

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF
CERAMIC COMPOSITES AND HARD MAGNETS FABRICATED BY
POWDER INJECTION MOLDING**

Ph.D. THESIS

Nil ÜNAL

Department of Advanced Technologies
Materials Science and Engineering Programme

JUNE 2012

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Thesis Advisor: Prof. Dr. M. Lütfi ÖVEÇOĞLU

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

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To my family,

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ABBREVIATIONS

MIM	: Metal Injection Molding
CIM	: Ceramic Injection Molding
PIM	: Powder Injection Molding
HIP	: Hot Isostatic Pressing
SPS	: Spark Plasma Sintering
LPS	: Liquid Phase Sintering
TZP	: Tetragonal Zirconia Polycrystals
PSZ	: Partially Stabilized Zirconia
Y-TZP	: Yttrium-stabilized Tetragonal Zirconia Polycrystals
τ	: Shear stress
γ	: Shear strain
Y	: Shrinkage factor
M(H)	: Magnetization loop
B(H)	: Induction loop
μ_0	: Permeability of free space
H	: Externally magnetic field
M	: Magnetization
H_{dm}	: Demagnetizing field
D	: Demagnetizing factor
P	: Working point
M_r	: Remanent magnetization
Br	: Remanent magnetic induction
B_{Hc}	: Coercivity
iHc	: Intrinsic coercivity
(BH)_{max}	: Maximum energy product
HDDR	: Hydrogenation-Disproportionation-Desorption-Recombination
HD	: Hydrogen Decrepitation
SEM	: Scanning Electron Microscopy
XRD	: X-Ray Diffractometer

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DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF CERAMIC COMPOSITES AND HARD MAGNETS FABRICATED BY POWDER INJECTION MOLDING

SUMMARY

General purpose of this thesis was to study and investigate powder injection molding technique and produce final sintered parts starting with powder processing. In recent years, powder injection molding (PIM) has become one of the common powder metallurgy (PM) technique which is used to produce complex shaped metal and ceramic parts. However, still some compositions were not examined practically and processed by PIM. Main aim of this study was to investigate and produce ceramic and metallic compositions which were not studied by researchers before. Ceramic and metallic injection molding has some slight differences between each other considering binder systems, debinding and sintering conditions. Depending on the composition and viscosity of the feedstock; injection pressure, temperature, speed and surface quality of the injected product can be variable between ceramic and metallic systems. In this thesis work, studies on ceramic systems were carried out on ZrO_2 ceramic composites. The friction resistance of ZrO_2 ceramic matrix composites was developed by micro- and nano- sized WC dispersions. This development was realized at Stuttgart, in IFKB Laboratories, Germany.

Second research was on Nd-Fe-B and Sm-Co permanent magnet materials which were processed by metal injection molding technique. Permanent magnets are the hot topic nowadays due to “clean energy and environment” studies. These magnets are frequently used for electrical vehicles, wind energy and electronic devices. Up to now, these magnets were produced by pressing and sintering or by embedding to polymer (bonded magnets). By pressing and sintering, it is not possible to produce complicated part shapes. Furthermore bonded magnets cannot provide magnetic properties well as sintered magnets. Therefore, injection molding and sintering technique was expected to be an excellent technique to produce high performance magnets. These investigations were performed in Fraunhofer Institute - IFAM, Bremen, Germany.

For the research on zirconia (ZrO_2) ceramic matrix composites; 10 - 40 vol% tungsten carbide (WC) were dispersed in 2, 2.5 and 3 mol% yttria stabilized zirconia matrix using commercial unstabilized ZrO_2 and 3mol% yttria stabilized ZrO_2 . Pre-studies of these powder compositions were carried out by hot pressing technique in order to compare the mechanical properties with the injected parts. Furthermore, with these pre-study, suitable WC compositions were figured out. Proper powder compositions were hot pressed at 1450-1550 °C under vacuum. 30 MPa pressure was applied for 1 hour. Following to metallographic preparations, mechanical and structural characterizations were applied. For ceramic injection molding process, similar powder compositions were firstly mixed with a commercial water-based binder using optimum solid content value and subsequently prepared feedstock

homogenized by extrusion machine. Granulated feedstocks were injection molded into different cavities. The effects of injection molding parameters (injection time, speed, temperature, back pressure, etc.) were observed during the process. The dimensions of the injected (green) parts were measured to control shrinkage. Parts were firstly solvent debinded and subsequently thermal debinded at 300 °C. Sintering was performed at 1550 °C. Before and after sintering several characterizations were performed on the parts. DTA/TG, Hg-Porosimetry and dilatometer tests were carried out following to debinding process to get information concerning sintering process. Final mechanical properties were identified by using 3 point bending tests, Vickers hardness, indentation toughness, microhardness, and unlubricated reciprocating wear tests. For microstructural and phase observations, SEM and XRD measurements were performed.

For the observations on injection molding and sintering of hard magnets, micron-sized jet milled irregular shaped single-crystalline commercial powders were obtained from a German company. Feedstock preparations were performed using various binder systems containing different polyethylene, wax and stearic acid contents. The solid content for each feedstock was arranged to obtain proper viscosity. The binder-powder mixture was mixed homogeneously by a z-blade kneader under Argon atmosphere inside the glove box. The effect of different residual impurity ratios of various binder systems on end-product was examined. The feedstocks were injection molded into different cavities in order to produce isotropic, axially single pole and multi pole magnetically aligned green parts. Binders were removed via solvent debinding in hexane under Argon atmosphere. Debinding atmosphere, rate and temperature parameters were studied in thermal debinding process and in the same run sintering were performed at 1080 °C and 1100 °C. The microstructure and phase analyses of the sintered parts were characterized by XRD, SEM/EDX analyses. The oxygen and carbon level of the sintered samples were measured via chemical tests. Magnetic properties of the isotropic and anisotropic parts were examined by a hystograph. Hysteresis loop, coercivity, remanence and max energy product values of the sintered parts were measured.

ENJEKSİYON KALIPLAMA YÖNTEMİ İLE ÜRETİLMİŞ OLAN SERAMİK KOMPOZİTLERİN VE SERT MİKNATISLARIN GELİŞTİRİLMESİ VE KARAKTERİZASYONU

ÖZET

Bu çalışmadaki genel amaç, toz enjeksiyon kalıplama tekniğini anlamak, geliştirmek ve toz üründen başlayarak çeşitli aşamalarla son ürünü üretmektir. Son yıllarda, toz enjeksiyon kalıplama tekniği, karmaşık şekilli metal ve seramik parçaların üretiminde kullanılan yaygın bir tekniktir. Ancak bu teknik daha henüz birkaç kompozisyon için pratik olarak denenmemiştir. Bu çalışmadaki amaç, henüz araştırmacılar tarafından çalışılmamış olan bazı seramik ve metal kompozisyonlarının araştırılması ve geliştirilmesidir. Seramik ve metal enjeksiyon kalıplama arasında malzemenin bağlayıcı sistemi, bağlayıcı giderme ve sinterleme koşulları bakımından küçük farklar vardır. Bağlayıcının cinsine ve vizkositesine bağlı olarak enjeksiyon kalıplama sırasında enjeksiyon basıncı, sıcaklığı, hızı ve ürünün yüzey kalitesi seramik ve metal sistemler arasında farklılık gösterebilir. Bu çalışmada seramik sistemler üzerine olan incelemeler zirkonya (ZrO_2) seramik kompoziti kullanılarak gerçekleştirilmiştir. ZrO_2 matriks kompozitlerinin aşınma direnci, mikro- ve nano- boyutlu tungsten karbür partikülleri disperse edilerek geliştirilmiştir. Bu araştırma Stuttgart-Almanya’da, IFKB laboratuvarlarında gerçekleştirilmiştir.

İkinci araştırma, Nd-Fe-B ve Sm-Co sert mıknatıslarının metal enjeksiyon kalıplama yöntemi ile üretilmesini geliştirmektir. Sert mıknatıslar son zamanlarda “temiz enerji ve çevre” çalışmalarından ötürü önemli bir ihtiyaç haline gelmiştir. Bu mıknatıslar rüzgar enerjisi üretiminde kullanılan rüzgar değirmenlerinin motorlarında, elektrik arabaların motorlarında ve bunun gibi önemli endüstriyel alanlarda talep görmektedir. Günümüzde bu mıknatıslar presleme ve sinterleme yöntemiyle veya polimerler içine karıştırılarak üretilmektedir. Ancak presleme ve sinterleme yöntemi ile, kompleks şekilli parçaların veya ince duvarlı silindirlerin üretilmesi mümkün değildir. Ayrıca, polimer içine karıştırılan mıknatıs tozlarının plastik enjeksiyon kalıplama yöntemi ile üretilmesi mümkün olduğu halde, bu ürünler sinterlenmiş mıknatıslar kadar yeterli manyetik özelliklere sahip değildir. Bu nedenle, enjeksiyon kalıplama ve sinterleme tekniği, yüksek performanslı karmaşık mıknatısların üretimine uygun mükemmel bir teknik olduğu düşünülmektedir. Sert mıknatısların metal enjeksiyon kalıplama yöntemi ile üretilmesi ve geliştirilmesi çalışmaları Fraunhofer Enstitüsü – IFAM, Bremen, Almanya’da gerçekleştirilmiştir.

Zirkonya (ZrO_2) seramik matriksi üzerine olan araştırmalarda 2, 2,5 ve 3 mol% yttria stabilize zirkonya matriksi içine 10-40 hacim% volfram karbür (WC) homojen olarak dağıtılmıştır. Bu toz kompozitleri ile gerçekleştirilen ilk çalışmalar, sıcak presleme tekniği kullanılarak yapılmıştır. Elde edilen mekanik özellik değerleri daha sonra enjeksiyon kalıplama ve sinterleme ile elde edilen sonuçlar ile kıyaslanacaktır. Yapılan ilk çalışmalar ile matrik içine dağıtılacak olan uygun WC oranları

incelenmiştir. Belli hacim oranlarında hazırlanan toz kompozisyonları sıcak presleme yöntemi ile 1450-1550 °C sıcaklıkta 30 Mpa basınç altında 1 saat boyunca preslenmişlerdir. Metallografik hazırlamanın ardından, mekanik ve yapısal karakterizasyonlar uygulanmıştır. Seramik enjeksiyon kalıplama prosesi için, benzer toz karışımları öncelikle optimum katı oranı kullanılarak ticari su bazlı bağlayıcı ile karıştırılmıştır ve ardından ekstrüzyon makinesi ile bu toz-bağlayıcı karışımı homojenize edilmiştir. Elde edilen granüle karışım farklı kalıplara enjekte edilmiştir. Enjeksiyon kalıplama parametreleri (enjeksiyon zamanı, sıcaklığı, hızı, kalıplama basıncı, vs.) işlem sırasında incelenmiştir. Enjekte edilen numuneler sinterleme sırasındaki boyutsal büzülmei incelemek adına ölçülmüştür. Numunelerin öncelikle çözücü içinde, ardından termal olarak 300 °C bağlayıcısı uçurulmuştur. Sinterleme 1550 °C'de gerçekleştirilmiştir.

Farklı sinterleme atmosferlerinin ve sinterleme sürelerinin etkisi incelenmiştir. Sinterleme öncesi ve sonrasında birçok karakterizasyon tekniği kullanılmıştır. DTA/TG, Hg-Por ölçümü ve dilatometre gibi incelemeler bağlayıcıyı uçurduktan sonra sinterleme karakteri ile ilgili bilgi edinmek adına yapılmıştır. Son mekanik özellikler üç noktalı eğme testi, Vickers sertlik testi, tokluk, mikro-sertlik ve yağsız vargel aşınma testi ile belirlenmiştir. Mikroyapısal ve faz incelemeleri ise ikincil elektron mikroskobu ve X-ışınları analizi ile gerçekleştirilmiştir.

Enjeksiyon kalıplanmış ve sinterlenmiş sert mıknatısların incelenmesi için, mikron boyuttaki jet-öğütme tekniği ile üretilmiş tek-kristalli ticari NdFeB ve SmCo tozlar alman firmalardan tedarik edilmiştir. Besleme stoğunun hazırlanmasında değişik bağlayıcı bileşenleri ve oranları kullanılmıştır. Bağlayıcıların içinde farklı oranlarda polietilen, mum ve stearik asit vardır. Katı oranı her besleme stoğu için enjeksiyon kalıplamada kullanılacak uygun vizkosite sağlanarak ayarlanmıştır. Bağlayıcı-toz karışımı z-tipi karıştırıcı kullanarak glove box'ın içinde Argon ortamında homojen olarak karıştırılmıştır. Kullanılan değişik bağlayıcı sistemlerin, son ürünün yapısındaki oksijen ve karbon impürütelerine etkisi incelenmiştir. Hazırlanan besleme stokları isotropik olarak veya kalıp içine yerleştirilen sert mıknatıslarla elde edilen manyetik alan içine yüzeysel tek kutup ve multi-kutup yönlenmeleri elde edilecek şekilde enjekte edilmiştir. İlk olarak numunelerin içindeki mum bağlayıcı hekzan içinde argon altında uzaklaştırılmıştır.

Termal bağlayıcı uçurma aşamasında, fırın atmosferi, hızı ve sıcaklığı incelenmiştir. Numunelerin sinterlenmesi termal bağlayıcı uçurmanın hemen devamında gerçekleştirilmiştir. NdFeB magnetler için sinterleme sıcaklıkları 1080 °C ve 1100 °C seçilip, vakum, yüksek vakum ve argon gibi sinterleme atmosferleri denenmiştir. SmCo için sinterleme sıcaklığı 1190 °C ile 1200 °C arasında değişip, sinterleme atmosferi olarak da argon kullanılmıştır. Sinterlemenin ardından numuneleri tavlamanın manyetik özelliklere etkisi araştırılmıştır.

Sinterlenmiş parçaların mikroyapı ve faz analizi X-ışınları analizi, ikincil elektron mikroskobu ile gerçekleştirilmiştir. Oksijen ve karbon miktarı kimyasal testler ile ölçülmüştür. İzotropik ve anizotropik parçaların manyetik özellikleri histograf ile ölçülmüştür. Numuneler 3 T (2380 kA/m) manyetik alan altında 3 kere manyetize edilmiştir. Sinterleme sırasında Curie sıcaklığının üzerine çıktığı için, manyetik moment değişmiştir. Bu nedenle bu moment'in geri kazanılması için anizotropik numuneler kolay eksen (easy axis) yönünde, isotropik numuneler ise herhangi bir doğrultuda yönlendirilmiştir. Numunelerin histerez diagramı, kuarsivitesi, remanensi

ve max enerji ürünü bulunmuştur. Enjeksiyon kalıplama ile üretilen mıknatısların yanı sıra, aynı NdFeB tozu kullanarak preslenmiş numuneler de hazırlanmıştır. NdFeB tozu içine %0,5 ağ oranında parafin katılarak oluşturulan karışım, uniaksiyal presle argon atmosferi altında 8 kN kuvvetle preslenmiştir. Preslenen ürün aynı sıcaklıklarda sinterlenmiştir ve elde edilen mekanik ve fiziksel özellikler enjeksiyon ürünleri ile karşılaştırılmıştır.

Sonuç olarak yapılan çalışmalarda görülmüştür ki enjeksiyon kalıplama yöntemi ile hem tungsten karbür disperse edilmiş zirkonya seramik kompozitleri hem de NdFeB ve SmCo sert magnetlerin üretimi mümkündür. Zirkonya matriksli kompozitler için enjeksiyon kalıplama ve sinterleme proseslerinin verimliliği göz önüne alındığında %20 hacim oranında tungsten karbür ilavesi en iyi sonucu vermiştir. Tungsten karbür oranı arttığı zaman hem sinterleme sıcaklığının da artması gerekmektedir ve bu da mekanik özelliklerde azalmaya neden olmaktadır. Sinterleme sıcaklığı 1550 °C'yi geçtiğinde ise ikincil porozite oluşumu görülmüştür. Sinterleme atmosferi olarak 950 °C'ye kadar hidrojen atmosferi kullanarak WC'ün oksitlenmesi engellenmiş ve geri kalan sinterleme argon altında gerçekleşmiştir.

Dört ve altı saat sinterleme süresi ardından numuneler isotropik olarak küçülmüştür. Sinterlenmiş ürünün mekanik özelliği sinterleme süresi ve WC oranı ile değişim göstermiştir. Düşük WC oranı hem yoğunlukta hem de mukavemet ve sertlikte daha iyi sonuç vermiştir. Zirkonya matriksi içine %20 hacim oranında disperse edilen sinterlenmiş kompozit 9,2 MPa.m^{1/2} tokluğa ulaşmıştır. Bi-modal partikül boyut dağılımı topaklanma probleminden ötürü, preslenen numunelerde elde edilen sonucun aksine, mekanik özelliklerde pozitif bir etki bulunmamıştır. Yağsız ortamda gerçekleştirilen triboloji testi sonucunda numunelerin düşük aşınma oranına sahip olduğu bulunmuştur. WC miktarı, sinterleme süresi ve bi-modal partikül boyut karışımından bağımsız olarak numuneler benzer aşınma katsayısına sahiptirler.

Sert mıknatıslarla yapılan enjeksiyon kalıplama ve sinterleme çalışmalarında görülmüştür ki birçok küçük parametre son ürünün manyetik özelliğini etkilemektedir. Manyetik özellikliğin değişimde en etkili rol oynayan parametre termal bağlayıcı giderme atmosferidir. Yapılan çalışmalarda görülmüştür ki hidrojen atmosferi son ürünlerdeki karbon oranını uygun değerlere düşürebilen tek atmosferdir. Bunun yanı sıra kullanılan bağlayıcı içeriği de sinterlenmiş ürünlerdeki karbon seviyesinde büyük önem taşımaktadır.

Bağlayıcıdaki karbon oranı polietilen seviyesinde değişim yapılarak minimuma indirilmiştir. Karbonun yanı sıra numunelerin manyetik özelliklerinde büyük rol oynayan oksijen impüriteleridir. Oksijen impüritesi arttığında ürünün kuarsivitesi ve max enerji ürününde büyük bir düşüş yaşanmaktadır. Bu nedenle besleme stoğu hazırlandıktan sonra argon altında saklanmalı ve enjeksiyon kalıplama yapılırken ilk enjekte edilen numuneler ile elde edilen yollukların tekrar enjeksiyonu sırasındaki oksitlenme göz önüne alınmalıdır.

Uygulanan enjeksiyon sıcaklığı oksitlenmeyi artırmamak için 90 °C'den yüksek olmamalıdır. Numunenin yoğunluğunun artması için uygulanan hafif sinterleme sıcaklığı artması, numunelerin yoğunluğunu arttırmadığı gibi manyetik özellikleri azaltmıştır. Aynı zamanda sinterleme süresini arttırmak tane büyümesine neden olduğu için manyetik özellikleri büyük ölçüde azaltmaktadır.

Diğer bir yandan enjekte edilmiş numuneler ile yapılan çalışmalar, aynı toz kullanılarak preslenip sinterlenmiş numuneler ile karşılaştırıldığında yoğunluğun ve kuarsivitenin daha çok yükseldiği görülmektedir. Preslenmiş numunelerin sinterlenmesi hidrojen atmosferi altında bağlayıcı gidermeye gerek olmadığı için doğrudan vakum altında gerçekleşmiştir. NdFeB yapısında, Nd₂Fe₁₄B matriks fazını, NdFe₄B₄ ve Nd-zengin fazını içermektedir. Nd-zengin faz oda sıcaklığından itibaren H₂ ortamında hidrojenize olmaktadır. Nd₂Fe₁₄B matrik fazı ise 650 °C'den itibaren hidrojenize olur. Bu nedenle bağlayıcı giderme işleminden sonra sıcaklık 600 °C'lerde iken yapıdaki hidrojen vakum ortamında tamamiyle uzaklaştırılmalıdır. Şimdiye kadarki enjeksiyon kalıplama numuneleri ile yapılan çalışmalarda, 500 °C'de 45 dk beklendiği halde hidrojen tamamen uzaklaştırılmadığı için yoğunluğun ve kuarsivitenin preslenen numunelere göre düşük olduğu düşünülmektedir.

1. INTRODUCTION

Powder injection molding (PIM) is a key manufacturing process in fabricating small, complex, precision parts in medium to high volume production using fine ($<20\text{ }\mu\text{m}$) metal or ceramic powders. The idea of using PIM process was developed from a synergy of traditional shape-making capability of plastic injection molding and the materials flexibility of powder metallurgy [1, 2]. The process consists of four main steps which are mixing, injection molding, debinding and sintering. In the mixing step, the powder is mixed with a binder, using a typical binder volume percentage of 35–50 vol.%, to form a homogeneous feedstock. The binder is a key component, which provides the powder with the flowability and formability necessary for molding [3]. After molding, the binder holds the particles in place. The remained binder is removed in the debinding step. Catalytic debinding, thermal and solvent debinding are common debinding methods used in the industry [4]. The debinded part is subsequently sintered to attain the required mechanical properties. The quality of the feedstock affects the quality of the molded and sintered parts [4].

By using Metal Injection Molding (MIM) and Ceramic Injection Molding (CIM), high volume - high precision components can be manufactured for various range of industrial use. MIM and CIM parts are currently found in all areas of life, from cars and trucks to watches, dental braces, mobile phones, IT equipment and much more [5].

The MIM process offers economical cost solutions for several applications compared to investment casting or machining, and improved mechanical properties in comparison to other net-shaping techniques such as zinc or aluminum die casting [6]. It also offers high-volume production, part to part consistency, high performance, excellent surface finish, weight savings, close porosity, surface finish, and high final density, among others [6]. There is a broad range of materials available manufactured by the MIM process. Traditional metal-working processes often involve a significant amount of material waste, which makes MIM a highly efficient

option for the fabrication of complex components consisting of expensive/special alloys [6]. These alloys are mainly cobalt-chrome, stainless steel; 17-4 PH, 304L, 316L, 430L, pure copper, Fe-Cr-Al-Y50, Fe-50Co, Fe-8Cr, Fe-Co-V, Fe-Cr-11Mn-3Mo, Fe-30%Ni, Fe-3%Si alloys; copper alloys; Cu-15Sn, Cu-Ni-Sn-P, Ni alloys; Ni-20Cr, Ni-Co-Cr-Al-Y and additionally WC-xCo (x:3-25), WC-xNi (x:3-25) and W-Ni-Fe. MIM is a viable option when extremely thin walls specifications (i.e. 0.2mm thickness) are required [7].

In this research, the aim has been to study and investigate the whole process of powder injection molding starting from powder preparation to characterization of the end parts. In this regard, production and development of ZrO₂/WC composites was performed utilizing CIM process and via MIM process production of NdFeB and SmCo permanent magnets were investigated and developed.

The inherent hardness of ceramics infers that manufacturing complex shaped ceramic components by standard machining processes can be expensive. CIM offers an economic solution for delivering repeatable, ultra high precision ceramic components. The injection molding of ceramics is a new and innovative process that provides cost effective solutions for design engineers requiring complex, repeatable ceramic components [8-10].

The processing of ceramic green body for the CIM process involves using polymeric binders consisting of distinct attributes to blend with ceramics powders forming a flow, uniform suspension so that the mixture can be shaped into a prescribed mold cavity at a given set of temperature and molding variables [11]. The binder formulation, in particular, has previously received more attention mainly because an ideal binder system suited for all different powder characteristics is still impossible to attain. The organic binder system used in ceramic injection molding usually consists of a major binder, a minor binder, a plasticizer or a lubricant, a wetting agent and a dispersant for processing ceramic powders [12]. Those additives that remain in the as-formed ceramic body after drying must be removed completely prior to component densification at elevated temperature [13-16].

ZrO₂-based ceramics have been demonstrated to be the strongest and toughest oxide yet produced [17, 18]. The excellent properties are attributed to the stress-induced

phase transformation from tetragonal to monoclinic ZrO_2 [17, 18]. However, for tribological applications, the limited hardness is a big handicap. Therefore to improve the modest hardness of ZrO_2 , refractory hard phases such as WC, TaC and TiC have been dispersed into the stabilized- ZrO_2 matrix [18-23]. Hot pressing experiments have demonstrated that WC secondary hard phase addition enhanced the hardness of ZrO_2 matrix while preserving its high toughness [17, 23].

Several research investigations have been focused on the production of ZrO_2/WC composites by hot pressing and spark plasma sintering (SPS) [17-19, 21, 24-26] and pressureless sintering techniques following cold compaction [27-29]. Currently, although there have been several studies based on the injection molding of ZrO_2 , this study revealed the first scientific data for the ceramic injection molding of ZrO_2 -based matrix ceramics. As an alternative processing route to pressing and sintering, the present study has shown that injection molding is a promising production technique for the fabrication of yttria stabilized ZrO_2/WC composites. The biggest advantage of injection molding over other techniques is that there is no need for machining the end products. The major challenge in this process is to determine the binder amount, debinding schedule and sintering conditions due to longer sintering times and temperatures compared with hot pressing. Different parameters in every step of the production were investigated to observe the structural and mechanical changes of the end product. Furthermore, the mechanical effect of bimodal particle size distribution of the secondly distributed WC phase was observed and reported.

Vleugels et al. [17, 19] in their studies have reported that when nanometer sized WC dispersoid is used, hardness, strength, and fracture toughness are higher than those containing micrometer sized WC. Moreover, Haberkorn et al. [18, 20, and 29] have indicated in their studies that secondly distributed micrometer sized WC particles increased the hardness although the toughness value remained relatively low. It can be concluded that fine WC particles increase the fracture toughness and hardness while composites with coarse WC particles can be sintered to higher densities [18, 20]. Proper combination of large and small reinforcement particles could result in higher wear resistance than a mono-size particle reinforced composite [30]. The larger particles mainly withstand the wear and the small dispersed particles preferentially strengthen the matrix [30]. In this study, it is expected that by mixing

proper amounts of nano-sized WC particles with micron-sized WC inclusions, an optimal balance between the overall hardness and ductility could be achieved, thus resulting in superior tribological properties.

As a following study, production investigations on NdFeB and SmCo magnets by metal injection molding process have been performed. First trials for injection molding of NdFeB were realized by Sumitomo Special Metals, the company that developed the NdFeB alloys in 1983. Despite the fact that they held the patents for MIM of NdFeB for many years, no further literature regarding MIM process was published by them. While a range of soft magnetic materials were already processed on a standard basis, MIM of hard magnets of the SmCo- or NdFeB-type have hardly been mentioned.

Since 1995, there have been very few research investigations on MIM of NdFeB, however the process has not been used for producing commercial parts [31-33]. Apparently there are many handicaps in this process such as, oxidation problems; residual carbon from the binders therefore debinding conditions took the attention on pressing and sintering technique.

Currently, commercially hard magnets are produced as bonded isotropic magnets with limited properties but complicated designs or as sintered anisotropic magnets with limited designs but maximum magnetic properties. MIM can allow the combination of both possibly opening up new markets. Since there are huge require on hard magnets especially for electrical vehicle parts, wind energy turbines and electronic applications, MIM will be the exact solution to response the demand.

The quality of permanent magnetic materials is quantified by its energy product $(BH)_{\max}$ which is determined by material's extrinsic and intrinsic parameters describing the amount of energy stored in magnets. Today, the permanent magnet choice for the main applications is based on intermetallic $\text{Nd}_2\text{Fe}_{14}\text{B}$ compounds. The developed NdFeB alloy ($\text{Nd}_2\text{Fe}_{14}\text{B}$) phase has greater coercivity and energy product than SmCo. Depending on the processing route and elemental additions, the $(BH)_{\max}$ for NdFeB commercial products was reported as high as 358 kJ/m^3 and for laboratory magnets, $398\text{-}413 \text{ kJ/m}^3$. As the $(BH)_{\max}$ value gets closer to its theoretical

value which is 509 kJ/m^3 , the end product would result in significant weight and size reductions [34].

SmCo and NdFeB combine strong anisotropy originating mainly from the rare-earth sublattice, accompanying with a reasonably high saturation magnetization provided by transition metal atoms [35]. High remanence is desirable in permanent magnets which certainly mean a high saturation magnetization [36]. Although SmCo has around 720°C Curie temperature, for NdFeB it reduces to $300\text{-}500^\circ\text{C}$ [36]. SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ type magnets are ideal when wide working temperature ranges (50°C - 250°C) are required. These magnets are high energy permanent magnets with magnetic fields stable over a variety of environmental conditions because of their high magnetocrystalline anisotropies and Curie temperatures [37].

The MIM process for the $\text{Sm}_2\text{Co}_{17}$ permanent magnets were tried by Chinese scientists in 2008 [38]. They have used water based binder and achieved $(\text{BH})_{\text{max}}$ 157 kJ/m^3 . In their studies as the binder concentration increased, the carbon impurities were increased significantly which lowered the density, remanence, coercivity drastically.

In this thesis study, for production of NdFeB and SmCo permanent magnets by MIM process, a thermoplastic binder was developed and a proper debinding route is investigated to prevent the end-product from oxidation and excessive carbon impurities.

Currently more than 80% of the world's rare earth reserves are in China [39] and 97% of all rare earth are produced there. Some of the main application areas for the permanent magnets are electric motors, generators, moving-coil meters, magnetic separators, frictionless bearings [36]. The demand is growing by the use of the permanent magnets in green technology.

In 2005 about 40,000 tones of sintered NdFeB magnets were manufactured worldwide, about 500 tones in Europe, 8,500 tones in Japan and the rest in China [40]. Permanent magnets have improved with regard to performance dramatically over the last five decades and they have become essential in modern life and industry. Thus, our lives depend directly or indirectly on the function of permanent magnets.

2. POWDER INJECTION MOLDING

Powder injection molding (PIM) is a new manufacturing technology that combines the shape complexity and productivity in order to produce ceramics and metals [11].

This process combines a small quantity of a polymer mixed with powder to form a feedstock which can be molded in a proper mold [1]. PIM is capable of producing a wide range of component sizes and complex-shape parts [11]. Following shaping, the polymer binder is extracted and the powder is sintered often to near-theoretical densities. The process is summarized in Fig. 2.1.

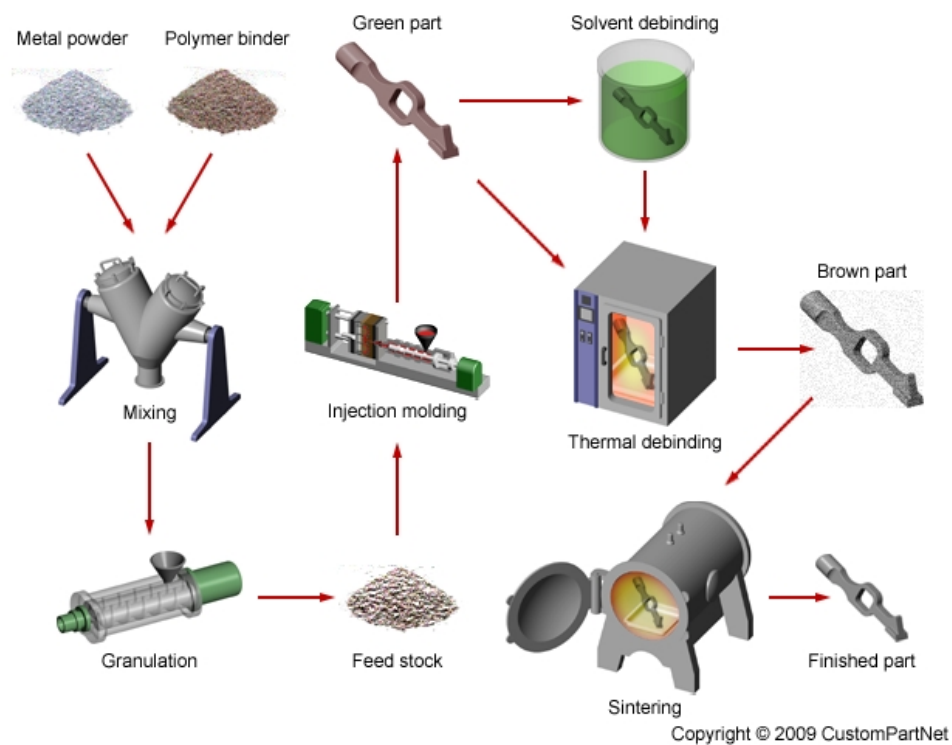


Figure 2.1 : The metal injection molding process (CustomPartNet) [41].

Widespread commercialization of PIM has started around 1980s [1]. PIM competes with other shaping technologies, namely, die and investment casting, machining, cold isostatic compaction and slip casting. PIM has overcome, the shape limitations of traditional powder compaction, the costs of machining, the productivity limits of

isostatic pressing and slip casting, moreover defect and tolerance limitations of casting [1].

PIM has been used to form section thickness with upper limits ranging from 10 to 50 mm and to form section thicknesses less than 0.5 mm. Dimensional tolerances are generally within 0.3%. Largest volume that can be produced is below 100cm³ however the cost of the powder and tool costs should be considered [1]. The feedstock material (runners, sprues, and damaged moldings) can be recycled which is very cost effective when costly raw materials are used [1]

Powder Injection Molding (PIM), which encompasses Metal Injection Molding (MIM) and Ceramic Injection Molding (CIM), is a major manufacturing technology with estimated sales of more than \$1 billion. MIM parts production accounts for about 90% of the market for the PIM products, with an estimated annual growth between 10% and 20% worldwide. PIM is a truly global business, with nearly 400 parts producers located worldwide. According to recent data, Asia is the world's largest PIM producing region by sales, followed by Europe and North America [5]. The world's PIM usage is summarized in graphs given in Fig. 2.2 [5].

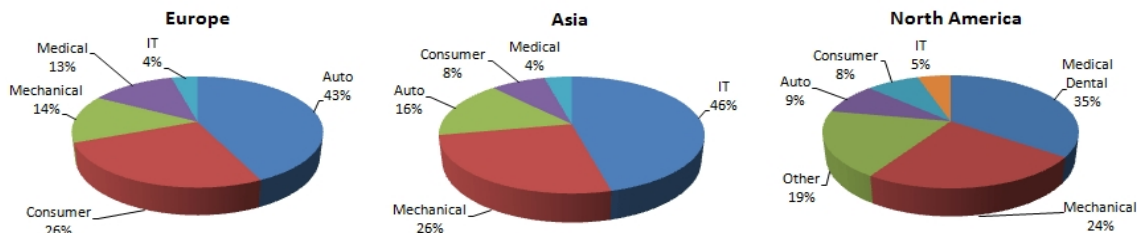


Figure 2.2 : The ratios of the PIM usage in world [5].

PIM is a desirable process because of providing ease of manufacture, including process control, flexibility and automation. This technique is associated with large production volumes, namely high rate (100,000 parts per day) or slow runs as few as 5,000 parts per year pointing that the production method is economical [1].

2.1 Ceramic Injection Molding

Although ceramic injection molding (CIM) has been used since 1930, until quite recently the technology has been relatively unknown [11]. Among the other major forming methods, such as, slip casting, extrusion, uniaxial pressing, tape casting,

recently CIM has received increased attention as a way to form complex ceramic parts in both traditional and advanced ceramics [11].

Forming of ceramics is the key process step in determining the cost competitiveness of engineering ceramics as high performance products [11]. The inherent hardness of ceramic means that manufacturing complex shaped ceramic components by standard machining processes can be expensive. Other manufacturing processes such as dry pressing or extrusion usually limit part complexity. CIM offers an economic solution for delivering repeatable, ultra high precision ceramic components [42]. The injection molding of ceramics is a new and innovative process that provides cost effective solutions for design engineers requiring complex, repeatable ceramic components [8, 9, 42, 43].

CIM process involves blending polymeric binders with distinct attributes with ceramic powders to form a flowable, uniform suspension so that this homogeneous palletized feedstock can be shaped into a prescribed mould cavity at a given set of temperature and molding conditions [42]. Binder blends used in CIM usually consists of a major binder, a minor binder, a plasticizer/lubricant, and a surfactant for wetting ceramic particles. Low molecular weight organic polymers and waxes are frequently used as the base for the binder [44]. After forming the part, green part goes through two thermal processes. First is pyrolysis to remove the binder, followed by sintering in a high temperature kiln to form a fully dense ceramic component. During sintering, the component shrinks uniformly by as much as 20% while retaining the complex shape [42].

Ceramics have significant advantages characterized by their outstanding physical, chemical, mechanical, thermal and/or electrical properties. This opens the door to a wide variety of application possibilities when other materials fail to perform, while maintaining great versatility and freedom in the design of components.

2.2 Metal Injection Molding

Many objects which people encounter in everyday life such as cars, mobile phones, watches, domestic appliances, cameras and power tools contain MIM parts [45].

The primary raw materials for MIM are metal powders and a thermoplastic binder. The binder is only an intermediate processing aid and removed from the products after injection molding. The properties of the powder determine the final properties of the MIM product. The subsequent binder removal process serves to obtain parts with an interconnected pore network without destroying the shape of the components [45]. After this stage, still some binder present in the parts holding the metal powder particles together, but the pore network allows to evaporate the residual binder quickly. The sintering process leads to the elimination of most of the pore volume formerly occupied by the binder. As a consequence, MIM parts exhibit a substantial shrinkage during sintering. The linear shrinkage is usually as high as 15 to 20% (Fig. 2.3). If required, sintered MIM parts may be further processed by conventional metal working processes like heat treatments or surface treatments in the same way as cast or wrought parts [45].

For certain applications, such as the automotive, medical and aerospace sectors, Hot Isostatic Pressing (HIP) can be used to completely remove any residual porosity. As MIM parts are typically small, this can be relatively cost effective for critical components [45].

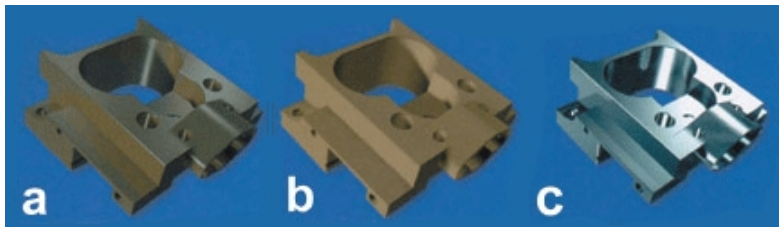


Figure 2.3 : MIM part (a) as molded, (b) after binder removal, (c) after sintering (Courtesy BASF AG, Germany) [45].

Fig. 2.4 shows some parts having different dimensions with various weights.



Figure 2.4 : A selections of MIM parts, ranging from 0.028g to 260g [45].

2.3 Feedstock Preparation

The feedstock is the pelletized mixture of powder and binder which will be used for injection molding. Powder characteristics, binder composition, powder-binder ratio, mixing method, and pelletization technique determine the characteristics of the feedstock. Ease of molding and control over final dimensions are the important aims. No voids and pores should be present in the feedstock therefore all the interparticle spaces are sufficiently filled with binder. Particle distribution and shape is important to obtain high packing density. Thus bi-model particle size distribution is usually preferred [1].

Feedstocks are generally prepared with slightly less powder than the critical solids loading which is the composition where the particles are packed as tightly as possible without external pressure and all space between the particles is filled with binder [1]. Typically 60 vol% solid content is used for PIM process.

Less binder than the critical loading would cause cracking and excessive binder would cause inhomogeneity, flashing, segregation and excessive shrinkage [4]. There are several techniques to determine the optimum critical solids loading of a powder-binder system [4]. The most common methods are the measurements of the density, melt flow, mixing torque or viscosity versus composition. The most common technique is using capillary rheometry in order to measure the viscosity by changing temperatures. For MIM solids loading varies between 45-75 vol%, and for CIM it ranges between 50-55 vol% [1].

Homogeneity of the feedstock is very important because inhomogeneities result in non-uniform viscosities, uneven molding and difficulties in sintering. The separation of particles from the binder leads to distortion of the final product. Small or irregular-shaped particles require longer mixing times. If the particle size is lower than 1 μ m and especially if the particle shape is irregular, agglomeration can happen easily. To enable easy homogenization, an extruder is needed which combines high shear rate with a short residence time at elevated temperatures. Mixing torque can be used to determine the homogeneity during mixing. The torque decreases as the agglomerates are broken apart and as binder becomes better dispersed in the mixture. On the other hand, contamination can increase with prolongation of mixing times [1].

The best mixing is obtained with a high shear, but not till the limit where the work of mixing damages the particles or overheats the binder. For thermoplastic binders, mixing is done at an intermediate temperature, where shearing is dominant. Mixing at very high temperatures degrades the binder or allows separation of the powder because of a low mixture viscosity. Mixing the surfactant with the powder before mixing the binder is the best and results in lubrication of the particles and a continual deagglomeration of clusters [1]. Fig. 2.5 shows types of twin and single screw extruders.

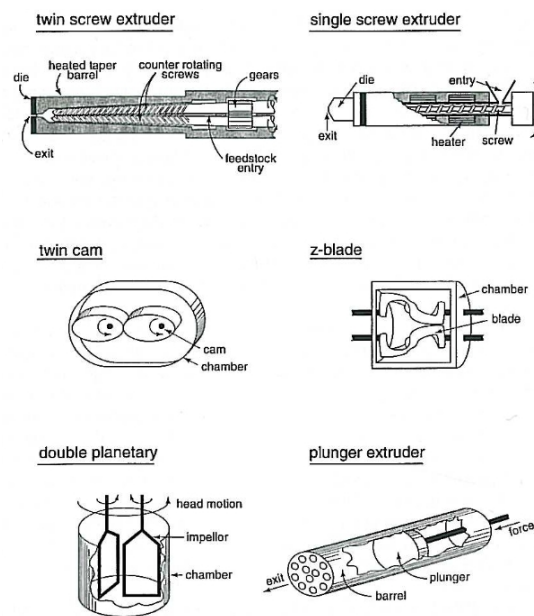


Figure 2.5 : Sketches of typical mixer geometries showing a double planetary, single screw, plunger extruder, twin screw extruder, twin cam, and z-blade mixers [1].

2.3.1 Rheology

Injection molding feedstock is a viscoelastic material which exhibits both viscous and elastic characteristics. At elevated temperatures, the feedstock has viscous character however at the room temperature it is elastic [1, 4]. Viscosity is the relationship of the shear stress to the shear strain rate. Shear stress (τ) is the force per unit area that causes PIM feedstock to flow over a surface, such as the die surface. The shear strain (γ) is the relative motion of the feedstock over the surface. $d\gamma/dt$ would give the shear rate. Fluid resistance to shearing is called viscosity " η ". The relationship between these parameters is given below in an equation (eq. 2.1);

$$\tau = \eta \left(\frac{d\gamma}{dt} \right)^m \quad (2.1)$$

"m" is the exponent used to characterize the fluid. For low molecular weight liquids like water, the viscosity depends on temperature and pressure but not on shear rate. These fluids have Newtonian flow. However, feedstocks have more complex behavior and their viscosity depends on shear rate as well as pressure and temperature, generally decreasing at higher shear rates due to shear thinning [1].

Powder particles affect the mixture behavior of the feedstock. The "shear stress" formula given in (eq. 3.1) is used to express the viscosity dependence on shear rate and stress where m is the exponent to characterize the fluid [1]. It should be taken into consideration that feedstock has high sensibility to temperature and pressure. As pressure and temperature increases due to the thermoplastic binder added, the feedstock becomes more viscous. On the other hand, at low temperatures, it exhibits an elastic behavior and has a yield point [4, 11].

If the viscosity increases as the shear rate increases (shear thickening), the substance has a dilatant flow. Shear thickening behavior is undesirable for injection process because of possible powder-binder separation. On the other hand, the viscosity of a pseudoplastic substance decreases as the shear rate increases (shear thinning) [1, 11]. Most PIM mixtures exhibit pseudoplastic behavior. However, several systems exhibit a combination of thinning and thickening behaviors depending on the shear rate [1]. The decreases in viscosity with increasing shear rate means particle / binder molecule orientation and ordering with flow. However higher shear rates increase particle-particle contacts that hinder flow. Small particles inherently have more surface area and interparticle friction [1, 11].

To measure the viscosity of the feedstock, capillary rheometry is the most common and relevant technique. It measures the pressure drop associated with a force flow rate through a small capillary tube. Corrections are needed for wall friction and the particle size must be small with respect to capillary diameter [1]. Since torque rheometers are regularly used in measuring viscosity during mixing, maximum torque values have been suggested. During molding, the shear rate generally ranges between 10^2 and 10^5 s^{-1} . In this range, the maximum useful viscosity for the mixture

is 10^3 Pa.s at the molding temperature. Moreover, it is most desirable to have little viscosity change over the molding temperature range. Consequently, flow of feedstocks is affected due to the binder, molding temperature, solids loading, shear rate or tool design [1].

Particle motion involves dilation of the particles, therefore the feedstocks exhibit yield strength. Surfactants are necessary in allowing particle sliding [1]. In a paraffin wax-based binder different contents of stearic acid (SA) is present as the surfactant. The viscosity of the feedstock decreases significantly when the SA is added. Besides, the wetting angle of the binder against the powder decreases greatly and the critical solid loading increases with the adding of the SA [46]. An excess of mobile liquid is needed as a lubricating layer to allow easy flow during molding, which is a major role of surfactant. In Fig. 2.6 the drawing shows the effect of the surfactant.

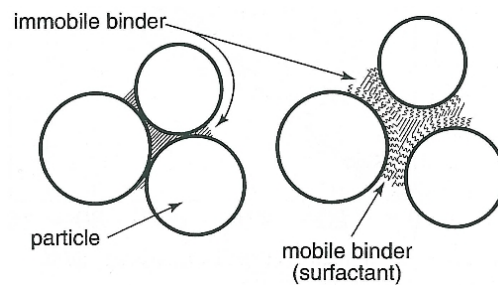


Figure 2.6 : Sketches of particles and the immobile liquid binder between the particles when they are in contact [1].

The role of the binder is to fill the spaces between the particles but it cannot facilitate the flow process. Therefore, the benefit of using surfactant is to allow sliding at the particle contacts, greatly reducing the system viscosity. Without the surface layer on the particles, the viscosity of the feedstock is too high for molding. Fig. 2.7 shows the relative viscosity change due to percentage of small particle content and the behavior indicates that better packing of the bimodal mixture allows more binder to act as a lubricant.

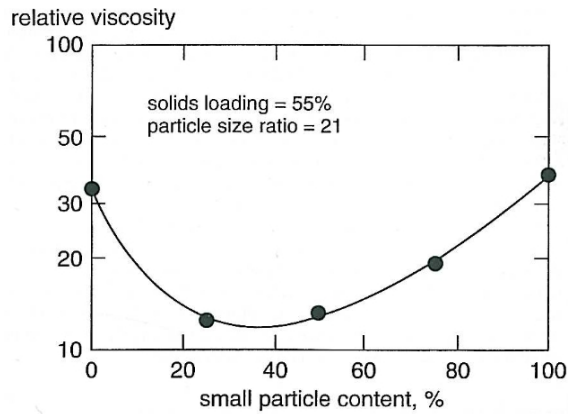


Figure 2.7 : Relative viscosity versus composition for a bimodal mixture having 55% solids loading and 21 particle ratio [1].

2.3.2 Feedstock - Molding Relationship

A feedstock has a viscoelastic behavior. In the mixing and molding temperatures it behaves viscous and during cooling in the mold, the behavior shifts to an elastic response. High molding temperature ease complete molding without the formation of void, however following molding, in the cooling stage depending on the rate, residual stresses in thermal and mechanical properties between the binder and the powder can cause distortion [1, 11]. To reduce the component distortion, the feedstock must exhibit a low, stable viscosity during molding but a large viscosity increase on cooling.

Consequently, the feedstock elastic modulus influences molding and distortion. The elastic modulus depends on the binder composition and solid loading. Temperature also has an effect on the elastic behavior. The elastic modulus decreases as temperature increases, but the relaxation of the stresses due to the thermal expansion coefficients between the powder and binder complicates the behavior [1, 4]. Ceramics are low conductivity powders, therefore the ceramic feedstock delays the cooling in the mold and has low residual stresses [1, 11].

2.4 Powders

In addition to the binder, powders have important effects on the PIM processing. Irregular particles exhibit better component-shape retention during binder removal; cause the degraded packing density is detrimental to high sintered densities. In order to standardize the PIM feedstock, it is important to know how the powder is fabricated. Additionally, particle size and distribution, particle shape, surface area,

interparticle friction as measured by flow, internal particle structure and chemical gradients, surface films is necessary to know because of its balance between rheological behavior, dimensional control in debinding, sintering response, binder wetting, mixing, debinding rate, and molding, respectively [1].

For ceramics, a narrow particle size distribution usually allows for easier molding, although bimodal particle size distributions improve packing and flow. Surface charge is significant for small size ceramic powders, and zeta potential measures it. Interparticle friction has an effect on powder flow and packing. As the particle size decreases, friction in a powder mass increases. If the interparticle friction is high, it interferes with mixing and molding. However, if it is low, it creates problems with component slumping and shape retention during debinding [1, 11].

Powder fabrication methods affect the size, shape, microstructure, chemistry, and cost of the powder [1, 2, 11]. Some of the micron-sized powder production techniques are compared in the Table 2.1.

Table 2.1 : Comparison of powder production techniques [1].

Technique	Particle Size µm	Shape	Materials	Cost
Gas Atomization	5 - 40	Spherical	Metals, Alloys	High
Water Atomization	6 - 40	Rounded	Metals, Alloys	Moderate
Centrifugal Atomization	25 - 60	Spherical	Metals, Alloys	Moderate to High
Plasma Atomization	2 - 40	Spherical	Metals, Alloys, Ceramics	High
Oxide Reduction	1 - 10	Polygonal to Rounded	Metals	Low
Carbonyl Decomposition	0.2 - 10	Rounded to Spiky	Metals	Moderate
Chemical Vapor Decomposition	0.1 - 2	Equiaxed, Needles	Ceramics	High
Precipitation	0.1 - 3	Polygonal	Metals, Compounds	Low to Moderate
Milling	1 - 40	Angular, Irregular	Brittle	Moderate
Fine Grinding	0.1 - 2	Irregular	Ceramics	Moderate
Reaction	0.2 - 40	Rounded to Spherical	Compounds	High

Jet milling, attritor milling, planetary ball milling and high-energy milling are the main powder milling and grinding techniques. Sharp asperities on milled powders inhibit packing and flow, making milled powders difficult to mold. Also contamination and lack of control over the powder characteristics can be the disadvantages for the alternative techniques [1, 11].

Very small ceramic particles are produced by decomposition of oxides, carbonates, acetates, alkoxides or oxalates. On the other hand, a classic form for metal powder fabrication is oxide reduction, such as reduction of milled WO_3 in a dry H_2 atmosphere at low temperatures. Final W particles have porosity therefore they need to be milled after reduction in order to use them for PIM [1].

Precipitation techniques are functional for forming refractory, reactive metals, ceramic and composite powders. For example, SiC is produced by reacting $\text{Si}(\text{OH})_4$ with methane [1].

Another useful technique is gas - fluid atomization. During atomization, liquid metal melts sprayed through a nozzle in order to produce spherical metallic powders. The fluid used to break up the molten stream can be air, nitrogen, helium, argon, water or oil. The molten stream is disintegrated by rapid expansion out of the fluid nozzle. Gas atomized powders are chemically homogeneous with high packing densities. The particles are spherical, and free from internal voids. These powders are used in PIM process like the water atomized powders.

In contrast to gas atomization (Fig. 2.8), water produces less spherical particle shape and smaller particle size. High pressure water is used to produce prealloyed particles such as stainless steel powder for PIM applications. Interaction of the molten alloy and water may result in oxidation therefore hydrogen reduction step should be followed up. Another technique is plasma atomization which enables the production of spherical refractory metal, ceramic, composite and traditional metal powders. In this technique, agglomerated material is fed into a plasma torch where melting and rapid acceleration occur [1].

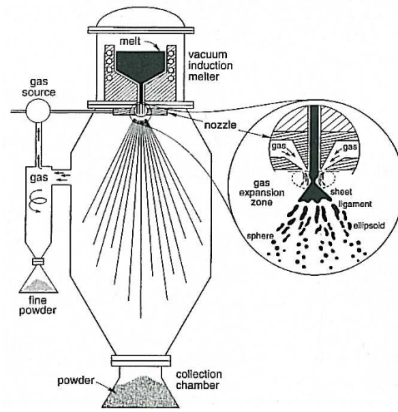


Figure 2.8 : Inert gas atomization process for production of small, spherical metallic powders from liquid metal melts, and extended view of the gas expansion nozzle [1].

Blending is used to create bi-modal or tri-modal particle size distributions for high packing densities. Gas or water atomized powders are often blended to adjust rheological properties. Deagglomerating and attritioning treatments reduce the mean particle size. Sometimes agglomerates can be broken apart in high shear mixing but the tendency to reagglomeration should be prevented by using surfactant [1, 11].

2.5 Binders

The binder is mixed with the powder to form the feedstock for molding. The binders usually have three components, such as backbone polymer which provides strength, a filler phase which can be easily extracted during debinding and a surfactant to bridge between the binder and powder. The binder wets the powder surface to aid mixing and molding, so various chemicals that modify wetting behavior are widely employed [1, 3, 4, 11].

Many binder systems are used in industrial PIM operations. Five main groups are: thermoplastic compounds, thermosetting compounds, water-based systems, gelatin systems and inorganics. It is important that the binder-powder mixture should provide mixing and molding without any defects. Binders should inhibit separation or agglomeration of the powder. If the viscosity is too low, the binder and powder will separate because of high shears encountered in molding. The shorter molecular chain length thermoplastic polymers generally enable good forming, and having isotropic properties so they are most desirable for PIM. Waxes and stearic acid prove ideal because of their small molecule size, thermoplastic character and low melting

temperatures. The effect of stearic acid on the viscosity of carbonyl iron feedstock is given in a graph in Fig. 2.9. Carnauba wax which has around 80-82 °C melting temperature, is also used to benefit from its hardness [1, 11].

In PIM, most of the polymers are hydrocarbon-based. Besides the major thermoplastic components, the binder can contain additives for die lubrication, powder wetting, viscosity control, residual stresses and debinding behavior. Successful binder formulations contain 20 to 80 vol% of a major component. Surfactants which improve powder wetting are very important.

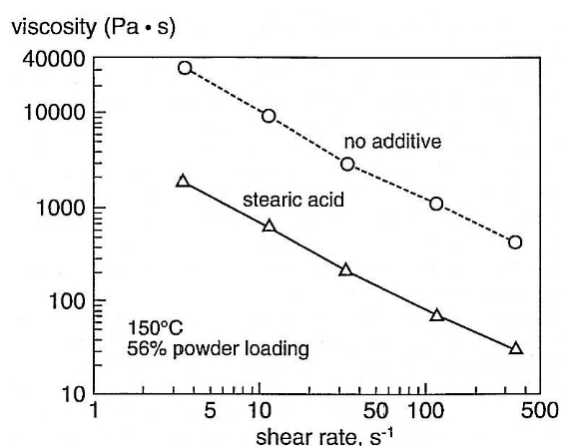


Figure 2.9 : Apparent viscosity versus shear rate for carbonyl iron in a wax-polymer binder at 150 °C showing the effect of an addition of 1% stearic acid [1].

If the binder component increases both the viscosity and glass transition temperature, there will be an increase in the molecular weight. In Table 2.2, properties of some polymers used in binders are given.

Binders are responsible for placing the particles into a close packing. The binder must wet the powder particles and provide low viscosity at a high solids loading. Therefore waxes and low molecular weight polymers are used as a base for a binder. The binder and powder should not react with each other.

Short chain-length molecules are easier to mix and to be removed during debinding. Moreover, it is advantageous if the binder can be recycled several times without degrading. Wax-polymer binder systems are forceful systems that are widely applicable to metals, ceramics, carbides, intermetallics and even amorphous materials [1, 11].

Table 2.2 : Some polymers employed as binder constituents [1].

Property	Poly-Pro-pylene	Poly-Ethy-lene	Poly-Styrene	Poly-Vinyl Chloride	Paraffin Wax	Poly-Ethylene Carbonate	Poly-Ethy-lene Glycol
Density (g.cc ⁻¹)	0.90	0.91	1.04	1.35	0.91	1.42	1.15
Melt Temp. (°C)	130-170	105-130	240	100-240	40-80	-	65
Melt Density (g.cc ⁻¹)	0.77	0.80	0.90	1.25	0.70	1.10	-
Thermal Conductivity (W.m ⁻¹ .°C ⁻¹)	0.2	0.3	0.1	0.2	0.3	0.2	-
Thermal Expansion (ppm.K ⁻¹)	100	200	70	140	400	-	740
Tensile Strength (MPa)	35	10	50	20	4	2	0
Failure Elongation (%)	200	400	2	300	-	1000	0

2.6 Tooling

For PIM, the cavity dimensions are close to the final component, even though some plastics swell on ejection. The cavity dimensions for PIM are oversized to accommodate subsequent sintering shrinkage. To control the tool temperature is also important to ensure final component dimensional control. The residual stresses would reduce and improve the uniformity of shrinkage [1, 11].

Abrasive wear of the screw, barrel and nozzle are problems with carbides, cermets, and ceramic powders therefore high hardness is necessary to improve resistance against abrasive conditions. New boride-tool steel composite coatings are excellent in reducing wear.

Cavity, the major part of the tooling, captures the component shape, which is oversized to allow for component shrinkage during sintering. The typical feedstock contains 60vol% solid and 40vol% binder. To attain the desired final component

properties, the linear shrinkage during sintering may be 15%. If the solid loading is similar or lower than 40vol% then the shrinkage can be 25%. The shrinkage in dimensions is known as the shrinkage factor (Y) and it is calculated from the feedstock solid loading ϕ and sintered fractional density ρ/ρ_T [1].

$$Y = 1 - \left(\frac{\phi}{\rho/\rho_T} \right)^{1/3} \quad (2.2)$$

where ρ is the final density and ρ_T is the theoretical density for the material. Equation (2.2) assumes isotropic shrinkage in sintering. The shrinkage factor is the change in a dimension divided by the original dimension. Since the target is the final component size, each dimension of the tool cavity is oversized to accommodate this shrinkage.

If the desired final dimension is L_f at a fractional density V_s from a feedstock with a fractional solids content of ϕ , then the initial dimension of the tooling is given in terms of the tool cavity expansion factor, Z ,

$$Z = \frac{1}{1 - Y} \quad (2.3)$$

According to these equations (2.2, 2.3), shrinkage Y is normalized with respect to the tool dimension, while the tool expansion factor Z is normalized with respect to the final dimension.

Non-uniform powder packing, gravitational factors in sintering, also polymer orientation in cavity filling, tool friction and wear, powder-binder separation cause slight but measurable anisotropic shrinkages [1, 4]. Therefore design of gates and vents in the cavity is also important. Fig. 2.10 shows the mold and cavity options of a mold.

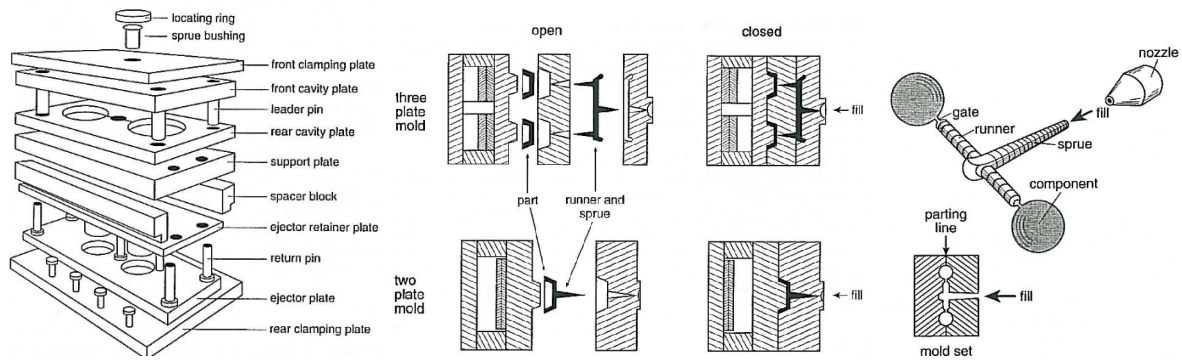


Figure 2.10 : View of (a) a typical injection molding tool set, (b) Contrast in design and sprue separation from the PIM component on old opening for two-plate and three-plate molds, (c) Feedstock flow the molding machine nozzle along the sprue then into the runner system to fill the cavity through the gate [1].

The feedstock takes the path of least resistance, making multiple gates and complex runner paths difficult to design and control. Runners should be short to reduce cooling during mold filling and to avoid jetting. Large runners result in wasted material, reduced shot volume available for the part and slow molding, while small runners result in more flow resistance and mold-filling problems. At the end of the runner is the gate leading into the die cavity. A small gate creates undesirable flow constrictions, leading to jetting and increased wear. Fast filling through a small gate causes jetting which forms internal shrinkage voids and weld lines. Most desirable is progressive filling with feedstock wetting the cavity walls, pushing air through the vent at the end of the cavity. Wetting is enhanced by filling at a corner [1, 11].

Vents are very thin relieves in the tooling sized to allow the escape of air while preventing feedstock penetration. Venting is also necessary to allow the part to be ejected from the tooling. For instance, a closed ended shape cannot be removed without creating a vacuum, so an additional pin built into the forming tool which is pulled first to the vent the mold to avoid part sticking [1, 11].

A high hardenability is needed in the tool material to attain uniform hardness throughout thick sections. To avoid wear and component adherence to the tooling, surface should be smooth, scratch free finish. In ceramic injection molding, chromium plated tools generally useful to have hard, smooth surface and rebuilding dimensions [1, 11].

For tooling, computer aided design would lower production and design costs, greatly decreases mistakes and the time required to design tooling. Many computer models exist but none are tuned to the special features of PIM yet.

2.7 Molding

The injection molding cycle starts by clamping the mold closed, injecting the preheated feedstock into the cavity, packing out the cavity until the gate solidifies and preparing the next charge while ejecting the cooled component [1, 11]. The flow from the nozzle passes through the sprue, runner and gate before filling the cavity. As the mold is cooler than the injected feedstock, the feedstock loses heat with a parallel increase in viscosity. Molding very quickly or heating the tooling can compensate the increasing viscosity. After the mold is filled, heat is extracted from the feedstock through the die. The ejected component is rigid [1]. The parts of the injection molding machines are given in Fig. 2.11 in detail.

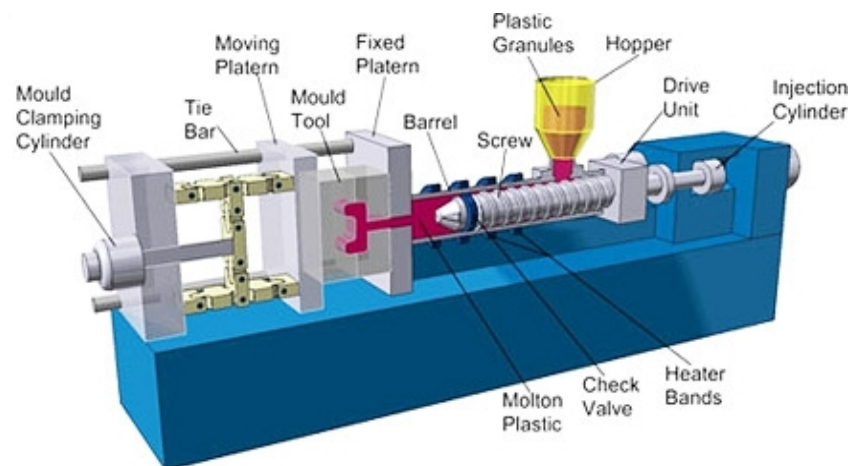


Figure 2.11 : The parts of the injection molding machine [47].

Uniform particle packing in the mold results in uniform dimensional change in sintering. Molding cannot be able to repair the errors caused by inadequate mixing.

Molding depends on particle characteristics, binder formulation, feedstock viscosity, tool design and machine operating conditions [1].

The most common molding machines are reciprocating screw, hydraulic plunger and pneumatic. Pneumatic machines apply gas pressure to move heated feedstock into the mold. Pneumatic or hydraulic plunger machines are usually applied to simple

shapes or slow molding operations because the control systems are usually simple therefore there can be problems with poor die filling and powder-binder separation [1, 11].

A very important part of molding is the design of the screw. During metering, the screw reciprocates and acts as a mixer to ensure uniform powder-binder distribution and heating. The screw has a check ring behind the tip that acts as a valve that allows feedstock flow into the front of the barrel during plastication. Screw rotation is controlled by a hydraulic motor. Design and construction of the screw for PIM is important to obtain minimized contamination [1, 11].

2.7.1 Moldability

Moldability is the evaluation of the speed and ease by which feedstock can be shaped to a given specification. The Fig. 2.12 treats the entire molding cycle. Changeover shows the screw speed control end till the cavity is full. Cavity pressure control is employed during packing and cooling. This stage is occurred after the changeover point (right side of the Fig. 2.12). Various defects can occur due to the values of screw speed or cavity pressure pathway [1].

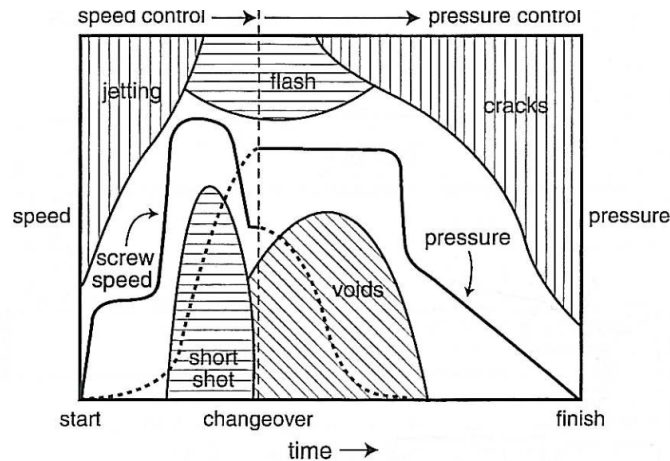


Figure 2.12 : Schematic diagram of the defects in molding and typical occurrence conditions in terms of the initial speed control and subsequent pressure control versus time [1].

Capillary rheometry is a useful method in characterizing the moldability. The viscosity is measured as a function of temperature and shear rate. Furthermore, zig-zag mold provides a quantitative basis for determining the suitability of PIM feedstock for molding complex shapes.

2.7.2 Molding Problems

2.7.2.1 Flashing

A slight interruption of molten feedstock between the moveable parts of the tooling is called flashing. The flash (in Fig. 2.13) is generally segregation of the binder since the intrusion space is small compared with the particle size. It can be avoided by tight tool fits and low packing pressures [1].



Figure 2.13 : Flashing due to over pressurization during mold filling [1].

High solids content raises the viscosity, requiring the pressure during molding. This high pressure alters the viscosity and contributes to flashing and separation of the binder from the powder. Furthermore, high nozzle temperatures cause flashing.

2.7.2.2 Jetting

Jetting involves filling too rapidly through a small gate, such that the high momentum of the feedstock causes plugging of the vent and trapped air. This high filling rate results from jetting additionally cause trapped air pockets, incomplete filling and many weld lines [1, 11]. To control jetting, a slow, progressive cavity filling process is needed [1]. The combination of high pressure, low viscosity and rapid die filling rates which lead to jetting should be avoided. However, too slow a speed, low pressure and temperature results in incomplete filling due to premature feedstock freezing which is called short shots. Intermediate temperatures and pressures provide good moldings. Fig. 2.14 illustrates the effects of small center gate and large side gate on filling stage.

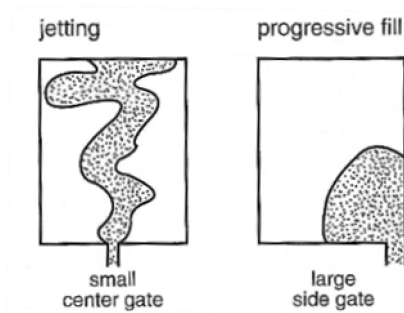


Figure 2.14 : Sketches of the fill patterns as a function of a gate size and position [1].

2.7.2.3 Sink marks

Incomplete packing will lead to cavities which is called sink marks on the compact surface. These cavities can be eliminated by ensuring sufficient packing pressure during the molding cycle with release of the packing pressure after the gate freezes. On the other hand, excessive packing pressure causes sticking problems in the die, resulting in severe ejection problems. Moreover, agglomerated powders contribute to uneven flow and subsequent cracks or other defects in the sintered compact [1, 11].

2.7.2.4 Weld lines

The feedstock splits and joints within the mold cavity can also cause another problem called weld lines. The weld line problem is another reason for a fast cavity fill, since hot feedstock better seals weld lines [1, 11].

2.7.2.5 Ventilation problem

At the beginning of molding, the die cavity is filled with air. As feedstock fills the cavity, this air is forced to escape through a vent at the end of the cavity opposite from the gate. If the vents are sealed, air becomes trapped in the component which causes voids at the edges of the part. The vents should be positioned at the highest point of the cavity or at a point filled late in the cycle. Relatively bigger vents can even cause flashing [1].

2.7.2.6 Ejector pin marks

As the molded feedstock cools down, it is ejected from the cavity. The force required for the ejection increases as the elastic modulus of the feedstock increase, contact area between the tooling and part increase and coefficient of friction and thermal contraction in the cavity increase. Ejector pins mark the component, since they

concentrate ejection force on a soft material. The damage is reduced by spreading the ejection force over a large area [1, 11].

Fig. 2.15 indicates the proper molding range depending on many parameters such as feedstock temperature, shear rate, screw speed, filling time and molding temperature.

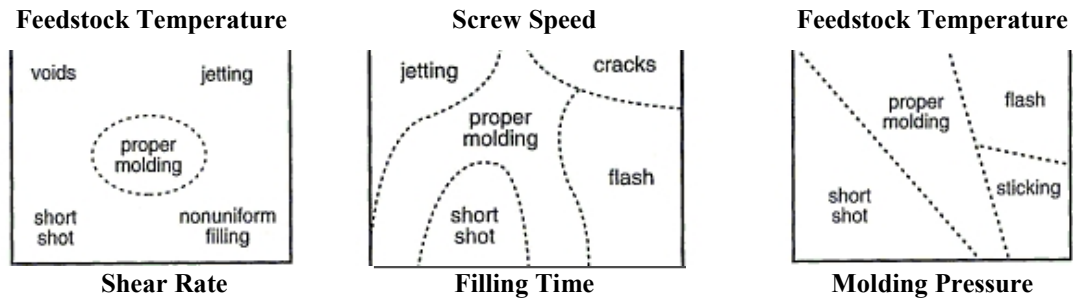


Figure 2.15 : Plots showing the regions where proper molding is applicable [1].

The molding temperature, pressure, material viscosity and molding shear rate have significant influences on successful molding due to their effects on viscosity. Besides, the pressure in the cavity is related to the component section thickness and the sprue and runner design. The best molding generally occurs when the temperature and shear rate are adjusted to give a feedstock viscosity less than 100 Pa.s. A large density difference between the powder and binder aids separation [1].

For molding easily, it is most desirable to have a bonder system with a low softening temperature, low viscosity, little viscosity variation at the molding conditions and high yield strength.

2.8 Debinding

The goal in debinding is to remove the binder in the shortest time with the least impact on the compact. When the binder is removed, until sintering the part becomes very fragile, therefore it must be strong enough to hold its shape [1].

Debinding is a key problem since the time for binder removal depends on the section thickness [1, 11]. Inappropriate debinding would result in component distortion, cracking and contamination. When the binder is heated, it becomes unable to withstand stress from gravity, temperature gradients or internal vapor pockets [1]. On the other hand, when the pores are partially open, capillary forces resist distortion as

the binder softens. Thus, stepwise binder removal is mandatory to hold the component in shape.

The alternative way to solvent debinding is to remove the binder by heat, either by degradation, evaporation, or liquid extraction using a contacting wick material. Using multiple component binder system is the key to rapid debinding. By this way, sufficient polymer remains after the first step to hold the particles in place. The backbone polymer holds the shape of the parts and provides strength during initial debinding till thermal debinding stage. If the backbone polymer content is high, then progressive damage of the pore structure at low temperatures becomes impossible [1, 11].

If the solids loading of the compact is less than the critical value particle migration and agglomeration exhibit during thermal debinding. In thermal debinding stage the compact is weak. Thus, capillary stresses generated by gradients in binder distribution are sufficient to cause warping or cracking. Slight differences in furnaces, geometries or molding conditions would tip the process into an uncontrolled situation with considerable variation.

Dimensional accuracy in PIM is measured by distortion and process repeatability. A dimensional standard deviation of 0.1% is possible and a standard deviation of 0.05% is held on many large and complex structures [1].

Subsequent to solvent extraction, the compact is dried to remove the solvent from the pores. The remained polymer is extracted by burnout which is the final stage debinding. The rate of burnout depends on the atmosphere and the temperature. In Fig. 2.16a, the graph shows the effect of various atmospheres in order to debind the Fe-2Ni feedstock. As the reducing character of the atmosphere increases, debinding occurs at lower temperatures and shifts away from CO and CO₂ products. On the Fig. 2.16b, defect formation during thermal debinding on the dependence of debinding temperature and heating rate is given.

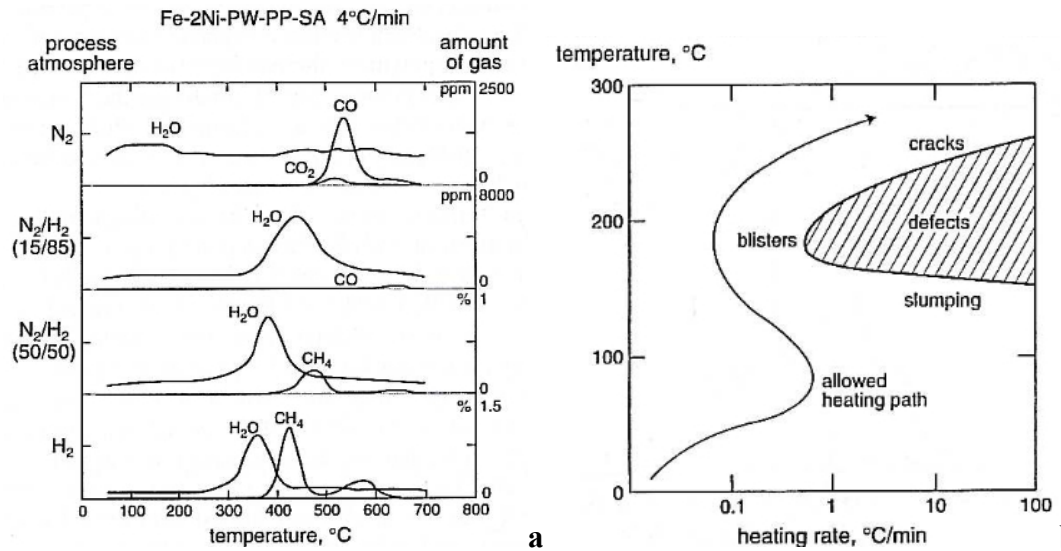


Figure 2.16 : (a) Process atmosphere effects on the debinding characteristics of Fe-2Ni with a paraffin wax, PE, SA binder. (b) Defect formation mapped for various combinations of heating rate and temperature [1].

Nitrogen gas is inert for many materials and provides control over carbon and oxygen levels not afforded by debinding under air atmosphere. It should be noted that rapid debinding causes surface defects and cracks during burnout [1].

3. SINTERING

Sintering is a processing technique used to produce dense materials by applying thermal energy [48]. In powder metallurgy (PM) practice on technique, sintering is an important stage which is a thermal treatment for bonding the particles into coherent, solid mass. During high temperature sintering, the pores are eliminated as part of particle bonding and consequently the component shrinks to a smaller dimension. As the sintering temperature increases, the atomic mobility and thus atom diffusion accelerates [1, 49].

During densification, the bonds between the particles grow by the motion of individual atoms via either solid-state or liquid-state events. Solid-state sintering occurs by the motion of atoms to form the particle bonds. Solid state sintering occurs when the powder compact is became wholly dense in a solid state at the sintering temperature, liquid phase sintering occurs when a liquid phase in the powder compact during sintering [48].

In eliminating the pores, mass flows along the particle surfaces (surface diffusion), across pore spaces (evaporation-condensation), along grain boundaries (grain boundary diffusion) and through the lattice interior (viscous flow or volume diffusion) as shown in Fig. 3.1. Furthermore, vacancies may migrate between pores, leading to the growth of larger pores while the smaller pores shrink [1]. For PIM parts, grain boundary diffusion is the main densification process where atoms move along the grain boundaries between near perfect crystal regions, creating a continual flow of mass into the pores. Grain boundaries are needed as vacancy sinks during pore elimination as part of sintering densification.

Following the debinding stage, the powder injection molded (PIM) components have generally 40% of the volume as open porosity (60% dense). Final density usually approaches 95 to 100% of theoretical. Therefore, such dimensional change can be a source of distortion. Shrinkage is inversely dependent on the green density [1].

Grain growth is a common difficulty during sintering, since grains enlarge and reduce the amount of desirable grain boundary area needed for sintering. The driving force of sintering is the reduction of the total interfacial energy. The main driving force for sintering is the lowering of free energy, which takes place when individual particles grow together, pores shrink and the high surface area of the compact decreases. The change in interfacial energy is due to densification and the change in interfacial area is due to grain coarsening [48].

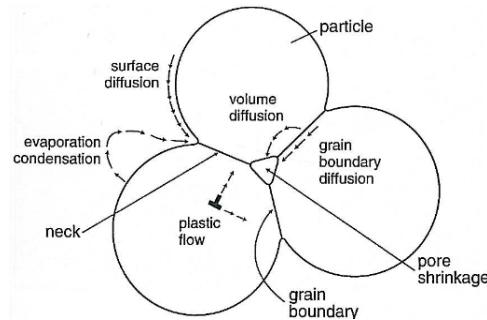


Figure 3.1 : The various transport possibilities are shown with three particles to indicate the possible mechanisms of sinter bonding [1].

At lower sintering temperatures, surface diffusion is often dominant, however it does not lead to full densification. Rapid heating can create a combination of pore size and grain size that leads to grain boundary breakaway from the pores resulting in diminished densification. Therefore, the microstructure can relatively be controlled by an optimum sintering cycle which consists rapid heating at low temperatures followed by slow heating in the intermediate temperatures (densification is active while grain growth is retarded) and with a final short-term high-temperature hold [1, 49].

Generally, liquid-phase sintering (LPS) produces a higher density and improved properties than those of solid-state sintered equivalents. LPS is a consolidation technique of powder compacts containing more than one component at a temperature above the solidus of the components and hence in the presence of a liquid [48]. Liquid phase helps in the densification of the compact. Liquids improve the mass transport rates leading to faster sintering [1, 48]. Liquid phases can be formed by melting one constituent or eutectic phase. Large amount of industrial PIM sintering is done in the presence of a liquid phase on account of cost and productivity

advantages. On the other hand, distortion is a common problem especially with high liquid contents [1, 49].

Grain boundaries play a vital role in sintering, since atomic transport is faster along these defective regions. Therefore sintering is enhanced by small grain sizes and small pores attached to the grain boundaries. Temperature and grain size provide more control over sintering as compared with extended times [1, 49]. The typical shrinkage value for the PIM materials is about 15%. Low green density regions undergo more shrinkage during sintering. On the other hand, isotropic green microstructures show uniform shrinkage. Moreover, temperature gradients in a furnace have a major effect on dimensional uniformity. Mechanical properties such as ductility, fracture strength, and fracture toughness are sensitive to sintered microstructure and final composition [1].

The sintering atmosphere is contained in the furnace to control reactions during sintering. Sintering atmospheres, such as, air, inert gas (Argon), hydrogen, hydrogen-nitrogen mixtures, and vacuum are used in PIM. In all of these atmospheres, the main concern is the concentration of reactive species. Inert gases are neutral and render little thermochemical interaction with the compact. Since inert gases are insoluble in the sintering material, gas filled pores do not close during sintering. Moreover, inert gases do not provide any reduction of oxides present in the compact. Hydrogen is the best reducing gas. However, moisture lowers the ability to reduce oxides and makes the atmosphere carburizing. Sintering in a vacuum at reduced pressure provides clean, reproducible and nonreactive environment. Besides, evaporation can be a problem leading to depletion of the higher vapor pressure elements. Introduction of a residual gas at high temperatures can minimize evaporation problem [1].

Oxides on the powder surface hinder sinter bonding and the development of properties. A reducing atmosphere provides protection from oxidation and reduces many oxides. For metallic structures, at high temperatures, a low dew point is desirable to provide both oxide reduction and carbon retention. The dew point must be selected to give oxide reduction and complete binder elimination.

Most frequent sources of problems in the sintering stage are associated with poor dimensional control or adverse reactions between the component and the sintering

atmosphere. Liquid-phase sintering systems are sensitive to temperature because low temperatures lead to residual porosity and high temperatures cause extended grain growth and component shape loss. Additionally, gravitational forces cause mostly distortion during sintering. A common cure for distortion is to use a slower heating cycle to induce more strength in the compact at low temperatures. Carbon control is also another important problem. An improper sintering atmosphere is a primary cause for this problem. Compositional changes also occur during cooling from the sintering temperature. Impurities segregate to interfaces resulting in embrittlement of the sintered material. Therefore, post sintering heat treatments are required by many materials [1].

3.1 Sintering of Permanent Magnets

Powder metallurgy (PM) is the most common method to produce magnets. In this process, a suitable ingot composition is pulverized into fine powder, compacted and densified via “liquid phase sintering”. Ferrites, SmCo and NdFeB magnets are all made by this method. Sintered NdFeB based magnets achieve their coercivity by virtue of an Nd-rich phase at the grain boundaries which acts to produce liquid phase sintering, smooth the boundaries and hence prevent nucleation of reverse magnetic domains.

Especially the high performance of sintered NdFeB magnets is obtained by the Nd-rich phase, which magnetically insulates the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and inhibits nucleation of reversed magnetic domains. Due to its low melting temperature, Nd-rich phase serves as a sintering aid [50].

Liquid phase sintering technique proved to be the key for the development of fully dense and stable SmCo_5 magnets, which became the first generation of rare earth magnets [51].

3.1.1 Detailed explanation of liquid-phase sintering

Metallic materials produced by pressureless sintering, such as hard metals, heavy metal alloys and permanent magnets, are all sintered in the presence of a liquid phase, which reflects the problems of sintering to a pore free material in the solid

state, but also indicate the ability to obtain dense materials by liquid phase sintering [52].

The microstructural development and the shrinkage during sintering in the presence of a liquid phase are governed by a number of basic principles. At sintering temperatures in all materials one or more phases are solid and at least one phase is liquid. After processing, the microstructure consists often of two solid (sometimes interpenetrating) networks.

Densification during liquid phase sintering (LPS) is based on rearrangement and shape change of the solid constituent particles as given in the schematic drawing in Fig. 3.2. In initial stage, the particles have pores in between and during heating the particles sinter. When a melt forms and spreads the solid grains rearrange. Subsequent densification is accompanied by coarsening. Pore annihilation as diffusion in the liquid accelerates grain shape changes that facilitate pore removal [53]. Figure 3.2 shows the stages of the LPS process [53].

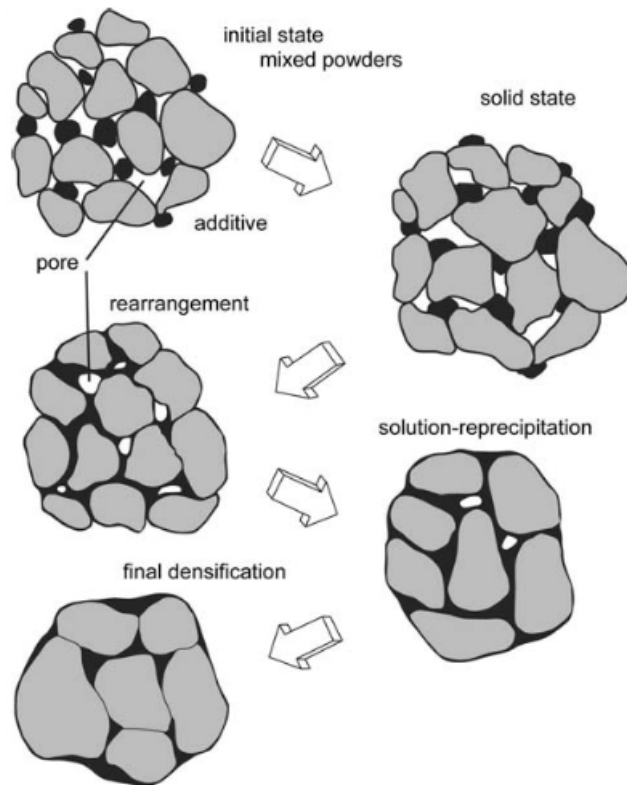


Figure 3.2 : Schematic view of the microstructure changes during LPS [53].

The driving force for both phenomena results from energy decreases caused by changes in the areas of the liquid/vapor, liquid/solid and solid/vapor interfaces during

rearrangement and/or shape change. Melt may originate from low melting point particles or areas which have built low melting point compositions by diffusion during heating [52, 54].

With good wetting, the liquid phase is pulled by capillary forces into particle necks and small pores. As a reaction to the capillary forces, solid particles are rearranged if their mobility allows it. This rearrangement of the solid particles is a necessary requirement for effective densification throughout the sintering process even during later sintering stages, when, for example, the rates of particle shape change also limit the rearrangement rate. Rearrangement may be primary or secondary [52, 54].

Shrinkage due to the shape change of the solid constituents always involves solution-reprecipitation processes, e.g., when during coarsening by diffusion controlled Ostwald ripening of the grains accommodates their shape to a changing environment. Major part of the shrinkage results from rearrangement when small particles are dissolved making way for the movement of larger particles [52].

Due to the effective shrinkage mechanisms, liquid phase sintering yields dense PM materials. Densification during liquid-phase sintering is based on rearrangement and shape change of the solid constituent particles [54]. Densification requires grain growth and rearrangement. Complete elimination of pores is thus limited to systems where either powder is fine initially or where large amounts of a suitable liquid phase are available. Typical examples of liquid phase sintered high performance materials are hard metals (e.g. WC-Co cutting tools) or hard magnets [52]. In Fig. 3.3, the microstructure of the liquid phase sintered NdFeB is given. In this image, the magnetic grains are indicated by line patterns (Kerr effect). The black areas are solidified eutectic melt (Nd-rich phase).

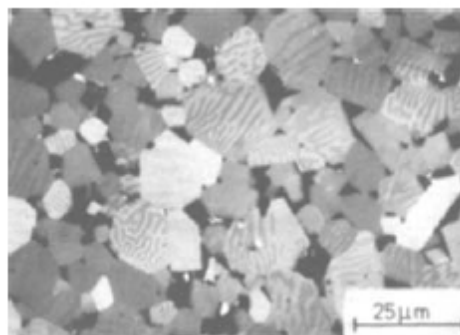


Figure 3.3 : Pore free microstructure of liquid phase sintered NdFeB [55].

In primary rearrangement, the rate is controlled by mechanical movements produced by capillary forces. In secondary rearrangement, the rate is controlled by dissolution and reprecipitation. Shrinkage resulting from the shape change of the solid constituents always involves dissolution – reprecipitation [54].

During liquid-phase sintering, the initial irregular or spherical shape of the single crystal grains becomes polyhedral [54]. Contact flattening is assumed to be a responsible mechanism for this shape change and the shrinkage that occurs during liquid-phase sintering. Contact flattening is dissolution – precipitation process which is driven by the high chemical potential of the solid matter in the contact area. A thin residual liquid film is assumed to exist between the particles. Under the assumption of local equilibrium, the solid phase dissolves at the contact region of two adjacent particles. In the liquid film, material is transported out of the contact area in a diffusion- or reaction-controlled manner and reprecipitated at the sites of the solid matter outside the contact region. The removal of material from the contact area leads to contact flattening. In contrast to the contact flattening theory, the shape accommodation theory assumes shape accommodation and shrinkage to be closely connected to grain growth [54].

Shrinkage is described as secondary rearrangement (controlled by a solution – precipitation process) which occurs when small particles dissolve, making way for the movement of larger particles. Grain growth during liquid phase sintering of PM materials determines their densification rate and their properties after processing [54].

The penetration of melt into grain boundaries is a further important dissolution– reprecipitation mechanism for liquid-phase sintering. Grain boundary penetration leads to skeleton disintegration, but also to contact dilatation, particle dilatation, and particle disintegration. Other important consequences are boundary alloying and liquid film migration. Dimensional changes during liquid-phase sintering due to grain boundary penetration are of commercial interest for structural parts. For example, in high-green-density compacts from iron and copper powder blends, copper-rich melt penetrates into the contact regions between adjacent iron particles and along grain boundaries [54]. Additional melt in prior contact areas and at prior

grain boundaries inside the iron particles causes contact and particle dilatation leading to macroscopic swelling [54].

3.1.1.1 Supersolidus liquid phase sintering

Traditional liquid phase sintering (LPS) relies on a mixture of two or more powders to form a liquid between the particles at the sintering temperature. For prealloyed powders, LPS creates a situation where liquid forms inside the particles. When prealloyed powders heated to a partially molten condition, high-diffusivity liquid provides rapid sintering densification. This process is called supersolidus liquid-phase sintering (SLPS), which is similar to viscous flow but involves a semisolid system [49]. The liquid forms within the particles, causing each particle to fragment into individual grains. Subsequent repacking of the fragments under the capillary force from the wetting liquid results in rapid densification [49].

Liquid within the grains has no effect on the densification process. Sinter bonds coated with liquid are evident at the contact points between particles, with little evidence of solid-state bonding between the particles. As the liquid volume fraction increases, it speeds up the densification but lowers dimensional control. Compared to solid-state sintering, the densification process, the SLPS is very sensitive to temperature. Prolonged high temperature dwellings cause density decrements or minor densification gain [49]. A prealloyed powder exhibits a high a rapid densification when it is heated slightly above the solidus temperature. Liquid is nucleated typically at grain boundaries or interdendritic spaces where the last solidification takes place. The liquid spreads on the grain boundaries causing particle disintegration. Solid-state sinter bonds are decomposed by this process. Densification is roughly proportional to the volume fraction of the liquid [49].

Vacuum sintering is usually best to avoid trapped gas in the pores during final densification. However, high sintering temperatures contribute to pore growth by Ostwald ripening, at shorter sintering times. Practically, high sintered density is favored by increases in the liquid-vapor surface energy, sintering time, sintering temperature, and liquidus-solidus separation. Selective alloying additions such as boron, silicon greatly improve the SLPS process if the addition segregates to grain boundaries forms a low-melting-temperature phase [49].

3.2 Sintering of Nd-Fe-B

The sintering of Nd-Fe-B (NdFeB) magnets is primarily determined by the liquid phase type of the sintering mechanism which involves the presence of a low melting, viscous Nd-rich eutectoid and secondly by the solid state type of sintering [56].

During sintering, the driving force for the densification of Nd-Fe-B magnets is the capillary pressure and the surface tension [56]. Both surface diffusion along grain boundaries and volume diffusion also play an important role during densification. Liquid phase sintering occurs most readily when the liquid thoroughly wets the solid particles at the sintering temperature. The liquid in the narrow channels between the particles results in substantial capillary pressure [56].

The particle size, sintering temperature and time, the uniformity of particle packing, the particle shape and the particle size distribution are extremely important parameters. Fine particle size powders can be sintered more rapidly and at lower temperature than coarser powders. If particle packing is not uniform in the pressed compact, it will be difficult to avoid porosity during sintering. Smaller particles exhibit a higher driving force for densification (higher capillary pressure and higher surface energy) than coarser particles [56].

The rate of liquid phase sintering is strongly affected by the sintering temperature. A small increase in temperature results in a substantial increase in the amount of liquid present, but on the other hand, this increase causes an excessive grain growth, which deteriorates the magnetic hardness [56].

Standard $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ magnets comprise three phases: 85 vol% $\text{Nd}_2\text{Fe}_{14}\text{B}$ (ferromagnetic), 3 vol% $\text{Nd}_1\text{Fe}_4\text{B}_4$ (non-ferromagnetic) and 12 vol% of Nd-rich (non-magnetic) phase [57]. Nd-rich phase is the eutectic phase having the $\text{Nd}_{95}\text{Fe}_5$ atomic formula [58].

A schematic drawing of the multiphase microstructure in Nd-Fe-B based sintered magnets revealed by transmission electron microscopy (TEM) is given in Fig. 3.4.

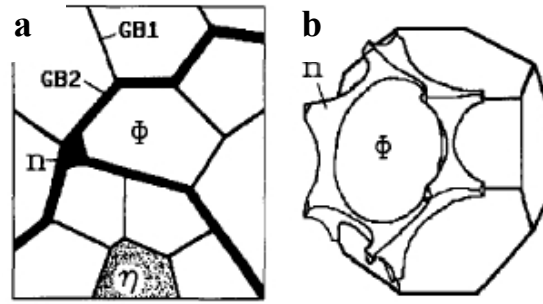


Figure 3.4 : Schematic drawing of (a) a typical multiphase microstructure of the NdFeB based sintered magnets revealed by TEM, (b) continuous network of the Nd-rich phase along the three grain junctions occurs if the dihedral angle exceeds 60° (Φ -phase: $\text{Nd}_2\text{Fe}_{14}\text{B}$, η -phase: $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ and η -phase: Nd-rich phase) [59].

In order to get a high amount of intergranular Nd-rich phases, a good wetting between η -phases and Φ -phases is favorable [59]. A high dihedral angle between the c-grains during the liquid phase sintering process restrains the liquid phase from penetration into the grain boundaries [59]. For a dihedral angle above 60° , the liquid becomes isolated at the triple points between grains and forms a continuous network along the three grain junctions (Fig. 3.4b) [59]. This is in good agreement with the analytical TEM investigations studied by Fidler et al [59].

The sintering of NdFeB magnets is assisted by a rare-earth rich, grain boundary phase, which is liquid well below the sintering temperature and wets the surface of the hard magnetic ($\text{Nd}_2\text{Fe}_{14}\text{B}$) matrix grains. As well as aiding densification, this phase plays an important role in smoothing and isolating grains to produce a microstructure conducive to good magnetic properties. Rare-earth hydrides were employed to vary the proportion and composition of the liquid phase during sintering [60].

Either liquid phase sintering of microcrystalline sintered NdFeB magnets and hot-compaction and deformation in nanocrystalline NdFeB magnets take place due to the existence of an intergrain Nd-rich phase that is liquid at working temperature ($T_{\text{sinter}} = 1080^\circ\text{C}$, $T_{\text{hot-working}} = 700^\circ\text{--}850^\circ\text{C}$) [61].

During deformation at a temperature of 1000°C , which significantly exceeds the melting point of the intergranular eutectic phase (the phase rich in neodymium), there is a very significant growth of grains of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [62]. A vertical section of the Nd-Fe-B phase diagram for a Nd : B ratio of 2 : 1 is given in Fig. 3.5.

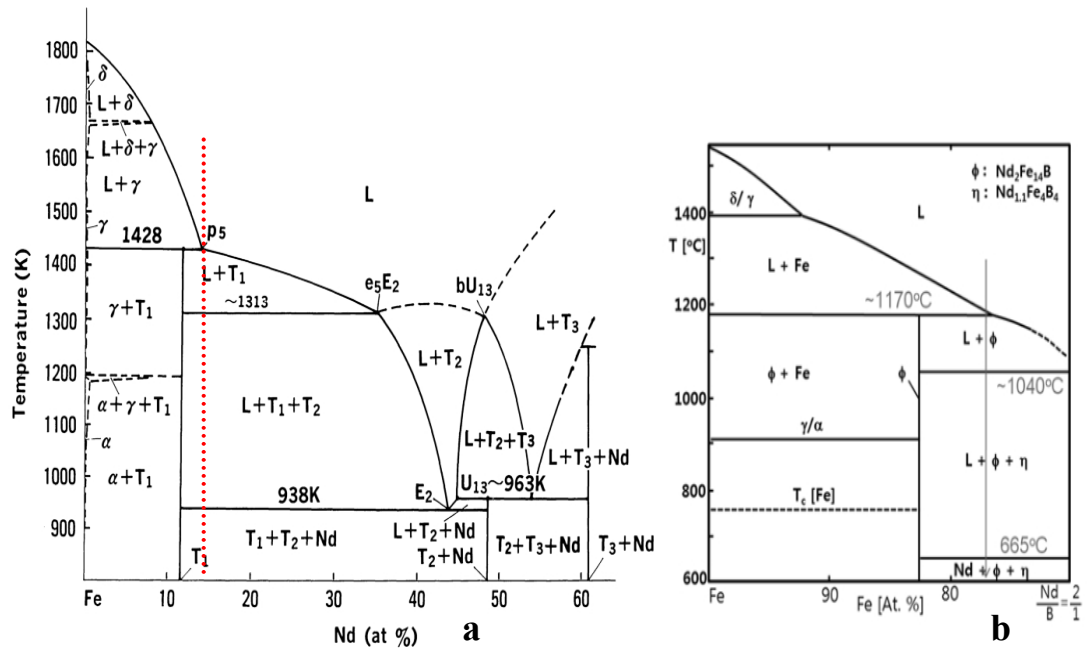


Figure 3.5 : (a) A vertical section of the Nd-Fe-B phase diagram for Nd : B = 2 : 1 (The T_1 phase is $\text{Nd}_2\text{Fe}_{14}\text{B}$, T_2 phase is $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$, T_3 phase is $\text{Nd}_2\text{Fe}_3\text{B}_4$), (b) with a different scale [63, 64].

The Nd-rich intergrain phase is vital in nanocomposite Nd-Fe-B (NdFeB) magnets for coercivity mechanism (pinning of the domain walls), deformation behavior (appearance of internal cracks in case of a non-homogeneous distribution) and also for texturing mechanism (through liquid phase diffusion and preferential orientation of the main $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains within the liquid Nd-rich intergranular region) [61].

A high volume ratio of intergrain phase reduces the magnetization directly through magnetic strength and indirectly, reducing the contribution of the short range exchange and long range dipolar coupling between the 2:14:1 grains. The hot-compaction and deformation in nanocomposite NdFeB magnets take place due to the existence of an intergrain Nd-rich phase that is liquid at the working temperatures. In addition, the texturing mechanism within these magnets is realized through liquid phase diffusion [61].

In the densification stage, Nd-rich liquid phase flows into the grain boundaries due to the capillary force between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases. The solubility and diffusivity decreases with decreasing sintering temperature according to Arrhenius relationship. Therefore, the sintering process at a low temperature suppresses the grain growth due

to the relatively low solubility and diffusivity of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in the Nd-rich liquid phase [67].

At sintering temperatures in the vicinity of 1100 °C, the volume of the liquid phase increases for higher B-contents due to the eutectic reaction between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and the $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ compounds [65]. Besides densification, the increased volume of the liquid phase probably also enables grain growth by a solution precipitation process. Besides the sintering temperature the grain growth kinetics depend on the volume of the liquid phase at sintering temperature [66].

Majima et al. [68] has shown that the boron content is an important parameter in determining the reactions by which Nd-Fe-B (NdFeB) will sinter. It has been concluded that, in alloys of composition $\text{Nd}_{15}\text{Fe}_{85-x}\text{B}_x$, there is a transition in how the liquid phase forms, which is related to the excess of B over stoichiometry. The phases and reactions can be clearly seen on the ternary phase diagram of the Nd-Fe-B system in Fig. 3.6.

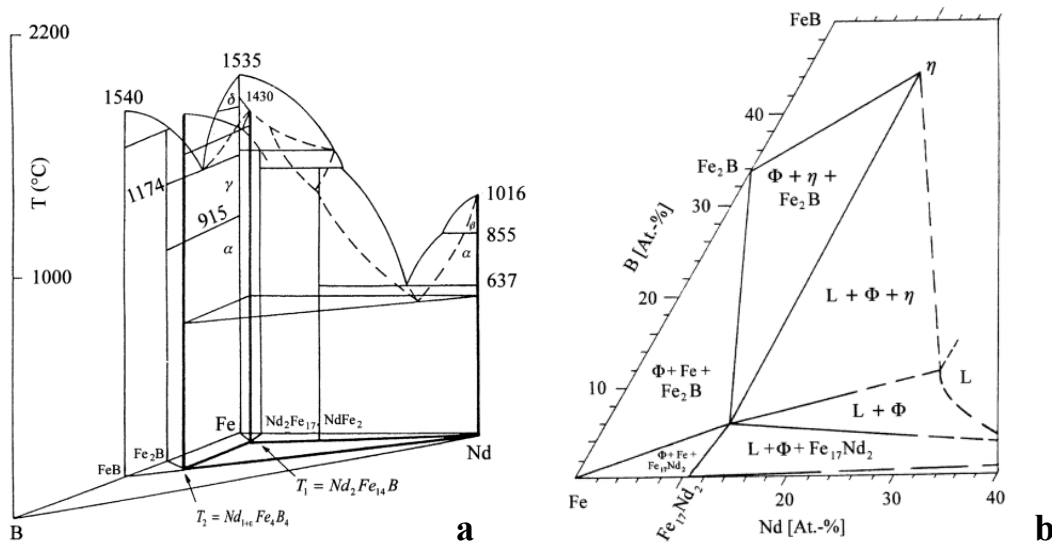


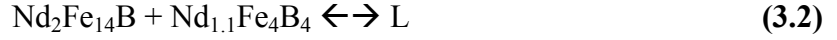
Figure 3.6 : (a) Ternary phase diagram of the Nd-Fe-B system [69], (b) Isothermal section of Nd-Fe-B at 1000 °C (The Φ phase is $\text{Nd}_2\text{Fe}_{14}\text{B}$, η phase is $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$) [70].

In the case of $x < 4$ at%, the $\text{Nd}_2\text{Fe}_{17}$ phase melts in a eutectic reaction with the Nd-rich phase at lower temperatures (690 °C), and then with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at elevated temperatures [60].

In the case where $x > 6$, as in the present study, initial liquid formation is attributed to the ternary eutectic reaction,



A second, binary eutectic reaction takes place at 1027 °C,



The formation of the liquid phase at 1027 °C is not a probable mechanism for the increase in sintering rate of $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ observed here. Initial densification is attributed to the formation of a liquid phase as the $(\text{Nd}_2\text{Fe}_{14}\text{B} + \text{Nd}_{1.1}\text{Fe}_4\text{B}_4 + \text{Nd-rich})$ eutectic melts at 655 °C [60].

Any subsequent eutectic reaction of $(\text{Nd}_2\text{Fe}_{14}\text{B} + \text{Nd}_{1.1}\text{Fe}_4\text{B}_4)$ would however, occur at too high a temperature to explain the observed increase in the rate of densification [60].

Harris et al. [60] mentioned that, this reaction sequence explain the sintering behavior seen as the rare-earth content was decreased. It was found out by Harries et al. that in the richer Nd samples, densification began below 700 °C and continued steadily to full density, with peaks in sintering rate noted at 750 °C and 980 °C. In the leaner Nd sample, there is not sufficient liquid formed by the initial reaction to promote densification at lower temperatures. Densification does however occur as the sintering temperature increases above 1027 °C; this corresponds to liquid formation through the $(\text{Nd}_2\text{Fe}_{14}\text{B} + \text{Nd}_{1.1}\text{Fe}_4\text{B}_4)$ reaction [60].

Consequently, the sintering behavior of $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ magnets has been shown to change between 800° and 900 °C. The densification of these magnets begins at 655 °C as the grain boundary eutectic melts, and increases linearly up to 800 °C. SEM analysis shows the change in microstructure as the distance between grains decreases and connectivity increases. At 900 °C an increase in the rate of densification is evident and, by 1100 °C, the density exceeds 98% of the theoretical maximum. This increase in rate at 900 °C is thought to be due to a change in the sintering mechanism [60].

Fracture surface micrographs show the initial stages to be dominated by neck growth with corresponding BSE images showing little redistribution of the Nd-rich liquid

phase [60]. This behavior suggests that the initial stage of sintering takes place in a limited number of activated sites. It is thought that the rapid increase in the rate of densification is due to a change in the nature of the liquid phase; there is effectively no liquid phase sintering until 900 °C at which point the liquid is able to wet the matrix grains leading to densification. This effect could be due to the formation of an oxide skin around the Nd particles at the powder processing stage. This would prevent the Nd-rich liquid from wetting matrix grains until the temperature is sufficiently high to allow liquid to become mobile. This leads to rapid rearrangement and, as grains begin to coalesce, solution/precipitation mechanisms complete the sintering process [60]. At relatively low sintering temperatures (~950 °C), the grain growth can be retained not only by the low solubility and diffusivity related to the solution and reprecipitation of the Nd₂Fe₁₄B, but also by the presence of the Nd_{1.1}Fe₄B₄ phase at the grain boundary junctions [67].

The Nd_{1.1}Fe₄B₄ phase commonly referred as the B-rich phase is formed at temperatures less than ~1000 °C according to the ternary phase diagram of the NdFeB system [67]. The Nd_{1.1}Fe₄B₄ phase cannot be affected by magnetic properties because it is a non-magnetic phase at room temperature. Nd_{1.1}Fe₄B₄ second phase particles at grain boundaries or triple junctions hinder grain growth during sintering process, a behavior referred to as the Zener effect [67]. These particles may act as pinning sites to suppress the grain growth. Pinning of the domain walls at grain boundaries (phases) is required to prevent complete reversal of the entire magnet from a single weak nucleation site [71]. Nucleation of the reverse domains and pinning can take place at various imperfections or inhomogeneities and this leads to lower values of coercivity [71].

Optimum heat treatment following sintering makes a smooth and sharp grain boundary. At such a boundary, nucleation of reversed domains is suppressed, even if they occur; the displacement of domain wall into the grain is hindered because of its steep gradient of domain wall energy [58]. It strongly increases the coercivity and improves the squareness of the demagnetizing J/H loops. Heat treatment (annealing) should be followed by fast quenching to optimize both the intrinsic coercivity and the loop squareness. With annealing, the systematic presence of the RE-rich phase film in the grain boundaries is obtained [72]. The morphology of the Nd-rich film/NdFeB

grain interface is the most important factor controlling the resistance to demagnetization [72].

3.2.1 The $\text{Nd}_{13}\text{Fe}_{80.5}\text{B}_{6.5}$ composition

Magnets of the composition $\text{Nd}_{13}\text{Fe}_{80.5}\text{B}_{6.5}$ reaches full density only when sintered above 1100 °C. Initial densification is suppressed due to the lower proportion of the Nd-rich eutectic phase, however significant densification takes place above 1027 °C due to the higher melting point of the $(\text{Nd}_2\text{Fe}_{14}\text{B} + \text{Nd}_{1.1}\text{Fe}_4\text{B}_4)$ eutectic. This behavior is demonstrated by a sharp peak in the rate of sintering centered at 1100 °C as shown in Fig. 3.7 [60].

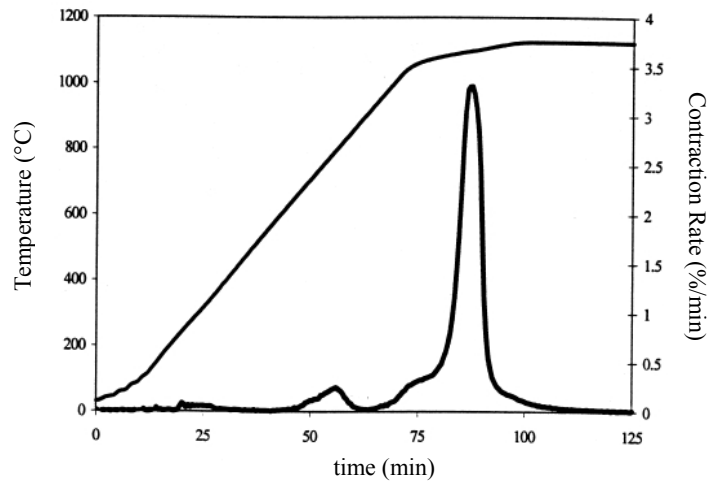


Figure 3.7 : Dilatometer sketch for $\text{Nd}_{13}\text{Fe}_{80.5}\text{B}_{6.5}$ [60].

Increasing the effective Nd content of these magnets to 15 at% by powder blending resulted in greater densification at lower temperatures (98% full density at 1060 °C determined from Fig.3.8a) [60].

The dilatometer curves for these magnets in Fig. 3.8b, show two peaks in sintering rate, at 750° and 980 °C. The first peak corresponds to initial rearrangement as the eutectic melts and solid state sintering begins.

The second peak does not however occur at a sufficiently high temperature to correspond to further eutectic melting and is thought to correspond to the proposed increase in mobility of the liquid phase above 900 °C [60].

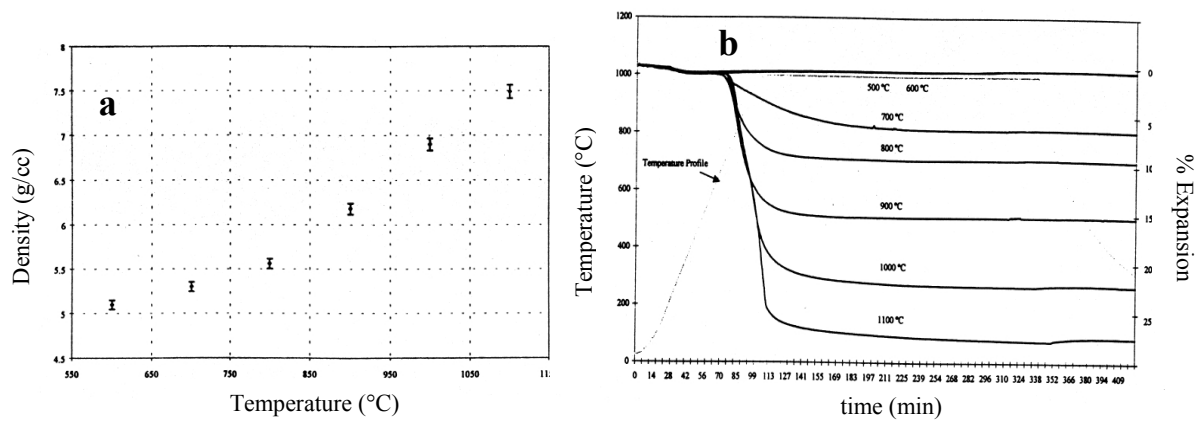


Figure 3.8 : (a) Density versus sintering temperature and (b) dilatometer curves for $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ [60].

3.2.2 The $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ composition

Sintered $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ magnets contain a multiphase microstructure. TEM observations reveal that the Nd-rich phase, which is an essential part of the liquid phase sintering process can be divided into at least 4 subtypes with different Nd : Fe - ratios [73].

During sintering, a liquid Nd-rich phase is formed in Nd-Fe-B compacts. The densification is probably due to the heavy alloy liquid phase sintering mechanisms and accelerated by the presence of vacant iron and boron lattice sites. Interdiffusion between phases and the capillary pressure is responsible for the movement and distribution of the liquid phase [73].

TEM studies reveal that Nd-rich phases formed during the sintering and post-sintering treatments [73]. Interdiffusion took place by lattice and surface diffusion processes especially near grain boundaries, whereby a high concentration of iron and boron vacancies is demanded. The nucleation of reversed domains primary determines the coercivity mechanism of the sintered Nd-Fe-B magnets. The expansion of reversed domain-nuclei is hindered by the existence of a continuous non-magnetic Nd-rich intergranular phase. The coercive force is proportional to the uniformity and completeness of the intergranular phase in the magnet [73].

Differential scanning calorimeter (DSC) analysis of the standard $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ sintered alloy is shown in Fig. 3.9a [74]. The first peak appeared at 312 °C representing the Curie temperature of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The second endothermic peak appeared at 677 °C which is the eutectic temperature between the Nd-rich phase (Nd metal) and

the matrix phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$). Above around 647 °C, the Nd-Fe-B ternary liquid is formed as a result of the eutectic reaction between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Nd metal [74].

The eutectic reaction between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Nd metal phases plays an important role for enhancing coercivity of the Nd-Fe-B permanent magnets. The eutectic reaction enables liquid phase sintering, which leads to densification of the alloy without significant grain growth [74].

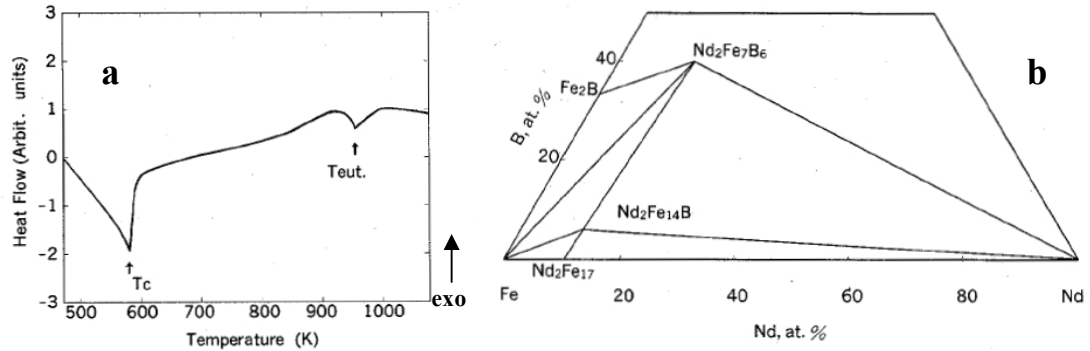


Figure 3.9 : (a) DSC analysis curve for sintered $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ alloy, (b) phase diagram of the NdFeB system below 647 °C [74].

For the post sintering heat treatment, the optimum temperature is just below the eutectic temperature and the coercive force decreases rapidly on heating above this temperature. Below the eutectic temperature, phase separation takes place [74]. It is considered therefore the enhancement of coercive force by post sintering heat treatment results from the removal of defects from the grain boundary areas concomitant with the phase separation [74].

Fig. 3.10 is a back-scattered electron (BSE) image of a typical sintered $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ magnet investigated by Harris et al. [60] showing a microstructure which is not ideal. The 2:14:1 matrix grains are seen to be irregular in shape and vary dramatically in size. The Nd-rich phase has to be more evenly distributed if it is to provide optimum grain isolation after sintering.

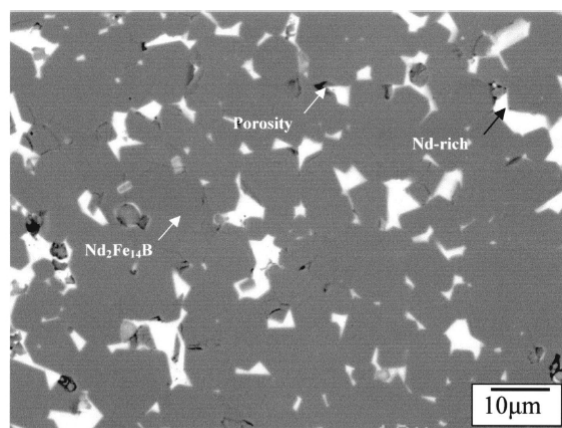


Figure 3.10 : BSE image of an Nd-Fe-B magnet [60].

The ternary alloy that forms the basis of many sintered NdFeB-type magnets is $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$. This is rich in Nd and B to facilitate sintering, however the large quantities of Nd-rich and $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ phases formed at this composition reduce the proportion of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase giving a lower remanence than the maximum theoretical value. Magnets can be produced using alloys with compositions close to stoichiometry but the processing becomes more difficult because of the reduced proportion of liquid phase and the risk of oxidation [60].

3.3 Sintering of Sm-Co

Cobalt and the congruently melting $\text{Sm}_2\text{Co}_{17}$ form a eutectic, while SmCo_5 is formed by a peritectic reaction between $\text{Sm}_2\text{Co}_{17}$ and the liquid phase which is seen in the Sm-Co binary phase diagram in Fig. 3.11 [75]. The SmCo_7 phase is also formed peritectically. Both SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ show a range of homogeneity at elevated temperatures [76].

SmCo_5 might be unstable below about 750-800 °C. SmCo_5 decomposes eutectoidally into SmCo_7 and $\text{Sm}_2\text{Co}_{17}$ [77, 78]. Martin & Smeggil [79] confirmed this by means of diffusion couples between Co and Sm. They analyzed the diffusion zones after annealing at 775 °C and between 820 °C and 1130 °C. At 775 °C, the SmCo_5 phase was absent, whereas at temperatures above 820 °C, Co, $\text{Sm}_2\text{Co}_{17}$, SmCo_5 , Sm_2Co_7 , SmCo_3 and SmCo_2 phases were all present [76]. Although Den Bröder et al. [77] and Buschow [78] detect the presence of Sm_2Co_7 and $\text{Sm}_2\text{Co}_{17}$ by metallographic

methods, they are unable to find any traces of Sm_2Co_7 by X-ray diffraction techniques [80].

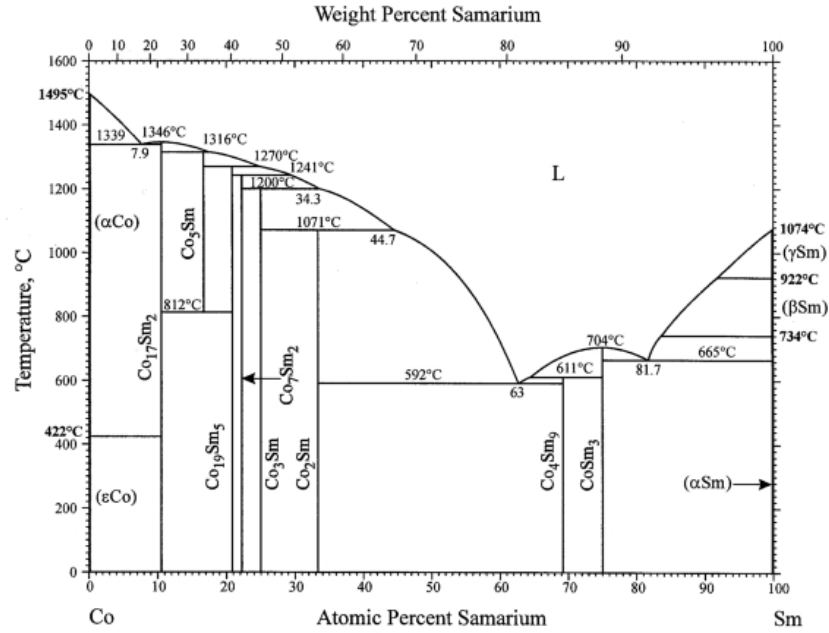


Figure 3.11 : The Sm-Co binary phase diagram [75].

The reaction $\text{SmCo}_5 \leftrightarrow \text{SmCo}_5 + \text{Sm}_2\text{Co}_{17}$ was found to be reversible between room temperature and 1150 °C. Above 1150 °C, Sm evaporates which may have been the reason for the non-reversibility of this reaction above 1150 °C. This reaction is in direct disagreement to the law of conservation of mass. Khan et al. [80] mentioned that characterizations reveal few additional weak X-ray diffraction lines which fit neither in the X-ray diffraction of the SmCo_5 of the CaZn_5 -type structure nor in that of $\text{Sm}_2\text{Co}_{17}$ and Sm_2Co_7 . On annealing SmCo_5 below 1150 °C, the phase SmCo_{5+x} , decomposes into SmCo_{5-x} and $\text{Sm}_2\text{Co}_{17}$ [80].

$\text{Sm}_2\text{Co}_{17}$ (2:17R) cells originate from nucleation and growth out of the 1:7 structure. This induces a related increase of Cu (according to Perry [81] the solubility of Cu in $\text{Sm}_2\text{Co}_{17}$ at 850 °C is only 4at.%) and Sm contents in the surrounding 1:7 matrix, that tends to 1:5 (SmCo_5) stoichiometry and forms the cell boundaries that have a thickness of 5 to 10 nm. The 1:7 and the 1:5 type structures are closely related to each other and have the same space group $\text{P6}/\text{mmm}$ [82]. TEM images given in Fig. 3.12 show the $\text{Sm}_2\text{Co}_{17}$ main phase, SmCo_5 cell boundary and the Z-phase [83].

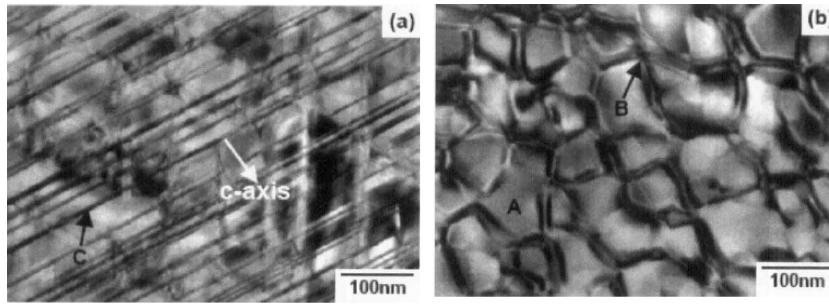


Figure 3.12 : TEM bright field images of sintered $\text{Sm}(\text{Co}_{0.784}\text{Fe}_{0.100}\text{Cu}_{0.088}\text{Zr}_{0.028})_{7.19}$ magnet with (a) nominal c-axis of $\text{Sm}_2\text{Co}_{17}$ main phase parallel, (b) perpendicular to imaging plane (A: $\text{Sm}_2\text{Co}_{17}$, B: SmCo_5 cell boundary and C: Z-Phase) [83].

The development of the specific form of the cellular precipitation structure is governed by the elastic energy due to lattice misfit of the SmCo_5 and the $\text{Sm}_2\text{Co}_{17}$ phases [84]. The cell interior (cell diameter of typically 100 nm) has the $\text{Sm}_2\text{Co}_{17}$ -type structure and shows boundaries of coherent twins in the basal plane [85]. The $\text{Sm}_2\text{Co}_{17}$ phase is the majority phase of the material. The SmCo_5 cell-boundary phase is coherent (or at least semi-coherent) with the cell interior [84]. Fig. 3.13 show BSE images of the sintered Sm-Co magnet, indicating the network of the SmCo_5 type cell-boundary phase, grain boundaries with Zr-rich regions [83].

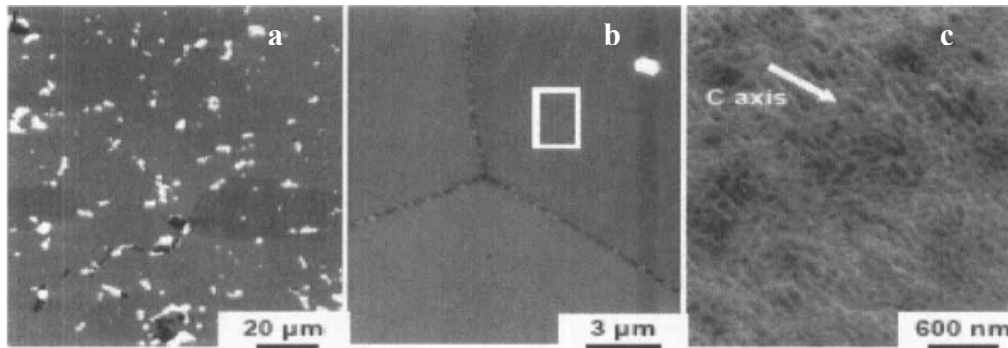


Figure 3.13 : BSE images of the sintered SmCo magnet. (a) Overview showing that average grain size is above 30 μm and that Sm rich precipitates can be found at the grain boundaries. (b) Grain boundaries with Zr-rich regions. (c) The image taken within the area indicated by frame in the middle image showing the network of SmCo_5 type cell-boundary phase and indications of lamellar phase (c-axis nearly parallel to imaging plane and perpendicular to lamellar phase) [83].

A so-called platelet phase (also referred to as lamellar or Z-phase) rich in Zr is observed additionally parallel to the $\text{Sm}_2\text{Co}_{17}$ (2:17R) basal plane. This Z-phase manifests itself as thin lines (1-3 nm) extending over many $\text{Sm}_2\text{Co}_{17}$ cells. On the

other hand, Fidler and Skalicky [85] found the 2:17H-type structure for the Z-phase, which is accepted by various authors. The Z-phase is considered to stabilize the cellular microstructure and, more importantly, to provide diffusion paths for Cu, Fe and Co, thereby modifying phase-ordering kinetics [86].

Permanent magnets fabricated from SmCo_5 alloy powders are today often produced by liquid-phase sintering. By this method, 25 MGOe (in 1978) maximum energy product can be attained in magnets and ensuring high thermal stability of their magnetic properties [87].

Sintering results in a transition from a two-phase $\text{SmCo}_5 + \text{SmCo}_2$ to a single-phase SmCo_5 structure. This phenomenon is due to the formation of samarium hydrides, oxides and also to partial vaporization of the samarium [87].

Raising the sintering temperature above 1130 °C led to pronounced samarium impoverishment of the boundary segregation zones of grains and precipitation of the compound $\text{Sm}_2\text{Co}_{17}$ at their boundaries. This was a consequence of increasingly rapid vaporization of samarium at grain boundaries [87].

The greatest distortion of texture is observed at the magnet surfaces, in regions of highest density of the material. The amount of the $\text{Sm}_2\text{Co}_{17}$ phase is a maximum at the magnet surfaces, while in the center of the magnet, this phase is absent. It would appear that the formation of the $\text{Sm}_2\text{Co}_{17}$ phase has a deleterious effect, because of the character of growth of its grains, on perfection of magnetocrystalline texture [87].

From the data obtained it follows that the presence of the samarium-rich compound SmCo_2 in liquid form not only compensates for the loss of samarium experienced during sintering and leads to relatively high magnet densities but also decreases texture distortion by bringing about the formation of epitaxial boundary regions hindering grain growth during sintering [87].

The liquid-phase sintered (LPS) permanent magnet material was fabricated by aligning a Sm-rich mixture of small particles in a strong magnetic field so that the c-axes of the crystallites are aligned approximately parallel to the applied field [88].

3.4 Sintering $\text{ZrO}_2 + \text{WC}$

Tetragonal ZrO_2 polycrystals (TZP) are usually doped with Y_2O_3 , CeO_2 , CaO or other oxides to stabilize the high temperature tetragonal phase at room temperature [27-29]. The transformation of tetragonal (t) to monoclinic (m) ZrO_2 phase contributes to excellent mechanical properties such as high fracture toughness and bending strength [26]. The phase changes due to increasing Y_2O_3 phase in ZrO_2 is shown on the $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ phase diagrams given in Fig 3.14.

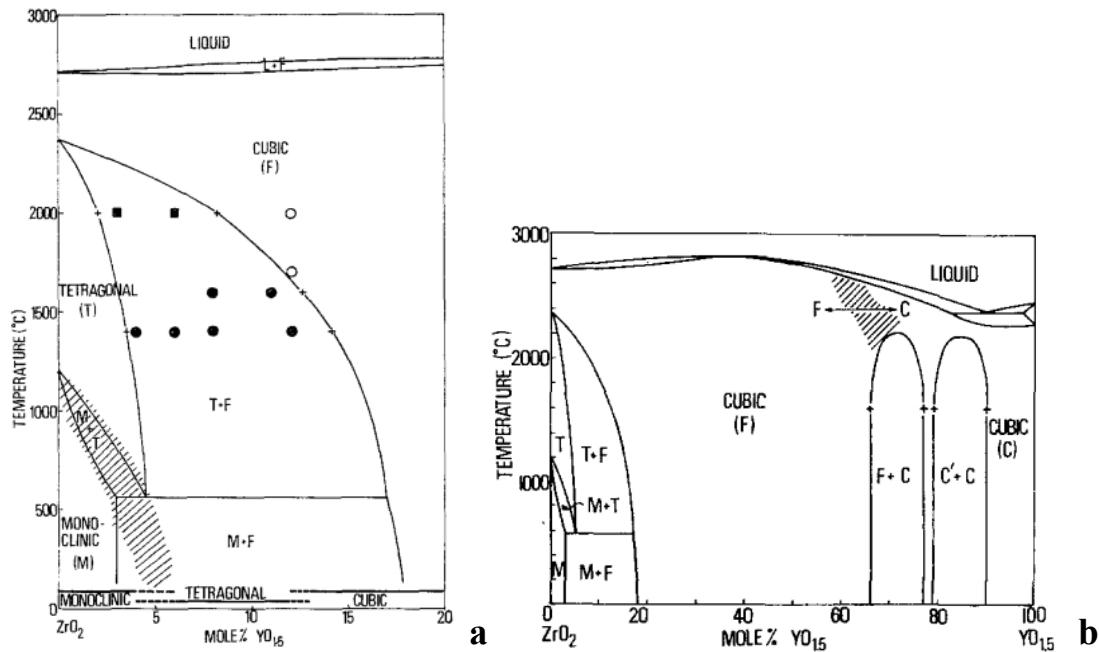


Figure 3.14 : Phase diagram for the zirconia rich portion of the zirconia-yttria ($\text{ZrO}_2 - \text{Y}_2\text{O}_3$) binary system. (a) Non-equilibrium homogeneous phases are indicated at lower margin. Phases found at room temperature are: monoclinic, tetragonal, cubic, monoclinic + tetragonal, monoclinic + cubic. Hatched region indicates non-equilibrium monoclinic-tetragonal transition; (b) Hatched region represents the apparently continuous fluorite-type C transition [89].

According to many authors, carbide or metal particles when introduced into TZP improved the mean values of hardness, stiffness, strength and fracture toughness [90]. The application of structural ZrO_2 ceramics can be broadened by the incorporation of hard carbide inclusions in the TZP matrix, such as in TZP-SiC [91, 92] TZP-TiC [93] and TZP-WC [17, 18, 29, 94-96] composites. Tetragonal zirconia ceramics show a relatively good reliability. Vleugels et al. [17, 19] have found out excellent combinations of hardness, fracture toughness and bending strength of hot

pressed ZrO₂–40 vol% WC composites, which may partially replace the traditional WC–Co cemented carbides for some specific applications. They mentioned, even though finer WC grades were difficult to densify by hot pressing, fracture toughness of the composites was generally higher than for monolithic ZrO₂ ceramics [26].

Vleugels et al. [26] sintered ZrO₂–WC composites by means of a very fast sintering technique, i.e. pulsed electric current sintering (PECS), which is also known as spark plasma sintering (SPS). The shrinkage started at 1050 °C upon increasing and rapid densification was achieved in the 1050–1450 °C range. Densification was nearly completed after dwelling for 1–2 min at 1450 °C under a pressure of 60MPa. Finally, all composites exhibited the same phase constitution, i.e. t-ZrO₂ + WC + m-ZrO₂ [26].

In monolithic TZP materials, the t- ZrO₂ to m- ZrO₂ phase transformation is a dominant toughening mechanism. The type and amount of stabilizers in ZrO₂ have a great impact on toughness. It can therefore be expected that the toughness of ZrO₂–WC composites can be manipulated by changing the type and amount of ZrO₂ stabilizers [26]. Both t-ZrO₂ grain size and stabilizer content can affect the transformability of t-ZrO₂ phase and the concomitant toughness [26].

In general, reduced stabilizer content leads to enhanced t-ZrO₂ phase transformability and related fracture toughness of Y–TZP ceramics, providing spontaneous transformation from t- ZrO₂ to m-ZrO₂ is not initiated during cooling. In ZrO₂–WC composites however, the high level of thermal residual stresses due to the coefficient of thermal expansion mismatch between the WC and ZrO₂ phases also contribute to the lower stability of the t-ZrO₂ phase in the composites [26].

All composites exhibit a much higher hardness than that of the monolithic ZrO₂, which can be explained by the harder WC inclusion, good coherence and chemical compatibility between WC and ZrO₂ components. The hardness however is strongly influenced by the WC source as well as the ZrO₂ matrix [26]. The t-ZrO₂ composites with low m-ZrO₂ content have a significantly higher hardness. The large amount of m-ZrO₂ in the other composites results in the formation of micro-cracks and a concomitantly lower hardness. The hardness of the ultra fine WC grained composites is slightly harder than that of the micrometer sized WC composite. The effect of the

m-ZrO₂ phase formation on the fracture toughness is not as significant as on the hardness [26].

Wear resistance depends mainly on densification. However, carbide inclusions restrain densification of the composites. Thus highest densities by pressureless sintering could be obtained with the smallest WC content (around 10vol %). High sintering temperatures causes extensive reaction between the components resulting in secondary porosity and formation of new phases. Due to the Zener effect, the carbide inclusions limit the zirconia matrix grain growth [27].

Due the crack deflection contribution of the secondary WC phase toughness is improved. Moreover, the size of the WC phase influences the composite toughness [26].

The flexural strength and hardness of the ZrO₂-WC composites is closely related. The composites with higher t-ZrO₂ content and higher transformability clearly exhibit a higher flexural strength and hardness than the lower t-ZrO₂ content composites with lower t-ZrO₂ transformability [26].

4. ZIRCONIA BASED COMPOSITES

4.1 Zirconia

Earlier than 1975, pure zirconia (ZrO_2 , zirconium dioxide) had very limited interest as a structural ceramic and its use was restricted to refractory applications (mp. 2680 °C) [97, 98]. Pure ZrO_2 exists in three different crystal structures (polymorphs), such as monoclinic, tetragonal and cubic [97].

At atmospheric pressure, ZrO_2 exists as a cubic structure above 2360 °C; below that temperature it is tetragonal. The tetragonal form is maintained to about 1200 °C, below which the transformation to the monoclinic structure begins. Below 1100 °C, the structure is entirely monoclinic [97]. This limit to application is attributable to the polymorphic tetragonal (t) to monoclinic (m) phase transformation, which occurs at around 950 °C on cooling in pure ZrO_2 and leads to a finite amount of volume change (4–5%) and a large shear strain (14–15%) [99]. The shape change in the transforming volume can result in catastrophic fracture, hence structural unreliability of fabricated components. However ZrO_2 has other intrinsic physical and chemical properties, including wear resistance, low coefficient of friction, elastic modulus, chemical inertness, ionic conductivity, electrical properties, low thermal conductivity and high melting temperature that make it attractive as an engineering material [97].

The most dramatic increase in its industrial applicability has been brought about by the discovery that the t→m transformation can be controlled by suitable material processing to become the source of transformation plasticity and transformation toughening in two-phase microstructures. t→m phase transformation in ZrO_2 can be used to enhance the strength and fracture toughness of materials of appropriate composition through careful microstructural control [98]. Polycrystalline ZrO_2 is generally grouped into three categories: a) partially stabilized zirconia (PSZ), b) tetragonal zirconia polycrystals (TZP) and c) zirconia-toughened materials [100].

Partially-stabilized zirconia (PSZ) is precipitation-toughened materials with enough of an additive in solid solution to partially stabilize the material in the cubic phase

such as Mg-PSZ and Ca-PSZ [100]. PSZ generally consist of a c-ZrO₂ matrix with a dispersion of tetragonal (t) precipitates. The goals are to form a uniform distribution of tetragonal precipitates within the grains to retain most of these in the tetragonal form at room temperature and to avoid large tetragonal precipitates at the grain boundaries [100].

PSZ is extremely strong at room temperature due to transformation strengthening. This occurs as a result of the transition from tetragonal structure to the monoclinic structure when the material is under stress. At high stresses, such as that at a crack tip, the material undergoes a phase transition. The phase transition has an associated increase in volume, this increase in volume that can then squeeze the crack shut. This prevents further crack growth. The phase transition also absorbs energy, increasing the amount of strain that the material can withstand resulting in a tougher ceramic material.

Zirconia-toughened materials are toughened with a dispersion of zirconia [100]. In order to obtain increase in toughness, dispersion of pure fine zirconia particles in polycrystalline alumina was invented. The change of bending strength of the yttria dispersed zirconia by adding alumina (Al₂O₃) is given in the Fig. 4.1 [101]. Strength and toughness follow quite different curves with the peak toughness being dependent on zirconia particle size. When the zirconia inclusions are above a critical particle size the fracture toughness is inversely proportional to the inclusion size and proportional to the volume fraction of the inclusions up to a maximum, above which the toughness falls with further increase in inclusion volume [100].

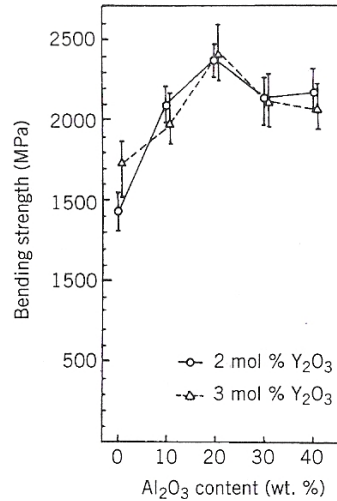


Figure 4.1 : Bending strength as a function of Al₂O₃ content in zirconia alloyed with yttria [101].

Tetragonal zirconia polycrystals (TZP) are ZrO₂ based ceramics where the matrix grains are stabilized generally to a single phase tetragonal form at room temperature. But in practice some amount of a second crystalline phase (generally cubic) may be present and some glassy grain boundary phase usually also exists [98, 100]. The most common forms are Y- or Y₂O₃- stabilized TZP. Yttrium-doped tetragonal zirconia polycrystals (Y-TZP) are generally added as Y₂O₃ in the range 2-3mol% to ZrO₂ or 7-8mol Y₂O₃ to ZrO₂ [98].

The t→m transformation in pure ZrO₂ (shown in the phase diagram in Fig. 4.2) commences at ~950 °C (M_s) on cooling and is reversible at ~1150 °C (A_s) on heating. Martensitic phase transformations have been identified in a range of ceramics considered as possible candidates for transformation toughening. In transformation toughening of ZrO₂ alloys, the strength and fracture toughness decrease with increasing temperature because the stability of the tetragonal phase increases and there is a decrease in the chemical driving force for the t→m transformation [98].

Polycrystalline TZP materials are generally fabricated from coprecipitated powders, i.e. ZrO₂ plus the alloying addition. Powders are in the size range 10-200 nm. Sintering temperature for Y-TZP is in the range of 1300 °C-1500 °C. The critical t-ZrO₂ grain size for stability within the fabricated body also depends on the solid content and the density of the fired compact.

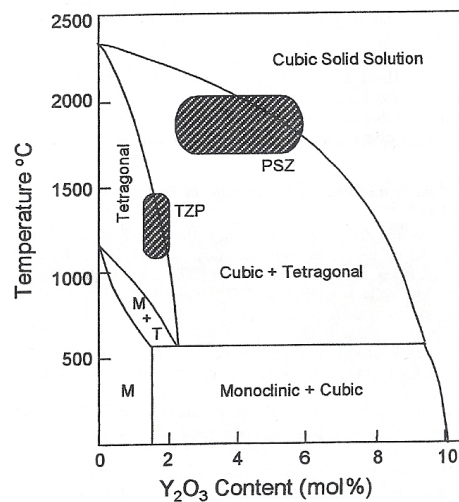


Figure 4.2 : ZrO_2 -rich sections of the ZrO_2 - Y_2O_3 phase diagram. Shaded areas indicate the compositions most commonly used for commercial engineering ceramics; arrows indicate the favored annealing or aging temperatures [98].

Early in the development of TZP ceramics, high densities were often difficult to achieve within a reasonable firing time because of the low sintering temperatures. To overcome low density problems, hot isostatic pressing (HIP) has become a favored technique to increase density without excessive grain growth [98]. By HIP'ing a combination of strength around 1400 MPa and toughness above $10 \text{ MPa}\cdot\text{m}^{1/2}$ is possible [100].

New powders having low amount of Al_2O_3 facilitate sintering and enabled densities higher than 98% of theoretical density to be achieved at 1400 °C, within a resultant grain size lower than 0.5 μm . Flexural strength changes of the Y-TZP as a function of yttria content is given in Fig. 4.3 for the parts which are sintered at 1400 °C by HIP and pressureless sintering [97].

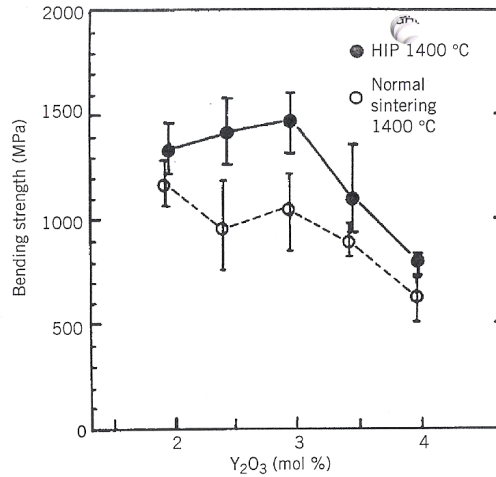


Figure 4.3 : Flexural strength of Y-TZP as a function of yttria content [97].

Green et al. [97] have prepared commercial Y-TZP materials in the composition range 1.75-3.5 mol% (3.5-8.7 wt%) Y₂O₃. Depending on composition, sintering time and temperature, the t-ZrO₂ content varies from 60% to 100% with the remaining phase being c-ZrO₂. In Fig. 4.4, the change in fracture toughness due to Y₂O₃ content indicates the effect of tetragonal or cubic ZrO₂ phase in the structure. As-sintered microstructures consist of uniform 0.5-2 μ m diameter equiaxed grains. A glassy grain boundary phase rich in SiO₂ and Y₂O₃ is almost always present in varying thickness depending on the method of manufacturing [98].

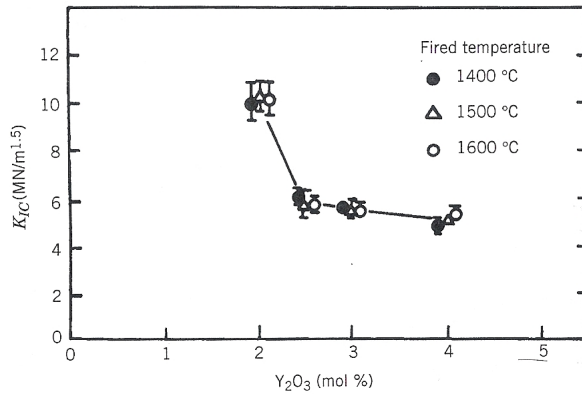


Figure 4.4 : Fracture toughness of Y-TZP as a function of yttria content [97].

With suitably fast cooling, the t' phase (so-called metastable, non-transformable tetragonal phase) can be achieved via a diffusionless, displacive c→t transformation and is generally considered to have a higher Y₂O₃ content than the equilibrium t phase [102]. The t' phase has not been observed to undergo the stress-induced t→m transformation [103].

To date, all such approaches to overcoming the surface sensitivity have generally resulted in an increase in the t-phase stability and a decreased in the desired mechanical properties. Additionally, higher t-phase solute content results in higher stability. Therefore, increasing the stability of the t phase continues to be the most favored approach [98].

At small particle sizes compared to the critical size (d_c), a very high critical stress is needed to overcome the constraint of the surrounding material thus toughening is small. As the particle size increases, the stress-induced transformation becomes easier and the toughness increases. The maximum toughness would occur if all the particles have a size just below d_c . For larger particle sizes, the transformation has been to some degree, spontaneous and the amount of t-ZrO₂ available for stress-induced transformation decreases [97].

Increasing the amount of t-ZrO₂ will increase the amount of toughening that is available, but it decreases the critical particle size [97]. The effect of particle size and volume fraction of zirconia on fracture toughness is given as a graph in Fig. 4.5 [97].

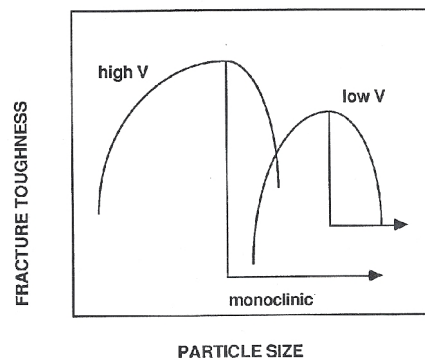


Figure 4.5 : Effect of particle size and volume fraction of zirconia on fracture toughness [97].

4.2 ZrO₂-WC Composite

Tetragonal zirconia polycrystalline (TZP) materials have excellent mechanical properties such as high bending strength and excellent fracture toughness, due to transformation toughening [17-19]. Although excellent toughness values could be achieved with an yttria-coated ZrO₂ starting powder, the increase in hardness aimed at by the addition of the hard secondary phases was rather modest.

The modest hardness property however limits their use in some advanced tribological applications. The addition of a secondary hard phase could increase the hardness, while maintaining the high toughness due to transformation toughening and crack deflection. The ZrO_2 –WC composites are substantially harder and stronger than the fine-grained Y-TZP, whereas the excellent toughness of Y-TZP is maintained. The hardness and bending strength of the composites increases, whereas the toughness hardly changes with increasing WC content. The ZrO_2 –WC composites were found to slightly plastically deform before fracturing during bending [17, 19].

WC has excellent high temperature strength and good corrosion resistance, being chemically and thermally stable even at high temperatures. WC is one of the hardest, stiffest material that posses high values of Young's modulus [104]. Thus, homogeneous distribution of WC hard carbide particles is expected to be a good method for increasing hardness and stiffness of the tetragonal zirconia polycrystals. Additionally, the presence of inclusions causes new toughening mechanisms to operate [17]. It leads to the higher fracture toughness than that of zirconia matrix. The hardness, strength as well as fracture toughness of the ultrafine grained composites with a nanosized WC source was significantly higher than with micron-sized WC [17].

It is well known that by means of milling, nanocrystalline composite powders can be produced and the component elements can be homogeneously distributed. Therefore, milling can be used to get nanocrystalline powders which will be used as reinforcement in composites [104]. The incorporation of hard carbide particles is a good method for increasing hardness and stiffness of the tetragonal zirconia polycrystals. Additionally, the presence of inclusions causes new toughening mechanisms to operate. It leads to higher fracture toughness values than that of zirconia matrix. The WC inclusion will increase the toughness by crack deflection, crack bridging and crack branching toughening effects, caused by these mechanisms, depend on the particle size and particle volume fraction [18, 20]. These two factors will also influence the grain growth kinetics of the matrix material and change their transformation ability [18].

According to some previous research investigations, ZrO_2/WC composites are generally produced by using hot pressing technique [17-19, 23, 28, 29]. However, this method does not provide to produce complex shaped materials. By using ceramic injection molding method, ceramic components of complexity, precision of micron-size would be achieved.

4.2.1 Powder preparation

In the processing of ceramic materials, very small grain sizes generally increase the surface to volume ratio of the particulate and promote sintering through increased diffusion. Mechanical milling is known to decrease grain sizes to the level of some tens of nanometers, and therefore it is potentially useful in the processing of nano-sized powders [104, 105]. The milling balls are normally of the same material of the vial [105]. Commercially available high energy milling media include carbide-based materials such as WC, as a consequence, the powder is milled to avoid cross contamination. However, by high energy milling process only small amount of powders can be obtained in one operation which is not suitable for industrial applications. Therefore, it would be feasible to mix milled nano-sized powders with un-milled micro-sized powders. In addition, it has been reported that a proper combination of large and small reinforcement particles result in higher wear resistance than a mono-sized particle reinforced composite [30]. In this manner, the mechanical properties of WC reinforced ZrO_2 composites will be improved.

An idea is to use WC powders which are blended with non-milled WC powders and disperse it into the ZrO_2 matrix. It has been reported that a proper combination of large and small reinforcement particles result in higher wear resistance than a mono-size particle reinforced composite [30]. The wear loss decreased when the volume fraction of large reinforcement particles increased. The larger particles mainly withstand the wearing force and the small dispersed particles preferentially strengthen the matrix so that it would be more difficult for the abrasive to abrade the relatively softer matrix. Since the average mechanical properties of the matrix can be adjusted by adding small dispersed particles, an optimal balance between the overall hardness and ductility could be achieved, thus resulting in superior tribological properties [30]. The view of the computer modeling of the composites with different reinforcement sizes is given in the Fig. 4.6 [30].

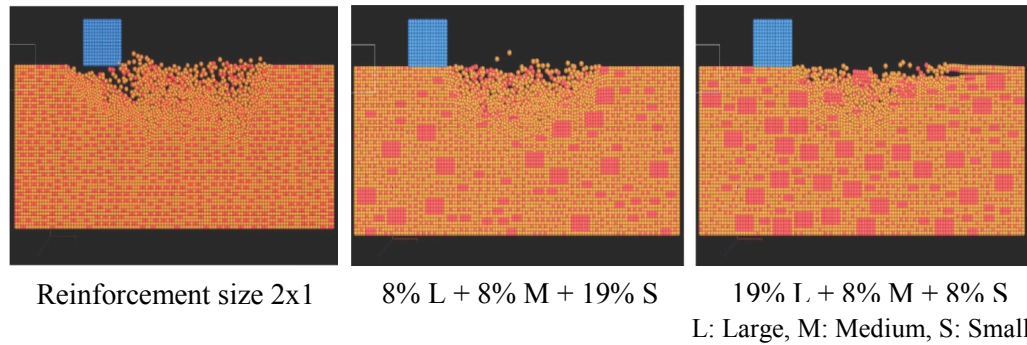


Figure 4.6 : The effect of the reinforcement size distribution on wear: Cross-sectional view of worn surfaces [30].

4.2.2 Feasibility

Injection molding of ceramics (CIM) is considered as a promising shaping technique. According to pertinent reports, the production of Y-TZP CIM parts appears to be feasible [42]. Ceramic parts often need expensive diamond machining after sintering in order to obtain required dimensional tolerance and surface finish. CIM becomes increasingly attractive because it offers a reliable production method to achieve near-net-shape components, which in turn, reduce post-sintering machining [106]. Considerable saving is possible since the machining cost would normally represent 30% to more than 50% of the overall product cost [106]. With good process control close tolerances can be obtained, therefore machining of the part after sintering is usually not necessary [42]. The cost comparison of CIM, rapid prototyped and machined parts is given in Fig. 4.7 [42].

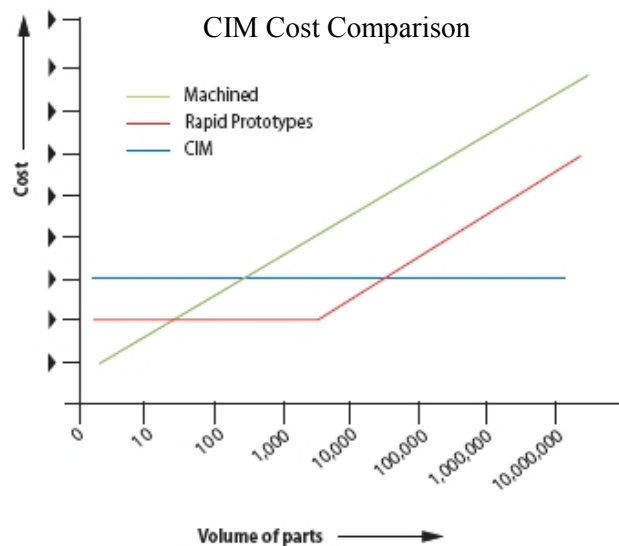


Figure 4.7 : CIM cost comparison with machined and rapid prototypes [42].

Considering that time and quality level are directly related to industrial costs, the optimization of debinding in CIM process can improve the production rate of compact ceramic parts, and minimize the defect that can be produced in the subsequent process steps. Therefore debinding step is important and many studies were carried out to improve this process step [8, 107-111]. Following debinding, sintering process is a significant step for regulating process costs.

4.2.3 Application areas

The 3 mol% yttria stabilized zirconia (Y-TZP) is well recognized for its high fracture toughness and it has been widely used in industry as a structural ceramic [112]. It has become an important advanced ceramic due to its high toughness, high thermal stability and other superior properties. For future industry applications, ceramic injection molding is adopted and sacrificing one of the most important factors: high green density. CIM of nano-sized Y-TZP powders hence offer attractive potential applications [112].

Ceramics, particularly ZrO_2 , are becoming increasingly popular with the dental industry as manufacturers look for ways to improve implant design and production. It has two key advantages. One is the better color match that ceramic provides, titanium abutments make the tooth prostheses appear unnaturally dark. The second is the inherent biocompatibility of the material, which gives improved soft tissue management after implantation [42]. Along with the superior strength, high resistance to wear and corrosion make Zirconia - CIM technology an ideal choice for demanding applications. Y-TZP is the material used in the manufacture of dental abutments and copings by CIM technique [42]. Fig. 4.8 is a picture of a ZrO_2 dental coping produced by CIM technique [42].

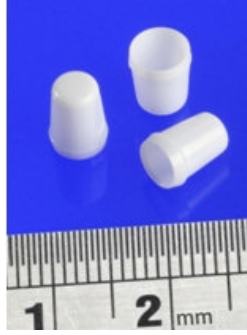


Figure 4.8 : Example of Zirconia dental coping manufactured using CIM [42].

In addition, injection molding is one of the interesting processing techniques for making fine ceramics in the past two decades. These ceramics, including Al_2O_3 , ZrO_2 , and Si_3N_4 , are fabricated by this technique for performance applications, such as ceramic turbines or ferrules [113].

Consequently, due to their high strength and toughness of ZrO_2 and ZrO_2 -based composites are very promising materials for ceramic machine components. Although ZrO_2/WC composites were produced by hot pressing up to now, ceramic injection molding technique (CIM) will facilitate producing high volume of complex shaped-parts in a unit time without extra machining which will lower the production costs.

5. PERMANENT MAGNETS

5.1 Magnetism

Solids which are magnetically ordered have atomic moments due to unpaired electrons. The atomic moments are coupled by exchange interactions that can give a net magnetization at all temperatures below the Curie temperature. Magnetization creates a magnetic field which is itself a non-linear and irreversible function of an externally applied field, illustrated on hysteresis loop. Hysteresis depends both on the microstructure of the material and its magnetic anisotropy [35].

5.2 Magnetization and magnetic fields

Magnetism is a property of materials that respond to an applied magnetic field. Permanent magnets have constant magnetic fields caused by ferromagnetism. That is the strongest type of magnetism. However, all materials are influenced differently by the presence of a magnetic field. Magnetic dipole moment is the key of the solid-state magnetism. The dipole moment of a magnet is the sum of the dipole moments of all its constituent electrons which are the elementary magnets in solids. The magnetic moment per unit volume is the magnetization, M . Magnetic field H created in free space by a magnet or by an electric current [35].

The relationship between the locally varying quantities M and H , known as the magnetic equation of state, is nonlinear, multivalued and depended on the size, shape and history of the magnet. The function $M(H)$ is known as the hysteresis loop and it is characterized by its intercepts M_r (remanence) and H_c (coercivity) [35]. Magnetic field (H') is expressed as the sum of the externally applied magnetic field (H) and the demagnetizing field (H_{dm}), as given in below equation:

$$H' = H + H_{dm} \quad (5.1)$$

$$\text{Flux density (induction), } B, \text{ is defined by } B = \mu_0 (H' + M) \quad (5.2)$$

μ_0 ($4\pi \times 10^{-7} \text{ N.A}^{-2}$) is the permeability of free space which is involved whenever externally magnetic field (H) interacts to exert a force on a magnet [35].

5.2.1 Dipolar fields and domain formation

As the magnetized material subject to no externally applied field, magnetic field (H') will be equal to demagnetizing field (H_{dm}). In Fig. 5.1, it is shown that magnetic field (H') produced by the magnet is oppositely directed to M in the volume of the magnet. Therefore the magnet produces its own demagnetizing field [35].

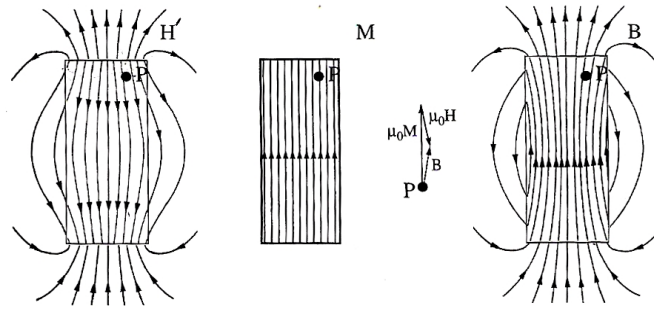


Figure 5.1 : Magnetic field (H') and flux density B due to a uniformly-magnetized bar-shaped permanent magnet of magnetization M [35].

As a consequence, the uniformly magnetized state of macroscopic magnets is at best metastable. Lower-energy states exist where the magnetization is broken up into domains magnetized in different directions so that the solid as a whole has no net magnetization. In a macroscopic state the magnetization over a scale which is large compared with the domain size, M is regarded as the average magnetization of the sample rather than the local magnetization in a domain. The magnetization shown in Fig. 5.2 in the M(H') hysteresis loop is a domain average [35].

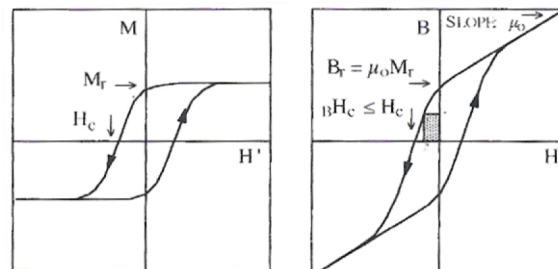


Figure 5.2 : Typical hysteresis loops for a permanent magnet. The M(H) and B(H) loops are obtained after saturating the magnetization. The shaded area indicates the max energy product $(BH)_{max}$ [35].

Spontaneous magnetization of iron is greater than any of the commercial magnet however the demagnetizing field makes it impossible to retain fully magnetized state which usually breaks up into domains [35]. General situations of the magnetization states are given in the sketches in Fig. 5.3 [35].

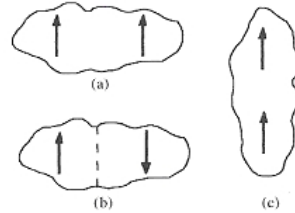


Figure 5.3 : Sketches of homogeneous and inhomogeneous magnetization states, (a) is magnetostatically much less favorable than multidomain configuration, (b) and would have to be maintained by strong uniaxial anisotropy. The prorated configuration (c) is comparatively stable and needs less anisotropy to remain permanently magnetized [35].

5.3 Atomic Scale Magnetism

The atomic scale magnetism is a quantum-mechanical phenomenon whereas the microstructural dependence of magnetic properties involves macroscopic phenomena such as magnetostatic interactions. Intrinsic magnetic properties refer to atomic scale magnetism and depend on crystal structure. On the other hand, extrinsic magnetic properties depend on microstructure. The main intrinsic properties are the magnetic moment, Curie temperature and magnetocrystalline anisotropy [35].

5.3.1 Magnetic order

In addition to the existence of a moment at the atomic level, permanent magnetism requires a macroscopic alignment of atomic moments. Ferromagnets such as iron are characterized by atomic moments pointing everywhere in the same direction in a crystal, whereas ferrimagnets, including many oxides and intermetallic compounds exhibit two magnetic sublattices with unequal and opposite sublattice magnetizations. When the sublattice magnetizations are equal, the material has no net magnetization and it is called antiferromagnet [35]. The position of the atomic moments in ferromagnetic, ferrimagnetic and antiferromagnet materials is given in the schematical sketch in Fig. 5.4 [35]. Above the Curie temperature, the material is paramagnetic, and usually exhibiting well developed but randomly oriented and fluctuating atomic moments [35].

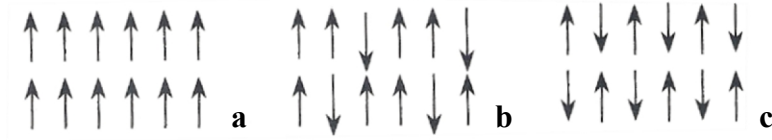


Figure 5.4 : Illustration of (a) ferromagnetic, (b) ferrimagnetic and (c) antiferromagnet order in a solid. The arrows represent atomic moments [35].

5.3.2 Anisotropy

There are several mechanisms contributing to the anisotropy of permanent magnets. It is important to differentiate the macroscopic shape anisotropy in small spherical particles and the magnetocrystalline anisotropy, which is an intrinsic lattice property. The shape anisotropy and a part of the magnetocrystalline anisotropy are two-ion anisotropies caused by magnetostatic dipole interactions [35]. However the large anisotropy of modern permanent magnets such as SmCo_5 and $\text{Nd}_2\text{Fe}_{14}\text{B}$ is due to the crystal field or magneto-electric contribution to the magnetocrystalline anisotropy. As opposed to shape and dipolar anisotropy, magneto-electric anisotropy may exceed typical magnetostatic energies by an order of magnitude which enables to exploit the full saturation magnetization of ferromagnetic materials for permanent magnet applications [35].

The magneto-electric anisotropy mechanism involves electrostatic crystal-field interactions and spin-orbit coupling and is also known as single-ion anisotropy. This mechanism is closely related to the magneto-elastic anisotropy which can be important in cubic and polycrystalline magnets [35]. The shape anisotropy, showing schematically easy and hard direction is given in Fig. 5.5.

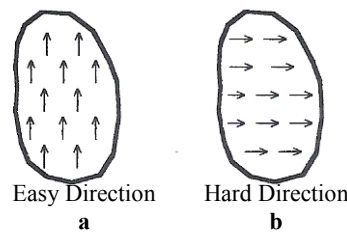


Figure 5.5 : Schematic shape anisotropy. The magnetostatic energy of configuration (b) is higher than that of configuration (a). Shape anisotropy is restricted to small particles, where the inter-atomic exchange ensures a uniform magnetization [35].

Magnetic anisotropy tends to fix the magnetization in well defined directions. In the simplest case, uniaxial anisotropy prefers alignment of the magnetization along an easy axis. Conventionally, the easy axis is denoted by the index "z" and it may match with the c-axis in hexagonal, tetragonal and rhombohedral crystals or the long axis of and acicular particle [35].

The intrinsic properties of a magnetic material may change completely when one element is replaced by a chemically similar one. For instance, $\text{Nd}_2\text{Fe}_{14}\text{B}$ is used to make excellent permanent magnets, whereas $\text{Sm}_2\text{Fe}_{14}\text{B}$ is useless for this purpose because of its easy-plane anisotropy [35].

Uniaxial anisotropy of a single domain particle is assumed to have neither magnetocrystalline anisotropy nor particle shape anisotropy. Stoner-Wohlfarth theory indicated that the coercivity of a system of single-domain particles was proportional to the coercivity [114, 115].

Domain-wall motion is much more difficult to describe theoretical than is domain rotation. Domain-wall mechanisms are probably the dominant factor in permanent magnet materials such as SmCo and NdFeB [116]. Some authors have argued that the high coercivity is due to difficulty in nucleating domains after the material has been magnetized to near saturation [117]. Others suggest that the high coercivity is due principally to domain-wall pinning [118]. Current evidence seems to favor the strong pinning mechanism [119].

In the context of permanent magnetism, the following basic coercivity mechanisms are of particular importance [35]:

- a. coherent rotation in aligned fine particles,
- b. magnetization curling in homogeneous single-domain particles,
- c. incoherent nucleation in slightly inhomogeneous magnets,
- d. domain wall pinning in strongly inhomogeneous magnets,
- e. localized rotation in isotropic nanostructures.

The first three mechanisms produce nucleation-controlled coercivities that are the formation of reversed domains inhibited by nucleation fields. By comparison, pinning coercivity means that reverse domains, once nucleated, do not immediately grow because the domain walls are unable to move.

The difference between nucleation-controlled and pinning controlled coercivities is illustrated in Fig. 5.6 [35]. Examples of nucleation type magnets are SmCo_5 and $\text{Nd}_2\text{Fe}_{14}\text{B}$. The second type of magnet in which the domain walls are pinned inside the grains is known as the pinning type. In these magnets, the domain walls encounter the same type of pins during the initial magnetizing process as they do during the demagnetizing process [71]. An example of this type is the precipitation hardened $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_7$ magnet [71].

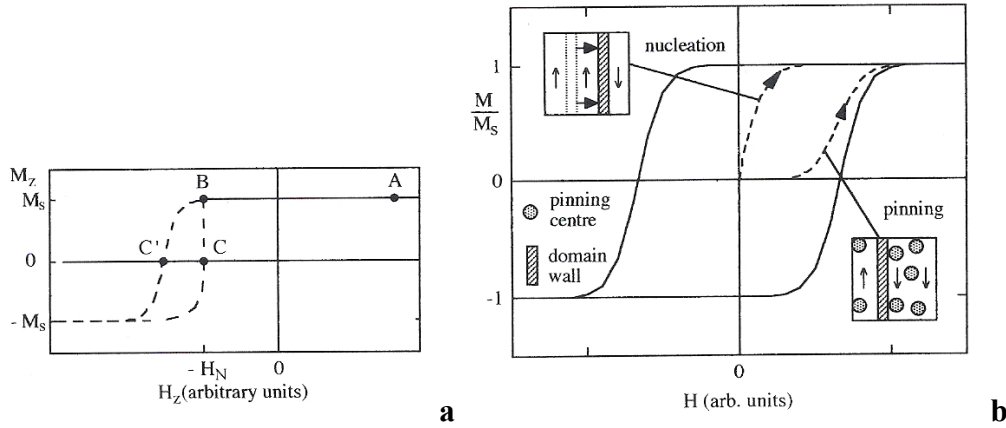


Figure 5.6 : (a) Nucleation and magnetic reversal, (b) Virgin curves for pinning-controlled and nucleation-controlled permanent magnets [35].

In Fig. 5.6a, the second quadrant of the major loop is given. Starting from the completely aligned magnetization (A), a reverse field gives rise to nucleation (B). The nucleation field establishes a lower bound to the coercivity (C), but due to domain-wall pinning the coercivity is more often higher than H_N (C'). On the other hand, the grain misalignment reduces the magnetization at which nucleation occurs, so that nucleation and pinning are more difficult to separate in isotropic magnets [35].

There are two main experimental methods used to distinguish between pinning and nucleation. These mechanisms are indicated as a schematical particle shown in Fig. 5.7. First, microscopy can be used to investigate the microstructure and to monitor domain wall propagation. Second, virgin curves (initial curves) of microstructured magnets are very different for pinning-controlled and nucleation-controlled magnets. After thermal demagnetization, domain walls in nucleation-controlled particles are very mobile, so that saturation is achieved in very low fields. In contrast, pinning hinders the domain wall motion in both virgin-curve and major-loop regimes [35].

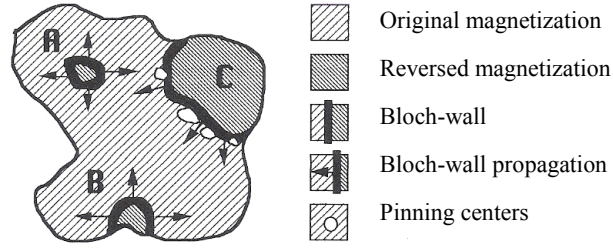


Figure 5.7 : Microstructural interpretation of nucleation and pinning. Nucleation may occur inside the particle (A) or at the surface (B), whereas pinning coercivity (C) is due to limited domain-wall mobility. (This figure assumes a common c-axis and therefore ignores the intermediate magnetization configurations relevant in random-anisotropy magnets [35].

5.4 Extrinsic Properties

5.4.1 Hysteresis loops

The behavior of a real magnet is given by its hysteresis loops which shows the response of a magnet to the total internal magnetic field. It may be measured in conditions where demagnetizing factor (D) is equal to zero ($D=0$), in which case the internal field H' is equal to the applied field H ($H'=H$) [35].

The main extrinsic properties are remanence (M_r), coercivity and energy product which are observed in the second quadrant of the loop after first saturating the magnetization. The equilibrium state of a macroscopic magnet is usually a multi-domain state with no net magnetization. The domain structure is gradually eliminated as the sample is magnetized to saturation along the virgin curve (dashed line in Fig. 5.8) in the first quadrant [35].

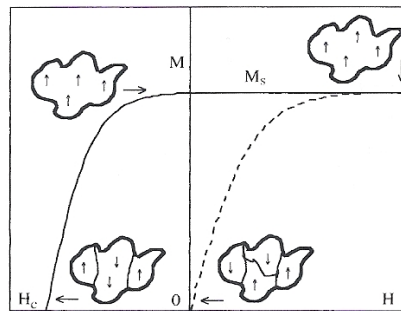


Figure 5.8 : Part of a hysteresis loop, showing the demagnetizing curve with the initial branch (virgin curve) as a dashed line. Domain structures are indicated in the graph [35].

5.4.2 Remanence

Remanent magnetization (M_r) of a magnet is defined as the magnetization which remains after saturation when the total field is reduced to zero. In practice, it is often taken as the magnetization remaining in zero external field. For $0 \leq M_r \leq M_s$, the magnetization within a domain is equal to spontaneous magnetization (M_s). The best permanent magnets are characterized by square loops where $M_r \approx M_s$. Squareness can be defined as M_r / M_s . The quantity $\mu_0 M_r$ gives the maximum flux density $B = \mu_0 H$ that can be produced outside a permanent magnet near its surface [35].

The remanence is the maximum residual magnetization which can be obtained only in a closed-loop configuration in which there is no demagnetizing field. No matter what the coercivity of the permanent magnet is, the remanent magnetization should be high. Therefore, a high remanence combined with a high coercivity is essential. All permanent magnets must be operated in an open circuit configuration, therefore the residual magnetization will always be below remanence value [36].

5.4.3 Coercivity

The internal magnetic field $-H_c$ at which the macroscopic magnetization disappears is the coercivity or coercive force. Since the magnetization is zero at H_c it follows that $H' = H$ so that H_c can equally well be taken as the external field required to reduce the magnetization to zero [35].

H_c is the magnetic field at which half of the atomic moments have reversed their orientation under the action of a reverse field. This change is realized by the formation and reversal of macroscopic domains, since the exchange coupling between spins makes the destruction of short-range ferromagnetic order energetically unfavorable [35]. Soft magnetic materials exhibit temporary magnetism in an applied field. They are characterized by as complete an absence of anisotropy and coercivity as possible [35]. Although it is not an intrinsic property in the sense of the term, the M-H loop coercivity H_c is sometimes referred to as intrinsic coercivity in the literature because it is independent of magnet shape. It can be denoted as iH_c to distinguish it from the coercivity BH_c defined as the field on the B(H) loop where $B=0$. Generally $BH_c \leq iH_c$ [35].

Since permanent magnets operate without an applied field, their ability to resist demagnetization is significant, therefore high coercivity is desirable. The coercivity is used to distinguish between hard and soft magnetic materials. Unlike soft magnetic materials, the magnetization of permanent magnets is not simply an approximate linear function of the flux density. Because the magnetic field values are much larger than in soft magnetic materials [36].

A decreasing Nd content leads to increased B_r and $(BH)_{\max}$ that is, however, accompanied by decreased coercivities. Careful control of the oxygen content is necessary because of the danger of forming Nd_2O_3 and resulting in densification problems. On the other hand, abnormal grain growth was observed for low oxygen contents, also lowering the magnetic properties [120]. As the grain size increases, the coercivity drops [121]. Oxygen contents higher than 1700 ppm (~1700–1950 ppm) grain growth was observed for the NdFeB sintered magnets. However, when the oxygen value is equal and higher than 3350 ppm, no abnormal grain growth was observed.

Oxygen (or oxides formed) may act as a grain growth inhibitor during sintering [121]. If the oxygen content is increased in the alloy, the α -Nd phase contains oxygen (presumably NdO_x) and this phase moves from the grain boundaries to the triple junctions [122]. On the other side, increase in carbon content may cause the Nd-rich phase to agglomerate in the triple junctions and also may stabilize the grain boundary Nd-rich phase against moisture attack [122].

5.4.3.1 The two hysteresis loops of a material: Magnetization loop $M(H)$ and induction loop $B(H)$

Magnetization loop of a hard magnet is characterized by its width, which indicates the value of the coercive field. A hard material with sufficient coercivity stores magnetic energy, and the amount stored depends both on the value of remanent magnetization and on the squareness of the loop. High squareness indicates that the magnetization varies little under the application of a reverse magnetic field until it reverses [39].

Another type of hysteresis loop may be plotted with the magnetic induction field B in the material replacing the magnetization M on the y-axis. This type of loop $B(H)$ is

sometimes more appropriate for describing the working properties of the material. It is called an induction loop or a B-H loop.

It is deduced from the magnetization loop by applying $B = \mu_0 (H + M)$ classical equation. For $H = 0$, $B = \pm B_r$ (remanent induction) and for $B = 0$, $H = \pm H_{CB}$ (the coercive field for induction) [39].

The physical origin of hysteresis is revealed more clearly in M-H loops, whereas B-H loops are useful for determining parameters for technical applications including the maximum energy product [35]. M-H and B-H loops are given on the same graph in Fig. 5.9 [35]. If the units of B and H are multiplied together, they are found to be equivalent to energy.

On the B-H graph, if 45° line from the origin is plotted, only one curve just touches the B-H curve at a single, tangent point. The value of this curve is called the BH product or maximum energy product [123].

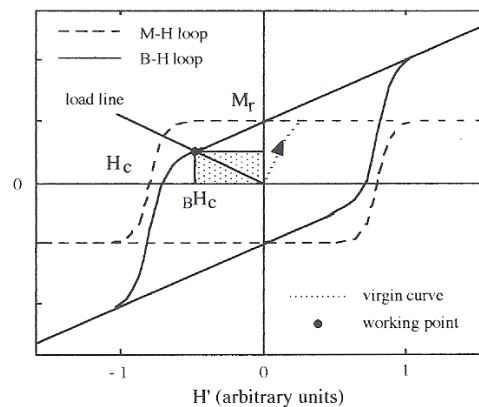


Figure 5.9 : Hysteresis loops. The dotted rectangle is the energy product. The load line and the working point are important for permanent magnet applications [35].

5.4.3.2 Demagnetization curve

In a permanent magnet, the field strength measured at the magnet surface has a direction opposite that of the induction inside the magnet, with positive induction the field strength is negative. The operating range of a permanent magnet therefore will be a portion of a second quadrant of the major hysteresis loop called the demagnetization curve (Fig. 5.10b). This is in contrast to the electromagnet in which both the induction and magnetization force having the same direction, with its operating range consequently in the first quadrant [124]. In Fig. 5.10, major

hysteresis loops obtained by varying the magnetizing force continuously between limits which will saturate the material in each direction is given [124]. The demagnetizing force required to reduce the normal induction, B , to zero is termed the inductive coercive force H_c . The field required to reduce the intrinsic induction, B_i , to zero is the intrinsic coercive force H_{ci} and is always greater than H_c .

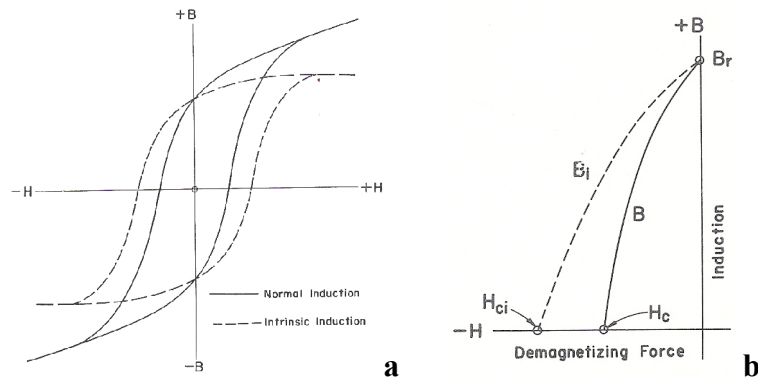


Figure 5.10 : (a) Major hysteresis loops, (b) The second or demagnetizing quadrant of a hysteresis loop [124].

The maximum energy product by itself gives insufficient information about the properties of a permanent magnet. A more useful way of displaying the magnetic properties of a permanent magnet is to plot the portion of the hysteresis loop in the second quadrant, which is from the remanence to coercivity. This is known as the demagnetization curve and is the information which is always used in order to decide on the suitability of a permanent magnet for particular applications. This curve gives not only the information of the maximum energy product but also contains additional information for the designer if the permanent magnet cannot be operated at its optimum condition. The strength of the demagnetizing field of a permanent magnet in an open-circuit configuration depends on the shape of the permanent magnet. Therefore, the choice of the material is dependent as much on its shape as on the intrinsic material properties [36].

The operating conditions for a permanent magnet are determined by the second quadrant of the magnetization curve which is the demagnetizing field. The operating point of a permanent magnet is the point of intersection of the load line with the demagnetization curve. If the length of the air gap or the total length of magnet that can be used is known, the designer must select a material with the largest possible value of BH on the load line [36].

A hard material with a remanence M_r , and intrinsic coercivity $iH_c = H_{cM}$, assuming it has an ideal $M(H)$ or $\mu_0 M(\mu_0 H)$ loop. The corresponding induction loop a 45° parallel, intersects the axes at $\pm B_r$ and $\pm H_{cB}$. The second quadrant which indicates $B = B_r + \mu_0 H$ equation is the demagnetization curve [39]. Magnetization and induction loops of an ideal material are presented in Fig. 5.11 [39].

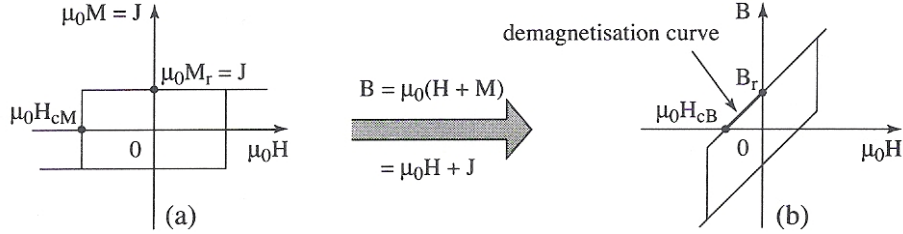


Figure 5.11 : The two hysteresis loops of an ideal material, (a) magnetization loop, (b) induction loop [39].

To characterize the performance of a permanent magnet material, the parameters are taken from one or other of the hysteresis loops of the material [39]. The principle parameters of hard magnets are summarized in Table 5.1.

Table 5.1 : Principle parameters of permanent magnet materials [39].

Parameters from the $M(H)$ Loop	Parameters from the $B(H)$ Loop
Remanent magnetization M_r (remnant polarization J_r) and Saturation magnetization M_{sat} (saturation polarization J_{sat})	Remanent magnetic induction B_r
Coercivity of the magnetization H_{cM} (intrinsic coercivity iH_c)	Coercivity of the magnetic induction H_{cB}
Squareness coefficient SQ of the loop	Maximum energy product $(BH)_{max}$ and corresponding ideal max energy product $(BH)_{max}^{ideal} = B_r^2 / 4\mu_0$
Orientation coefficient of the material	

5.4.4 Magnetic domains

Magnetic materials consist of a large number of domains within each of which all spins are pointing in the same direction. The domains are separated by domain walls, which have characteristic width and energy associated with their formation and existence. The motion of domain walls contributes to magnetization [125]. The comparison between grain structure and interaction domains (imaged by Magnetic

Force Microscopy) directly proves that the domains extend over several correlated grains as seen in Fig. 5.12 [126].

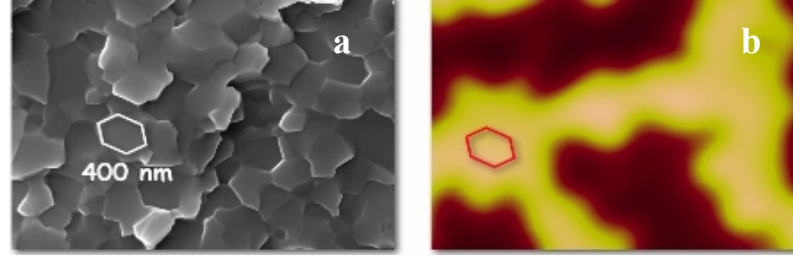


Figure 5.12 : Grain structure and interaction domains: (a) SEM and (b) Magnetic Force Microscopy images [126].

In the past, the model of domains was introduced to explain why two pieces of soft iron do not attract each other. In 1907, Weiss argued that soft iron is ferromagnetic on a local scale but loses its net magnetization by domain formation (Fig. 5.13) [35, 127] . Based on this idea, Bloch in 1932 suggested the domain wall [35].

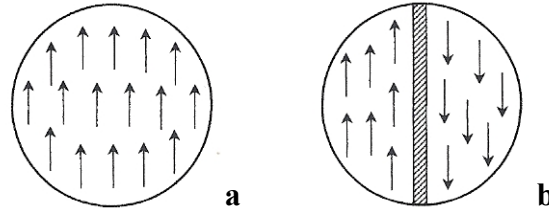


Figure 5.13 : The domain formation in a sphere schematically: (a) single-domain particle and (b) two-domain particle [35].

Further examples of domain structures are given schematically on a cubic structure in Fig. 5.14 [35].

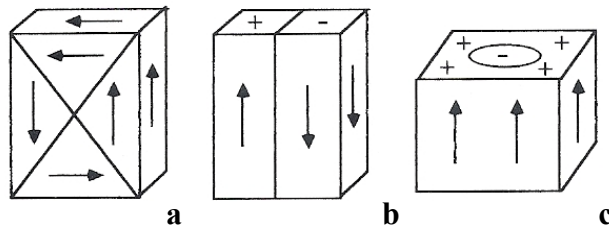


Figure 5.14 : Schematic domain structures for (a) cubic and (b, c) uniaxial anisotropy. The arrows show the magnetization direction [35].

Flux-closure domain configurations as given in the Fig. 5.14a have low magnetostatic self-interaction energy, whereas surface charges are magnetostatically unfavorable. This situation can be seen clearly in Fig. 5.15a [35].

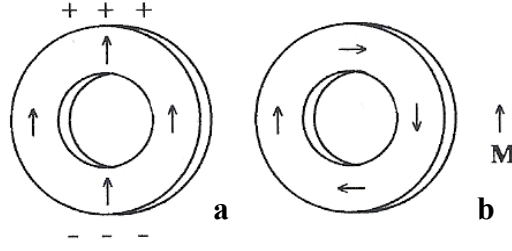


Figure 5.15 : Flux closure in ring-shaped magnets; (a) in an open circuit, (b) closed circuit [35].

In the uniformly magnetized ring (Fig. 5.15a) there is an inhomogeneous demagnetizing field, so that magnetostatic interaction is bigger than zero ($E_{ms} > 0$). However, in the closed configuration (Fig. 5.15b), demagnetizing factor (D) is equal to zero ($D=0$) and $E_{ms} = 0$. Since the gain in magnetostatic energy competes against the exchange and anisotropy energy stored in domain walls, the domain structure cannot be derived from magnetostatic considerations only [35].

A permanent magnet can usually be regarded as a metastable system, although it may be stable as an alloy. By thermally demagnetizing a permanent magnet, such as heating beyond the Curie point and subsequent cooling, the stable non-magnetic (magnetically compensated) system, consisting of a large amount of small (Weiss-) domains is obtained.

The interplay between different magnetic configurations and the activation energies between different magnetic states determined the actual magnetic configuration. This interplay is reflected in the hysteresis loop [128].

5.4.4.1 Domain walls

The transition layers between the domains called domain walls, in which the magnetic moments undergo a reorientation. This theory was first suggested by Bloch [129]. Domains in uniaxial materials are separated by 180° domain walls which are known as Bloch walls whose width is approximately shown by the Eq. (5.3) found by Kittel in 1949.

$$\delta_B = \pi \sqrt{\frac{A}{K_1}} \quad (5.3)$$

Here A is a constant, K_1 ($J.m^{-3}$) is the first anisotropy constant [35]. Unfortunately there is no such a simple equation for the size of the domains in bulk materials. In

some magnets which contain defects whose size is of the order of δ_b the extrinsic properties are managed by the pinning of the domain walls in the neighborhood of the defects.

Typical domain walls are much thicker than inter-atomic distances but much smaller than the domain size [35]. The schematic drawing of the Bloch wall and domain wall width is shown in Fig. 5.16.

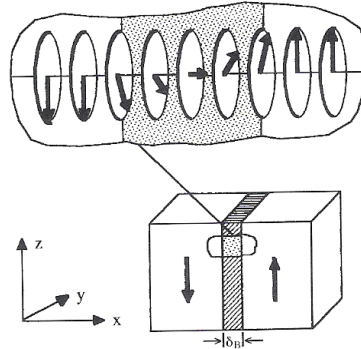


Figure 5.16 : The schematic Bloch wall. δB is the domain-wall width [35].

Domain and domain wall observations made with an optical microscope and polarized light (Kerr effect microscopy) or an electron microscope (Lorentz microscopy) accompaniment measurements [39]. Lorentz and Kerr microscopy studies indicate that the domain walls are pinned or nucleated at grain boundaries, possibly at the disturbed layers of 2:14:1 grains neighboring the Nd-rich grains [71].

5.4.5 Energy product and extrinsic properties

The maximum energy product $(BH)_{\max}$, which is an extrinsic property, is the maximum amount of useful work that can be performed by the magnet. It is the maximum value of (BH) obtained in the second quadrant; area enclosed by the hysteresis loop or the total hysteresis loss [36]. The second quadrant of the $B - H'$ loop showing the working point and the corresponding energy product derived from the $B - H'$ loop is shown in Fig. 5.17.

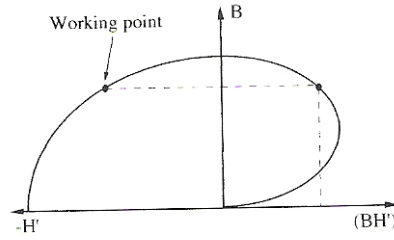


Figure 5.17 : The working point and the corresponding energy product derived from the second quadrant of $B - H'$ loop [35].

Since the energy product scales with the square of the magnetization, any reduction of the magnetic moment per unit volume by imperfect crystallite alignment or non-magnetic dilution rapidly degrades the magnetic properties [35].

The ratio of coercivity to remanence determines the best shape for the magnet and the working point in the second quadrant [35]. Remanence can never be greater than the saturation magnetization. A high energy product requires moderately strong coercivities [35, 36].

Independent upper limits to the energy product are $\mu_0 \cdot B_c \cdot M_r$ and $\mu_0 \cdot M_r^2 / 4$ (μ_0 : permeability of free space, B_c : coercivity and M_r : remanent magnetization), which indicate that both remanence and coercivity must be large to yield a useful permanent magnet [35]. The working point (P) of an ideal material is shown on the demagnetization curve (second quadrant) in Fig. 5.18 [39]. Demagnetization curve and load line have α -slope, and their intersection is the working point P.

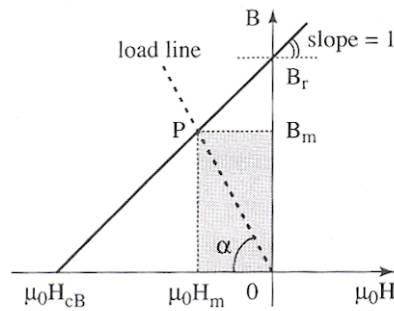


Figure 5.18 : Demagnetization curve and load line, with a slope α , of an ideal material; their intersection defines the working point P [39].

5.5 Microstructure

Each magnet has an optimum microstructure, resulting from a very carefully controlled preparation process. There are various of characteristics defines the

microstructure, notably, the particle size, grain size, arrangement of the particles, and grains in the presence or absence of intergranular phases and secondary phases, the optimization of these phases by the addition of chosen additives or particular heat treatments, the alignment of crystallites in a magnetic field, etc. [39]. Gallium (Ga) addition for instance, can decrease the surface energy of NdFeB phase which leads to smoothed grain boundaries, and improved corrosion properties [120]. Additionally, Ga can improve the hot workability of the HDDR powder remarkably, possibly due to a modified melting point and viscosity of the intergranular phase [120].

Any permanent magnet requires a microstructure or nanostructure which hinders the nucleation and growth of reverse domains [35]. Gutfleisch [120] mentioned that there are two basic concepts for the prevention of nucleation and growth of reverse domains from the fully magnetized state (magnetization reversal): (a) for microcrystalline sintered magnets and (b) for single-domain grains found in nanostructured magnets obtained by melt spinning, mechanical alloying or HDDR. The earlier concept is realized initially in the nucleation type, as found in sintered NdFeB-type magnets consisting of multi-domain grains in the thermally demagnetized, equilibrium state. Here the spontaneous nucleation of reverse domains is hindered by smooth grain boundaries, which also decouple the individual crystallites and thus obstruct propagation [120]. The idea of producing a very fine microstructure for permanent magnets by HDDR process has little to do with the anisotropy (shape or otherwise) but a lot to do with the creation of a large number of barriers to domain wall motion, both through the particle or grain sizes and through the presence of localized residual strains which pin domain walls and lead to higher coercivity [36].

Secondly, it is realized in the pinning type as found in sintered $\text{Sm}(\text{Co}_{\text{bal}}, \text{Fe}_w, \text{Cu}_x, \text{Zr}_y)_z$ magnets where the growth of reverse domains is prevented by pinning the existing domains at inclusions or defects. The nucleation and pinning type can be easily recognized from their respective virgin curve [120].

For instance, in Fig 5.19b microscope image shows a melt-spun NdFeB alloy where 50nm crystallites of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are randomly oriented to produce an isotropic structure. The domain walls follow the grain boundaries and apart from

minor spatial fluctuations, there is a common magnetization direction in each crystallite [35].

The second microstructure (Fig. 5.19a) belongs to an oriented sintered $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ magnet, where aligned crystallites of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase which are $10\mu\text{m}$ in size are separated by an Nd-rich grain boundary phase. Each crystallite is multi-domain in the virgin state, but a saturating field in the first quadrant removes the walls and the nucleation of reverse domains in the second quadrant is inhibited by the uniaxial anisotropy. Moreover, the grain boundary phase inhibits the propagation of the magnetic reversal from grain to grain [35].

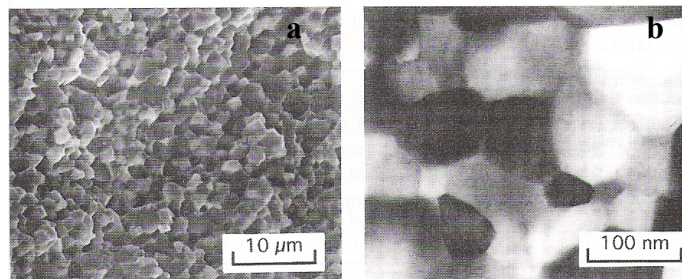


Figure 5.19 : Microstructure of two permanent magnets: (a) sintered $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ with aligned crystals of $\text{Nd}_2\text{Fe}_{14}\text{B}$ separated by a Nd-rich grain boundary phase and (b) melt-spun NdFeB with an anisotropic nanostructure of randomly oriented $\text{Nd}_2\text{Fe}_{14}\text{B}$ [35].

5.5.1 How to enhance coercivity

Coercivity defines materials capability to resist reversal of its magnetization "M" when it experiences magnetic field applied antiparallel to "M". Once the magnetization reversal has occurred, the magnet properties are lost. Two conditions must be fulfilled if a magnetic material is to resist reversal in significant reverse magnetic fields. The first of these conditions involves an intrinsic property of the material; its anisotropy, this must be uniaxial and as large as possible. The second condition concerns the microstructure; in which defects are controlled must be developed. Due to this second condition, coercivity is considered as an extrinsic property of the material [39].

The magnetization reversal process begins at magnetic defects in the material (compositional defects, crystal defects, stresses, etc.) and is not a collective phenomenon as it involves only a small area of the material at a given time [39].

The first phase of the process is localized at and in the vicinity of triggering defects which is the nucleation phase of the magnetization reversal. The wall created around an initial nucleus grows and driven on by reverse field, it crosses the entire sample. An increase in the magnetization reversal field requires materials with a strong uniaxial anisotropy and a reduction in the number and influence of defects in the material so as to retard reversal nucleation [39].

When nucleation intervenes at low fields, the domain walls created may be pinned by suitable defects, thus retarding domain wall propagation and consequently retarding magnetization reversal [39].

5.5.2 Importance of fine particles

Grain refinement is known to be very effective for increasing coercivity due to the inhibition of domain wall motion in an applied field [130]. A granular microstructure should be developed in order to have max coercivity, max remanent induction and a rectangular magnetization loop. The particle size refers to the physical entity while grain size refers to the crystallite size; one particle may contain many grains, or alternatively each particle may be a single crystal [39].

5.5.3 Reduction into grains to suppress nucleation

In the nucleation phase, the magnetization reversal process begins at those particular defects which are most detrimental and the magnetization then reverses throughout the magnetic volume containing the defect once the applied magnetic field allows the propagation of the domain wall. Thus, major defects must be isolated to reduce their influence. This is the reason why the material is divided into independent magnetic particles [39].

The optimum particle size for SmCo_5 and NdFeB is between $0.5\mu\text{m}$ to $10\mu\text{m}$ and for ferrites it is around $1\mu\text{m}$. After milling, the particles are usually single crystalline. Although milling increases the coercivity of SmCo_5 and ferrites, in the case of NdFeB , the grains of NdFeB are not coercive, the surface of the grains is oxidized on contact with air. Only at the end of the process, during a post-sintering anneal, NdFeB magnets become coercive. During this step, an intergranular phase appears which plays an essential role in protecting the grains, and allowing coercivity to develop these magnets [39].

5.6 Oriented (Textured) and Isotropic Magnets

The performance thus the hysteresis loop of a permanent magnet depends on whether the magnet is oriented or isotropic. In certain magnet types each grain is a tiny single crystal, however on the other types (such as bonded magnets); each grain consists of a large number of entangled, randomly oriented crystallites [39].

If the grains are single crystallites, before assembly their easy axes may be oriented along a unique direction by an external magnetic field. The easy axes are then distributed within a cone, which is more or less open, around the field direction [39]. In Fig. 5.20a, the magnetic NdFeB crystallites (white phase) are separated by a non-magnetic Nd-rich phase (grey phase) and the individual magnetic moments are more or less oriented along the same z direction.

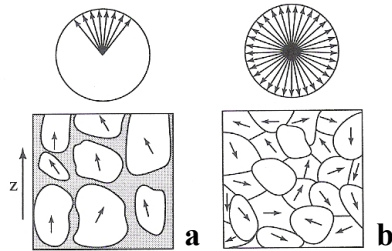


Figure 5.20 : (a) Textured NdFeB magnets, (b) Isotropic magnets [39].

In Fig. 5.20a, the grains have their magnetization vectors pointing in the same direction, but they are separated from each other by an intergranular phase which serves to magnetically isolate the individual grains, for instance, the exchange interactions between neighboring grains are suppressed [39].

Because of the orientation of the crystallites, the value of B_r is close to the max attainable value for B , i.e. $J_s = \mu_0 \cdot M_s$, the saturation polarization which characterizes the material. This situation is very favorable for the magnetic performance. When the grains are polycrystalline or single crystalline but non-oriented (Fig. 5.20b), the magnetic moments oriented randomly. These are known as isotropic magnet [39].

Although the application of an external field activates the same magnetization processes in both oriented (anisotropic) and isotropic magnets, their hysteresis loops $M(H)$ are quite different due to difference in the orientation distribution of their easy magnetization directions [39]. The hysteresis loop of an oriented and isotropic permanent magnet is given in Fig. 5.21.

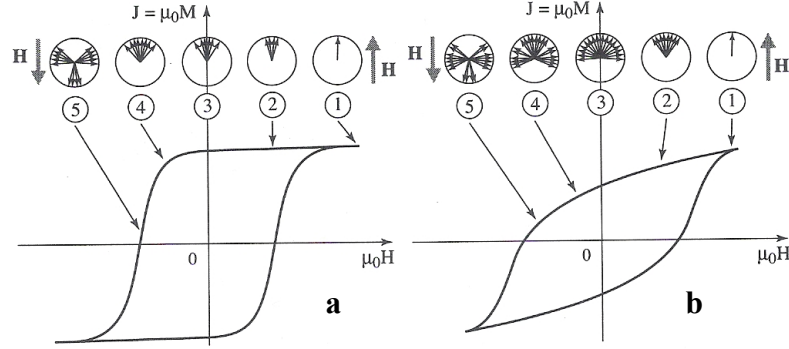


Figure 5.21 : Hysteresis loop of an oriented magnet (a) and an isotropic magnet (b), respectively [39].

Stage 1 is the complete saturation. In oriented magnets, the external magnetic field used to saturate the magnet is applied along the axis of the cone containing the easy magnetization axes of the individual crystallites. In isotropic magnets, the field is applied in any direction. In these both cases, saturation is achieved by applying a sufficiently high field so as to remove all domain walls, and then to align the moments of the crystallites along the field. For the maximum field $H_{\max}$, we then have: $M \sim M_{\text{sat}}$ [39].

Stage 2 and 3 is the change from saturation to remanence. When the magnetic field is reduced from $H_{\max}$, the magnetic moments of the crystallites progressively return to their respective closest easy directions of magnetization. The resulting magnetization is the remanent magnetization (M_r). The value of M_r for the oriented magnet is around 88% to 97% of M_{sat} . The process is similar for an isotropic magnet, though the value of M_r is much lower; it is exactly equal to half of the M_{sat} [39].

Stage 4 and 5 is the increasing negative field. Reversal of the magnetic field happens and the moments of the individual crystallites reverse, one after the other. Each moment orients itself along its easy axis which is closest to the applied field direction. Rotation and reversal of the moments occur simultaneously. The decrease in M under the influence of the applied reverse field is much stronger in isotropic than oriented magnets, in the isotropic magnets the moments are more spread out around the field direction, and thus experience a stronger torque. Consequently, oriented magnets have squarer hysteresis loops which are a property that improves their magnetic performance [39]. The coercive field (H_{cM}) does not depend much on whether the magnet is isotropic or oriented.

5.7 Permanent Magnet Materials

There are three main classes of permanent magnet materials, such as 3d oxides, 3d itinerant moment alloys and rare-earth (4f) transition-metal (3d) intermetallic compounds [35]. Materials that were considered "hard" magnetic materials in the past are in many instances not recognized as hard materials today because of the great improvement of magnetic properties such as coercivity and max energy product [36]. A permanent magnet does not need an electrical current flowing in a coil or solenoid to maintain the magnetic field. The energy needed to maintain the magnetic field has been stored when the permanent magnet was magnetized initially to high field strength and to remanence when the applied field was removed [36].

A total of 10,000 tones of rare earth magnets were produced in 1998. Two countries dominate the market: China and Japan, each producing 4,000 tones while the reminder (2,000 tones) was produced in the US and Europe. In 2005 about 40,000 tones of sintered Nd-Fe-B magnets were manufactured worldwide, about 500 tones in Europe, 8500 tones in Japan and the rest in China [131]. The global neodymium industry is worth \$91,415 per ton/annum and has grown at a rate of 30% in the past six months. Currently 97% off all rare earth magnets are produced in China.

Magnetite, permanent magnet steels which have 1%C, alnico alloys were investigated in till the half of 20th century. Hard ferrites, also known as ceramic magnets, were developed in the 1950s as a result of Stoner-Wohlfarth theory which indicated that the coercivity of a system of single-domain particles was proportional to the coercivity [36]. The development of the $(BH)_{\max}$ of hard magnetic materials in the 20th century is given in Fig. 5.22.

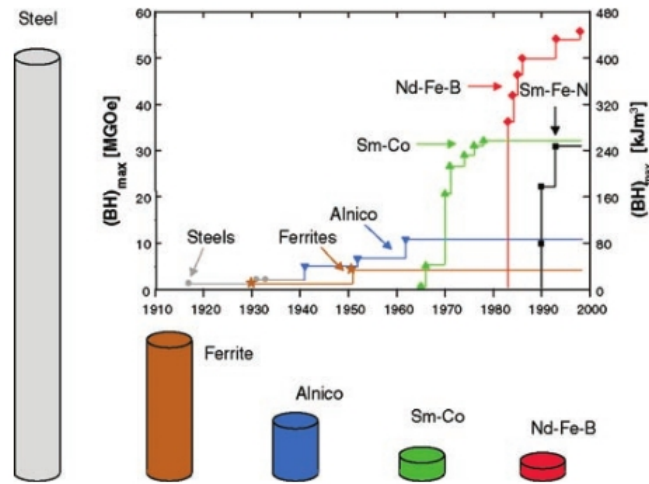


Figure 5.22 : Development in the energy density [120].

This led the permanent magnet manufacturers to try to develop highly anisotropic materials in the form of aggregations of single domain particles. The cause of anisotropy could be either crystalline or small-particle shape effects. However instead of the theoretical predictions, mechanisms other than coherent domain rotation are always available and lower the coercivity. Ferrites are often used to produce as embedded (bonded) magnets [36]. High remanence is desirable in permanent magnets which certainly mean a high saturation magnetization. High permeability and low conductivity properties which are desirable for soft magnetic magnets are irrelevant in hard magnetic materials [36].

SmCo and NdFeB combine strong anisotropy originating mainly from the rare-earth sublattice, accompanying with a reasonably high saturation magnetization provided by transition metal atoms [35]. The magnetic properties of selected hard magnets are given in Table 5.2.

There is a wide range of applications of permanent magnets from heavy current engineering such as in electrical motors and generators to very small scale uses like control devices for electron beams and moving coil meters and intermediate powder range applications such as microphones and loudspeakers [36]. The first group consists of the ferrites and NdFeB magnets which provide energy at a lower price, as a result, represent the greater share of the market [39].

Table 5.2 : Important magnetic properties of selected permanent magnets [36].

Material	Composition	Remanence (T)	Coercivity (kA/m)	$(BH)_{\max}$ (kJ/m ³)
Steel	99%Fe, 1%C	0.9	4	1.59
36Co Steel	36%Co, 3.75%W, 5.75%Cr, 0.8%C	0.96	18.25	7.42
Alnico 5	8%Al, 15%Ni, 3%Cu, 50%Fe, 24%Co	1.2	57.6	40
Ba Ferrite	BaO.6Fe ₂ O ₃	0.395	192	28
Remalloy	12%Co, 14%Mo, 71%Fe	1	18.4	9
SmCo	SmCo ₅	0.9	696	160
	Sm ₂ Co ₁₇		800	260
NdFeB	Nd ₂ Fe ₁₄ B	1.3	1120	320

5.7.1 Samarium-Cobalt

SmCo permanent magnet material was developed in the late 1960s. Sm(CoFeCuZr)₇₋₈ also called as SmCo₅ and Sm₂Co₁₇ are high performance magnets and Sm is the most expensive rare earth elements [39]. The structure of Sm₂Co₁₇ is derived from that of SmCo₅ by replacing one third of the Sm by dumbbell pairs of cobalt atoms. Sm₂Co₁₇ is usually crystallites in the rhombohedral form [35]. The Sm-Co binary phase diagram is given in Fig. 5.23.

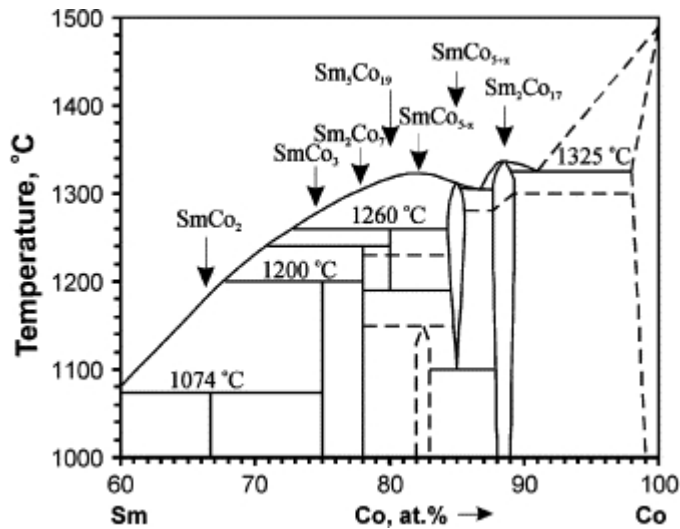


Figure 5.23 : The Sm-Co equilibrium phase diagram.

SmCo₅ and Sm₂Co₁₇-type magnets have high magneto-crystalline anisotropies and Curie temperatures. The 1:7 and 1:5-type structures are closely related to each other and have the same space group: P6/mmm. The 2:17R phase is the majority phase of the material. The 1:5 cell boundary phase is coherent (or at least semi-coherent) with the cell interior [37]. Coercivity drops to zero at about 475 °C which is the Curie temperature of the Sm₂Co₇ phase [132]. The Curie temperature of Sm₂Co₁₇ is 650 °C which is higher than Sm₂Co₇ [133].

The anisotropy of SmCo₅ is already substantial, indicating that 40% of the anisotropy energy is due to Cobalt and 60% is due to Samarium. The Sm₂Co₁₇ compound has a larger magnetization and Curie temperature on account of the lesser amount of rare earth in the structure. The dumbbell substitution (stacking sequence ABCABC...) has a dramatic effect on the cobalt anisotropy, destroying the easy axis character and making Sm₂Co₁₇ weakly easy-plane.

Unlike SmCo₅, it is difficult to develop adequate coercivity for a permanent magnet in pure Sm₂Co₁₇ because the anisotropy is a factor five weaker [35]. Increasing the anisotropy of Sm₂Co₁₇ can be achieved by replacing the 6c cobalt dumbbells which destroy uniaxial anisotropy of Co sublattice, is to use a non-magnetic atom such as Zr. Optimized formula therefore would be Sm(CoFeCuZr)₇₋₈ [35].

5.7.1.1 Microstructure and coercivity of Sm-Co magnets

Real crystals are never perfect and their magnetic reversal occurs via nucleation of reversed magnetized domains at defects followed by the movement of the domain wall through the crystals. Two cases are possible: (a) Domains of reversed magnetization are difficult to nucleate, whereas the domain walls can easily move; and (b) there are many nuclei with reversed magnetization in the crystal but the movement of the domain walls is hindered at defects or pinning centers [76].

Magnetization reversal of single domain particles starts by nucleation of reversed domains in regions with reduced crystal anisotropy. Once a reversed domain has been nucleated in a demagnetizing field the domain wall moves easily through the particle [76].

μm-sized particles exhibit nucleation-controlled hysteresis when they are free of defects larger than the domain wall width which is 4nm for SmCo₅. Typical

crystallites in SmCo_5 magnets are about $5\mu\text{m}$ in size so they are usually multi-domain. The walls move freely across a crystallite in an applied field and saturation is readily achieved. In Fig. 5.24 Initial magnetization curves and second-quadrant hysteresis loops for different types of SmCo magnets are given. Fig. 5.24a is typical of a nucleation-type SmCo_5 magnet, Fig. 5.24b is a pinning type $\text{Sm}_2\text{Co}_{17}$ magnet and Fig. 5.24c is $\text{Sm}_2\text{Co}_{17}$ magnet with a distribution of pinning centers.

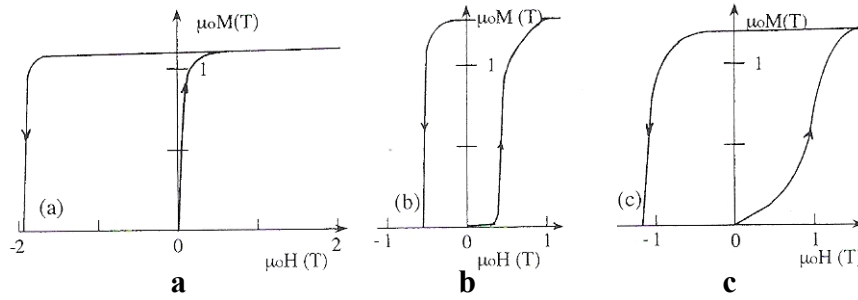


Figure 5.24 : Initial magnetization curves and second-quadrant hysteresis loops for (a) nucleation-type SmCo_5 , (b) pinning type $\text{Sm}_2\text{Co}_{17}$ and (c) high-coercivity $\text{Sm}_2\text{Co}_{17}$ magnets with a distribution of pinning centers [35].

Once the domain structure has been eliminated, the magnetization remains saturated until a large reverse field creates nuclei from which reverse domains propagate and the magnetization switches. Reducing the particle size to a fine size limits the defects that act as nucleation centers, which may reserve without affecting all the others.

Despite a coercivity which can reach high values of 2T or more, the SmCo_5 magnets are rather easy to magnetize. They are typical nucleation-type magnets. The defects which act as nucleation centers for reverse domains are mostly associated with the surface of milled powder particles, so coercivity can be increased by annealing or etching away the surface layer [35]. The domain reversal of sintered SmCo_5 magnet is schematically shown in Fig. 5.25.

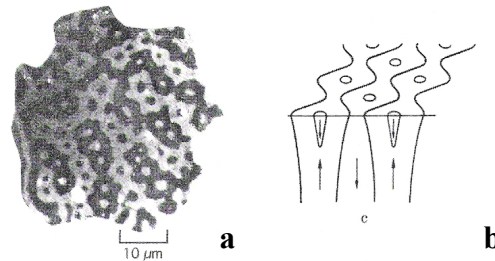


Figure 5.25 : Kerr effect micrographs illustrating domain reversal in the second quadrant for SmCo_5 sintered magnet [35].

A different coercivity mechanism occurs when some copper is substituted for cobalt. A homogeneous Cu-rich precipitate appearing inside the grains of the 1:5 phase hinders domain-wall movement. Provided the homogeneously distributed defects are on the scale of the domain-wall width, the walls are pinned at the defects and an initial magnetization curve of type will occur (Fig. 5.25b) [35].

Pinning-type coercivity was fully exploited in the second generation Sm-Co magnets which have a composition close to $\text{Sm}(\text{CoFeCuZr})_{7.2-8.5}$. Iron is added to increase the remanence and Cu, Zr help form the required microstructure. Absorbed oxygen may also play a role as domain-wall pinning centers.

The composition is intermediate between 1:5 and 2:17, and the main feature of the microstructure is a network of small ($\sim 100\text{nm}$) rhombohedral 2:17 structure cells separated by thin ($\sim 10\text{nm}$) boundary layers with the 1:5 structure which serve to pin the domain walls. With suitable heat treatment, lamellae of a platelet phase form which incorporate much of the Zr in the hexagonal 2:17 structure. All three phases are crystallography coherent, with a common c-axis [35]. The microstructure of a $\text{Sm}(\text{CoFeCuZr})_{7.8}$ magnet showing the cellular arrangement with 1:5 boundary layers which pin domain walls between the 2:17 grains is given in Fig. 5.26.

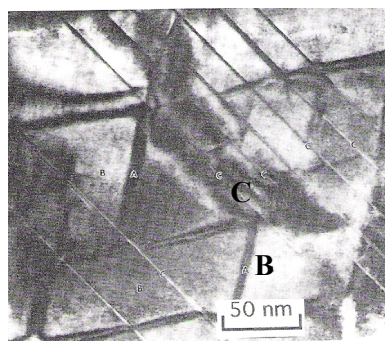


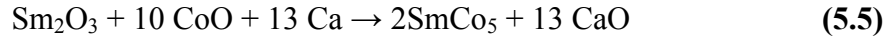
Figure 5.26 : The microstructure of a $\text{Sm}(\text{CoFeCuZr})_{7.8}$ magnet showing the cellular arrangement with 1:5 boundary layers which pin domain walls between the 2:17 grains (B). The coherent lamellae are (C) [35].

5.7.1.2 Producing of Sm-Co magnets

For SmCo (1:5) the starting point can be an ingot of the alloy produced by batch melting of the elements or mixture of a eutectic Sm-Co master alloy and cobalt in an induction furnace. It has to be reduced to a fine powder by crashing and milling. An aid is here hydrogen decrepitation, where the alloy is exposed to an atmosphere of

hydrogen which is absorbed, provoking a volume expansion of the order of 8%, causing the ingot to fragment and fissure [35].

As an alternative, it is possible to produce fine SmCo_5 powder directly by reducing the rare earth oxide powder with calcium. The possible reactions are:



These reactions are exothermic, being conducted at about 1100 °C in vacuum. Excess Calcium (Ca) is removed by washing, leaving an alloy powder which is suitable for further processing [35].

Following to powder processing, pressing the in a magnetic field (about 1T) to align the crystallites of the powder. Alignment and densification are critical steps as they directly influence the magnetization of the sintered magnet. Typically the green compact has 65% of bulk density [35].

The sintering conditions and heat treatment depend on the composition and microstructure required. For SmCo_5 , due to the phase diagram, the phase is only stable above 805 °C. Normally the magnets are sintered at about 1150 °C and aged at 900 °C to eliminate inhomogeneities before quenching [35].

For $\text{Sm}(\text{CoFeCuZr})_{7.8}$ composition, more complex series of heat treatments is needed to develop the cellular microstructure which leads to pinning-type coercivity. A typical composition is $\text{Sm}(\text{Co}_{0.73}\text{Fe}_{0.20}\text{Cu}_{0.05}\text{Zr}_{0.02})_{7.5}$. The alloy is first sintered at about 1180-1200 °C and then quenched to room temperature before ageing at 800 °C to precipitate the Zr-rich hexagonal phase and develop the coherent microstructure of the 2:17 matrix and 1:5 grain-boundary phases. A subsequent slow cool to 400 °C or annealing at 40 °C is required to develop coercivity. Large magnetizing fields up to 5T may be needed for the high coercivity precipitation hardened material [35]. During the sintering cycles the improvement in the coercivity of $\text{Sm}_2\text{Co}_{17}$ magnets is given in Fig. 5.27.

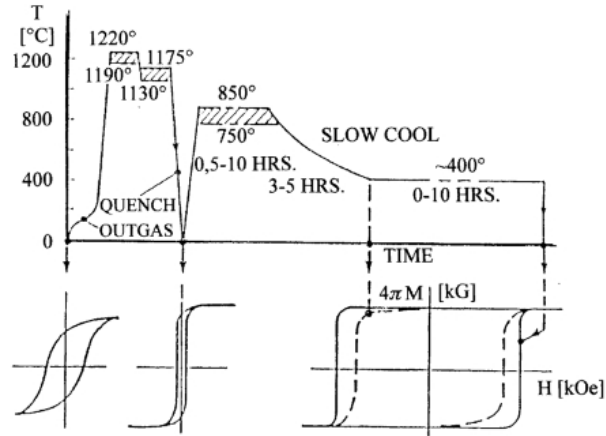


Figure 5.27 : Development of coercivity in $\text{Sm}_2\text{Co}_{17}$ magnets [128].

An example of the magnetic properties of SmCo sintered magnets is given in Table 5.3.

Table 5.3 : Properties of Sm-Co sintered magnets [35].

	$\mu_0 M_r$ (T)	H_c (kA.m^{-1})	$(BH)_{\max}$ (kJ.m^{-3})
SmCo_5	0.92	1500	160
$\text{Sm}_2\text{Co}_{17}$ (high remanence)	1.20	1100	260
$\text{Sm}_2\text{Co}_{17}$ (high coercivity)	1.07	1700	215

Due to their high temperature behavior and their usability in potentially corrosive environments, 2-17 type SmCo magnets have kept their market share for applications where performance and reliability are a priority over cost [39], for instance, in aeronautic and military applications such as frictionless earrings or co-axial starter motors/generators, magnetic couplings in hot environments.

The use of SmCo_5 type magnets has moved to special applications where partial substitution of Gd for Sm results in materials with constant induction over a wide temperature range [39].

5.7.2 Neodymium-Iron-Boron

In the early 1980s due to the problems with the supply of cobalt, there was a need for a new permanent magnet material to replace SmCo. There had been some attempts to develop Nd-Fe materials which were known to have high coercivities but the

properties of these alloys were not sufficiently reproducible. The addition of a small amount of boron was found to improve the properties dramatically [36]. The new material was discovered in 1983 in Japan by Sagawa [134] at Sumitomo Special Metals and independently in the USA by Croat and Herbst at General Motors was a ternary phase stabilized by a small amount of interstitial boron (or carbon) [35].

The developed NdFeB alloy ($\text{Nd}_2\text{Fe}_{14}\text{B}$) phase has greater coercivity and energy product than SmCo. The magnetic properties of NdFeB are very sensitive to the metallurgical processing. The material has been produced either by powdering and sintering or by rapidly quenching from the melt [36].

Both the Nd and Fe sublattices are aligned parallel in $\text{Nd}_2\text{Fe}_{14}\text{B}$ producing a room temperature magnetization of 1.6T, the largest of any rare-earth metallic that can be used for permanent magnets. The dysprosium compound has very large anisotropy and small quantities of Dy are often substituted for Nd to improve the coercivity of NdFeB magnets [35].

5.7.2.1 Microstructure and coercivity of NdFeB magnets

The $\text{Nd}_2\text{Fe}_{14}\text{B}$ ferromagnetic phase is the carrier of the high saturation magnetization of the materials. This phase comprises 85% of the magnet volume and present in the structure with two paramagnetic phases, Nd-rich phase (nearly 10%vol) and NdFe_4B_4 (η) (about 2%vol). These paramagnetic phases produce an optimal microstructure that strongly enhances the magnets coercivity [135].

Sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets are composed of oriented grains of several micrometers in size which are multi-domain in the unmagnetized state. The critical single-domain radius is $0.12\mu\text{m}$ whereas the domain-wall width is 4.2nm. The walls move freely across the crystallites in an applied field as the virgin sample is magnetized to saturation. The coercivity depends on the ability of the magnet to resist nucleation and growth of reverse domains in a reversed magnetic field. This is more difficult to achieve in $\text{Nd}_2\text{Fe}_{14}\text{B}$ than in SmCo_5 because the anisotropy field is five times smaller [35].

The optimum microstructure to obtain coercive sintered magnets was found to be $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$, which is both Nd- and B- rich with respect to stoichiometric $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ composition. This would be the region where the three phases coexist at 1050 °C,

$\text{Nd}_2\text{Fe}_{14}\text{B}$, NdFe_4B_4 , and an Nd-rich liquid. The microstructure of the sintered NdFeB magnet is given in Fig. 5.28. Nd-rich liquid promotes liquid-phase sintering where the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are wetted by a surrounding liquid film [35].

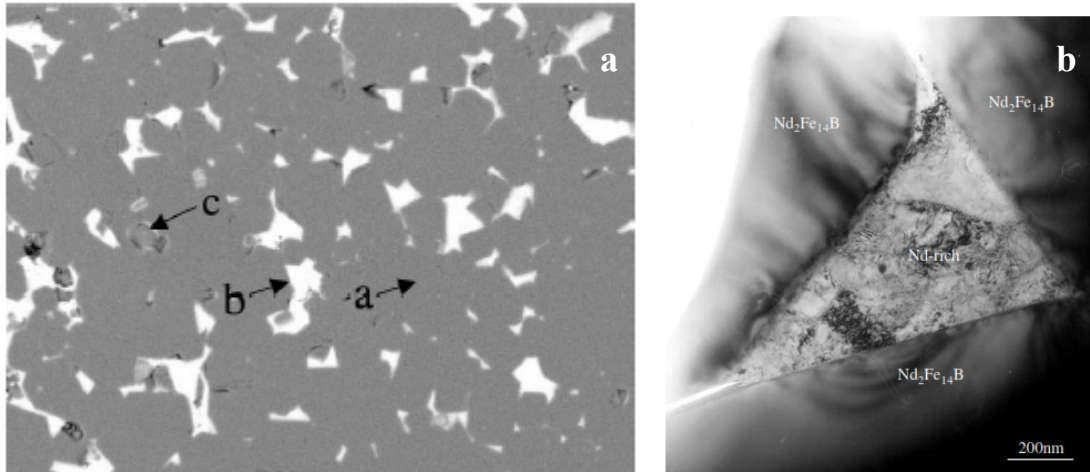


Figure 5.28 : (a) The microstructure of an $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ sintered magnet; (a) indicates the grains of $\text{Nd}_2\text{Fe}_{14}\text{B}$, (b) is Nd-rich intergranular phase, (c) is NdFe_4B_4 [136], (b) $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains and Nd-rich grain boundary phase [137].

The surfaces of the hard-magnetic grains are smooth and intergrain interactions are negligible, so the microstructure tends to prevent nucleation of reversed domains and the propagation of reversal from grain to grain. By contrast, a Fe-rich composition would include μm -sized grains of $\alpha\text{-Fe}$ in the microstructure which act as nucleation centers and prevent the development of coercivity. The ideal two-phase microstructure in an NdFeB sintered magnet consists of fully aligned grains of $\text{Nd}_2\text{Fe}_{14}\text{B}$ separated by the minimum amount of a non-magnetic intergranular phase [35].

A complete range of commercial grades of NdFeB magnet exists, some including substitutions of Dy or Co to improve the anisotropy and magnetization, and additives such as V, Mo or Zr to refine the microstructure. A typical composition of a high-coercivity grade is $\text{Nd}_{13.5}\text{Dy}_{1.5}\text{Fe}_{76}\text{NbB}_8$, whereas a high-remanence grade may have composition $\text{Nd}_{13}\text{Fe}_{81}\text{B}_6$ [35].

A decreasing Nd content leads to increased remanence and max energy product, however, accompanied by decreased coercivities. Therefore, careful control of the oxygen content is necessary because of the danger of forming Nd_2O_3 and resulting in

densification problems. On the other hand, abnormal grain growth was observed for low oxygen contents, also lowering the magnetic properties [120, 138].

5.7.2.2 Producing of NdFeB magnets

There is more than one way to produce hard magnetic NdFeB material. However there are two main groups; the microcrystalline powder routes used to make oriented sintered magnets and the nano-crystalline routes used mostly for bonded magnets [35].

Sagawa et al. [134] developed the powder metallurgical method. The constituents (Nd, Fe and ferroboron) are strip cast or induction melted in an alumina crucible under an argon inert atmosphere to prevent oxidation. The ingot is crushed and jet-milled into a powder having 3 μ m particle size often with aid of hydrogen decrepitation (HD).

The induction melted alloy consists of ferromagnetic matrix phase; Nd₂Fe₁₄B and Nd-rich, grain boundary eutectic which readily absorbs hydrogen at room temperature and at <1 bar hydrogen pressure.

By HD process, hydrogen atoms penetrate into the interstitial sites of the Nd₂Fe₁₄B lattice and Nd-hydride is produced from the Nd-rich phase. The initial failure is predominantly intergranular in nature and the exothermic nature of the reaction causes the alloy to heat up and hydrogen is absorbed subsequently by the matrix phase to form Nd₂Fe₁₄BH_x solution.

Hydrogen is first absorbed by the non-magnetic phase enriched with Nd (inter granular phase) at temperatures between 150 °C and 300 °C. If the alloy is continuously heated a further dramatic absorption occurs at about 650 °C during which the hard magnetic main phase of Nd₂Fe₁₄B crumbles [139].

Materials become brittle and decrepitate into a powder as a result of the large volume expansion of the lattice of both the matrix and the intergranular phases. The bulk alloy absorbs around 0.4 wt% of hydrogen during the initial decrepitation stage and this hydrogen is desorbed during the subsequent vacuum sintering [140].

This way of powdering known as HD is well-established stage of manufacturing technologies of sintered and bonded NdFeB magnets. The HD-powder is extremely

friable and can be readily jet-milled to the final powder size of a few microns required to produce the fully dense, sintered magnet [135].

The interstitial hydrogen in the ferromagnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase reduces significantly its anisotropy field. That is why desorption of hydrogen is necessary in order to recover the high values of the intrinsic magnetic coercivity of the magnets [135].

The presence of hydrogen in the powder markedly reduces the intrinsic coercivity and hence the material is not directly usable as a permanent magnet, e.g. by resin bonding [141].

The rare earth di-hydrides are more stable than the corresponding metal powders thus reducing the amount of oxidation during processing. Once the hydrogen has been desorbed the powders become very reactive thus aiding the sintering process. The presence of hydrogen can enhance solid state diffusion [140]. The schema of the powder production is given in Fig. 5.29.

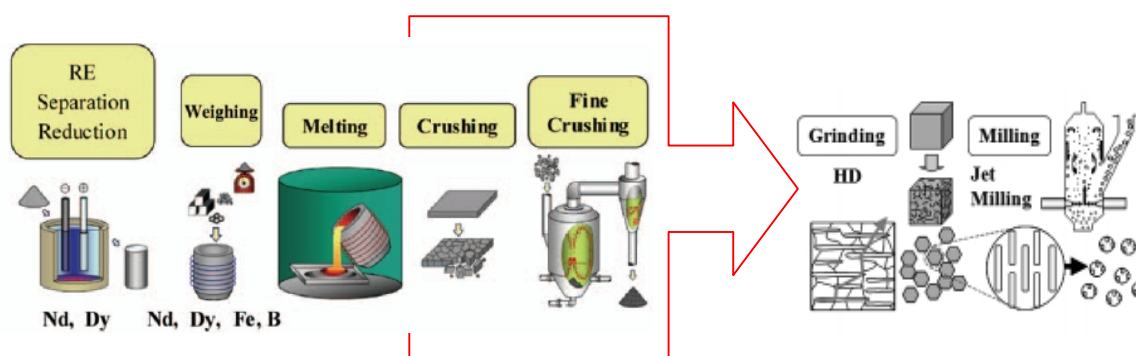


Figure 5.29 : NdFeB powder production.

If the permanent magnets are produced by using the HD Process, fine single crystal powder is then aligned in a magnetic field prior to compaction to form an aligned ‘green compact’ which is ~50% dense. These compacts do not exhibit any coercivity and are therefore easy to handle. The hydrogen is still contained within the compact but is removed completely during the subsequent vacuum sintering operation [142]. The hydrogen partial pressure versus temperature graph is given in Fig. 5.30 showing the phase changes due to hydrogen lost at temperatures starting around 150 °C and in final stage Nd is obtained at temperature around 600 °C.

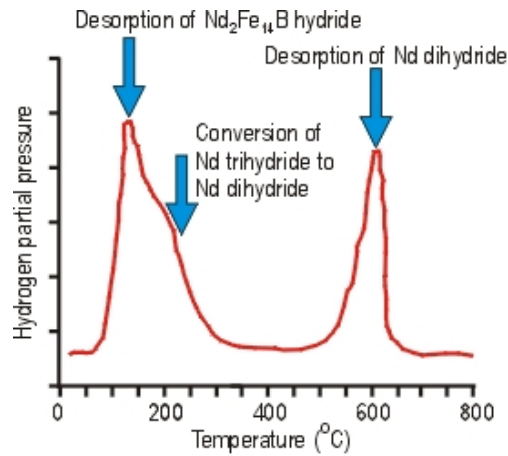


Figure 5.30 : The loss of hydrogen during vacuum sintering [142].

Once the hydrogen is fully desorbed, the Nd-rich material melts and liquid phase sintering is achieved at around 1000 °C. The sintering temperature and time have to be carefully controlled to avoid excessive grain growth, which degrades the magnetic properties, in particular the coercivity. In addition to the normal reduction in volume during sintering, there is also anisotropic shrinkage and substantial machining is often required to achieve the final dimensions [142].

The particles are aligned in 800kA/m field, while compacting under 200MPa pressure and then sintered in an argon atmosphere or a under vacuum at temperatures in the range 1050-1150 °C. This process is followed by a post-sintering anneal [35, 36]. A two-step heat treatment is used for the Nd₁₅Fe₇₇B₈ alloy, a sintering step at about 1080 °C for about 1h to develop a dense three phase material by liquid phase sintering, followed by a soak for 1-2h at about 600 °C to establish the coercivity [35].

Typical sintered blocks are rectangular shaped and magnetization direction along the short axis. They are sliced and ground or cut by spark erosion into desired shapes, coated with anti-corrosion layer such as Ni and magnetized in a field of the order of 2T. On the other side, radially oriented segments have been produced by hot extrusion of as-cast ingot material or compact isotropic powder [35].

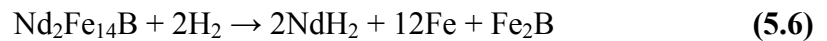
Sintering is the best way of making fully dense NdFeB magnets, grades with a high remanence tend to have less coercivity and vice versa. A standard grade has a remanence of 1.2T and an energy product of 250kJ.m⁻³, while remanence in a premium grade approaches 1.5T and energy product to 400kJ.m⁻³ [35, 39].

The rapid quenching process, known as "magnequench" was developed by Croat et al. [143]. A typical composition is Nd₁₄Fe₈₀B₆. Constituents are arc melted together by melt-spinning in an argon atmosphere by ejecting the molten alloy through a hole in the quartz crucible on to a rapidly rotating copper substrate where the metal cools rapidly to form ribbons. Overquenched coercive ribbons produce the required nano-structure in a subsequent annealing step. Flakes of melt-spun material, known by the trade name Magnequench (MQ), are typically 50µm thick and 500µm wide. This fine-grained microstructure of the equilibrium is Nd₂Fe₁₄B phase. The flakes are suitable for bonding with polymer to make isotropic magnets by compression or injection molding. Alternatively, they may be hot pressed to reach full density to yield a dense isotropic material [35, 36].

Energy products of 100kJ/m³, and remanence of 0.80T are characteristic for fully dense, isotropic NdFeB. Typical energy products are 60kJ/m³ for injection molding and 80kJ/m³ for compression molding [35].

Similar coercive powders can be produced by high-energy ball milling of the elements, yielding a partly amorphous alloy which is annealed to give the necessary microstructure. The mechanically alloyed powder can then be pressed in one of the same ways as the rapidly quenched flakes [35].

The hydrogenation-disproportionation-desorption-recombination (HDDR) process is a method of refining the grain structure of a cast alloy or coarse powder to make it coercive. Unlike the more straightforward HD-process, the HDDR route involves heating the bulk alloy in around 1 bar of hydrogen to ~800 °C where the disproportionation reaction begins to occur:



This is an exothermic reaction and the disproportionated alloy consists of an intimate mixture of fine rods of NdH_{2±x} in α-Fe matrix. The Fe₂B phase forms isolated grains. The hydrogen is then removed from the NdH₂ by pumping by a vacuum and the finely divided mixture of Nd, Fe and Fe₂B is recrystallized into numerous submicrometre Nd₂Fe₁₄B crystallites [35, 142]. The schematic representation of the conventional HDDR procedure consisting of heating from room temperature to 800-900 °C in hydrogen and desorption/recombination under continuous pumping and of

the modified HDDR procedure consisting of; stage 1: heating under vacuum; stage 2: solid disproportionation; stage 3: slow recombination under a partial hydrogen pressure and stage 4: full desorption is shown in Fig. 5.31.

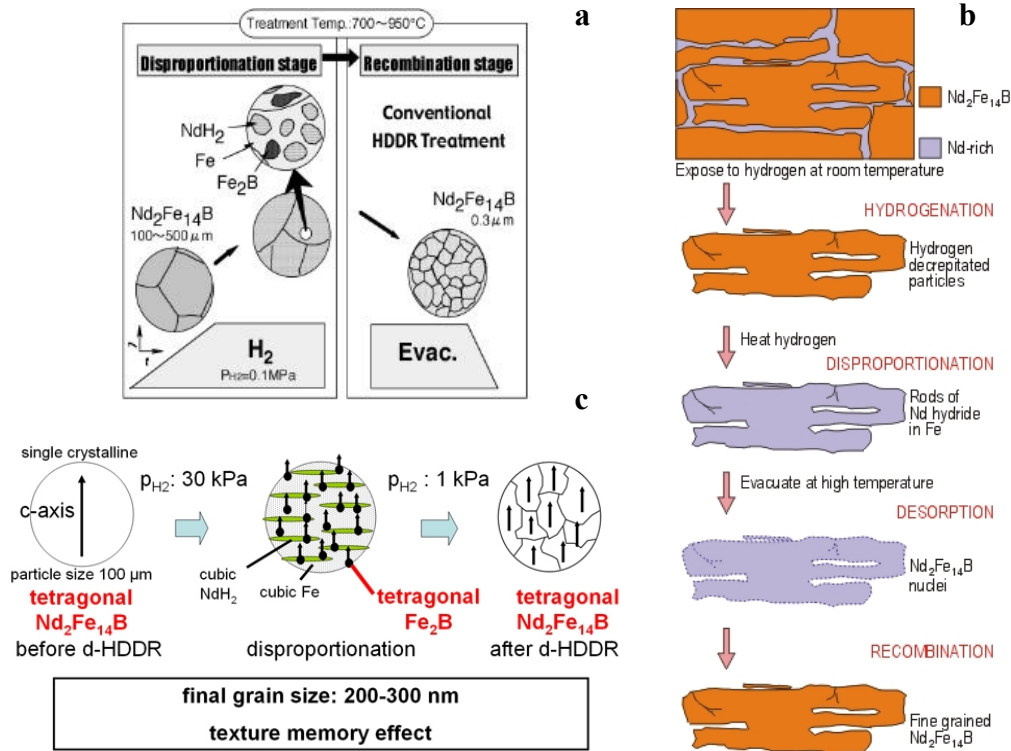


Figure 5.31 : (a) The conventional HDDR procedure heating from room temperature [120], (b) the steps of the HDDR process [142], (c) the steps of d-HDDR process [144].

The most significant aspect of the HDDR process is that there is a dramatic change in the microstructure from an initial grain size of typically 150 μm to a very fine, uniform grain size of about 0.3 μm . On magnetization, the HDDR powder exhibits an appreciable coercivity which means in its simplest net shape form, the powder can be mixed with a thermosetting resin to produce an isotropic permanent magnet by compression molding. HDDR powder exhibits excellent hot pressing characteristics and fully dense, near net shape, isotropic magnets can be produced by hot pressing at 750 °C in an inert atmosphere [142].

The processed material composed of tiny crystallites as shown in Fig. 5.31b with an isotropic distribution of c-axis orientation, although some methods exist for texturing the material to make it anisotropic so that easy axes become partly aligned. The initial magnetization process is relatively difficult as the domain walls tend to be

trapped at the boundaries between the crystallites. The remanent state is composed of multigrain domains composed of groups of crystallites where the c-axis lies in roughly the same direction. Magnetization reversal is rather extended in the field, proceeding by nucleation and growth of reverse domains as in sintered magnets. The pseudo domains with the greatest misorientation to the applied field tend to be the last saturate [35].

Modification of both the composition of the start material and the processing conditions can also result in the production of anisotropic powder with a substantial improvement in the magnetic properties. Due to the controlled pressure of hydrogen in the d-HDDR (dynamic-HDDR) process (Fig. 5.31c) the formed NdH_2 nanograins work as nucleation sites during the recombination and keep the orientation of the former $\text{Nd}_2\text{Fe}_{14}\text{B}$ mono-crystal. During recombination step aligned NdH_2 sites provides that the new $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains follow this orientation after the recombination and keep the same alignment of the mother-grain [144].

Small additions of 0.1wt% Zr have the dramatic effect of generating a textured array of submicrometre crystallites which tend to have their c-axes aligned towards the c-axis of the crystallites in the original coarse powder from which they came. In this way, an isotropic coercive powder is available for bonding [35].

Energy products of 150 kJ/m^3 are significantly greater than for isotropic bonded magnets and this facilitates saving of weight or increase of torque in small electrical machines [35].

5.7.3 Comparison of SmCo to NdFeB

The advantage of NdFeB compared to SmCo is the NdFeB's alloy constituents are cheaper. SmCo has around 720°C Curie temperature, for NdFeB it reduces to $300\text{--}500^\circ\text{C}$ [36]. It was found that the cobalt-rare earth alloys had higher anisotropies than the nickel- or iron-rare earth alloys. Furthermore the alloys with the light rare earths generally had higher saturation magnetizations [36].

In sintered form NdFeB possess the highest energy densities, as their remanent magnetizations equal those of AlNiCo magnets [39]. They are also easily oxidized on exposure to air, with the result that grains which are in direct contact with air are non-coercive. The magnets surface must be protected. To date, this has made it

impossible to prepare coercive, oriented NdFeB powders [39]. Permanent magnets have much higher surface energies and correspondingly thinner domain walls than the soft magnetic materials such as iron, nickel and cobalt [36]. A domain structure exists within the grains of sintered NdFeB and SmCo₅ magnets in the thermally demagnetized state. The domain configuration develops under the influence of a magnetic field which easily moves the domain walls. The grains of the NdFeB magnets made from melt spun ribbons are generally single domain [39]. The domain and domain wall properties of NdFeB and SmCo magnets are given in Table 5.4.

Table 5.4 : Magnetic properties of domains and domain walls [36].

	Domain Wall Surface Energy (mJ/m ²)	Domain Wall Width (nm)	Single-Domain Particle Diameter (μm)
Nd ₂ Fe ₁₄ B	30	5.2	0.26
SmCo ₅	85	5.1	1.6
Sm ₂ Co ₁₇	43	10.0	0.66

The microstructure of Sm₂Co₁₇ magnets consist of precipitation of a Sm(CoCu)₅ high coercive phase within a Sm₂(FeCo)₁₇ phase of lower coercivity. The grains are separated by boundaries consisting of the 1-5 phase of thickness 5 to 10 nm. The magnetic domains of a thermally demagnetized sample, observed by Lorenz microscopy, seem to follow the cell boundaries with the domain wall taking of a zig-zag shape (Fig. 5.32a). The Bloch walls forming saw-tooth lines which follow the cell boundaries confirms the domain walls are pinned at the intergranular phase boundaries (Fig. 5.32b) [39].

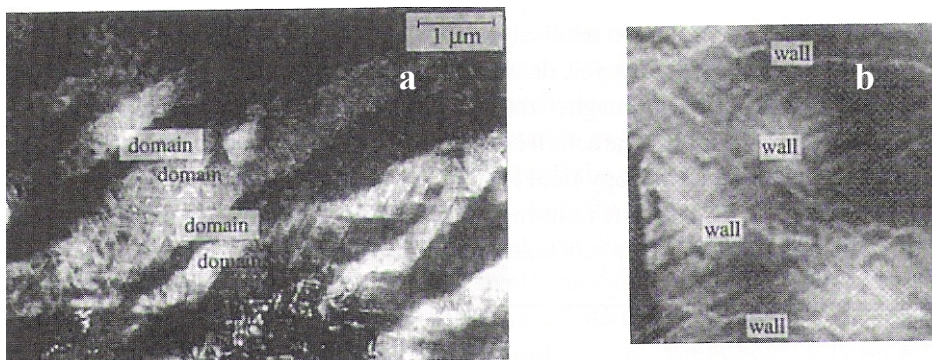


Figure 5.32 : Visualization of domains (a) and domain walls (b) in a Sm₂Co₁₇ type magnet [39].

The grain boundaries act as effective barriers against any movement of domain walls from one grain to a neighboring one. In sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets this effect is caused by the non-magnetic Nd-rich grain boundary phase which gives a nearly complete decoupling of exchange interaction.

On the other hand, in sintered SmCo_5 magnets which have been annealed under optimal conditions the individual grains act almost independently from each other like as $\text{Nd}_2\text{Fe}_{14}\text{B}$ but the reduction of exchange interaction is not as strong as in $\text{Nd}_2\text{Fe}_{14}\text{B}$. So, in SmCo_5 there is a partial decoupling only which could be explained by impurities around the grain boundaries such as foreign atoms or vacancies which reduce the exchange coupling as well as the crystal anisotropy [132]. With increasing magnetizing field, domain walls will be concentrated around pores and non-magnetic regions such as oxides, carbides or borides. When the magnet is approaching saturation, pores will act like reversed domains with magnetization [132].

5.8 Production Ways

To produce high performance magnet components, the composition, microstructure and processing are the critical factors. Three common fabrication routes can be used to categorize as conventional pressing and sintering, polymer bonding via compression or injection molding and hot deformation. By conventional pressing and sintering, full density, relatively simple shape and energy products around 30-50 MGOe ($240 - 400\text{kJ/m}^3$) can be obtained. On the other hand, the bonded magnets have lower energy products around 10-18 MGOe ($80 - 140\text{kJ/m}^3$), and lower density. However, this technique provides net shapes [145]. Hot deformed magnets possess full density, around 15- 46 MGOe ($119 - 366\text{kJ/m}^3$), energy product having isotropic or anisotropic properties. The magnetic properties of the hard magnetic materials produced using different techniques summarized in Fig. 5.33.

The bonded magnets have good mechanical properties but low magnetic properties, on the other hand, sintered magnets have high magnetic properties but less complexity of the part shapes and low mechanical properties. Therefore MIM of sintered hard magnets would fill this gap.

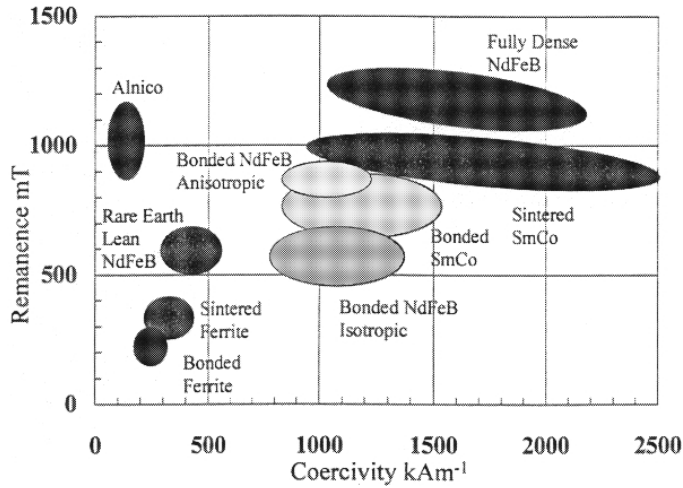


Figure 5.33 : Magnetic properties of hard magnetic materials [60].

5.8.1 Sintered magnets

Microcrystalline magnets tend to be sintered to a fully dense shape using a traditional powder metallurgy route. The ingot is cast with a relatively high rare-earth component (Nd, Dy ~15 at%) because rare-earth limits α -Fe precipitation and facilitates the subsequent liquid phase grain boundary sintering operation. The ingot is pulverized by a coarse grind and then jet milling [145]. The various processes used for each of the principle magnet types are given below in the Table 5.5. Powder metallurgy route is the reference process [39].

Table 5.5 : The various processes used for each of the principle magnet types.

	Sintered Ferrite	Sintered NdFeB	Sintered SmCo ₅	Sm ₂ Co ₁₇	AlNiCo
Principal Phase	BaO-6Fe ₂ O ₃ SrO-6Fe ₂ O ₃	Nd ₂ Fe ₁₄ B	SmCo ₅	Sm ₂ (CoFe) ₁₇	FeCo
Anisotropy	Magnetocrystalline				Shape
Reduction into grains	by milling			by thermal phase segregation + Milling	by thermal phase segregation
Inter-granular phase	BaO-nFe ₂ O ₃ SrO-nFe ₂ O ₃	Nd-rich eutectic	Sm eutectic	Sm(CoCu) ₅	NiAl
Orientation of grains	by compression under field				by heat treatment under field

The quality of crystalline alignment is a function of the strength of the magnetic field applied and the compression method used. Compression is carried out directly after alignment in a pulsed magnetic field of about 4T without handling the sample in between two steps. There are four ways of compression, such as axial, transverse, isostatic and quasi-isostatic pressure. After each the degree of alignment (M_r/M_{sat}) is approximately; 87%, 92%, min. 95% and min. 95%; respectively [39].

The room temperature remanence and coercivity comparison of the commercial sintered magnets is given in Fig. 5.34.

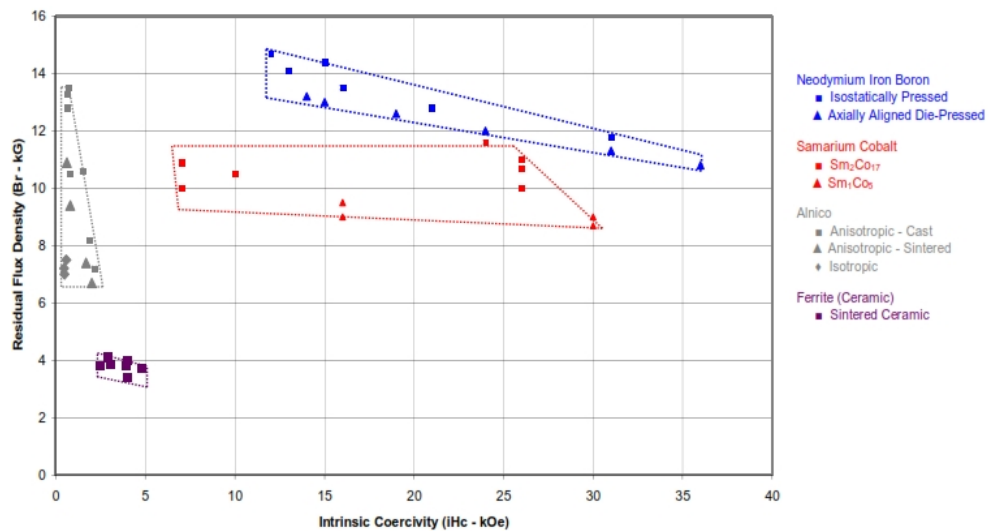


Figure 5.34 : Typical material property ranges at room temperature [146].

5.8.2 Bonded magnets

Magnetic powders having permanent magnet properties and a typical particle size between 10 and 200 microns are suitable to prepare bonded magnets. NdFeB powders are produced by rapid quenching or mechanical milling or HDDR. The quenching takes place in a He or Ar controlled atmosphere chamber to make a ribbon. This technique was projected by Croat and Herbst of General Motors in 1983 [143]. The pieces of ribbon thus processed consist of crystallites with an average grain sizes about 50nm which is about a hundred times smaller than the crystallites of sintered magnets. The anisotropy axes of these crystallites are randomly oriented therefore they are isotropic [39]. The ribbon pieces are annealed and mixed with resin. Shaping is processed by cold compaction or by plastic injection molding. The route to processing bonded isotropic magnets by compaction is given in Fig. 5.35.

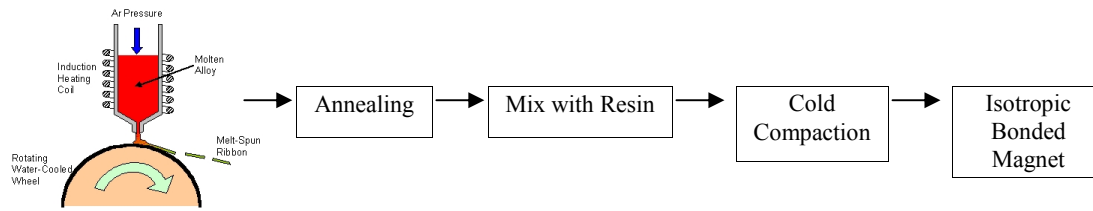


Figure 5.35 : Fabrication process for a bonded isotropic magnet [39].

Most hard magnetic materials are used to make composite magnets, using a metallic or polymer matrix. These magnets are called bonded magnets and they are often isotropic. The magnetic powder is bonded by a polymer, a resin or even a low melting point metal, such as zinc. These products have low production costs, ease of forming and mechanical resistance. Oriented bonded magnets have a magnetization which is two-thirds that of an equivalent sintered magnet [39]. The second quadrant of the hysteresis loop of oriented and isotropic bonded and sintered magnets is shown in Fig. 5.36. The bonded NdFeB type magnets can be used up to about 100 °C however sintered magnets may be used up to 150-200 °C.

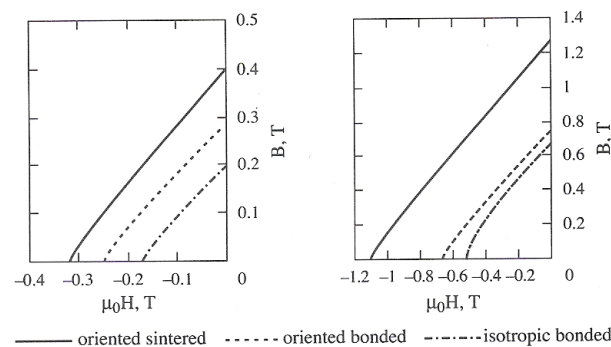


Figure 5.36 : Comparison of the performances of oriented sintered magnets, and isotropic and oriented bonded magnets [39].

5.9 Stability of Permanent Magnets

It is significant to be aware of which conditions could degrade the performance of the permanent magnets. Temporary effects due to operating temperatures beyond the material was designed and secondly, permanent deterioration of the magnetic properties caused by exposure to very high fields (demagnetization) or by alternation of microstructure caused by exposure to elevated temperatures (ageing). The permanent changes which occur as a result of exposure to elevated temperatures are caused by acceleration of the ageing process. Many permanent magnets exist in a metastable metallurgical state so that a phase transformation does occur. At room

temperature it proceeds so slowly, however in high temperatures the phase transformation is very rapid [36]. Other factors like mechanical treatments, corrosion and radiation effects can alter the properties of permanent magnets [36].

In warm and humid atmospheres, the Nd-rich intergranular phase in conventional NdFeB sintered magnets tends to form Nd hydroxides and some free hydrogen, which causes hydrogen embrittlement and therefore conventional magnets are usually coated [120]. The corrosional properties can also be improved by additions of Co, Cu, Al and Ga, their main effect is to transform the intergranular phases into more noble compounds [120]. The low Curie temperature (312 °C) of NdFeB magnets is the major reason for their poor temperature performance. If Co is added to replace Fe, large increases in Curie temperature occur at the expense of some of the magnetic coercive force. Adding small amounts of Al along with Co additions helps retain coercive force with little effect upon Curie temperature increase. Dysprosium (Dy) decreases the energy product but increases the coercivity and therefore also the temperature performance [128]. Hence it improves corrosion resistance [122]. Fully dense, sintered magnets require significant amounts of Dy substitution for the Nd [145].

5.10 Applications

Permanent magnets generate stable magnetic fields without continuous expenditure of electrical energy. Some of the main application areas are electric motors, generators, moving-coil meters, magnetic separators, frictionless bearings [36].

Electric motors, in which electrical energy is converted into mechanical energy, and electric generators in which mechanical energy is converted into electrical energy are the most important application. The size of the motors can be reduced greatly by the use of stronger permanent magnets. The size change can be easily seen on the dc motors shown in Fig. 5.37. NdFeB magnets are also being used in magnetic resonance imaging system [36].

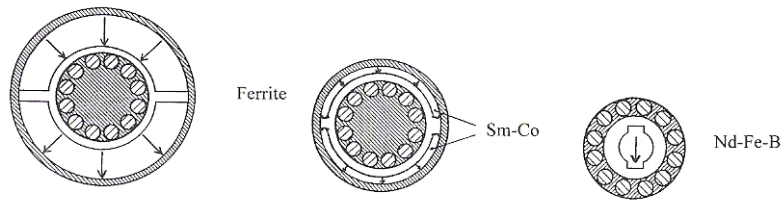


Figure 5.37 : The influence of permanent magnet properties on the design of dc motors [35].

The standard uses of NdFeB magnets depend on the magnet grade, for instance; High J_r sintered magnet: reading head actuators for hard disks, loudspeakers, High H_c sintered: DC motors, magnetic couplings, sensors (ABS) and Bonded NdFeB is for hard disk drive motors, and stepper motors [39].

Permanent magnets are rather brittle. Especially SmCo and ferrites are extremely brittle while sintered NdFeB is less. Therefore magnets should not be incorporated as load-bearing members in a design, particularly in tension or shear. Moreover they should not be treated with threads or pins to serve as mechanical fasteners [146]. Typical applications of permanent magnets depending on the energy density are given in Fig. 5.38.

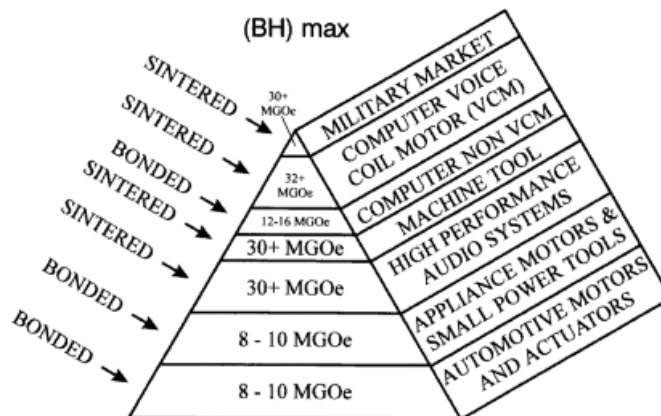


Figure 5.38 : Typical applications of permanent magnets depending on the energy density $(BH)_{max}$ [128].

6. EXPERIMENTAL PROCEDURE

In order to give a brief idea about the mechanical and structural properties of the ZrO₂/WC composites, hot pressing was realized initially to optimize the parameters and to facilitate the CIM process. Since injection molding process requires consuming huge volume of feedstock; concerning the feasibility, pre-investigations were realized by hot pressing. Further on, ceramic injection molding of ZrO₂/WC composites was performed using the selected compositions and approximate sintering temperatures.

Additional studies on powder injection molding process were realized with metal powders namely permanent NdFeB and SmCo magnet powders. Different binder systems, mixing and molding techniques were performed and observed. Following to injection, investigations on debinding and sintering steps were carried out to produce injection molded sintered hard isotropic and anisotropic (oriented) magnets.

6.1 Hot Pressed ZrO₂/WC Composites

Y-TZP/WC composites were prepared by mixing commercially available co-precipitated 3 mol % Y₂O₃ stabilized ZrO₂ powder and 0-40 vol% WC particles homogeneously by attrition milling. Milling was performed in n-propanol to break the agglomerates mechanically and hence to obtain a homogenous microstructure. Milling were carried out for 1 hour in a steel vial using 1 mm Ø WC/Co balls with 6:1 ball to powder ratio (BPR).

As-milled powders were retrieved by drying the resulting dispersions in a rotating vacuum dryer and sieving with 35 mesh. For the preparation of the nano-WC powders, high energy Spex[™] mixer mill was used in dry conditions for 10 min in a WC/Co milling system. A ball to powder weight ratio of 10:1 and a 400 rpm speed were adopted. Totally 200g ball was used. The loading and unloading of the powders into and from the vial were always done in argon filled glove box. The properties of the starting powders are listed in Table 6.1.

Table 6.1 : The characteristics of the starting powders.

Powder Material	Particle Size	S_{BET} (m²/g)	Supplier	Grade
3Y-TZP	590 nm ^a	6.80 ^b	Tosoh	TZ-3YS-E
Coarse-WC	1.49 μm ^a	0.93 ^a	Alfa Aesar	WC
Fine-WC	184 nm ^a	1.64 ^a	Milled	WC

a: measured data, b: supplier's data

Powders were hot pressed in vacuum atmosphere using a heating rate of 50°K/min under 30 MPa for 1 hour in thin boron nitride coated graphite molds. Different sintering temperatures ranging from 1450-1550 °C were applied to optimize mechanical properties.

Using standard metallographic procedures, the hot pressed disks were ground and polished for further tests. Archimedes method was carried out in ethanol to measure the densities of the composites. 3 point bending tests using the DIN EN ISO 6872 standard [147] was applied to five bending bars of each sample at room temperature to determine the flexural strength.

Vickers hardness measurements were carried out on the hot pressed samples using a 10 kg load for 10 sec. By utilizing the Niihara equation [148], the fracture toughness values of the composites were calculated from the crack length measurements obtained with HV₁₀ indentations. The Niihara equation for Median (MED) cracks is given in Eq. 6.1a and for Palmqvist (PQ) cracks in Eq. 6.1b.

$$\left(K_{1c} \phi / Ha^{1/2} \right) \left(H / E \phi \right)^{2/5} = 0.129 \left(\frac{c}{a} \right)^{-3/2} \quad (6.1a)$$

$$\left(K_{1c} \phi / Ha^{1/2} \right) \left(H / E \phi \right)^{2/5} = 0.035 \left(\frac{l}{a} \right)^{-1/2} \quad (6.1b)$$

In the Niihara equation (6.1a and 6.1b), H is the hardness, a is the indent half-diagonal, E is Young's modulus, $\phi (= H/\sigma_y \approx 3)$ is the constraint factor, l is the Palmqvist crack length and c is the radial crack size.

Young's modulus and Vickers microhardness values were determined using a Fischerscope™ HCU microhardness test machine by applying 10 indentations under a load of 100 gr for 10 sec on each sample.

Unlubricated reciprocating wear tests were performed using a pin-on-disc machine (Johann Fischer™) with a 5 mm diameter WC/Co pin at ambient temperature and humidity. The balls were renewed for each experiment. The normal load and sliding speed was 55 N and 0.07 m/s, respectively. For each test, a total sliding distance of 45 km was traveled on a 5 mm stroke. Fig. 6.1 is a sketch representing a brief model of the reciprocating wear (friction) test which was performed on the polished surface of the composites.

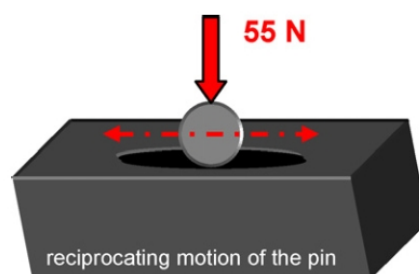


Figure 6.1 : The sketch of the tribological reciprocating wear test.

Friction force was monitored simultaneously using a force transducer. Surface profiles of the worn surfaces and the wear volumes were measured using a profilometer (Mahr™ Perthometer PGK).

Microstructural investigations and observations of the wear traces were carried out using a Leo™ VP 438 scanning electron microscope (SEM) operated at 15 kV. X-ray diffraction (XRD) investigations of the sintered samples were carried out using a Bruker™ D-8 Advance XRD (Cu K α radiation, $\lambda = 0.15418$ nm) diffractometer at 40 kV and 40 mA settings in the 2θ range from 25° to 80° . All XRD experiments were conducted on the polished composite surfaces.

6.2 Ceramic Injection Molded and Sintered ZrO₂/WC Composites

To optimize the stabilizer amount and WC fraction, commercial coarse-WC powders in the amounts varying between 10 vol% to 40 vol% were dispersed in yttria stabilized ZrO₂ matrix. 2, 2.5 and 3 mol% yttria stabilized zirconia were prepared

using suitable mixtures of commercial powders which were unstabilized (pure) ZrO_2 and 3mol% yttria stabilized ZrO_2 (3Y-TZP).

To obtain fine-WC powders, a high energy SpexTM mixer mill was used in dry conditions for 10 min with a WC/Co milling system. The vial and the balls were made of similar material as the powder being milled to avoid cross contamination. A ball to powder weight ratio of 10:1 and a 400 rpm speed were adopted. Totally 200g ball was used. The loading and unloading of the powders into and from the vial were always done in argon filled glove box. Mean particle size of the powders was determined by a MalvernTM Laser particle size analyzer. The properties of the powders are shown in Table 6.2.

Table 6.2 : The characteristics of the starting powders.

Powder Material	Particle Size (D_{50})	S_{BET} ($\text{m}^2.\text{g}^{-1}$)	Supplier	Grade
Pure ZrO_2	560 nm ^a	15.90 ^b	Tosoh	TZ-0
3Y-TZP	590 nm ^a	6.80 ^b	Tosoh	TZ-3YS-E
Coarse-WC	1.49 μm^a	0.93 ^a	Alfa Aesar	WC
Fine-WC	184 nm ^a	1.64 ^a	Milled	WC

a: measured data, b: supplier's data

Commercially available water-soluble (LicomontTM EK 583G) binder was used to prepare the feedstocks. Solid content was varied between 44-51 vol% according to fine and coarse WC content in the composition. Feedstocks were mixed in a double sigma blade kneader (Hermann LindenTM Maschinenfabrik) with a twin screw extruder (ThermofisherTM) unit at 120 °C followed by homogenization of granulated feedstocks in a twin screw extruder at 140 °C.

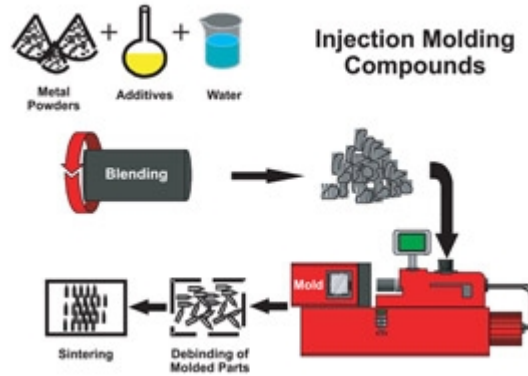
Some extruded bars (30x3x5) were spared for optimizing sintering conditions. Following to homogenization, a capillary rheometer (ThermofisherTM Rheomex) unit was attached to the extruder and rheometer measurements were performed between 130-160 °C and using a nozzle having a diameter (D) of 2.0 mm and length per diameter (l/d) of 15. Granulated feedstocks were injection molded into 2 different molds using optimized parameters given in Table 6.3.

Table 6.3 : Injection molding parameters of the feedstocks.

Molding Variables	3Y-TZP/10WC	3Y-TZP/10WC (75% coarse)	3Y-TZP/20WC	3Y-TZP/40WC
Solid content vol%	46	44	47	51
Mold Temp. (°C)	65	65	65	60
Nozzle Temp. (°C)	160	160	160	155
Injection Speed (cm ³ .s ⁻¹)	40	40	40	35
Injection Pressure (bar)	1350	1350	1550	1600
Hold Pressure (bar)	1400	1400	1400	1200
Cooling Time (s)	20	20	20	20

The given data was used for the mold which has plate and bar cavity.

The dimensions of the first molds were: 7 x 7 x 70 mm stick and a ring that has an outer diameter (øi) of 19.9 mm, a wall thickness (b) of 4 mm and a height (h) of 3.4 mm. As a second mold system, a plate with the dimensions of 32 x 3 x 45 mm and an additional core which has a diameter of 0.3 mm and a bar cavity with the dimensions of 4 x 3 x 30 mm in the same mold were used. The ceramic injection route is summarized in the drawing shown in Fig. 6.2.

**Figure 6.2 :** Injection molding process route [149].

Produced parts were debinded firstly in distilled water at 60 °C for 24 hours, followed by drying at the same temperature. Thermal debinding was carried out at 300 °C using a heating rate of 10 K/hour for 12 hours in air. After all debinding steps shape and weight differences were measured dimensionally. Hg-porosimetry measurements on the brown parts (after debinding) were carried out in a

ThermoScientific Mercury Porosimeter PASCAL 440™ with a mercury surface tension of 480 dyn/cm and a contact angle of 141.3° in average to calculate the pore size distribution. Furthermore, DTA/TG investigations of the green and brown parts were conducted in a Netzsch™ DTA/DSC/TGA up to 1590 °C using a heating rate of 5 K/min. For the green parts (before debinding), DTA/TG measurements were carried out in air, and for the brown parts in Argon (Ar) atmosphere.

To observe the sintering behavior of the debinded parts, dilatometer measurements were conducted in a Netzsch™ dilatometer up to 1590 °C using a heating rate of 5 K/min. On the basis of the dilatometer tests, sintering was performed at 1550 °C with 4 hour and 6 hour dwelling times, using a heating rate of 5 K/min. H₂ gas flowing conditions were employed up to 950 °C without any dwell and followed by Ar gas up to the sintering temperatures and cooling down to the room temperature.

Archimedes density measurements were done using ethanol for sintered samples and followed by metallographic preparations for microstructural analyses. Scanning electron microscope (SEM) (Leo™ VP 438; operated at 15 kV) and X-ray diffraction (XRD) investigations of the sintered samples were carried out using Bruker™ D-8 Advance XRD (Cu K α radiation, λ = 0.15418 nm) diffractometer at 40 kV and 40 mA settings in the 2 θ range from 25° to 80°.

3 point bending tests using the DIN EN ISO 6872 standard [150] were carried out on five bending bars of each sample at room temperature to measure the flexural strengths. Young's modulus and Vickers microhardness values were analyzed using a Fischerscope™ HCU microhardness testing machine by applying 10 indentations under 100 gr load for 10 sec on each sample. Vickers hardness measurements were carried out with a 10 kg load for 10 sec. Using the Niihara equation (Eq. 6.1a and 6.2b), palmqvist and median indentation toughness values of the composites were calculated by the crack length measurements obtained with HV₁₀ indentations [20].

Unlubricated reciprocating wear tests were performed using a pin-on-disc machine (Johann Fischer™) with a 5 mm diameter tungsten carbide ball pin at the ambient temperature and at ambient humidity. The balls were renewed in each experiment. The normal load and sliding speed were 55 N and 0.07 m/s, respectively. For each test, a total of 45 km total sliding distance was performed on a 5 mm stroke. Friction

force was monitored simultaneously using a force transducer. Surface profiles of the worn surfaces and the wear volume were acquired using profilometer (Mahr™ Perthometer PGK).

6.3 NdFeB and SmCo Sintered Isotropic and Anisotropic Permanent Magnets Formed by Metal Injection Molding

Generally, commercial ingots, which are supplied mostly from China and England, are the end products for the raw material suppliers due to shipping restrictions. There are very limited rare earth permanent magnet powder manufacturer in Europe. For NdFeB powders; Magnequench and Ms-Schramberg, for SmCo powders; Ms-Schramberg and Vacuumschmelze are the only companies in Germany that provide commercial-powder. These companies process the NdFeB ingots by hydrogen decrepitation (HD) process and crash them into micron size by jet-milling under inert atmosphere.

In this study, considering the oxidations problems during milling, mainly commercial NdFeB and SmCo powders were preferred. The suppliers and the physical properties of the ingot and powders used in the experiments are indicated in the Table 6.4.

In the very beginning of the experiments, investigations were carried out using an NdFeB ingot provided from China. The ingot (named as CNFB) was crashed utilizing feedstock crusher without applying HD process. Following to coarse crashing, planetary ball milling was realized in dry conditions for 5 hours under N₂ atmosphere.

In every 30 minutes of milling, the system cooled down. The vial and the balls were stainless steel. Into each vial 500g of powder were loaded under Argon atmosphere in the glove box. Ball to powder ratio was 2:1 and 2 balls having 32mm diameter were used for milling. Subsequently powders (shortly m-CNFB powders) were sieved under 63μm in the glove box and around 270g of powder obtained.

Initially obtained SmCo commercial powder from Vacuumschmelze Company (named as VSC) had 139μm particle size. This powder was very coarse for injection molding. Therefore planetary ball milling process was applied in two batches (3 hours and 5 hours milling) under Argon atmosphere. Milling conditions kept the same as NdFeB milling. Following to 3 hours (named as m-VSC powder) and 5

hours (shortly 5m-VSC powder) milling and sieving, 481g and 498g powders obtained, respectively. The rest of the investigations were carried out using the commercial micron-sized powders clarified in the Table 6.4.

Table 6.4 : Properties of the raw material.

Code	Powder	Company	D ₅₀ (μm)	Density (g/cm ³)	Production
MQP	NdFeB	Magnequench	41.25	7.43	HDDR
CNFB	NdFeB	Chinese Company	as-cast ingot	7.6 - 7.7	Melt spun
m-CNFB	NdFeB	Chinese Company	-	7.6 - 7.7	Planetary Milling (3 hours)
SNFB	NdFeB	Ms- Schramberg	4.6	7.60	Jet milled
VSC	Sm ₂ Co ₁₇	Vacuumschmelze	139.1	8.2 - 8.7	Jet milled
m-VSC	Sm ₂ Co ₁₇	Vacuumschmelze	50.31	8.2 - 8.7	Planetary Milling (3 hours)
5m-VSC	Sm ₂ Co ₁₇	Vacuumschmelze	-	8.2 - 8.7	Planetary Milling (5 hours)
SSC	Sm ₂ Co ₁₇	Ms-Schramberg	6	8.25	Jet milled
VSC2	Sm ₂ Co ₁₇	Vacuumschmelze	5.0 - 6.0	8.40	Jet milled

Polymeric binders were prepared in different compositions. Except polyoxymethylene (POM) binder, other binder compositions were defined by Fraunhofer, IFAM. In these binder systems, polyethylene was used as back-bone. Different contents of stearic acid (SA) were added as a surfactant. The details of the binder compositions are mentioned in the Table 6.5.

Table 6.5 : Binder compositions used in the study.

Binder Name	Company	Polyethylene wt%	Waxes wt%	Stearic Acid wt%	Density (g.cc⁻¹)
POM	Atect - Japan				0.96
B41	IFAM	25	73	2	0.91
B32	IFAM	50	49	1	0.93
B27	IFAM	30	69	1	0.92
B39	IFAM	15	83	2	0.91

The solid content for each feedstock were arranged for every composition depending on powder particle size and shape. All the feedstocks were mixed homogeneously in the glow box using Femix™ kneader under Argon atmosphere to inhibit oxidation. The mixing temperature was selected as 120 °C and the inner temperature that thermocouple was measured was around 107 °C. At this temperature, 25rpm rotation frequency was applied and the torque was around 38Nm. The volume of each kneading process was changed due to the volume needed. Subsequent to mixing special cooling schedule were figured out to obtain homogeneously distributed palletized feedstock to be used directly for injection.

Hek™ Injection molding machine was used to mold all different feedstock compositions. Hek™ machine is an old injection molding machine working by air pressure. Air pressure pushes down the top part of the injection insert and this part pushes down the feedstock thus the feedstock comes out from a nozzle tip. The volume of the feedstock in the machine is not digitally recognizable. Additionally the feedstock amount coming out of the nozzle can only be arranged by injection pressure (the pressure obtained through the top part of the injection insert) however it is not precise. The only parameters that the user can change are the injection pressure, the time during pressure apply, injection temperature. Hek™ injection machine does not have the same work mechanism like as usual higher capacity hydraulic injection molding machines where feedstock is pushed forward by a screw. Therefore, the biggest disadvantage of the Hek™ injection machine is that the heated feedstock exposes to air during molding. Moreover, since the injected volume is not adjustable, the over-floated feedstock was re-fed to the nozzle. In Fig. 6.3, the

powder injection molding machines used in the Fraunhofer Laboratories are given. The Arburg™ 320C injection molding machine shown in Fig. 6.3b, is a hydraulic injection molding machine, having 320mm tool width and 50 tones clamp force.

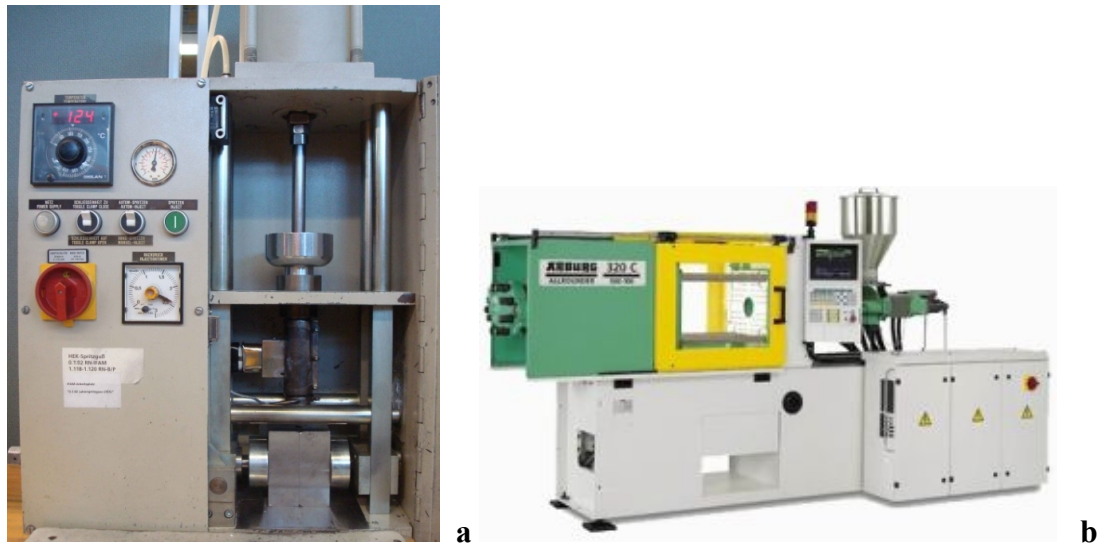


Figure 6.3 : (a) HEK™ and (b) Arburg™ powder injection molding machines.

Arburg™ machine is a conventional screw-type injection molding machine consists of clamping unit, injection unit and control system. The mold, comprising two halves, is mounted in the clamping unit. The screw feeds the compound, compresses it and the nozzle via which the compressed and heated material is injected into the mold under pressure.

Besides isotropic parts, axially single pole and multi pole magnetically aligned green parts were molded using Hek™ and Arburg™ injection molding machines. Magnetic field was created via internally inserted N48 grade NdFeB permanent magnets in the cavity. Commercially available anisotropic NdFeB magnet (N48) discs supplied from Schallenkammer Magnetsysteme, had 1370 - 1430mT remanence, 358 - 382 kJ/m³ max energy product and 80 °C working temperature. These magnets which have magnetic poles on the top and bottom layer, placed inside aluminum (Al) inner molds and the feedstock was injected between these magnets. Magnetic field was obtained on the c-axis of the disc shape cavity. The close loop of magnetic field was provided by the steel mold. Disc and ring shapes were produced via changing the mold insert. The predicted magnetic field in the mold during anisotropic molding is schematically given in Fig. 6.4.

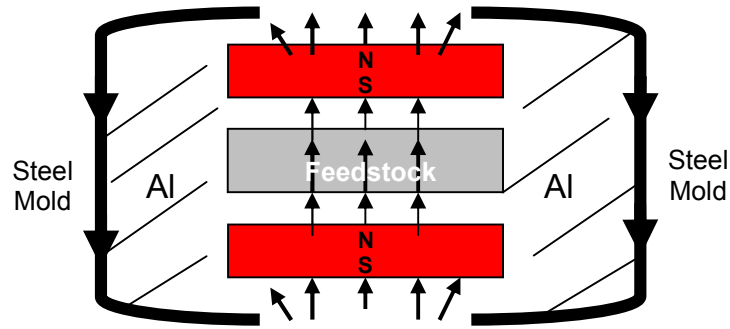


Figure 6.4 : Schematic view of the magnetic field in the mold.

Two different mold inserts were used during molding which are disc and ring shape. The detailed drawing of the disc shape mold insert is given in Fig. 6.5.

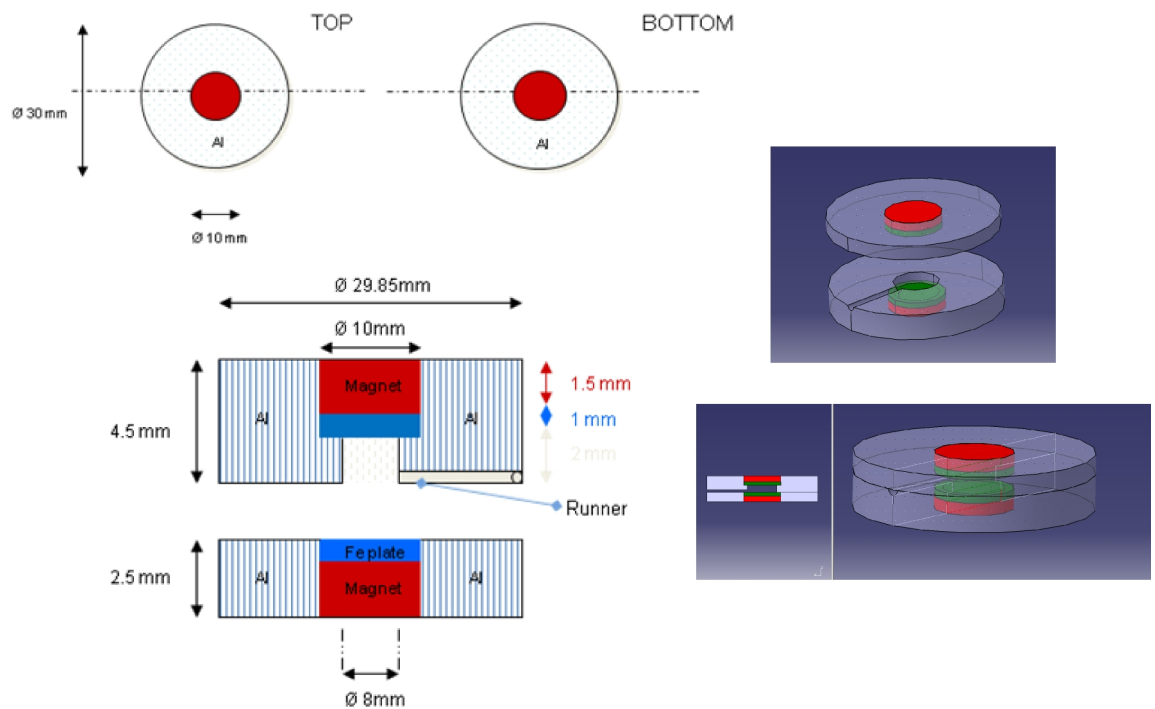


Figure 6.5 : Schematic view of the mold insert for disc shape cavity.

In Fig. 6.5, the red color indicates the N48 grade NdFeB commercial sintered disc shaped magnets ($\text{Ø}10\text{mm}$) and blue color parts represent the 1mm thick stainless steel discs ($\text{Ø}10\text{mm}$). Feedstock flow was enabled by the runner on one side of the inner mold. The cavity has 8mm diameter (Ø) and 2.5mm height. The drawing for the ring shape cavity is given in the Fig. 6.6.

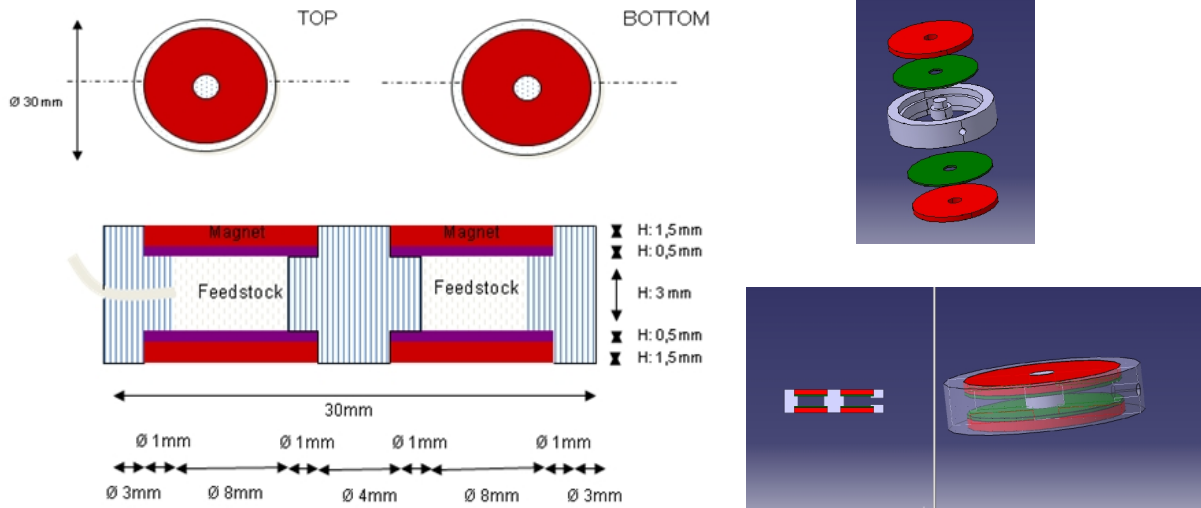


Figure 6.6 : Schematic view of the mold insert for ring shape cavity.

Fig. 6.6 shows the top and bottom look of the inserted inner mold and the cross section drawing of the cavity with the inner mold insert is given. N48 grade NdFeB commercial sintered ring shaped magnets ($\varnothing 10\text{mm}$) and purple color parts represent the 0.5mm thick stainless steel discs ($\varnothing 10\text{mm}$). The main mold is steel and the inner mold constructed using aluminum parts and the commercial magnet ring and stainless steel discs placed inside as shown in Fig. 6.6. The green part have 3mm height and 22mm diameter ($\varnothing$) and its inner hole 6mm $\varnothing$.

For molding isotropic and anisotropic NdFeB, SmCo parts via Hek™ machine, injection pressures around 4 to 6 bars were preferred. Injection temperature was mostly 90 °C in the nozzle. Injection time was taken as 3s and mold temperature was 50 °C. The green densities obtained by Hek™ machine did not provide 100% green densities probably due to insufficient injection pressure problems.

The waxes contained in the green parts were removed totally in hexane after certain of a time. Previous experiments reveal that debinding in room temperature for each 2mm thickness takes 24 hours. The samples placed on pierced stainless steel plates and between the samples and steel plate, paper with holes placed to increase wax absorption. During solvent debinding and drying, the samples were placed under Argon atmosphere.

The polyethylene content in the solvent debinded parts can only be removed thermally. Thermal debinding and sintering were applied in the same cycle without replacing the samples. Elnik™ sintering and debinding furnaces for injection

molding were used in this stage. Thermal debinding process was affected sensitively by the parameters such as, debinding atmosphere, rate and temperature. Different atmospheres such as, argon, vacuum and hydrogen were examined utilizing also different partial pressures and it is found out that only hydrogen was able to remove carbon adequately.

Debinding rate was also played a big role on the remained carbon content. Debinding rates higher than 1 K/min resulted in very low magnetic properties due to the higher carbon levels. Debinding temperature was chosen as 500 °C. Starting from room temperature to 250 °C - 280 °C, 3K/min debinding rate was applicable.

The samples were placed on Yttria coated W plates. Ti traps were placed around the plates to trap the oxygen. However these traps were also absorbed H₂ during hydrogen debinding.

Different sintering atmospheres, for instance, high vacuum, argon and vacuum were examined. Sintering rate was chosen as 5K/min. 1080 °C and 1100 °C sintering temperatures were processed and additionally 1 hour and 4 hour dwelling times were examined in order to check the properties of the sintered part.

The microstructure and phase analyses of the sintered parts were characterized by XRD, SEM/EDX analyses. XRD (Cu K α radiation, $\lambda = 0.15418$ nm) diffractometer at 40 kV and 40 mA settings in the 2 θ range from 25° to 65° with 30sec/step speed. All XRD experiments were conducted on the polished composite surfaces. Before observing by SEM, samples were prepared. They were grinded and polished before etching. Choosing proper etching was a key process to investigate the samples. The Nd-rich phase is sensible to etching and it should be keep in mind that some of this phase can be etched away. On the other hand, it is needed to etch some amount of the Nd-rich phase to observe the grain boundary phase. Due to the literature search, 1g picric acid, 5ml HCl acid and 95cm³ ethanol solution was used as etcher. The SEM micrograph of an NdFeB sintered magnet subsequent to picric acid etching is given in Fig. 6.7. HNO₃ and Aqua regia etchers were also observed. HNO₃ solution was not proper to observe the grain boundaries because it removes the Nd-rich phase and the grain boundaries are not clearly observable. Aqua regia is very strong etcher

which etches away the Nd-rich phase. None of the tried solutions give sufficient microstructure view as picric acid solution.

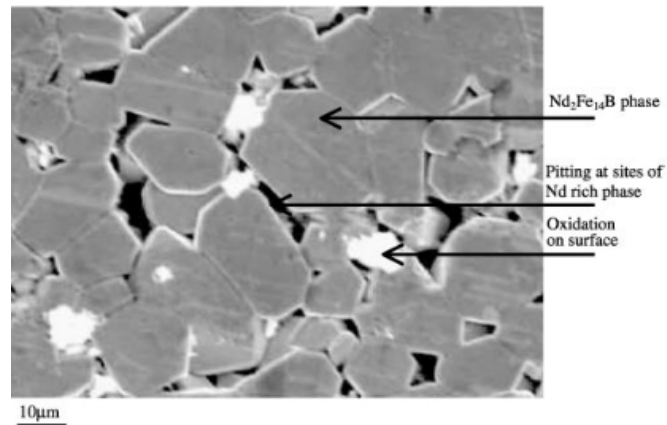


Figure 6.7 : Secondary electron micrograph of etched sample via picric acid solution [151].

The oxygen and carbon level of the sintered samples were measured by chemical tests. The density of the final parts was measured by Archimedes in ethanol and additionally by dimensional calculations.

Magnetic properties of the isotropic and anisotropic parts were examined by Brockhaus™ Hystograph. Before measuring, the samples were magnetized by 2000V Brockhaus™ magnetizer using a 3T (2380 kA/m) magnetization field. Hysteresis loop, coercivity, remanence and max energy product values were measured for each sintered sample.

7. RESULTS AND DISCUSSION

7.1 Hot Pressed ZrO₂/WC Composites

Structural ceramics combining high hardness, toughness, strength and wear resistance can be interesting materials for engineering applications such as cutting tools, punching and stamping dies. Zirconia (ZrO₂) is an example of such structural ceramics. Enhancement in toughness for ZrO₂ ceramics is associated with the martensitic phase transformation from metastable tetragonal phase to monoclinic phase [152-154].

Hence to increase the metastability of the tetragonal phase, stabilizers such as MgO, CaO, Y₂O₃ and CeO₂ were used in literatures [155]. Y₂O₃ is used mostly to improve mechanical properties [97, 155]. Transformability of the tetragonal phase is strongly influenced by the Y₂O₃ content [155]. In order to reach a high value of fracture toughness, tetragonal grain size has to be maintained under a critical size which depends on the yttria (Y₂O₃) content, processing conditions and the degree of mechanical restriction [19, 155].

High fracture toughness value improves the wear resistance of ZrO₂ as well as its hardness [152]. However, hardness of ZrO₂ is only moderate, thus addition of hard phases such as transition metal carbides, borides or nitrides (e.g. TiN and WC) can substantially contribute to hardness increases without affecting the toughness of the ZrO₂ matrix [19].

There are two main factors which enhance the wear performance of a composite; first is the mechanical properties of the reinforcing phase and the matrix, secondly microstructure of the composite which is influenced by particle size and distribution, volume fraction, shape of the reinforcement [30]. Monolithic ceramics generally are not able to withstand abrasive environments due to their relatively low strength and fracture toughness. However, for the ceramic matrix composites, finely and homogeneously dispersed harder particles enhance the mechanical properties of the matrix [157]. It has been shown by Jiang et al. [19] that WC enhances the hardness

and wear resistance of the $\text{ZrO}_2\text{--WC}$ nanocomposites since generally carbide additions hinder the grain growth of the matrix.

Wear of composites also depends on the spacing between reinforcement particles, which can be adjusted by adding small reinforcement particles dispersed in the matrix [30]. Large reinforcing particles usually bear most of the wearing force [158, 205] while uniformly dispersed small particles contribute to strengthening of the matrix [159, 160]. Therefore, if a composite consists of both large and small reinforcing particles, it could have higher resistance to wear than the one reinforced by either only large particles or small particles.

In this study, the effect of mechanical and microstructural properties of Y-TZP/WC composites on their tribological behavior was investigated. The obtained data would be cooperative for the further investigations on these composites performed by ceramic injection molding process.

In prior studies, it was found out that for co-precipitated zirconia powders, 3 mol% Y_2O_3 stabilizer content was the optimum amount to achieve the highest Young's modulus, hardness, and indentation toughness values [23]. The indentation toughness value of the 2Y-TZP/WC (40 vol% WC) composite was $5.20 \text{ MPa.m}^{1/2}$ which was increased to $6.54 \text{ MPa.m}^{1/2}$ for the 3Y-TZP/WC (40 vol% WC) composites; sintered at 1450°C . The expended results for varying Y_2O_3 mol% amount and sintering temperature are summarized in the Table 7.1.

Table 7.1 : Mechanical properties of Y-TZP matrix 40vol% WC dispersed composites with varying Y_2O_3 mol% and sintering temperature.

Y_2O_3 (mol%)	T ($^\circ\text{C}$)	Rel. Density %	Strength (MPa)	HV _{0.1} (GPa)	E (GPa)	K_{IC} ($\text{MPa.m}^{1/2}$)
2.00	1450	94	360	9.51 ± 0.83	216 ± 7	5.20 ± 0.32
2.50		94	518	10.32 ± 0.61	261 ± 6	5.35 ± 0.29
3.00		95	652	15.25 ± 1.33	312 ± 14	6.54 ± 0.20
3.50		94	378	10.30 ± 0.53	164 ± 6	4.24 ± 0.47
2.00	1550	93	525	17.35 ± 0.86	329 ± 9	5.89 ± 0.35
2.50		96	782	15.82 ± 0.78	316 ± 7	6.19 ± 0.23
3.00		99	843	18.58 ± 0.69	374 ± 6	6.89 ± 0.15

Either the stabilizer content increased or decreased from 3 mol%, the fracture toughness lowers considerably. Hardness and strength is also considerably higher in 3Y-TZP/WC. It is known that Young's modulus (E) is influenced by the WC amount in the matrix according to the phase rule. Even though the WC amount kept as 40 vol% for all compositions, the E was changed significantly with yttria stabilizer amount. In accordance with the Niihara's formula [148], toughness increases with rising hardness and Young's modulus. Thus, the increase of toughness is likely to be an artefact of different relative density. Low crack-to-indent ratio size was present in the samples which indicate Palmqvist cracks. For the Palmqvist cracks, the equation is given in Eq. 7.1,

$$\left(\frac{K_{IC} \phi}{H a^{1/2}} \right) \left(\frac{H}{E \phi} \right)^{2/5} = 0.035 \left(\frac{l}{a} \right)^{-1/2} \quad (7.1)$$

where H is the hardness, a is the indent half-diagonal, E is Young's modulus and c is the radial crack size [148].

Therefore, in 3Y-TZP composites, stabilizer content is enough to keep the tetragonal phase stabilized at room temperature and maintain stress induced phase transformation to improve fracture toughness. The Vickers hardness and indentation toughness results of the 3Y-TZP/WC (32 vol% WC) composites with respect to sintering temperatures are shown in Fig. 7.1. Hereafter, 3Y-TZP/WC composite having 40 vol% WC phase will be named as 3Y-TZP/40WC and the other compositions will be named similarly as well.

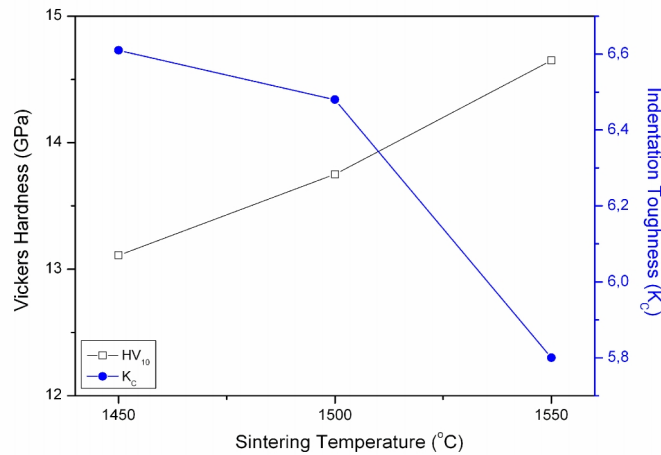


Figure 7.1 : The mechanical properties of the 3Y-TZP/32WC composite with respect to sintering temperature [23].

In order to optimize the sintering temperature, samples were hot pressed at 1450 °C, 1500 °C and 1550 °C. Although for 3Y-TZP/40WC composites sintering at 1550 °C improved the results, for the composites having less than 40vol% WC indentation toughness values were declined sharply in contrast to hardness and density enhancement. Furthermore, the flexural strength value of the 3Y-TZP/32WC composites decreased slightly from 1179 MPa to 990 MPa as sintering temperature increased from 1450 °C to 1550 °C. Samples were fully densified ($\rho > 98\%$ relative) even at 1450 °C, therefore this sintering temperature was chosen for the rest of the experiments.

Detailed information about the grain size of the WC dispersion phase was obtained by back scattered electron images (BSE) given in Fig. 7.2. Figs. 7.2a and 7.2b are the BSE images taken from the crack path of 3Y-TZP/32WC composites sintered at 1450 °C and at 1500 °C, respectively. On top of each image, there is a 5kX magnified version of the non-cracked surface. The light grey phases indicate the WC phases and the Y-TZP matrix was determined as the dark grey phase.

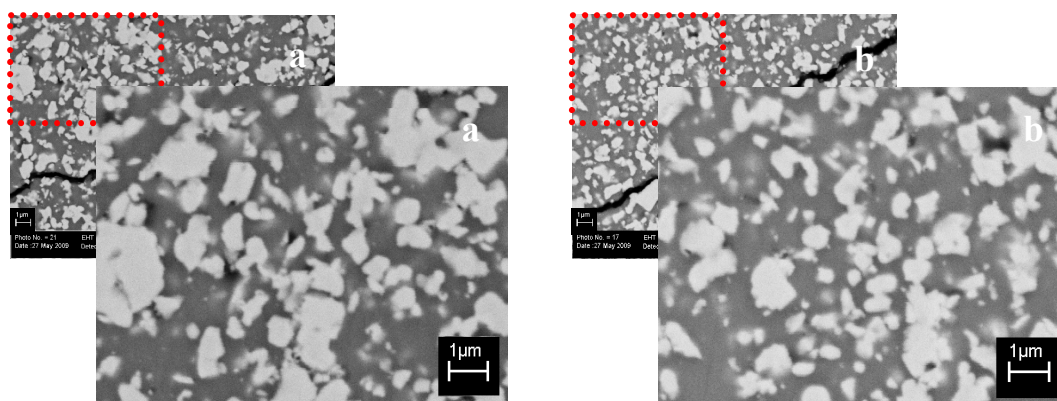


Figure 7.2 : Back-scattered electron (BSE) images of the 3Y-TZP/32WC composites sintered at: (a) 1450 °C and (b) 1500 °C. From a selected part of the 5kX BSE images, equally magnification applied to create the top detailed images, WC (white phase), 3Y-TZP matrix (grey phase).

It is commonly believed that fracture toughness increases with decreasing grain size as composition and other microstructural variables are held constant [161-163]. For transformation toughened composite materials, this is only partially true as the increasing size of zirconia grains leads to increase in transformability and increasing fracture toughness owing to an increasing transformation zone size [164, 165]. However, this effect should not be overstressed as grains exceeding a critical

threshold size will transform to monoclinic during cooling with a significant decrease in tetragonal content and thus cause toughness decreases [165]. According to BSE images in Fig. 7.2, with increasing sintering temperature, WC grain growth was not observed. On the other hand, the sizes of ZrO₂ grains could not be precisely measured since the grain boundaries were not distinctly etched using both thermal and chemical etching. Nevertheless, the study of Singh et al. [166] pointed out that, as the sintering temperature increased from 1450 °C to 1550 °C, the grain size of pure co-precipitated 3Y-TZP ceramic increased slightly from 400 nm to 700 nm. However, the fracture toughness values remained constant at around 5 MPa.m^{1/2}. Our previous study [23] revealed that as the sintering temperature increased from 1450 °C to 1550 °C, the indentation toughness of the 3Y-TZP/32WC composite decreased slightly although density, hardness and Young's modulus values were improved. Therefore, it is expected that at higher temperatures, larger grains tend to transform to monoclinic phase during cooling which lowered the toughness.

The XRD patterns of the 3Y-TZP/32WC composites sintered at 1450 °C, 1500 °C, and 1550 °C are given in Fig. 7.3a, 7.3b and 7.3c, respectively. Three major peaks in all figures matched the ICDD card values of the stable ZrO₂ phase (Bravais lattice : primitive tetragonal, Space Group : P42/nmc) [167], the WC phase (Bravais lattice : primitive hexagonal, Space Group : $P\bar{6}m2$) [168] and the W₂C phase (Bravais lattice : primitive hexagonal, Space Group : P6₃/mmc) [169]. The W₂C phase emerges in the microstructure at 1450 °C and its amount continuously increases with increasing sintering temperatures (traces B and C of Fig. 7.3). The peak which is around 45° could not be identified. Since this peak was observed in all XRD scans, it is believed that it was reflected from the base-holder.

According to XRD results presented in Fig. 7.3, the reduction of the indentation toughness at higher sintering temperatures can most probably be attributed to increasing amount of ditungsten carbide (W₂C) phase. Zirconia (ZrO₂) seems to react with tungsten carbide (WC) forming ditungsten carbide (W₂C) and carbon monoxide (CO) due to the equation 7.2 [27]:



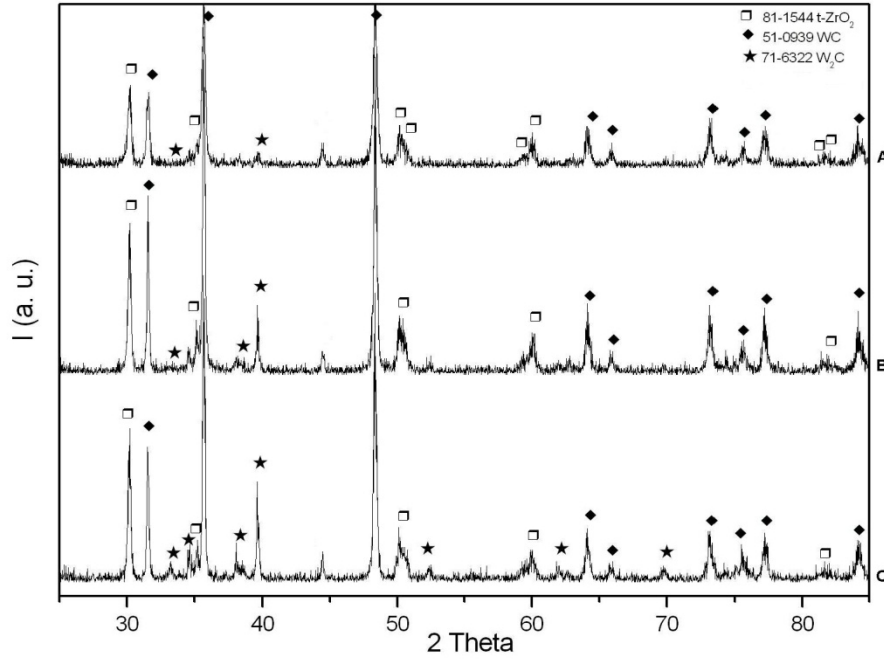


Figure 7.3 : XRD patterns of the 3Y-TZP/32WC composites hot pressed at 1450 °C (A), 1500 °C (B), and 1550 °C (C).

Equation 7.2 can be shown thermodynamically using Factsage program. The free energy-temperature graph shown in Fig. 7.4 reveals that at higher than 1800 °C the equation will go to the productions direction. However the process temperatures that we have used were around 1450 °C. The reason why this reaction goes to the production side at these lower temperatures can be explained by Van't Hoff equation given in Equation 7.3.

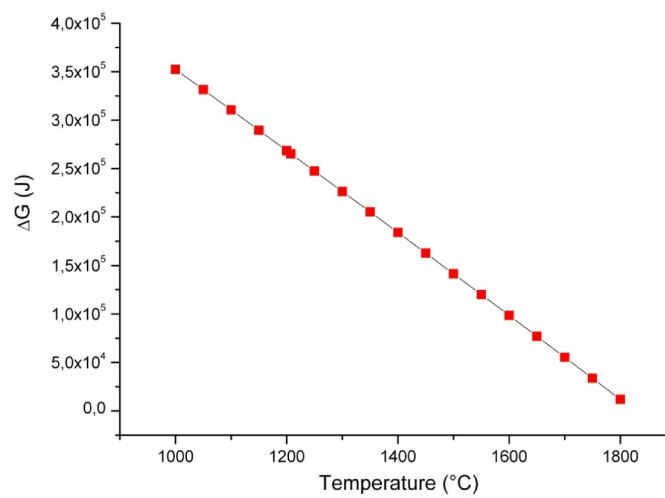


Figure 7.4 : $\Delta G - T$ diagram of Equation 7.2.

Equation 7.3 shows the Van't Hoff equation relates the change in temperature T to the change in the equilibrium constant K, given the standard enthalpy change ΔH for the process gas constant free energy equation.

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$\Delta G = -R \cdot T \cdot \ln K \quad (7.3)$$

$$K \text{ (equilibrium constant)} = \frac{[W_2C]^3 \cdot [CO]^2}{[ZrO_2]^1 \cdot [WC]^6 \cdot [ZrC]^1}$$

gas

We can assume that under vacuum conditions since the CO gas will leave the system, and the equation will need to compensate and forced to be to the productions direction.

On the basis of XRD measurements, Haberkro et al. [27] reported the formation of the ZrC phase in the 20 vol% WC dispersed ZrO₂ matrix composites sintered at 1700 °C. Moreover, they also identified the ZrC phase in TEM investigations of the samples sintered around 1400 °C. It is supposed that ZrO₂ incorporated some carbide either into the anionic sublattice or as nanoscale zirconium carbide making the reaction product very difficult to be detected in the XRD patterns. Anionic lattice stabilization by carbon or nitrogen can stabilize tetragonal phase and lower transformability. W₂C phase is equally hard but more brittle than WC and may contribute to the loss of toughness at higher sintering temperatures [170].

The effect of WC amount on the mechanical and microstructural properties of the fine 3Y-TZP matrix composites was observed by reinforcing with 5-40 vol% micron-sized WC particles.

The most significant influence of WC addition was the increase of the indentation toughness while hardness remained similar. The carbide reinforcements hinder densification of the composites with increasing WC addition.

The mechanical and physical properties of the 3Y-TZP matrix composites containing different WC contents are given in Table 7.2.

Table 7.2 : Mechanical properties of the 3Y-TZP/WC composites hot pressed at 1450 °C.

WC (vol %)	Relative Density (%)	Strength (MPa)	E (GPa)	HV ₁₀ (GPa)	K _C , PQ (MPa.m ^{1/2})	K _C , MED (MPa.m ^{1/2})
40	95.26	452	312 ± 14	13.80 ± 0.50	6.54 ± 0.20	8.52 ± 0.39
32	98.34	1179	312 ± 5	13.11 ± 0.29	6.52 ± 0.21	8.56 ± 0.41
20	98.87	969	273 ± 3	13.60 ± 0.45	6.48 ± 0.28	8.64 ± 0.58
10	99.20	1476	272 ± 2	12.85 ± 0.38	5.67 ± 0.11	7.13 ± 0.25
5	99.60	1282	265 ± 2	14.22 ± 0.04	5.22 ± 0.08	6.11 ± 0.17
0	100.00	1291	235 ± 3	14.24 ± 0.18	5.05 ± 0.03	5.97 ± 0.06

Toughness measurements were calculated by Niihara palmqvist (PQ) and median (MED) equation

Following sintering at 1450 °C, 3Y-TZP matrix composite samples were ground and polished. As can be seen in Table 7.2, relative density % values decrease with increasing WC content, inferring that WC impurities restrain the densification. Nevertheless, except for the sample containing 40 vol% WC, the density values of all sintered samples (3Y-TZP and 3Y-TZP/WC composites) were fairly good.

The flexural strength values fluctuated with increasing WC contents, but the 40 vol% WC containing composite displayed the lowest strength value. This composite also had the lowest density value as a result of incomplete sintering. Regarding the indentation toughness measurements, no evidence was found whether the cracking mode was palmqvist or median. However, Niihara's palmqvist crack equation (Eq. 7.1) is more suitable to our case as crack to indent ratio size (l/a) is low. For all samples, indentation toughness and hardness values increased systematically with increasing WC content.

The thermal expansion mismatch between the 3Y-TZP matrix and WC particles was probably caused by residual thermal stresses within and around WC particles during furnace cooling to room temperature. The thermal expansion value of the 3Y-TZP matrix (α_m) is $11.0 \times 10^{-6} \text{ K}^{-1}$ [20] and the WC particle (α_p) is $5.2 \times 10^{-6} \text{ K}^{-1}$, i. e. $\alpha_m > \alpha_p$ [20]. Subsequent to cooling, the interface was left under compressive load. Depending on the strength of the interface, tangential tensile stresses could cause

radial microcracks around the WC particles in the ZrO_2 matrix associated with transformation around WC grains. On the other hand, during cooling this would lower the toughness [20, 28, 171]. A weak interface will facilitate crack deflection which would improve toughness.

Lange [172] has pointed out that the incorporation of a second phase with high modulus increases toughness significantly. Thus, the high Young's modulus of WC (700 GPa) will contribute strongly to toughness of the composites. Increase in toughness values with WC content indicates that mechanisms hindering crack propagation were dominant [173]. On the basis of Table 7.2, the 3Y-TZP composite containing 32 vol% WC has the best overall mechanical properties.

Figures 7.5a, 7.5b and 7.5c are the SEM micrographs taken from the 3Y-TZP matrix reinforced with 20 vol%, 32 vol% and 40 vol% WC particles, respectively. Due to the activation of the crack deflection, crack branching and bridging mechanisms observed on the etched crack surfaces shown in Fig. 7.5, toughness increased.

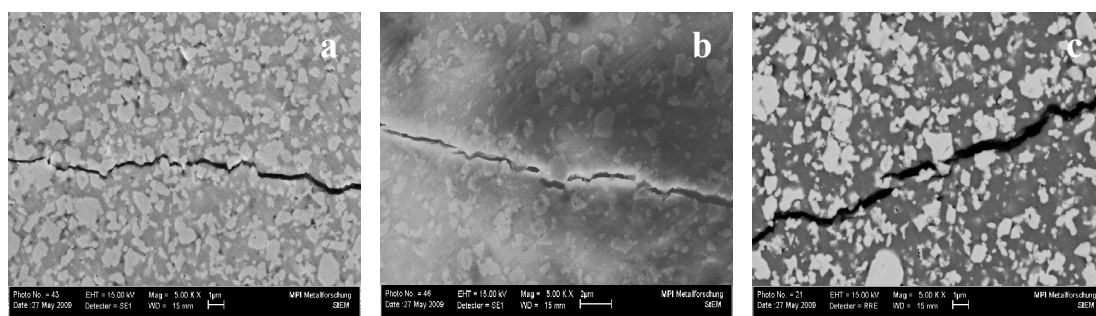


Figure 7.5 : Propagation of an indentation crack on the 3Y-TZP matrix containing: (a) 20 vol% WC, (b) 32 vol% WC and (c) 40 vol% WC.

Figure 7.6 shows XRD patterns taken from the 3Y-TZP/WC composites hot pressed at 1450 °C reinforced with : A) 0 vol% WC, B) 20 vol% WC, C) 32 vol% WC and D) 40 vol% WC particles. As seen in Fig. 7.6, with increasing WC content in the 3Y-TZP matrix, more W_2C phase was formed. It is believed that zirconia powders formed a gas tight matrix at lower sintering temperatures and prevented the escape of gaseous products like CO which eventually enabled the formation W_2C . This concept was followed by Jiang [19] successfully using the more silica rich and sinterable Daichi HSY-3U zirconia powder.

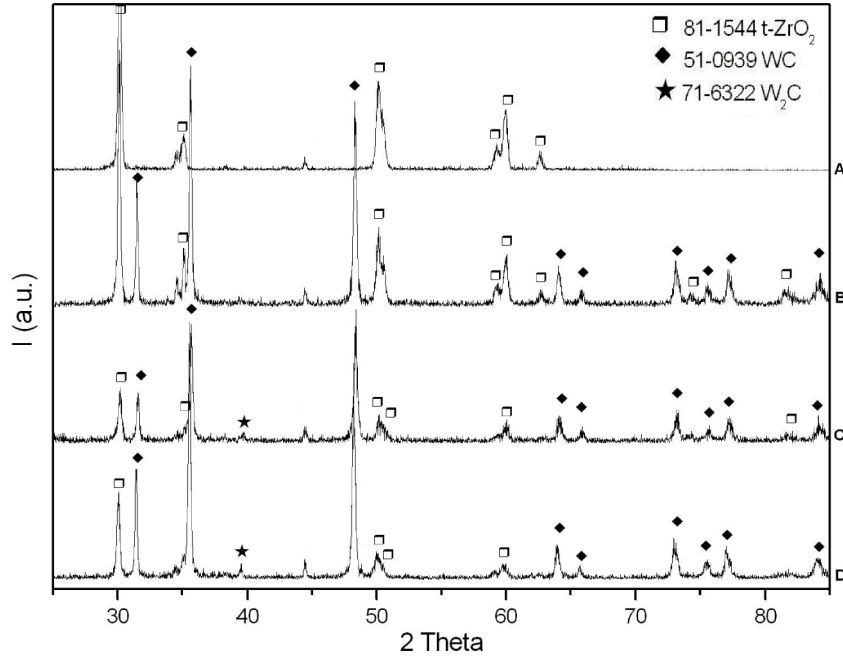


Figure 7.6 : XRD patterns of the 3Y-TZP/WC composites hot pressed at 1450 °C reinforced with: (A) 0 vol%, (B) 20 vol%, (C) 32 vol% and (D) 40 vol% WC particles.

Fig. 7.7 shows in-situ high temperature XRD patterns of the 3Y-TZP/40WC composite taken between room temperature and 1450 °C at temperature increments of 50 °C. These in-situ XRD patterns during heating up from RT to 1300 °C indicated that in addition to some unidentifiable peaks occurring at very low 2θ angles, no evidences of any phase changes were observed.

As expected, less than 20°, monoclinic ZrO₂ had a peak with a low intensity which is marked in Fig. 7.7b. According to the analyses, this phase started to form at temperatures above 1000 °C.

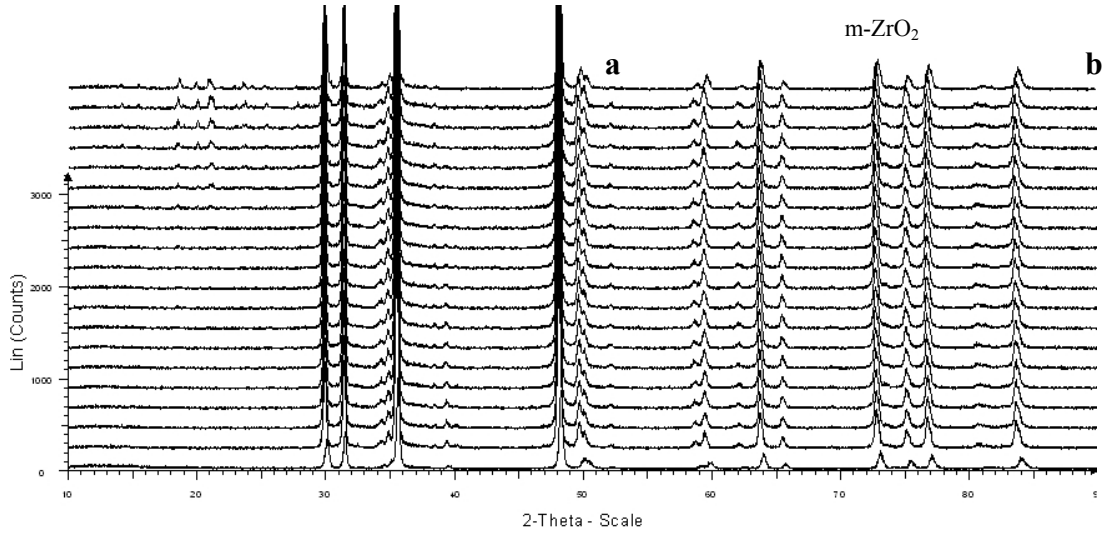


Figure 7.7 : In-situ XRD patterns of 3Y-TZP/40WC composite starting from ambient temperature up to 1450 °C with 50 °C increment (a), detailed view up to $2\theta = 30^\circ$ (b).

Thus, on the basis of the presented data, increasing the sintering temperature in order to obtain higher density and better mechanical properties seems an invalid strategy. Based on existing literature the assignment of toughness reduction to a single cause seems incorrect.

The effect is probably caused by a superposition of several phenomena. However, it can be assumed that the main reason for high indentation toughness results in general are due to the combination of martensitic phase transformation with crack deflection, crack branching and bridging mechanisms.

The effect of WC amount on wear performance was examined via unlubricated sliding pin-on-disc tests. The volumetric wear rate (kv) was calculated by using Archard's Equation [174] given in equation 7.4:

$$kv = \frac{V_{wear}}{F_N \times s} \left(\frac{mm^3}{N.m} \right) \quad (7.4)$$

Where F_N is the normal load, s the sliding distance, V_{wear} is the wear volume and kv is the wear rate. Wear test results of 3Y-TZP/WC composites hot pressed at 1450 °C are listed in Table 7.3.

Table 7.3 : Dry reciprocating wear test results of 3Y-TZP/WC composites under 55N normal load with a sliding distance of 45 km against WC-Co.

WC (vol %)	Friction Force (N)	Friction Coefficient (μ)	Wear Volume (mm ³)	k_v (10 ⁻⁸ mm ³ /N.m ⁻¹)
40	21.31	0.39	0.02	0.80
32	22.92	0.42	0.03	1.21
20	26.58	0.48	0.04	1.62
0	37.40	0.68	0.15	6.06

As clearly seen in Table 7.3, the presence of homogeneously dispersed hard WC particles added in increasing amounts significantly enhanced the tribological behavior of 3Y-TZP matrix composites. The worn volume was reduced nearly 15 percent with 40 vol% WC addition.

Although the hardness, strength, and density of 3Y-TZP/40WC were lower than the pure 3Y-TZP matrix, the improvement in wear resistance could be attributed to the high indentation toughness because the critical load of crack propagation was influenced by toughness. Bhushan [175] stated that low toughness reduces wear resistance by introduction of micro-fracture at contact surfaces in sliding.

Fracture toughness (K_{IC}) and friction coefficient (μ) values of the ZrO₂/WC composites with respect to WC amount are presented in Fig. 7.8. As the toughness increases with increasing WC amounts, the friction coefficient decreases, implying that the wear resistance increases.

In the present study, it may be speculated that higher contents of WC will increase the thermal conductivity and thus the long term stability of the zirconia by preventing heating up. The fact that the worn surfaces did not show any evidence of spallation or cracking support this assumption that the matrix remained stable during the wear test and was able to keep hold of the dispersed WC.

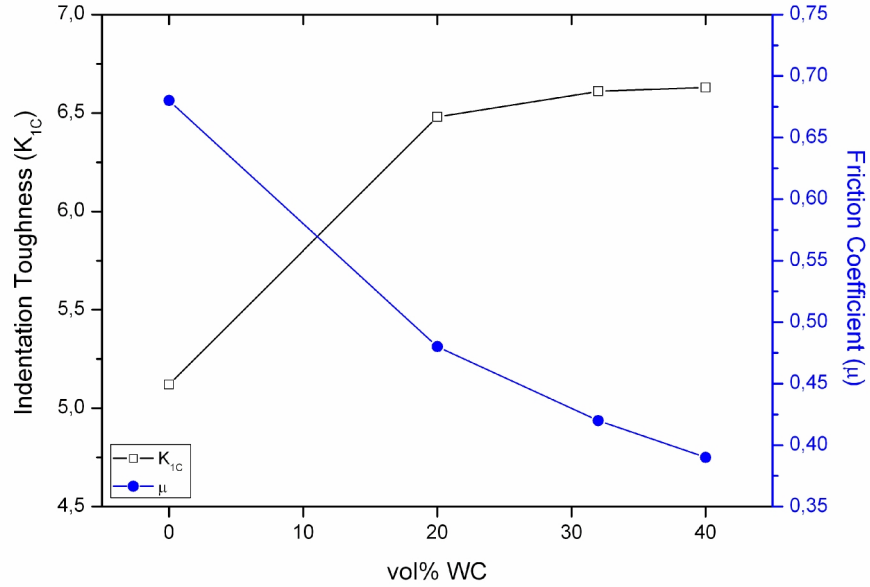


Figure 7.8 : Indentation toughness (K_{IC}) and Friction Coefficient (μ) values of the ZrO_2/WC composites with respect to WC vol% amount.

7.1.1 Effect of bimodal WC particle size distribution

In order to enhance the mechanical properties of the compacts further, different percentages of nano-WC particles were mixed with micron-sized WC particles. Packing density of the bi-modal composites was increased by increasing particle size distribution broadening.

In addition to improved sintered density, higher Young's modulus and indentation toughness was achieved. In Table 7.4, relative densities and some mechanical properties of the 3Y-TZP/WC (40 vol%) composite as a function of the vol% coarse WC are listed.

Table 7.4 : Relative density % values and mechanical properties of 3Y-TZP/40WC composites sintered at 1450 °C as a function of coarse-WC content.

Coarse WC (vol %)	Relative Density (%)	Strength (MPa)	E (GPa)	HV ₁₀ (GPa)	K_{IC} , PQ (MPa.m ^{1/2})	K_{IC} , MED (MPa.m ^{1/2})
100	95.26	452	312 ± 14	13.80 ± 0.50	6.54 ± 0.20	8.52 ± 0.39
75	97.00	763	367 ± 4	13.82 ± 1.05	6.84 ± 0.64	8.89 ± 1.31
25	98.01	827	371 ± 3	15.92 ± 0.30	6.85 ± 0.35	8.56 ± 0.68

Toughness measurements were calculated by Niihara palmqvist (PQ) and median (MED) equation

The reason for the slight increase in the hardness and enhancement in the indentation toughness of the 75 vol% coarse WC dispersed 3Y-TZP/40WC composite can be explained by XRD phase analysis. According to Fig. 7.9, it's clear that W_2C phase formation was increased with higher nano-WC addition. Brittle W_2C enhanced hardness but indentation toughness was decreased slightly when nano-WC increased to 75 vol%.

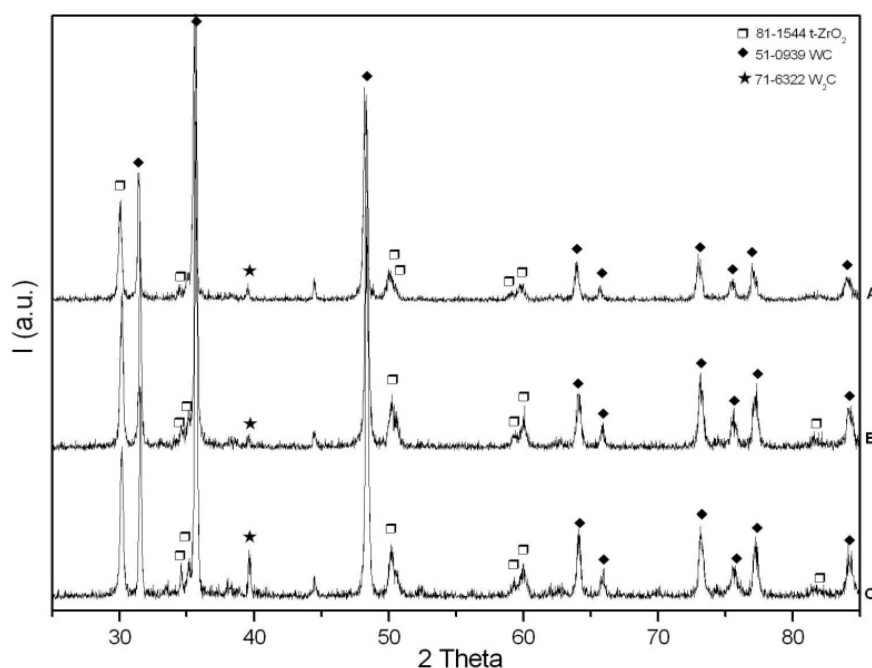


Figure 7.9 : XRD patterns of the bimodal particle size distributed 3Y-TZP/40WC composites; coarse WC particle dispersion value of 100 vol% (A), 75 vol% (B), 25 vol% (C), respectively.

In addition to improvements in indentation toughness and strength, wear resistance of the composites were enhanced significantly by nano-WC additions. As indicated in Table 7.5, the wear rate was decreased from 0.8×10^{-8} to $0.12 \times 10^{-8} \text{ mm}^3/\text{N.m}^{-1}$.

Even with dry sliding conditions under relatively high normal load and long operation conditions the worn volume was 0.003 mm^3 for the 25% coarse nano-WC distributed 3Y-TZP/40WC composite. The wear resistance was enhanced significantly and the value is satisfactory compared to those reported in the literature [176, 177].

Table 7.5 : Dry reciprocating wear test results of 3Y-TZP/40WC composites as a function of coarse-WC content under 55N normal load with a sliding distance (s) of 45 km.

Coarse WC (vol %)	Friction Force (N)	Friction Coefficient (μ)	Wear Volume (mm ³)	k_v (10 ⁻⁸ mm ³ /N.m ⁻¹)
100	21.31	0.39	0.02	0.80
75	20.36	0.37	0.01	0.40
25	19.38	0.36	0.003	0.12

Coefficient of friction (COF) was recorded simultaneously by the computer and the values are shown in Fig. 7.10. Figs. 7.10a through 7.10e present the coefficient of friction values (μ) versus sliding distance (in km) of the 3Y-TZP composites hot pressed at 1450 °C.

In Fig. 7.10, the lines represent the samples by order of without WC addition (Fig. 7.10a) and containing 20 vol% WC (Fig. 7.10b), 40 vol% WC (Fig. 7.10c), 40 vol% WC (75% coarse + 25 vol% nano-sized), (Fig 7.10d) and 40 vol% WC (25% coarse + 75 vol% nano-sized) (Fig 7.10e). For a constant normal load, the friction force fluctuated with respect to sliding distance.

However, the fluctuations were very small in the 25% coarse WC dispersed 3Y-TZP/40WC composites. In general, the COF curve of the pure 3Y-TZP material has a shape different oscillation; it was just decreased from the constant COF value. This behavior can occur due to hard on soft WC-Co/ZrO₂ sliding contact which cause adhesion.

On the other hand, with hard WC additions to the matrix, hard on hard WC-Co/WC sliding increased the friction coefficient. Steady state regime was obtained after about 35 km sliding distance of the all range particle size distributed 3Y-TZP/40WC composites. The friction coefficient levels decrease with increasing WC content. Best and most constant values were obtained with 40 vol% WC (25% coarse).

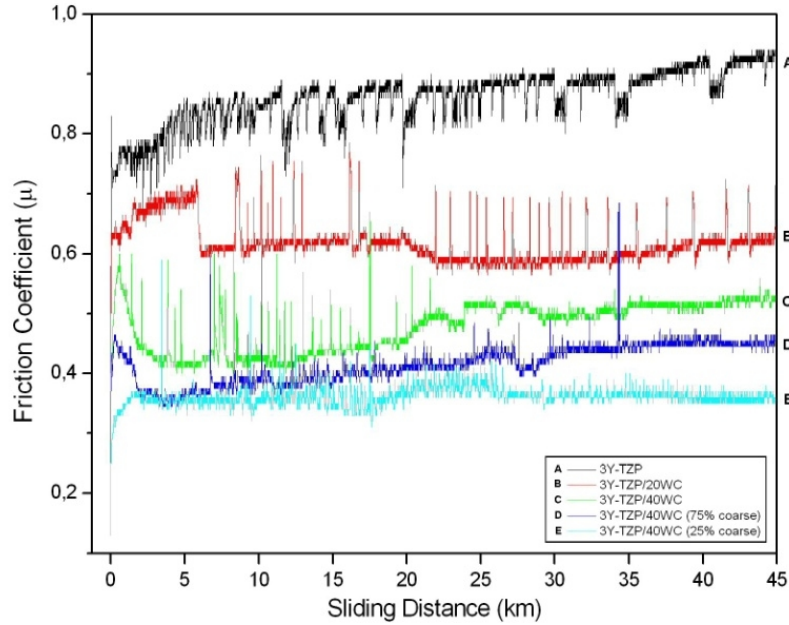


Figure 7.10 : Friction coefficient curves of the 3Y-TZP composites hot pressed at 1450 °C as a function of sliding distance under 55N constant normal load with a sliding velocity of 0.07m.s^{-1} : (A) 3Y-TZP composites without WC addition and containing, (B) 20 vol% WC, (C) 40 vol% WC, (D) 40 vol% WC (75% coarse + 25 vol% nano-sized) and (E) 40 vol% WC (25% coarse + 75 vol% nano-sized).

The inverted profiles of the abraded surfaces are given in Fig. 7.11. By means of the 3-D surface topographies, it is clear that the 3Y-TZP matrix structure without WC reinforcement had a deeper wear track than the ones with WC additions.

Relatively flat and shallow abraded surface of 3Y-TZP/40WC (25% coarse) was obtained with bi-modal particle size WC-reinforcement. Consequently, these large and small WC reinforcing particles enhanced the wear resistance considerably more than those containing only large or small WC particles.

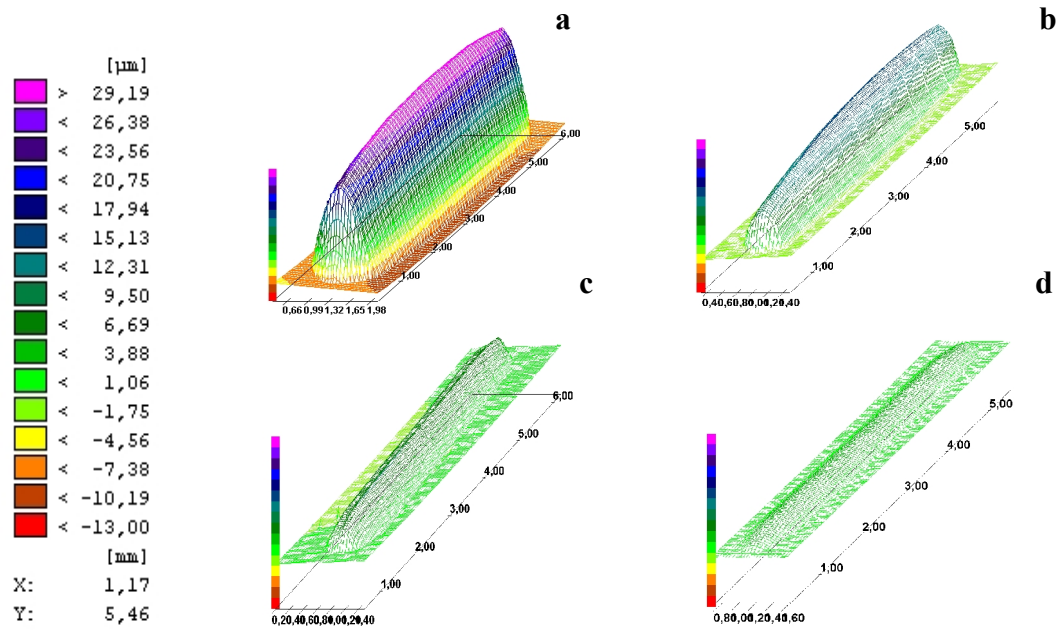


Figure 7.11 : Inverted 3-D surface profiles of the parts after 45 km unlubricated wear test run. The tracks belong to (a) 3Y-TZP, (b) 3Y-TZP/20WC, (c) 3Y-TZP/40WC and (d) 3Y-TZP/40WC (25% coarse), respectively.

Figure 7.12a, 7.12b, 7.12c are respective SEM micrographs taken from the middle part of the wear traces of the 3Y-TZP matrix composites without WC addition and those containing 40 vol% WC, and 40 vol% WC (25% coarse +75 vol% nano-sized) at a total sliding distance of 45km under a normal load of 55N.

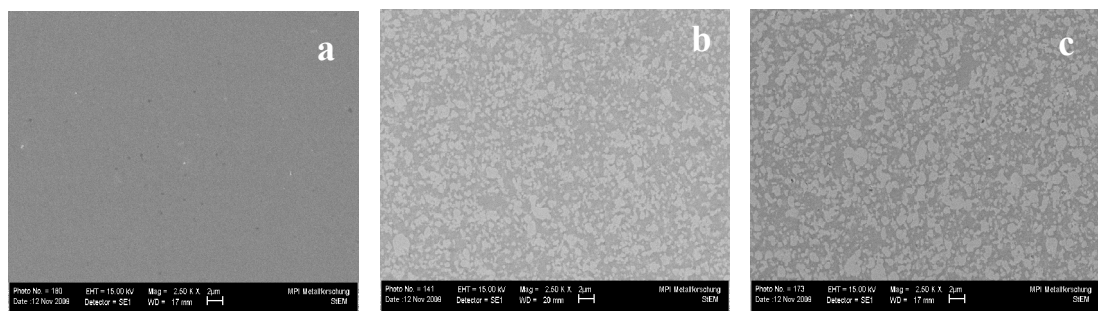


Figure 7.12 : SEM images taken from the middle part of the wear traces of ZrO_2/WC composites after 45 km run, (a) 3Y-TZP, (b) 3Y-TZP/40WC and (c) 3Y-TZP/40WC (25% coarse), respectively.

The SEM images of Fig. 7.12 reveal that on the wear layer there was neither an adhesion of the debris nor any microcracks along the wear trace. Initially, all the abraded material was removed from the debris layer and did not stick onto the wear layer afterwards. The same wear behavior was found in all composites. The bimodal

particle size distribution did not have any effect on the surface morphology of the worn surface.

7.2 Ceramic Injection Molded and Sintered ZrO₂/WC Composites

Ceramic injection molding (CIM) is an innovative forming technique in manufacturing a range of components, including those with a high geometric complexity and offering an economic solution for difficult production problems. CIM has become a highly attractive process for the production of geometrically complex ceramic parts in large scale manufacturing [8]. The inherent hardness of ceramics infers that manufacturing complex shaped ceramic components by standard machining processes can be expensive. CIM offers an economic solution for delivering repeatable, ultra high precision ceramic components. The injection molding of ceramics is a new and innovative process that provides cost effective solutions for design engineers requiring complex, repeatable ceramic components [8, 9, 43].

Tetragonal zirconia polycrystalline (TZP) materials have high bending strength and excellent fracture toughness by martensitic stress-induced phase transformation from tetragonal to monoclinic [17]. To increase the modest hardness of Y-TZP material, homogeneously distributed hard phase is expected to increase the hardness and wear resistance [19] since generally carbide additions hinder the grain growth of the matrix. Although B₄C, TaC and TiC phases have higher hardness values than WC, they need higher sintering temperatures resulting in fracture toughness loss of the zirconia matrix [20-22]. WC has excellent high temperature strength and it is chemically and thermally stable even at high temperatures. It is reported that ZrO₂/WC composites have sufficient bonding between two phases which is expected to improve mechanical properties [18, 19]. Consequently, homogeneously distributions of WC hard carbide particles are expected to be a good method for increasing hardness and stiffness of the tetragonal zirconia polycrystals. Additionally, the presence of inclusions causes new toughening mechanisms to operate leading to higher fracture toughness than the pure zirconia matrix. Hot pressing experiments have demonstrated that WC secondary hard phase addition enhanced the hardness of ZrO₂ matrix while preserving its high toughness [17, 23].

Up to date, although there are many studies which are based on injection molding of pure zirconia [43, 113, 178-180], hard phase reinforced zirconia matrix ceramics were mostly produced by hot pressing technique to obtain high mechanical properties with the help of applying pressure during sintering [18, 171, 181, 182]. In the present study, it is revealed that by using optimized production parameters and suitable sintering conditions, pressureless sintering after injection molding would give similar results as processing with hot pressing technique. The difficulty of CIM processing was to determine the binder amount, optimize the debinding schedule with respect to the oxidation sensitivity of WC and sintering conditions. Longer sintering times and higher temperatures compared to hot pressing are required. Different compositions, injection molding and thermal processing parameters were tried and characterized in order to develop a feasible production process. Furthermore, the mechanical effect of bimodal particle size distribution of the secondly distributed WC phase was observed and reported.

7.2.1 Optimization of injection molding and pre-sintering parameters

To observe the rheological behavior of the feedstocks, capillary rheology measurements on homogenized 2 mol% Y_2O_3 stabilized ZrO_2 matrix composites with 40 vol% WC addition (2Y-TZP/40WC) were carried out using a nozzle with a $D = 2.0$ mm and $l/d = 15$ dimensions. Fig. 7.13 shows capillary rheometer measurement results (shear viscosity vs. shear rate) taken at the temperatures of 130 °C, 140 °C, 150 °C and 160 °C, revealing viscosity lowered linearly with increasing shear rate up to 160 °C. At 160 °C, shear thinning behavior was observed until the shear rate reached to $100s^{-1}$ but with increasing shear rate the viscosity stayed stable. For the measurements at 150 °C, the viscosity value even declined to 525Pa.s as the shear rate was $250s^{-1}$. Therefore, 150 °C was selected as suitable temperature for injection molding.

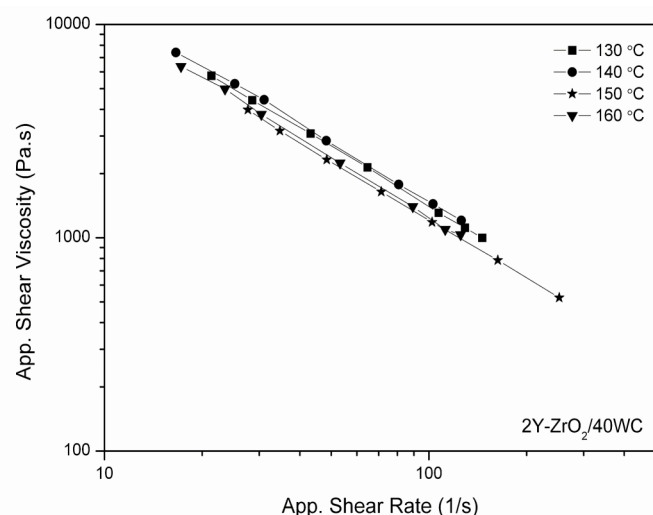


Figure 7.13 : Capillary rheometer measurements of the 2Y-TZP/40WC feedstocks at different temperatures.

Due to the pressure limit (100 bar) of the rheometer device, the viscosity at higher shear rates could not be measured. Similar flow behavior with increasing temperature was observed for other feedstocks. Consequently, it was observed that injection molding could be performed without problems at the plasticization temperature of 150 °C. The samples were injection molded into two different molds with optimized injection parameters. Injection pressure was increased from 1350 bar to 1600 bar with increasing WC amount. General injection molding parameters of the WC added 3Y-TZP feedstocks are given in Table 7.6.

Table 7.6 : Injection molding parameters of the feedstocks.

Molding Variables	3Y-TZP/10WC	3Y-TZP/10WC (75% coarse)	3Y-TZP/20WC	3Y-TZP/40WC
Solid content vol%	46	44	47	51
Mold Temp. (°C)	65	65	65	60
Nozzle Temp. (°C)	160	160	160	155
Injection Speed (cm ³ .s ⁻¹)	40	40	40	35
Injection Pressure (bar)	1350	1350	1550	1600
Hold Pressure (bar)	1400	1400	1400	1200
Cooling Time (s)	20	20	20	20

The given data was used for the mold which has plate and bar cavity. The detailed injection parameters were not mentioned above.

As seen in Table 7.6, when the system had 25 vol % fine-WC powders, the binder amount was slightly getting higher. As the amount of WC phase in 3Y-TZP matrix increase, higher injection pressures and lower speed were needed, though it complicated processing. In addition, with higher WC amount, flow lines and jetting problems were observed.

Prior to debinding, DTA/TG measurements were carried out on extruded green samples under air to optimize the debinding conditions. Figures 7.14a and 7.14b are the DTA/TG graphs of the 3Y-TZP/40WC composite and the starting WC powders, respectively.

It is evident from Fig. 7.14 that the green bodies continuously lost weight starting from 200 °C until 490 °C. At 490 °C, oxidation took place and the parts gained weight. To observe oxidation, DTA/TG measurements were carried out with the same conditions on the WC powders.

Oxidation rate reached its maximum at 498.2 °C, indicating that WC was oxidized to form WO₃. XRD investigations revealed the formation of the WO₃ phase in these samples due to the possible oxidation reaction: $WC + 5/2O_2 \rightarrow WO_3 + CO_2$.

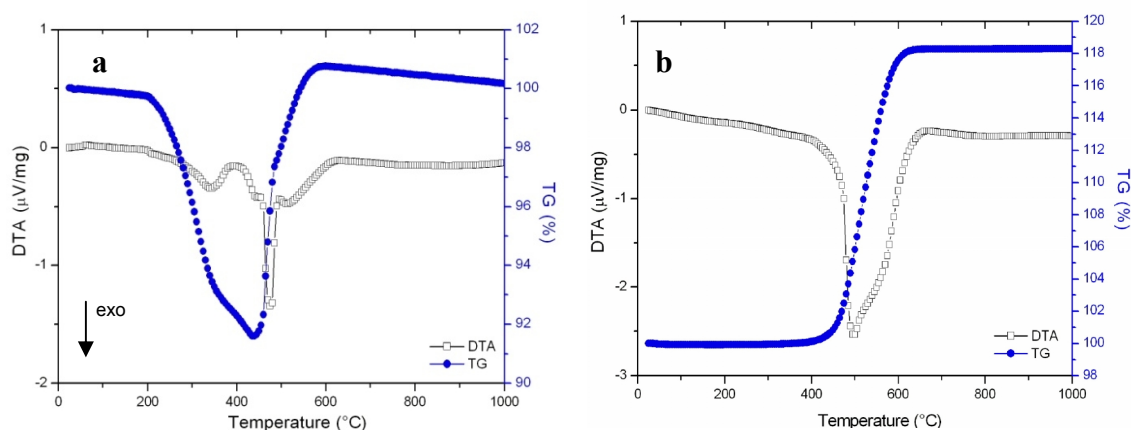


Figure 7.14 : DTA-TG graph of the (a) 3Y-TZP/40WC composite before water debinding and (b) DTA-TG graph of the starting WC powder.

The first exothermic peak, which occurred around 370 °C, is associated with the decomposition temperature of the binder. Therefore, the thermal debinding temperature should be kept below this temperature.

Since no dwelling can be performed in DTA/TG experiments, the thermal debinding temperature could not be precisely determined. To verify the optimum conditions,

several tests were done and it was found out that temperatures higher than 300 °C would cause oxidation problems after a dwell of 12 h.

Following thermal debinding, to get a general idea about the shrinkage characteristics and thermal analyses, DTA/TG and dilatometer measurements were carried out under argon (Ar) atmosphere. The DTA/TG and dilatometer curves of the thermally debinded 3Y-TZP/40WC composite are given respectively in Figs. 7.15a and 7.15b.

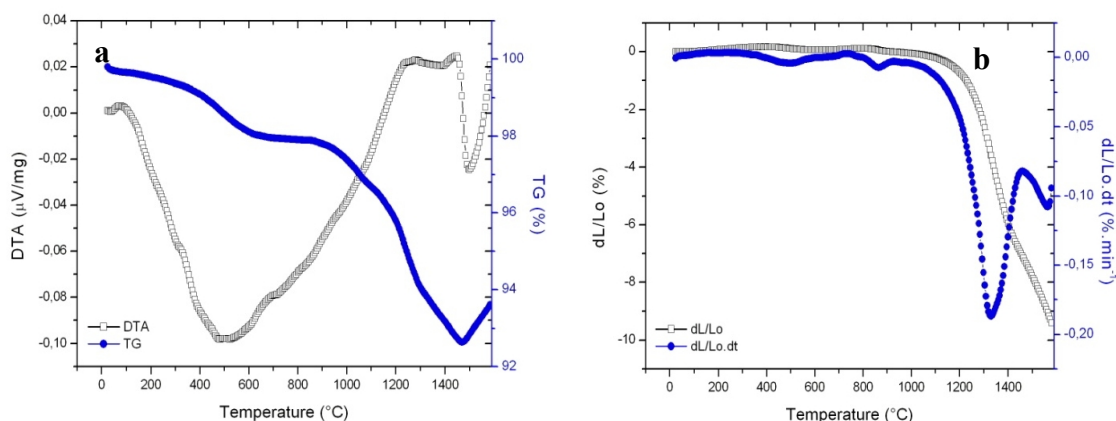


Figure 7.15 : (a) DTA/TG and (b) dilatometer curves of the thermal debinded 3Y-TZP/40WC composite.

As seen in Fig. 7.15, the DTA/TG and dilatometer measurements until 1590 °C revealed that even at this temperature, the shrinkage was not completed. Therefore, longer dwelling times were assumed to be required. Furthermore, when DTA/TG observations on thermally debinded extruded samples were examined, for the 3Y-TZP/40WC samples at temperatures higher than 1400 °C, weight increase was observed which can refer to oxidation even under Ar atmosphere.

XRD analyses given in Fig. 7.19 reveals that ZrO₂ and WC phases decomposed at this temperature and new phases such as W₂C, ZrC, W₂Zr and WO₃ oxide phase was formed. For this reason, choosing the proper sintering temperature and atmospheres for the injection molded composites requires a careful evaluation of XRD analyses combined with DT/TG and dilatometer analyses.

Shrinkage rates of the composites with different WC amounts as a function of temperature are plotted in Fig. 7.16.

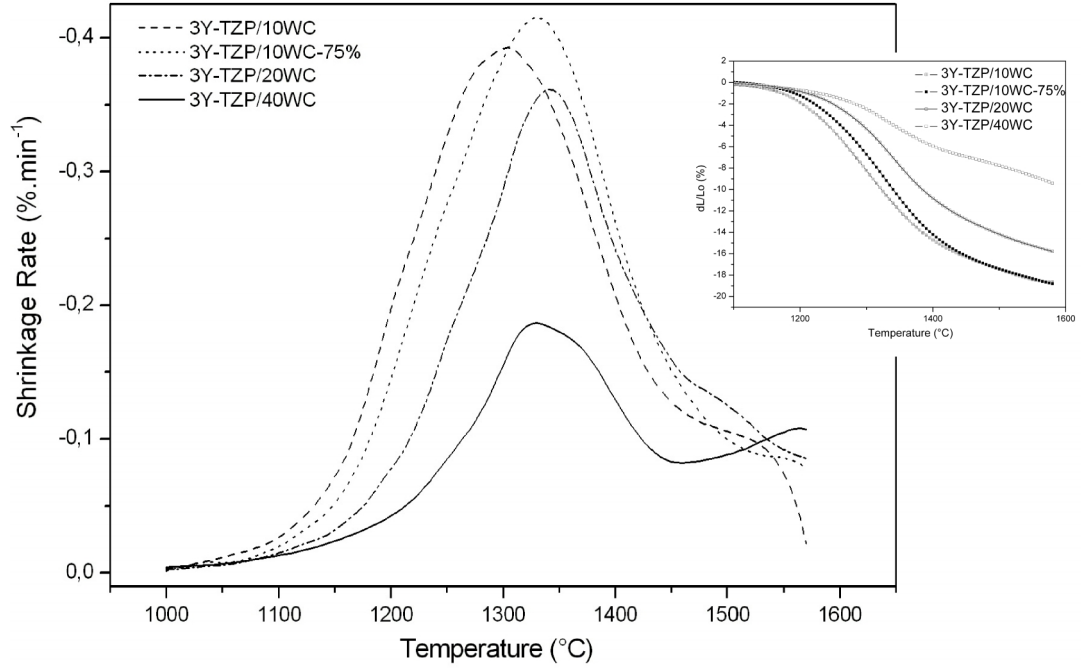


Figure 7.16 : The shrinkage rate versus temperature graph of the extruded composites.

Fig. 7.16 reveals that with increasing WC amounts in the matrix, the shrinkage rate decreased. We believe that WC pins the dislocations at the grain boundaries and for this reason excess energy is required for atom movement from the boundary. Therefore, the presence of WC second phase diminished the sintering kinetics. It is clear from the graph that WC fine-particles provided higher diffusion rates and consequently enhanced the shrinkage rate. Sintering was not finalized even at 1550 °C for all the compositions. Therefore, long dwelling times are needed.

On the basis of the thermal and mass analyses data obtained by extruded samples given in Figs. 7.14 and 7.15, the water and thermal debinding conditions for the injection molded parts were figured out. The injection molded samples were thermal debinded at 300 °C for 12 hours. However, higher temperatures or longer dwelling times caused oxidation. Weight loss was measured in every debinding step. The % binder loss percentage of the plates and bars are shown in Fig. 7.17.

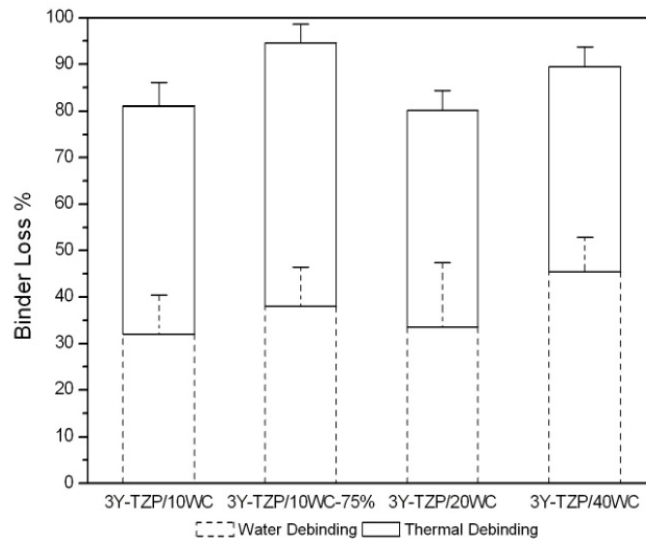


Figure 7.17 : Percentage binder loss after water and thermal debinding related with the compositions. The binder loss of the plates are represented with the columns and the bars are represented with lines (T).

As seen from Figure 7.17, debinded plates lost less binder than the bars due to dimensional differences. The debinding rate was increased as the part became smaller. Likewise, as the parts include smaller particle size, as in the case of the 3Y-TZP/10WC (75% coarse) composite, more binder was removed at the same debinding schedule. After water debinding step, more than 30% of binder was removed in each composition which would further improve thermal debinding. German et al. [1] claimed that 30% of the binder has to be removed to create an open pore network which is necessary to avoid cracking and blistering during thermal debinding.

Porosimetry results reveal that total open porosity was slightly higher when 25% fine WC particles were used in the 3Y-TZP/10WC composite. On the other hand, smaller pore radius (72 nm) and higher apparent density was obtained with this composition. Lowest porosity was obtained for the 3Y-TZP/20WC composite which had 43vol% total open porosity with relatively higher average pore radius. 3Y-TZP/40WC had the largest mean pore radius due to higher amount of WC particles whose mean particle size was larger than that of the 3Y-TZP matrix.

Sintering was carried out at 1550 °C using two different dwelling times with determined stages under controlled atmosphere. Earlier sintering experiments were carried out under Ar atmosphere or in vacuum but in neither of these investigations

resulted with sufficient densification although several temperatures and dwelling times were observed. Therefore, attention was paid on the sintering atmosphere to obtain good resultant mechanical properties of the sintered compacts. It was found out that when H_2 gas was used up to a proper temperature followed by flowing Ar gas until the end of sintering, the mechanical properties were significantly improved. However, when sintering was performed at a temperature of 1600 °C higher than 1550 °C, secondary porosity was observed in the microstructure. Haberkro et al. [27] also found secondary porosity formation at 1700 °C, which were located close to the carbide grains. They related this formation due to the CO release caused by the reaction between WC and ZrO_2 . Therefore, sintering temperature of 1550 °C was chosen as the optimum sintering temperature and higher temperatures were avoided.

Isotropic shrinkage was investigated for the injection molded plates and bars after sintering at 1550 °C for 4 and 6 hours. The shrinkage was between 20-22 % at all directions for the 10 vol% WC dispersed 3Y-TZP samples.

As the WC amount was increased, shrinkage lowered to 17-19 % for the 20 vol% WC, and to 13-15% for the 40 vol% WC containing composites. WC particles pinned the ZrO_2 grain boundaries therefore it inhibited sintering kinetics of the ZrO_2 matrix [48, 183]. The shrinkage amounts were slightly the same at longer dwelling times. The shrinkage model of the 10 vol% WC dispersed composite is shown in Fig. 7.18. The outer transparent profile refers to the dimensions of the debinded part, and after sintering it got the dimensions shown with red profile.

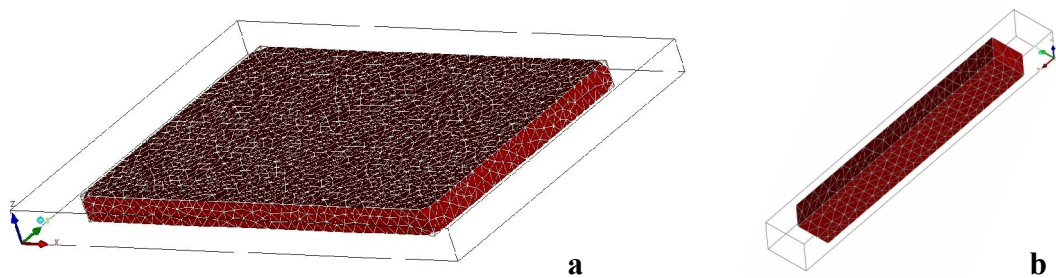


Figure 7.18 : The shrinkage model of the 3Y-TZP/10WC (a) plates and (b) bars. Debinded and sintered composites are represented as outside rectangle and inside rectangle, respectively.

Injection molded and sintered 40vol% WC dispersed composites which have around 92% relative density, have extremely low hardness and Young's modulus values according to the high porosity level. As mentioned earlier [184], sintering at higher temperatures also did not improve the properties due to secondary pore formation. Additionally, sintering at longer times (longer than 4 h) caused bending and cracking.

Hence, the composites with a WC amount more than 20 vol% should be sintered under pressure at lower sintering temperatures and times, similar to those employed in our previous investigation [23]. Hot pressed 32 and 40vol% WC dispersed ZrO₂ matrix composites had 98% and 96% relative density, respectively [23].

On the other hand, if the system had lower amount of the secondary hard phases (less than 40vol% WC), the relative densities and mechanical properties were measured to be higher. Measured physical and mechanical properties such as % relative density, Young's modulus, flexural bending strength, Vickers hardness and fracture toughness values of the 10 vol% and 20 vol% WC dispersed 3Y-TZP/WC composites sintered at 1550 °C for 4 h and 6 h are given in Table 7.7.

Table 7.7 : Mechanical properties of the 3Y-TZP/WC composites sintered at 1550 °C at the dwell times of 4 h and 6 h.

Composite	Dwell Time	R.D. %	Hv _{0.1} (GPa)	E (GPa)	Flexural Strength (MPa)	Hv ₁₀ (GPa)	K _{IC} (MPa.m ^{1/2})
3Y-TZP/10WC	4 h	99.1	16.4 ± 0.2	287 ± 3	824 ± 96	13.2 ± 0.3	6.3 ± 0.2
	6 h	100.0	16.1 ± 0.3	278 ± 2	1087 ± 112	13.6 ± 0.3	6.2 ± 0.1
3Y-TZP/10WC (75% coarse)	4 h	95.4	13.8 ± 0.5	246 ± 3	568 ± 42	11.3 ± 0.1	6.0 ± 0.1
	6 h	96.9	13.7 ± 0.7	251 ± 2	661 ± 41	11.8 ± 0.4	6.1 ± 0.3
3Y-TZP/20WC	4 h	86.6	10.8 ± 0.4	225 ± 3	305 ± 60	10.0 ± 0.3	5.8 ± 0.5
	6 h	93.4	14.0 ± 0.3	270 ± 2	703 ± 93	11.8 ± 0.1	9.2 ± 0.6

As seen in Table 7.7, the 3Y-TZP/10WC composite sintered at 1550 °C for 6 h had the best overall mechanical properties. It is interesting to note that the 3Y-TZP/10WC samples containing 75 vol% coarse + 25 vol% fine-WC particles sintered

at the dwell times of 4 h and 6 h did not have the best mechanical properties, indicating that fine WC powder did not improve the hardness, strength and fracture toughness of the composites.

However, in our previous hot pressing investigation [23], fine-WC addition enhanced the density, strength, hardness and toughness related with the microstructural changes. Thus, following injection molding the presence of dispersed fine-WC particles in the 3Y-TZP matrix did not facilitate sintering but they behaved as inhibitors during the pressureless sintering step. It can be assumed that the fine-WC particles dispersed around the grain boundaries of zirconia and caused reduction in sintering rate. SEM observations would help to clarify this assumption.

7.2.2 Characterization of as-sintered 3Y-TZP/WC composites

XRD patterns of the sintered 3Y-TZP/WC composites comprising 10 vol % WC, 10 vol% WC (75% coarse), 20 vol% WC and 40 vol% WC, all sintered at 1550 °C for 6 hours are given in Fig. 7.19.

XRD reflections matched the ICDD card values of the t-ZrO₂ (simple tetragonal Bravais lattice, space group: P42/nmc) [167] and WC phases (hexagonal Bravais lattice, space group: $P\bar{6}m2$) [168] for the 3Y-TZP/WC composites comprising 10 vol % WC, 10 vol% WC (75% coarse WC + 25% fine-WC), 20 vol% WC (XRD patterns of A, B and C), indicating that no reaction took place between the matrix and the dispersion for WC contents up to and including 20 vol%.

However, when the WC amount increased to 40 vol% (Fig. 7.19 - pattern D), the microstructure of the sintered composite contains new metastable and stable phases (W₂C, W₂Zr, W₃O, ZrC) which resulted from kinetic reactions between ZrO₂ and WC. The additional C peak (fcc Bravais lattice, $F\bar{4}3m$ space group) [185] at around 45° for every measurement was analyzed because of the background measurement.

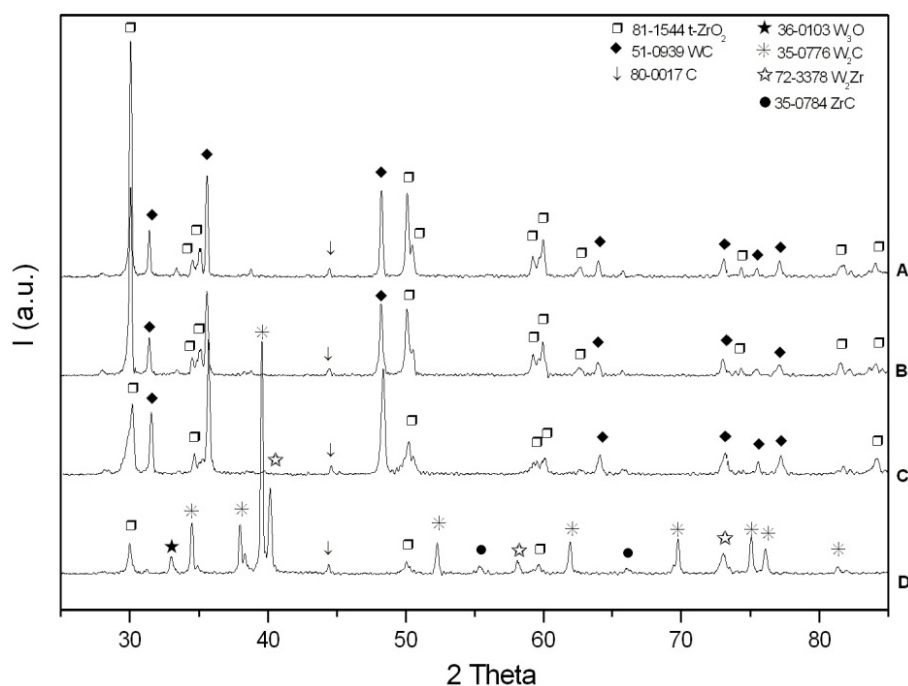


Figure 7.19 : XRD patterns of the 3Y-TZP/WC composites containing 10 vol% (A), 10 vol% - (75% coarse) (B), 20 vol% (C) and 40 vol% (D) WC sintered at 1550 °C for 6 hours.

Fig. 7.20 are the SEM micrographs of the indentation traces of the composites sintered at 1550 °C for 4h (a,b,c) and 6h (d,e,f), revealing crack deflection, crack branching and bridging mechanisms for all samples. These mechanisms enhanced the fracture toughness of the composites.

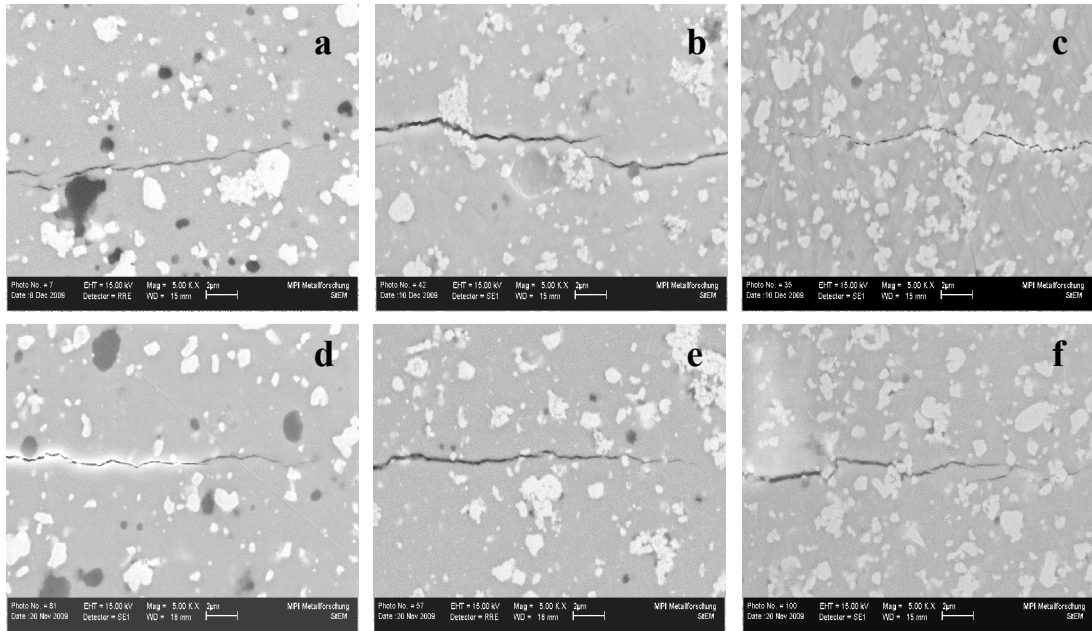


Figure 7.20 : SEM/BSE images of the crack propagation of the (a) 3Y-TZP/10WC, (b) 3Y-TZP/10WC (75% coarse), (c) 3Y-TZP/20WC composites sintered at 1550 °C for 4 h and (d) 3Y-TZP/10WC, (e) 3Y-TZP/10WC (75% coarse) and (f) 3Y-TZP/20WC composites sintered at 1550 °C for 6h.

On the basis of the microstructural observations of Fig. 7.20, the most prominently increase in fracture toughness of the 3Y-TZP/20WC composite could be a combination of martensitic phase transformation and crack deflection, crack branching and bridging mechanisms.

SEM images in Fig. 7.20 (c and f) reveal that longer sintering times did not have any effect on the grain size of WC particles. Furthermore, the SEM micrographs belonging to the 3Y-TZP/10WC composite having 25% fine + 75% coarse WC dispersion (Fig. 7.20b and 7.20e) indicate that fine WC particles tend to agglomerate which would deteriorate the mechanical properties. Powder agglomerates are often suppressive to the particle packing characteristics, sintering behavior and ensuing properties especially in ceramic systems [186-190].

In the present investigation, it is very likely that the agglomerations of fine WC particles caused high total open porosities which eventually caused density reductions. A similar observation was also concluded by Suri et al. [191] on the effect of agglomerates for a W-based heavy alloy fabricated powder injection molding and sintering. Thus, on the basis of SEM micrographs shown in Fig. 7.20b

and 7.20e, the agglomerates were not destroyed sufficiently during feedstock preparation.

Wear performances of the polished injected parts were examined with unlubricated sliding pin-on-disc test machine. The volumetric wear rate (k_v) was calculated by using the Archard's Equation (7.4). The calculated tribological values of the composites up to 20 vol% WC addition which were sintered using two different dwelling times (4h and 6h) are listed in Table 7.8.

Table 7.8 : Surface roughness (R_a) of the polished surfaces and dry reciprocating wear test results of 3Y-TZP/WC composites under 55N normal load with a sliding distance (s) of 45 km against WC-Co.

Composite	Dwell Time	R_a (μm)	Friction Force (N)	Friction Coefficient (μ)	Wear Volume (mm^3)	k_v ($10^{-8} \text{ mm}^3/\text{N.m}^{-1}$)
3Y-TZP/10WC	4h	0.003	29.10	0.53	0.06	2.4
	6h	0.005	31.32	0.57	0.06	2.4
3Y-TZP/10WC (75% coarse)	4h	0.011	30.59	0.56	0.09	3.6
	6h	0.004	33.87	0.62	0.06	2.4
3Y-TZP/20WC	4h	0.008	33.14	0.60	0.14	5.7
	6h	0.004	31.05	0.56	0.05	2.0

The tribology results indicated that the parts were wear resistant in the unlubricated environment even with long operation conditions under relatively high normal load.

Literature values of friction coefficient of ZrO_2 are in a range between 0.4 and 0.9 in the unlubricated wear conditions and this value is 0.9 for the PSZ (partially stabilized zirconia) [192, 193]. In a previous study [23], with the same tribology conditions, the friction coefficient and wear rate of the hot pressed 3Y-TZP were measured as 0.68 and $6.06 \cdot 10^{-8} \text{ mm}^3/\text{N.m}^{-1}$, respectively. With WC addition the friction coefficient lowered till 0.39 for hot pressed 3Y-TZP/40WC composites [23].

The friction coefficient values of the injection molded sintered samples were almost similar in every composite, therefore WC amount, dwelling time and bi-modal particle size distribution did not have much influence on the wear resistance, as

expected. The 3Y-TZP/20WC sample which had the highest toughness value of 9.2 MPa.m^{1/2} also had the lowest wear amount. With longer dwelling time, the toughness of this composite increased nearly by 59% (Table 7.7) and this reflected on the wear performance.

The inverted 3-D surface topographies of the abraded wear surfaces of the composites are given in Fig. 7.21. The polished composite surfaces which had roughness values listed in Table 7.8, worn off between 24 µm to 37 µm deep subsequent to unlubricated reciprocating wear tests under 55N load and 45 km sliding distance.

Homogeneously straight abrasion was obtained all along the wear track in all composites. Comparison of the wear traces shown in Fig. 7.21d representing 3Y-TZP/10WC composite with those in Fig. 7.21e representing 3Y-TZP/10WC composite having 25% fine + 75% coarse WC dispersion reveals that the wear resistance was not enhanced as it had for similar composites fabricated by hot-pressing [184].

Similar to the effect on overall densities, the agglomeration of fine WC powders restricted the enhancement of the mechanical properties and that hardness, strength and fracture toughness of the composites were not improved. Therefore, no positive effect of bimodal particle size distribution on mechanical properties could be observed. Higher dwelling time lowered the depth of the abraded surface and the most shallow wear track was obtained for the 3Y-TZP/20WC composite.

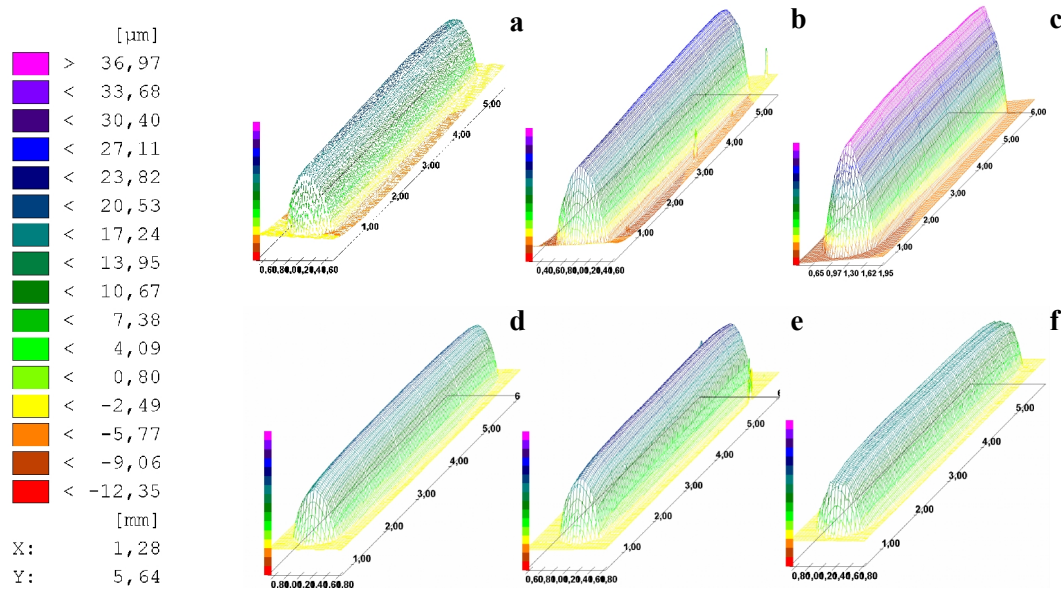


Figure 7.21 : Inverted 3-D surface profiles of the composites subsequent to 45 km unlubricated reciprocating wear test. The tracks belong to 3Y-TZP/10WC (a,d), 3Y-TZP/10WC (75% coarse) (b,e) and 3Y-TZP/20WC (c,f). Sintering at 1550 °C, for 4h dwell (a,b,c), 6h dwell (d,e,f).

Fig. 7.22a, 7.22b, 7.22c are the SEM micrographs of the wear traces belong to the 3Y-TZP matrix reinforced with 10 vol% WC, 10 vol% WC (75% coarse particles) and 20 vol% WC particles, respectively. Additionally surface topography of the 3Y-TZP/10WC composite is given. SEM micrographs represent the middle part of the wear traces obtained after 45 km sliding distance.

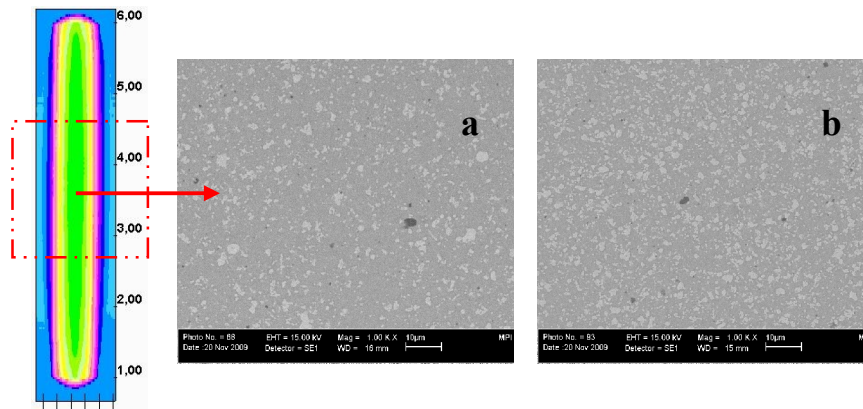


Figure 7.22 : SEM images taken from in the middle part of the wear traces of composites sintered at 1550 °C for 6 h, 3Y-TZP/10WC (75% coarse) (a), 3Y-TZP/20WC (b); the vertical view of the 3Y-TZP/10WC trace is given as an example on the left.

SEM images in Fig. 7.22 indicate that there was neither an adhesion of the debris nor any microcracks along the wear trace. The abraded surfaces were removed away from the debris layer and smooth wear layer remained after a distance of 45 km even at the unlubricated conditions. The bimodal particle size distribution did not have any effect on the surface morphology of the worn surface.

7.3 NdFeB and SmCo Sintered Isotropic and Anisotropic Permanent Magnets Formed by Metal Injection Molding

7.3.1 NdFeB parts

7.3.1.1 Samples prepared by Magnequench (MQ) powder

MQ powder which is a HDDR (hydrogenation-disproportionation-desorption-recombination) powder was obtained from Magnequench™ Company. Due to its production method, the grain size is a few hundred nanometers. Therefore, it is known from the literature that this powder can be used for production of NdFeB type hot pressed or bonded magnets.

In this study, as a pre-work some experiments were carried out using MQ-powder in order to analyze the properties of the end product produced by MIM route. The oxygen and carbon levels of the MQ powder is given in Table 7.9. Results reveal that the starting-powder had very low oxygen content when it is compared to HD (hydrogen decrepitation) powders.

Table 7.9 : Properties of the MQ powder.

Powder	O wt%	C wt%
MQ-Powder	0.049 ± 0.001	0.080 ± 0.001

Four different feedstocks having 68vol% solid content were prepared by MQ powder. The binders and debinding/sintering conditions are given in Table 7.10. The details of the binder compositions were explained in the Table 6.5. For thermal debinding of the parts hydrogen atmosphere were used.

Table 7.10 : Sintering details of the MQP feedstocks.

Feedstock	Binder	Debinding				Sintering			Heat Treatment	
		R	T	Atm	P.P.	T	Atm	D.	T	D.
F1-MQP	B41	3	500	H ₂	800	1100	HV	4	500	2
F2-MQP	B32									
F3-MQP	POM									
F4-MQP	B27									

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

The feedstocks were injection molded by Hek™ and Minijet™ machine. Due to the segregation problems, Minijet™ was not used further for injection. For Hek™ machine, injection temperature was selected as 90 °C and around 5 bar pressure was applied. During injection process, sticking and filling were injection problem for these feedstocks. The surface quality of the parts after injection was poor.

Solvent debinding stage was realized under air in hexane. For sintering, the samples were placed on Tantalum boxes without any coating on box surface. After sintering of these batches it is observed that the end products had very dark (black) color on their surface. XRD analyze was applied on the cross section of the F3-MQP sintered part to analyze the phase changes.

High iron content in addition to Nd₂O₃ was observed by the characterization. High oxidation possibly during in the debinding stage caused dark layer formation on the surface of the sample. Furthermore, due to fast debinding (3K/min), carbon could not remove the part totally which was resulted in free Fe phase. NdFeB composition was decomposed as the impurities increased. The relative densities were around 88%.

In Fig. 7.23, BSE images of the F1-MQP sintered part is given. The phase analyses were made on the marked areas A and B, and found out that dark phase was nearly pure Fe phase.

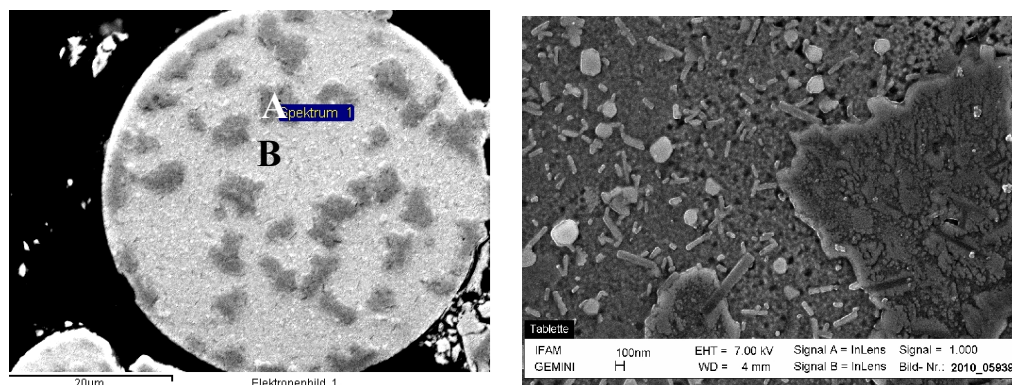


Figure 7.23 : BSE images of the F1-MQP sintered part.

EDX analyses carried out on the A and B points in Fig. 7.23 showed that the dark phases were iron (Fe) and the light grey matrix phase was Nd-poor magnetic phase.

According to the XRD analyses obtained for MQP samples given in Fig. 7.24, it is determined that the parts had mainly α -Fe phase and additionally Nd_2O_3 phase.

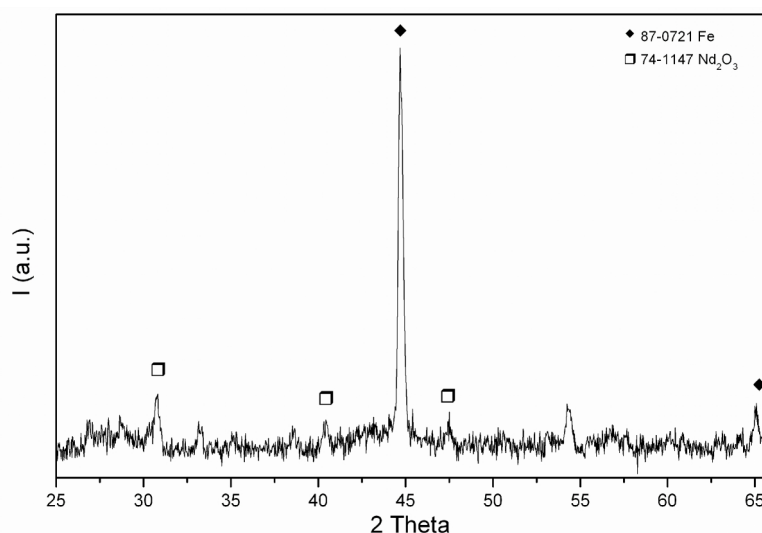


Figure 7.24 : XRD analyze of F1-MQP sintered part.

The soft iron phase severely decreased the magnetic properties of the parts. Moreover high amount of oxygen impurities lowered the coercivity dramatically. Therefore it is confirmed that MQ powder was not suitable for processing by injection molding and pressureless sintering.

7.3.1.2 Samples prepared by CNFB powder

CNFB powders were processed by planetary ball milling of the NdFeB ingot supplied from China. The ingot firstly crashed mechanically by a feedstock crusher

under Argon without applying HD process. Planetary ball milling was applied in dry conditions via 2 milling balls ($\varnothing$ 32mm) for 5 hours. The loading of the powder were realized in glove box under Ar atmosphere. The oxygen level of the milled powder was measured 0.7 wt% which was extremely high. There can be many reasons for obtaining high oxygen level; such as oxidation of the ingot during transportation from China since it was not stored under Argon atmosphere. Additionally, during mechanical milling since the vials could not be totally air isolated, oxidation could have happened.

For injection molding, first of all 68vol% solid content was applied however the feedstock was very dry to be injected. Thus, the solid content was lowered to 55% and injected by Hek™ machine. Segregation of the wax and air pocket formation were the problems during injection. Furthermore samples tend to break while removing the mold. Only small discs could be injected without any problem. These problems also pointed out that 55% solid content was low for proper injection process.

Solvent debinding of the F1-CNFB green parts were carried out under Ar in a stainless steel box. For thermal debinding and sintering, samples were placed on Y₂O₃ coated W plate and Ti traps were placed surrounding the samples for to prevent the parts from excessive oxidation. The sintering conditions are given in Table 7.11.

Table 7.11 : Sintering details of the CNFB feedstock.

Feedstock	Binder	Debinding				Sintering			Heat Treatment	
		R	T	Atm	P.P.	T	Atm	D.	T	D.
F1-CNFB	B27	3	500	H ₂	800	1100	HV	4	500	2

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Chemical analyses reveal that high amount of impurities were remained in the sintered structure due to the high oxygen content in the starting powder. Furthermore, improper debinding and sintering caused free α -Fe phase. Additionally by XRD characterizations, phases such as; Fe, Nd oxides and boron carbide were

observed. The microstructure was analyzed further by optical microscope and SEM/EDX. The micrographs are given in Fig. 7.25.

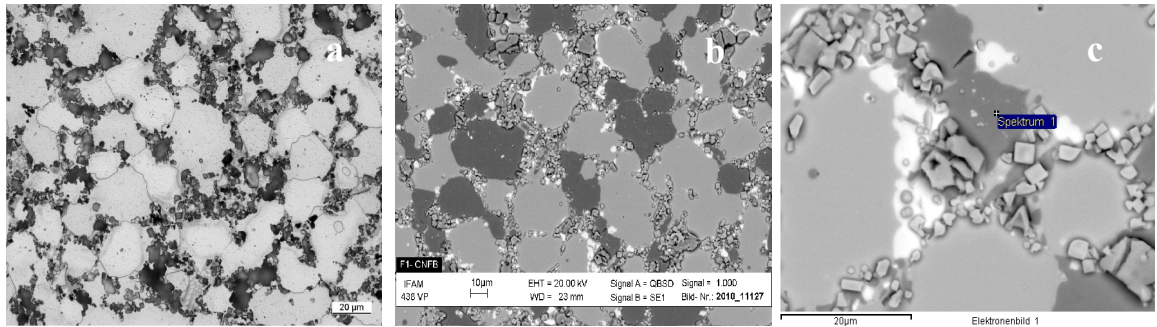


Figure 7.25 : BSE images (a, c) and optical microscope image (b) of the CNFB sintered part.

In the micrographs in Fig. 7.25, the grey phase indicates the magnetic phase, white parts are Nd-rich phase which was distributed mainly to the grain boundaries and dark grey areas are free α -Fe phase. Fig. 7.25c also point out there are different phases with cubic topography which were observed as an Nd-rich phase with a different composition than white areas. Mapping of the sintered unetched CNFB parts given in Fig. 7.26 also shows clearly that α -Fe phase is dominant in the structure.

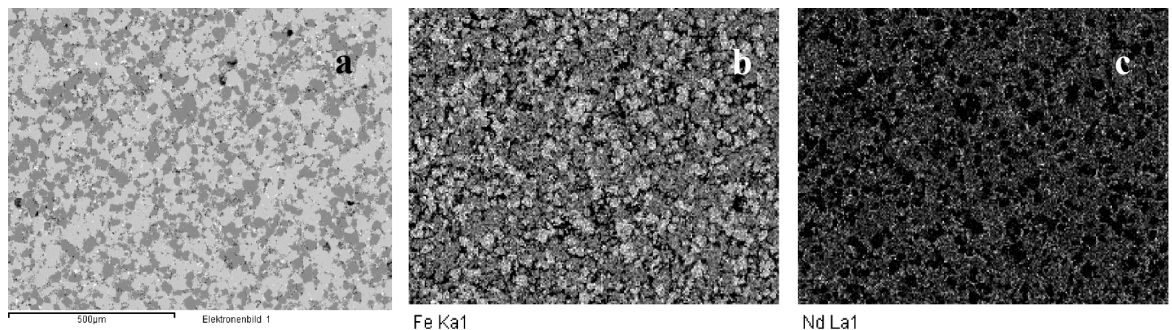


Figure 7.26 : Mapping of the sintered unetched CNFB parts.

High amount of the α -Fe phase resulted in huge coercivity decrease since the sintered magnet behaved as like a soft magnet.

7.3.1.3 Samples prepared by SNFB powder

SNFB powders were obtained commercially from Ms-Schramberg Company. These powders were produced by jet milling under Argon atmosphere following to the HD process of the melt spun NdFeB ingot. The particles had single grain structure which gives the powder anisotropic property. Due to the jet milling, the powder particles

had irregular shape. The powder composition was $(\text{Nd,Dy})_{14.35}\text{Fe}_{79.4}\text{B}_{6.14}$ and had 0.3wt% oxygen content. Mean particle size is 4.6 μm . The further powder properties obtained from the supplier are summarized in Table 7.12.

Table 7.12 : Properties of the SNFB powder.

	wt%	at %	Br (mT)	(BH) _{max} (kJ/m ³)	BHc (kA/m)	iHc (kA/m)	Density (g/cc)	O (wt%)	C (wt%)
B	1	6.14							
Fe	66.9	79.4	1022	188	620	660	7.6-7.7	0.356 $\pm$ 0.005	0.069 $\pm$ 0.001
Nd	25.1	11.5							
Dy	7	2.85							

Magnetic properties were measured at 150 °C.

XRD analyses were carried out for the powder to analyze the phases and impurities of the SNFB powder. The XRD graph given in Fig. 7.27 showed that only $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was detected which is actually the matrix of the $(\text{Nd,Dy})_{14.35}\text{Fe}_{79.4}\text{B}_{6.14}$ structure.

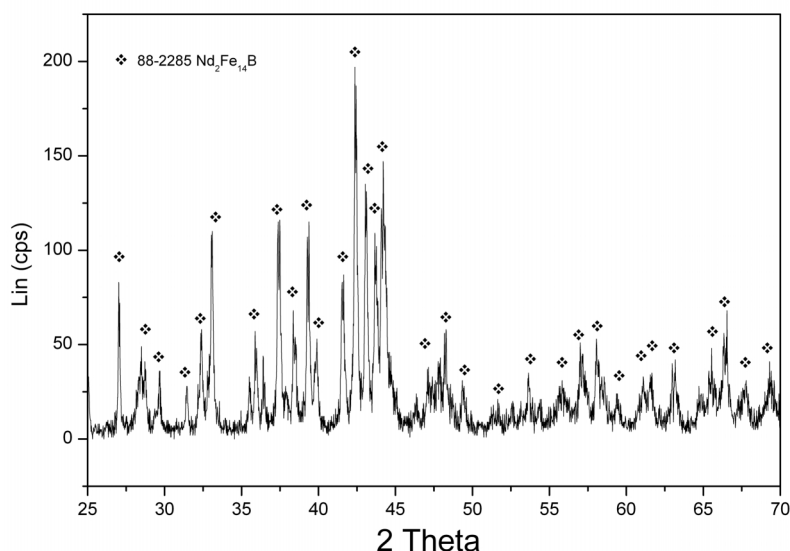


Figure 7.27 : XRD analyze of SNFB powder.

Additionally to XRD characterizations, etched commercial SNFB powder particle was observed by SEM/EDX analyses. As seen in the Fig. 7.28, the powder particles had nearly homogeneous size which is around 5 μm .

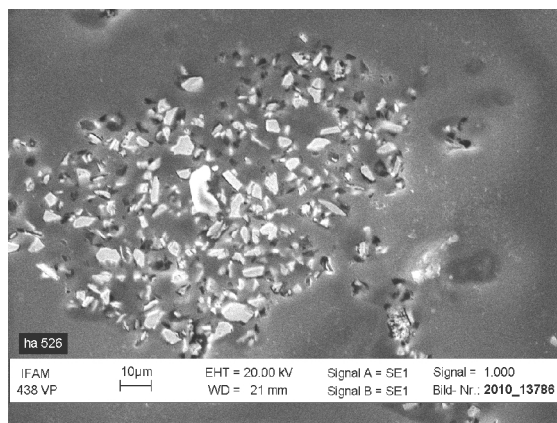


Figure 7.28 : BSE image of SNFB powder particle.

General EDX analyze of the powder reflect that there was additionally Cobalt (Co) phase. The exact composition found as $(\text{Nd, Dy})_{15,4-x_1}(\text{Fe,Co})_{84,55-x_2}\text{B}_{x_1+x_2}$. Cobalt phase mostly contain in the commercial powders to replace Fe since it helps to increase the Curie temperature and helps retain coercive force by Curie temperature increase.

So as to observe the effect of the different binders to the magnetic and physical properties of end products, four different binder compositions having various polyethylene contents were examined. The polyethylene backbone plays an important effect on the final properties since it contains the high carbon content. In Table 7.13, the type of binders mixed with SNFB power and injection molding observations are given. In total, four different feedstocks were prepared with SNFB binder using different solid contents.

Table 7.13 : Properties of SNFB feedstocks.

Feedstock	Binder	Solid Content vol%	Injection
F1-SNFB	B27	55	No problem
F2-SNFB	POM	55	No filling /burned
F3-SNFB	B39	68	No filling
		60	No problem
F4-SNFB	B41*	68	No filling

The prepared four different feedstocks were injection molded via HEK™ machine. The powder metallurgy process is schematically given in Fig. 7.29. The SNFB powder was mixed homogeneously with different binder compositions and additive (stearic acid) via kneader in the glove box. The details of the binder contents were indicated in the Table 6.5.

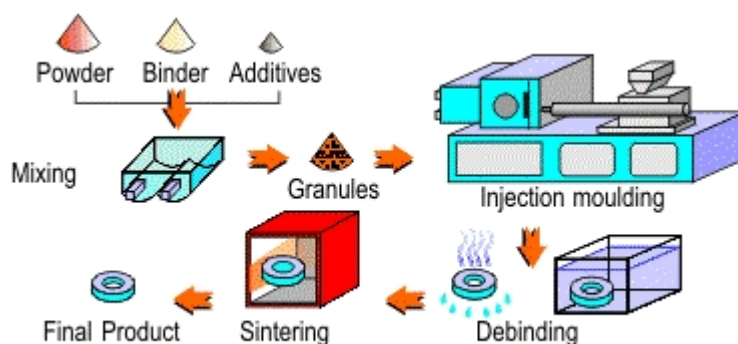


Figure 7.29 : Route for ceramic injection molding and sintering process [194].

The granules were obtained following to kneading, consequently isotropic and anisotropic green parts were injection molded for all the compositions. The magnetic field was provided by the N48 type hard magnets placed in the mold cavity. For the binder compositions marked as F1 (55% solid content) and F3 (60% solid content), the injection molding process were applied without any injection problems. Around 5 - 6 bar injection pressure and 80 - 85 °C injection temperature was performed for F1, F3 and F4 feedstocks. However the rest of the compositions had flowing problems during molding although different injection temperature and pressure values were performed to optimize the parameters.

Especially POM binder feedstock needed to be injected around 150 - 160 °C which was too high and resulted in feedstock burn during injection. Yamashita [195] found out in his studies that oxidation of NdFeB alloy powder was started from 100 °C and oxidation showed a dramatic increase in the region of 250 °C. Therefore he stated that in order to suppress the oxidation of NdFeB alloy powders in air, the temperature of the MIM process from mixing to molding needs to be kept below 100 °C. For this reason, POM (Polyoxymethylen) binder is not suitable for this alloy since it needs to be injected at around 170 °C. The green parts were solvent debinded under Argon in hexane. The thermal debinding and sintering schedules for F1-SNFB

feedstocks are summarized in Table 7.14. It was expected that the heat treatment of sintered NdFeB magnets would increase the coercivity of the parts.

Table 7.14 : Sintering conditions of the injected F1- SNFB feedstocks.

Feedstock	Debinding						Sintering		Heat Treatment		
	R ₁	T ₁	R ₂	T ₂	Atm	P.P.	T	Atm	D.	T	D.
F1-SNFB-1	3	500			H ₂	800	1100	HV	4	500	2
F1-SNFB-2	3	550			Ar	800	1080	HV	1	630	1
F1-SNFB-3	3	550			Ar	100	1080	HV	1	630	1
F1-SNFB-4	3	550			Ar	100	1080	HV	1		
F1-SNFB-5	3	250	1	500	H ₂	850	1100	Ar	1		
F1-SNFB-6	3	400	1	500	H ₂	850	725/30min+1100	HV	1		
F1-SNFB-7	3	250	1	500	H ₂	850	725/30min+1100	HV	1		

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

For the first five cycles (F1-SNFB-1 to F1-SNFB-4), different debinding atmospheres; such as reducing (H₂), inert (Ar), vacuum were performed. The debinding rate was kept as 3K/min till 550 °C. The carbon test analyses shown in Table 7.15 revealed that all these different atmospheres resulted in high carbon level. It is supposed that 3K/min was very rapid for sufficient debinding. Thus, for the further sintering steps (F1-SNFB-5 to F1-SNFB-7), debinding was realized in two steps. 3K/min debinding rate were carried out till 250 °C afterwards 1K/min rate were performed till 500 °C under hydrogen atmosphere.

The reason for choosing hydrogen is that it is most effective atmosphere to remove the rest of the binders. In fact, the optimum debinding temperature and rate of the green parts could have been found by DTA/TG analyses; however, since the system can not be connected to hydrogen gas, samples could not be analyzed. The reason for slow debinding between 250 °C and 500 °C for F1-SNFB-5 to F1-SNFB-7 samples was that, it was assumed, the polyethylene removed out in this temperature range. In

this respect, carbon analyses also proved, two step debinding was successful to lower the carbon level. Additionally, 3K/min rate till 400 °C was also tried instead of 250 °C to speed up the debinding process however 400 °C was also a high temperature to remove the binder sufficiently and it was resulted in high carbon content plus significant cracking.

In the Table 7.15, the magnetic and structural properties of the sintered F1-SNFB parts are given. These results belong to the anisotropic disc samples, with dimensions: 8.20mm Ø, h = 1.95mm. Before the magnetic measurements, the disc was magnetized by 3T magnetic field.

Table 7.15 : Properties of sintered F1-SNFB feedstocks.

	Rel. Den %	O level wt%	C level wt%	Br (T)	B_{Hc} (kA/m)	i_{Hc} (kA/m)	$(BH)_{max}$ (kJ/m ³)
F1-SNFB-1	98	0.552	1.047	0.514	10.05	10.33	1.03
F1-SNFB-2	93	0.787	0.639	0.642	14.10	14.50	2.20
F1-SNFB-3	96	0.568	0.601				
F1-SNFB-4	91			0.693	14.70	15.10	2.40
F1-SNFB-5	91	0.743	0.157	0.528	16.75	17.50	1.70
F1-SNFB-6	89			0.479	18.17	19.08	2.15
F1-SNFB-7	92			0.485	15.52	16.10	2.09

In overall, the magnetic properties of these samples were very poor. The reason should be the high carbon and oxygen level in the sintered samples. Although different sintering temperatures (1080 °C and 1100 °C), atmospheres (Argon and high vacuum) and heat treatments were applied, their effect on the magnetic and physical properties cannot be clearly observable due to the high carbon and oxygen levels.

SEM observations (Fig. 7.30) were carried on the cross section area of the F1-SNFB-1 sintered sample to analyze the phases and do EDX on unetched sample. Nd-rich phase which was reacted with oxygen was localized mainly surrounding the dark

grey areas (Fe-rich phase). Moreover, the phase marked as Spectrum 4 contain extreme oxygen level.

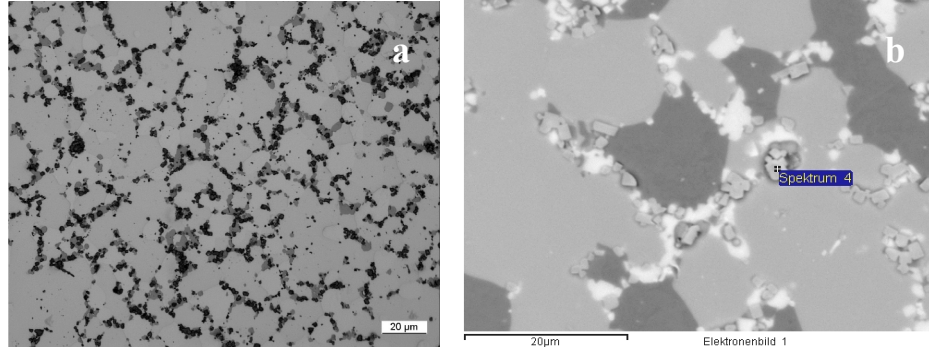
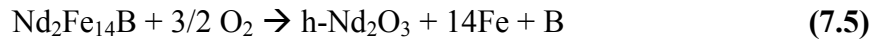


Figure 7.30 : (a) The optical microscope and (b) BSE images of the unetched F1-SNFB-1 sintered part.

In this study, α -Fe phase seems to be formed according to oxidation reaction of the matrix phase given in the following equations:



Oxygen reacts with $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase causes free α -Fe and boron (B) phase. With further oxidation results in oxidation of Fe and B which destroys the magnetic properties. These oxidation reactions can be also thermodynamically shown by Gibbs free energy versus temperature graphs given in Fig. 7.31.

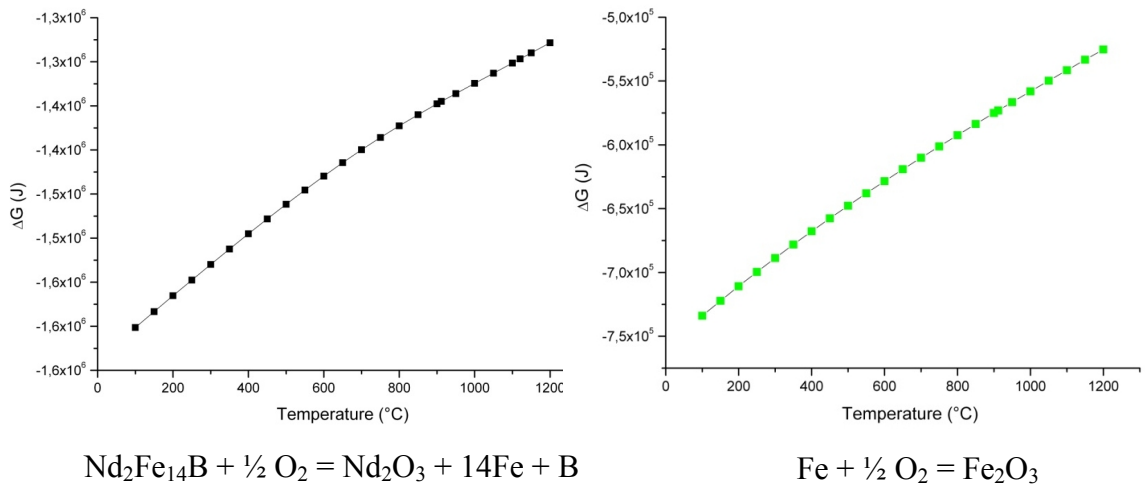


Figure 7.31 : Gibbs free energy versus temperature graphs for oxidation reactions of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe.

The free energy value increases with increasing temperature which means, the oxide phase even get more stable with elevated temperatures. General EDX analyze of the sintered F1-SNFB-1 part is given in Table 7.16 which revealed that Fe level was higher than normal ratio. Which means $\text{Fe (at\%)} / (\text{Nd, Dy (at\%)})$ was higher than 7 ($14(\text{Fe})/2(\text{Nd})$). As the (Fe,Co) atomic weight compared by (Nd,Dy) amount by general EDX, it was found out that the structure was Fe-rich which had supported the comments. The high amount of carbon resulted in an increase in the Fe level which dramatically reduced the magnetic properties. It was highly supposed that the high carbon level in the sintered F1-SNFB parts should be resulted by the improper binder system (B27) which had 30wt% polyethylene casing high carbon impurities.

Table 7.16 : General EDX of sintered F1-SNFB-1 sintered part.

Elements	Al K	Fe K	Co K	Nd L	Dy L
at %	0.59	85.83	3.38	7.75	2.44

No structural characterizations were carried out for the rest of the samples of the F1-SNFB series. Due to the high polyethylene level in the binder composition, the magnetic properties could not be improved although different debinding and sintering regimes were performed. The photo of the sintered anisotropic F1-SNFB parts is shown in Fig. 7.32.



Figure 7.32 : The picture of the sintered anisotropic single-pole F1-SNFB samples, from left to right: F1-SNFB-1 to F1-SNFB-6.

F2-SNFB feedstocks had serious problems during injection molding. Because of using POM binder in this feedstock, the injection molding temperature was around 170-180 °C. The temperatures higher than 100 °C caused the feedstock oxidize quickly, and around 170-180 °C it was burned while injecting.

The feedstocks which were prepared with 68vol% solid content named as F3-SNFB and F4-SNFB had also problems during injection. The solid content was too high therefore although many different injection parameters were tried; the feedstocks could not flow properly through the nozzle and were not able to fill the mold.

In a new batch, F3-SNFB feedstocks were prepared using 60vol% solid content. The binder (B39) used for this feedstock had 15wt% polyethylene which was expected to result in lower carbon level in the sintered samples. The rheology experiments for the F3-SNFB feedstocks were carried out using a nozzle with a $D = 1.0$ mm and $l/d = 16$ dimensions at temperatures 90 °C and 95 °C. The result obtained for 90 °C is given in the Fig. 7.33.

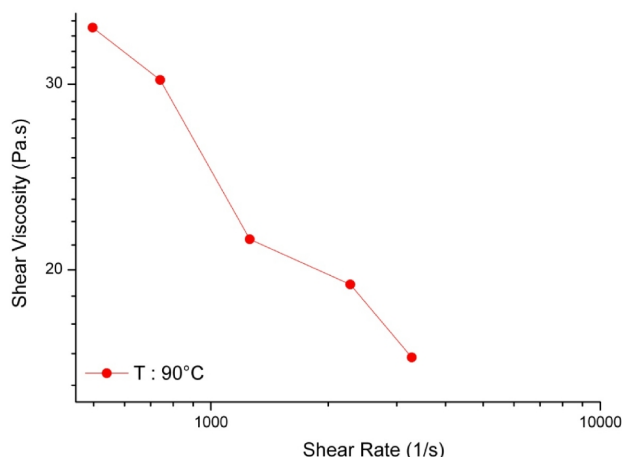


Figure 7.33 : Capillary rheometer measurements of the F3-SNFB (60 vol%) feedstock at 90 °C.

Fig. 7.33 shows capillary rheometer measurement results (shear viscosity vs. shear rate) taken at 90 °C. Viscosity lowered linearly with increasing shear rate. Injection molding is suitable at this temperature. Additionally lower injection temperature lowers the possibility for oxidation. The processed debinding and sintering cycles for F3-SNFB feedstocks were summarized in the Table 7.17.

Several thermal debinding and sintering schedules were performed for the molded F3-SNFB feedstocks. First of all, Argon atmosphere was tried using fast (3K/min) and consequently very slow (0.1 K/min) debinding rates to remove the binder. These cycles were marked as F3-SNFB-1 and F3-SNFB-2 in the Table 7.17; respectively. However the carbon results on these sintered samples given in the Table 7.18 revealed that Argon atmosphere was not proper to remove the carbon sufficiently. Therefore for the rest of the cycles (F3-SNFB-3 to F3-SNFB-15) Hydrogen (H_2) was performed as a thermal debinding atmosphere.

Table 7.17 : Sintering conditions of the injected F3-SNFB feedstocks.

Feedstock	Debinding						Sintering		
	R ₁	T ₁	R ₂	T ₂	Atm	P.P.	T	Atm	D.
F3-SNFB-1	3	550			Ar	100	1080	HV	1
F3-SNFB-2	3	300	0.1	550	Ar	100	1080	HV	1
F3-SNFB-3	3	250	0.1	500	H ₂	850	1080	HV	1
F3-SNFB-4	3	250	1	500	H ₂	850	1100	HV	1
F3-SNFB-5	3	250	0.5	500	H ₂	850	1100	HV	4
F3-SNFB-6	3	250	1	500	H ₂	850	1100	HV	4
F3-SNFB-7	3	250	1	500	H ₂	850	1080	HV	1
F3-SNFB-8	3	250	5	500	H ₂	850	1100	HV	1
F3-SNFB-9	3	250	1	500	H ₂	850	1100	HV	1
F3-SNFB-10	3	250	0.1	500	H ₂	850	1100	HV	1
F3-SNFB-11	3	250	1	500	H ₂	850	1100	V	1
F3-SNFB-12	3	250	1	500	H ₂	850	1100	V	1
F3-SNFB-13	3	250	1	500	H ₂	850	1100	Ar (10mbar)	1
F3-SNFB-14	3	400	1	500	H ₂	850	725/30min+1100	HV	1
F3-SNFB-15	3	250	1	500	H ₂	850	725/30min+1100	HV	1

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Different debinding rates; such as 0.1, 0.5 and 1 K/min were observed. Firstly up to 250 °C faster debinding rate (3K/min) was used to speed up the sintering time and between 250 °C and 500 °C, 1K/min was performed. Conversely in one cycle (F3-SNFB-14) 1K/min debinding rate started at 400 °C, in order to observe the difference in carbon level.

To observe various parameters for the sintering stage, different sintering atmospheres such as; high vacuum (HV), vacuum (V) and Argon (Ar) was performed. Two different sintering temperatures (1080°C and 1100 °C) was carried out with 1h or 4h dwelling. Firstly, achievement of good magnetic properties and density was aimed

without heat treatment process. Therefore heat treatment was applied at 630 °C for one hour just to F3-SNFB-1 and F3-SNFB-11 sintering cycles.

In the Table 7.18, the magnetic and structural properties of the sintered F3-SNFB parts are given. These results belong to the anisotropic disc sample, with dimensions: 8.20mm Ø, h = 1.95mm. Before the magnetic measurements, the discs were magnetized by 3T magnetic field.

Table 7.18 : Properties of the sintered F3-SNFB feedstocks.

	Rel. Den %	Shrinkage %	O level wt%	C level wt%	Br (T)	B_Hc (kA/m)	iHc (kA/m)	$(BH)_{max}$ (kJ/m ³)
F3-SNFB-1	90	14	0.600	0.517	0.739	17.33	17.88	3.71
F3-SNFB-2	96	16	0.659	0.490	0.640	14.53	15.00	2.09
F3-SNFB-3	85	12	0.663	0.045	0.798	108.50	151.43	18.38
F3-SNFB-4	90	12			0.461	13.60	14.10	1.57
F3-SNFB-5	93	14	0.679	0.070	0.484	13.51	14.15	1.04
F3-SNFB-6	88	12			0.528	13.23	13.64	1.78
F3-SNFB-7	74	2			0.605	20.77	21.82	3.04
F3-SNFB-8	95	15			0.528	16.41	16.92	2.56
F3-SNFB-9	92	14			0.475	15.76	16.27	2.09
F3-SNFB-10	85	10			0.575	20.74	21.44	3.86
F3-SNFB-11	83	7			0.515	22.72	24.37	2.42
F3-SNFB-12	88	11			0.466	21.14	22.68	1.84
F3-SNFB-13	82	9	0.882	0.082	0.653	27.10	28.74	4.64
F3-SNFB-14	83	7			0.556	25.30	26.72	3.29
F3-SNFB-15	85	9		0.129	0.639	26.36	27.77	3.80

As it was expected, the first two cycles (F3-SNFB-1 and F3-SNFB-2) which were debinded under Ar had very high carbon contents. Due to high carbon contents, free Fe phase was present in the microstructure which pulled down the coercivity of the

sintered parts. As the Fe content increased in the microstructure, coercivity decreased but remanence stayed the same.

Although Fe has high saturation magnetization, huge amount of ferromagnetic elements (Fe, Co) in the grain boundary phase result in low coercivity owing to easily demagnetization. XRD characterizations of the F3-SNFB-1 sintered sample shown in Fig. 7.34 indicated the high Fe content in the structure.

For the cycle F3-SNFB-3 and F3-SNFB-10, between 250 °C-500 °C, 0.1K/min slow debinding rate was used. With this slow debinding rate, sintering cycle took around 2 days which was not financially positive. However the highest coercivity and remanence was obtained with this cycle. The carbon level achieved for sintered F3-SNFB-3 parts were lower than 0.05wt% and oxygen level were similar to the prior samples. When 1100 °C sintering temperature was used instead of 1080 °C, the magnetic properties were declined. This decrease in remanence and coercivity could be due to the grain growth.

However, it should be kept in mind that, these results were obtained for the small disc parts. When bigger samples are considered, 1080 °C was not high enough for sufficient densification. The F3-SNFB-3 samples were distorted - concaved as like F3-SNFB-10 samples which were sintered at 1100 °C. It was expected that sintering temperature increase would improve the density however even the shrinkage got lower. The same tendency was observed also in comparison of the cycles F3-SNFB-7 and F3-SNFB-9.

This time 1°K/min was used for debinding rate and 1080 °C sintering temperature was used for cycle F3-SNFB-7 and 1100 °C for F3-SNFB-9. Coercivity and remanence was higher at lower sintering temperature however the samples approached to nearly full-density with higher sintering temperature.

XRD observations on the F3-SNFB-3 sintered part (Fig. 7.34B) showed that still high Fe phase present in the microstructure due to the high oxidation amount in the sintered part given in Table 18. Since the carbon level was lower than F3-SNFB-1 parts, barely higher amount of Nd₂Fe₁₄B phase is observable.

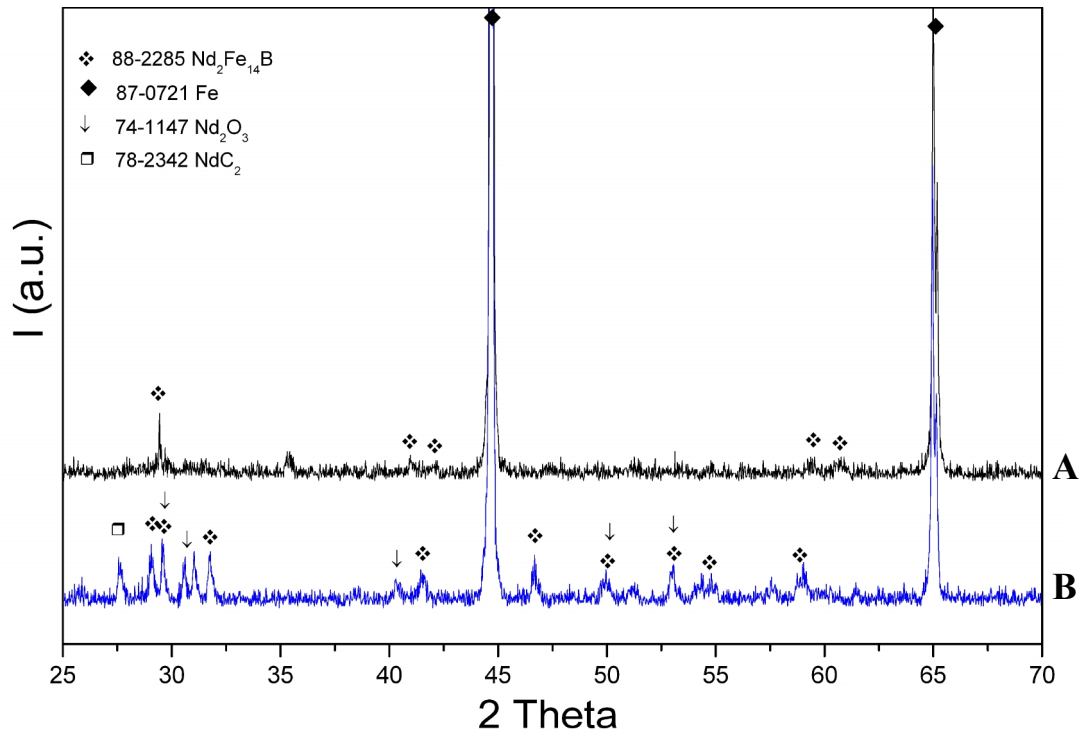


Figure 7.34 : XRD analyze of sintered F3-SNFB-1 (A) and F3-SNFB-3 (B) sample.

SEM/BSE micrographs of the etched F3-SNFB-3 sintered part given in Fig. 7.35, mainly reflected a pores structure and visible grain boundaries. White phase representing the Nd-rich phase mainly observed on the triple junctions of the grain boundaries where big pores placed. These pores could be formed by the etcher which etched partly the oxide phases.

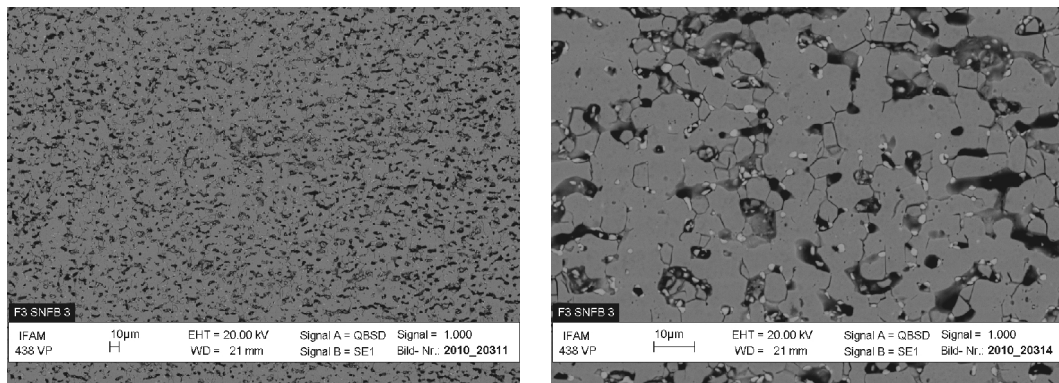


Figure 7.35 : BSE images of sintered - etched F3-SNFB-3 samples.

F3-SNFB-4 and F3-SNFB-9 cycles had the same sintering schedule. These small discs were sintered together with big tensile test specimens. The discs were placed in between these specimens. The sintered densities were relatively higher than the average however since the magnetic properties were poor, further investigations were

not carried out. The picture of the sintered anisotropic F3-SNFB parts is given in Fig. 7.36.



Figure 7.36 : The image of the sintered anisotropic single-pole F3-SNFB parts, from left to right: F3-SNFB-1 to F3-SNFB-4.

In cycles F3-SNFB-5 and F3-SNFB-6, dwelling time was applied for 4 hours instead of 1 hour. The grains tended to grow drastically which degraded the coercivity and energy product. Significant grain growth was determined by dwelling longer than 2 hours. In fact, it is also possible that solid solution in-homogeneity during liquid phase sintering caused peak broadening for the F3-SNFB-5 sample.

SEM/BSE micrographs of the etched F3-SNFB-5 sintered part given in Fig. 7.37 shows less pores structure than F3-SNFB-3 parts since shrinkage was 2% higher. The high grain growth was not clearly visible since the grain boundaries were not well observable.

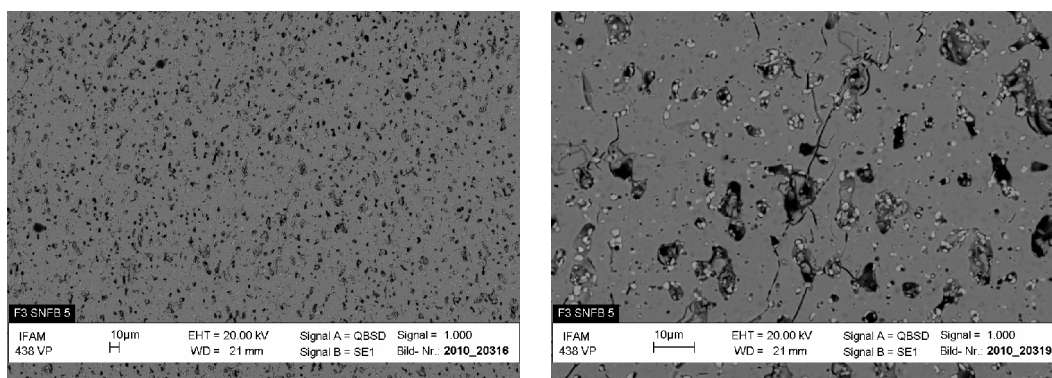


Figure 7.37 : BSE images of sintered - etched F3-SNFB-5 samples.

Vacuum (10^{-3} to 10^{-4} mbar) was used instead of high vacuum (10^{-5} to 10^{-6} mbar) for F3-SNFB-11 and F3-SNFB-12 cycles. The samples did not have good magnetic properties except small amount of coercivity increase than high vacuum sintered samples.

As the cycles F3-SNFB-12 (sintering under vacuum), F3-SNFB-13 (sintering under Argon), and F3-SNFB-9 (sintering under high vacuum) are compared, it is found out that better magnetic properties were achieved by Argon atmosphere sintering. However the lowest density also obtained by Argon sintering. In order to increase the

density, increasing dwelling time caused grain growth as explained above. Therefore it is very critical for the small sized samples to arrange the sintering atmosphere, temperature and dwelling time parameters.

For cycle F3-SNFB-14, in order to observe the debinding behavior, debinding in slow rate started at 400 °C. Sintered samples had many cracks on the surface following to sintering and had dark surface which refers to high carbon level.

The pressure respect to temperature data stored by the computer during sintering of the previous sintering cycles up to F3-SNFB-14 was examined. It is found out that, after debinding; in the beginning of the sintering stage, high amount of gas exit out of the samples under high vacuum till around 750 °C. It is considered that this gas should be hydrogen coming out of the samples by breaking down NdFeBH_x formation following to sintering stage. Moreover most of this gas was coming from the Ti getter which absorbed high amount of Hydrogen in the debinding stage. Therefore, for cycle F3-SNFB-14 and F3-SNFB-15 a small step was given at 725 °C with 30min dwell in order to remove the absorbed hydrogen before starting sintering stage. The magnetic properties did not improve with this small additional step at 725°, furthermore higher carbon level was observed than the samples sintered under Argon (F3-SNFB-13) without this additional step. Moreover, as the density compared with F3-SNFB-9, the shrinkage was reduced.

In contrast to small anisotropic disc samples, isotropic tensile test specimens had higher densities around 96% relative density. Various sintering atmospheres such as high vacuum, argon and vacuum were examined, however the carbon levels were similar and approximately 0.08wt% and oxygen level 0.3-0.4wt% which were significantly lower than the values for small discs. Lowest oxygen was achieved by high vacuum sintering and highest oxygen level was obtained by sintering under vacuum.

The remanence of the isotropic tensile test specimens which was around 0.3 T was lower than the anisotropic small disc specimens as it was expected. The coercivity levels varied due to the sintering atmospheres. These isotropic tensile test parts were saturated by 3T magnetic force. The highest intrinsic coercivity was achieved by

vacuum sintered sample which was 921 kA/m. This measurement was applied via Brockhaus™ Hystograph having max field strength of 1500 kA/m.

However, when the isotropic samples were saturated by 5T magnetic force, the samples sintered under argon and high vacuum had same coercivity level which was 1775 kA/m. During sintering process, the temperature went over the Curie temperature ($\sim 312^\circ\text{C}$), therefore magnetic moments changed.

Parts should be re-magnetized in the easy axis to get the magnetic moments back. For the anisotropic parts even 3T magnetization was enough to saturate the material due to remained crystalline anisotropy in the material. However, as for isotropic parts, higher saturation was needed because there is no easy axis.

For comparison to the injection molded and sintered parts, uniaxial pressed isotropic parts were also prepared. Uniaxial hand press also placed in the glove box in order to inhibit oxidation. Parts were pressed in an $\varnothing$ (10mm) mold with a pressure of 8.0 - 8.4kN. The first composition which is called as C-SNFB-1 was mixed with 5 drops of 2-Butanol (99.9%) inside the glow box.

C-SNFB-1 parts were tending to break down very easily therefore 2-Butanol was not a suitable lubricant for this SNFB (NdFeB) powder system. For the rest of the compositions, instead of 2-Butanol, 0.5wt% of paraffin wax was mixed to improve stability of the green parts.

C-SNFB-1 composition was sintered outside the glove box, and it was carried to the furnace in a closed stainless steel container. Sintering was performed without debinding stage in a high vacuum atmosphere at 1080°C . The sintering details for the C-SNFB parts are given in Table 7.19.

The C-SNFB-1 sintered samples were highly cracked and had oxidized surface. The oxidation probably appeared during transportation of the parts although parts were carried to the furnace in a closed container. Probably the parts tend to oxidize in the very beginning of the sintering cycle while the furnace started to make high vacuum. High vacuum took some minutes to warm up the vacuum pump. Therefore the compositions (C-SNFB-2 to C-SNFB-4) were sintered under vacuum atmosphere in a furnace which was placed inside the glove box. At 200°C a step was given to

remove the paraffin totally and inhibit possible cracking. C-SNFB-5 parts were sintered together with injected molded samples.

Table 7.19 : Sintering conditions of pressed C-SNFB parts.

Feedstock	Debinding						Sintering		Heat Treatment		
	R ₁	T ₁	R ₂	T ₂	Atm	P.P.	T	Atm	D.	T	D.
C-SNFB-1							1080	HV	1		
C-SNFB-2	2	200			V		1080	V	1		
C-SNFB-3	2	200			V		1100	V	4		
C-SNFB-4	2	200			V		1100	V	1		
C-SNFB-5	3	250	1	500	H ₂	850	1100	V	1	630	1

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Nearly full densification was obtained for the samples C-SNFB-2, C-SNFB-3 and C-SNFB-4 which were sintered under 10^{-2} mbar vacuum in the glove box. However the sintered parts belonging to cycle C-SNFB-3 and C-SNFB-4 resulted in highly distortion. C-SNFB-3 samples were concaved from the top layer which shows long dwelling time was definitely not suitable for liquid phase sintering of this composition. Shorter dwelling was applied this time for the C-SNFB-4 samples, however concave behavior was observed this time on the bottom of the sample which indicated improper pressure-atmosphere. The image of the sintered C-SNFB samples is given in Fig. 7.38.



Figure 7.38 : Isotropic pressed and sintered C-SNFB samples, from left to right: C-SNFB-1 to C-SNFB-5.

The magnetic properties of C-SNFB-1 were not measured since it was severely oxidized. Although C-SNFB-2 samples had more than 0.1wt% carbon, the intrinsic coercivity level was relatively high. There was no texturing (alignment) during pressing of these samples therefore the remanence values were low. The density and microstructural properties of the parts are mentioned in Table 7.20.

Table 7.20 : Properties of the pressed - sintered C-SNFB parts.

	Rel. Den %	Shrinkage %	O level wt%	C level wt%	Br (T)	B_{Hc} (kA/m)	H_{ci} (kA/m)	$(BH)_{max}$ (kJ/m ³)
C-SNFB-2	97	8.2	0.307	0.146	0.207	106.15	419.50	5.44
C-SNFB-3	98	9.2			0.187	26.22	34.73	1.07
C-SNFB-4	97	9.5			0.257	110.69	350.34	6.66
C-SNFB-5	83	0.5			0.331	89.48	146.15	7.24

C-SNFB-5 parts were exposed to H₂ atmosphere in the "debinding" step since they were sintered with the injection molded samples. Thus, hydrogenation of the Nd-rich phase which takes place at room temperature [196, 197] should be realized. The samples were sintered under vacuum (around 10⁻² mbar) till 1100 °C. However at around 725 °C, it is known that H₂ gas was exhausted from the Ti getters. Therefore till 725 °C, hydrogen was present in the sintering atmosphere and afterwards vacuum was reached around 900 °C. It can be possible that hydrogen process was realized efficiently consequently NdFeBH_x and NdH_x phases could still be present in the structure leading to low density and coercivity of the sintered C-SNFB-5 samples.

7.3.2 SmCo Parts

7.3.2.1 Samples prepared by VSC powder

Sm₂Co₁₇ powders were commercially supplied from Vacuumschmelze™ (Vacomax 240-AK) Company. The mean particle size of the initially delivered powder (named as VSC) was 139.1µm. The feedstock (F1-VSC) was prepared using 68vol% solid content with this VSC coded coarse particle sized powder; however injection molding could not be performed due to the flowing problems through the nozzle tip.

The particle size of VSC powders were reduced by planetary ball milling in dry conditions under Argon atmosphere by using 1:2 ball to powder ratio. Milling was carried out for 3 hours and for 5 hours and these powders were named as 3m-VSC and 5m-VSC; respectively. Powders were loaded and unloaded to the vials in the glove box, under Argon atmosphere. Milling was stopped in every 30 min and let it cooled down for the next cycle. Following to 3 hours milling, the mean particle size was reduced nearly to 50.31µm. The laser particle size analyses for the magnetic

powders could not be precisely measured even with surfactants due to the precipitation and agglomeration problems. The oxygen and carbon level after 5 hour milling (5m-VSC powder) is shown in Table 7.21.

Table 7.21 : Properties of the 5m-VSC powder.

Powder	O wt%	C wt%
5m-VSC-Powder	0.536 ± 0.019	0.021 ± 0.000

Subsequent to milling oxygen level of the powder was increased around 0.1-0.2wt%. The optical and BSE pictures of the etched 3m-VSC powders following to etching by picric acid is given in Fig. 7.39. During metallographic preparation, the brittle powder particles tend to break down. In Fig. 7.39a, it is clear that the particle size distribution was in a wide scale. Grains were irregular and some of them had more than 40 μ m grain size which is very large. By BSE image given in Fig. 7.39b, it is observed that one particle had many sub-grains which also pointed out that these particles did not single poles. Therefore remanence should not be expected to be high because reverse domains would decrease the remanence.

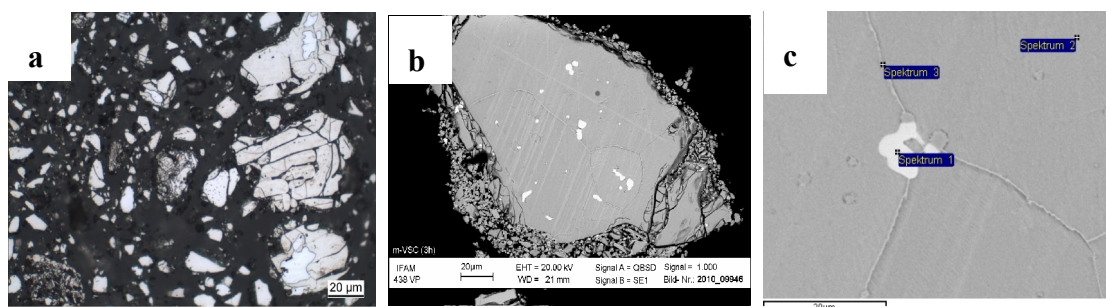


Figure 7.39 : Optical microscope (a) and BSE image (b) of the etched 3m-VSC powder (c) SEM/EDX analyses on etched 3m-VSC powder particle.

EDX analyses were performed on the white areas (spectrum 1), matrix phase (spectrum 2) and on the grain boundary of the powder particle (spectrum 3). Results pointed out that these white areas were oxide phases with Sm_2O_3 composition having around 4 μ m diameter size. Spectrum 2 was taken from the matrix phase which had a $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_{16.55}$ composition which fit to our initial powder composition. Additionally, it was aimed to make a measurement on the grain boundary phase shown as spectrum 3. However since the grain boundary was very thin, the reflections were probably collected also from the matrix phase, thus spectrum 3 had

nearly the same values as spectrum 2. Four different feedstocks were prepared by coarse and as-milled Vacomax 240-AK powder by mixing with the same binder composition (B27). The details are given in Table 7.22.

Table 7.22 : Properties of VSC feedstocks.

Feedstock	Powder Code	Binder	Solid Content vol%	Injection Machine	Injection Observations
F1-VSC	VSC	B27	68	Embedding Machine	No flowing
F2-VSC	3m-VSC		68	HEK	No filling
F2-VSC (2)	3m-VSC		55		Segregation, Air pockets
F3-VSC	5m-VSC		55		No problem

F2-VSC feedstock having 68vol% solid content was prepared using 3 hour milled irregular shaped VSC powders. Injection F2-VSC feedstock resulted in severe segregation and filling problems as like F1-VSC feedstock. As the solid content was lowered to 55vol% (F2-VSC (2)), flowing was no longer a problem however, segregation, and air pocket formation was observed.

As the VSC powder was milled for 5 hours, it was managed to reduce the particle size in a proper ratio to enable accurate flow. The prepared feedstock with 55vol% solid content, the injection molding process was carried out without any injection problems.

The green parts of the prepared feedstocks were sintered separately in the Elnik 2 furnace. Same sintering schedule was applied for each cycle. Subsequent to thermal debinding, samples were heated to 1200 °C with a 5°K/min sintering rate and hold for 30 min under high vacuum. In the following step, sintering was continued in Argon atmosphere (800mbar partial pressure) till 1220 °C for 1hour.

Homogenization treatment was realized at 1175 °C for two hours, and continued with precipitation hardening cycle at 850° for 8 hours. From 850 °C very slow cooling (0.7°K/min) to room temperature was carried on to improve coercivity. F1-VSC samples sintered on Tantalum Plates using Ti traps surrounding the samples. No sticking problem was analyzed. In the following cycles, green parts were sintered

on Y₂O₃ coated Tungsten plates with Ti traps and half-covered lid. The sintering conditions of the VSC feedstocks are given in Table 7.23.

Table 7.23 : Sintering conditions of the injected VSC feedstocks.

Feedstock	Debinding				Sintering			Heat Treatment		
	R	T	Atm	P.P.	T	Atm	D.	T	D.	Cooling
F1-VSC					1200	HV	0.5			400
F2-VSC (2)	3	500	H ₂	800	1220	Ar	1	850	8	(0.7 rate)
F3-VSC					1175	Ar	2			

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Gutfleisch et al. [37], found out in their observations that slow cooling (0.7 K/min) from the aging temperature of 850 °C confirmed evolution of the magnetic domain structure because high-performance 2:17-type SmCo magnets are generally pinning-dominated magnets. Additionally the nature of the magnetic domain structure (the domain width) is very sensitive to details of the processing procedure, which enables high coercivity. In literature it is stated that maximum coercivity obtained by slow cooling and a very fine magnetic domain contrast was observed by Kerr microscopy [83].

The main effect of slow cooling is the redistribution of the elements, namely the diffusion of Cu from the 2:17R cell interior into the 1:5 cell boundary phases, thereby changing the intrinsic magnetic properties of the latter [37]. On the other hand, if the cooling rate is too fast, microscopic cracks and internal stresses are created which negatively influence the stability of the magnets against oxidation and the coercivity [198].

Following to sintering, the sharp edges of the green F3-VSC parts had rounded curve-shape as shown in Fig. 7.50. All samples color was light grey without any contamination signs.

The relative dimensional densities of the samples were enhancing by increasing milling time of the powder. F1-VSC parts had 63% relative density as the reference density taken as 8.45 g/cc. F2-VSC (2) had 84% relative dimensional density and F3-VSC had 90%. Archimedes densities are mentioned in the Table 7.24.

Table 7.24 : Properties of the sintered F3-VSC feedstock.

	Rel. Den %	Shrinkage %	Br (T)	B_{Hc} (kA/m)	i_{Hc} (kA/m)	$(BH)_{max}$ (kJ/m ³)
F3-VSC	96	20	0.168	19.12	22.03	0.80

The new formed phases after sintering F2-VSC samples were characterized by SEM/EDX analyses. EDX analyses were carried out on each phase of the un-etched sintered F2-VSC part and they are marked on the image given in Fig 7.40.

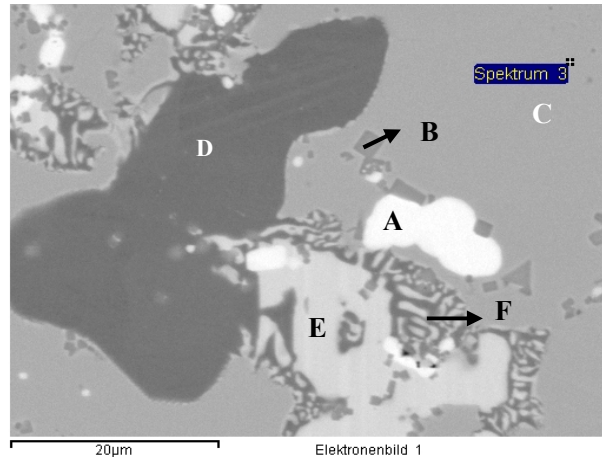


Figure 7.40 : SEM image of the un-etched F2-VSC sintered sample.

Six different phases were determined on un-etched F2-VSC sintered sample and phase A had the highest oxide phase. Since the oxide and carbide analyses cannot precisely measurable by EDX analyses, the exact phase composition of phase A could not be measured directly. Nevertheless this phase assumed to be Sm_2Co_3 phase.

Phase B was a platelet structure. This phase was also determined in many studies in the literature [83, 199-201]. It is stated that this so-called platelet phase (also referred to as lamellar or Z-phase) was rich in Zr and it was observed additionally parallel to the 2:17R basal plane [83, 199]. This statement suit to the results obtained by EDX analyses in this study. Phase B had the highest Zr content in 3m-VSC parts which was 87.71at%.

Additionally, Z-phase manifests itself as thin lines extending over many 2:17R cells. Thickness of the lamellae was informed as very small ranging from 1 nm [199] to 3

nm [200]. The lattice structure of the Z-phase is still somewhat controversially discussed.

The Z-phase is considered to stabilize the cellular microstructure and, more importantly, to provide diffusion paths for Cu, Fe and Co, thereby modifying phase-ordering kinetics [83]. Table 7.25 outlines all the compositions of these six phases mentioned in Fig. 7.40.

Table 7.25 : EDX analyses of the sintered un-etched F2-VSC part.

	at%					
	A	B	C	D	E	F
Fe K		2.42	18.88	30.85		23.85
Co K	3.72	7.73	64.38	67.74	49.68	61.55
Cu K		0.74	6.05	1.03	0.97	1.12
Zr L		87.71				1.99
Sm L	96.28	1.40	10.68	0.38	49.35	11.48

Phase C was the matrix phase which had $\text{Sm}_{10.68}(\text{Co,Fe,Cu})_{89.31}$ shortly, $\text{Sm}_2\text{Co}_{17}$ composition. Phase D had the biggest grain size than the other phases. The identified CoFeCu phase had nearly $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ atomic formula. On the other hand phase E, had SmCo phase composition. Phase F had zigzag shaped morphology. EDX analyzes on sintered un-etched F3-VSC parts indicated five different phases and they were marked on the Fig. 7.41.

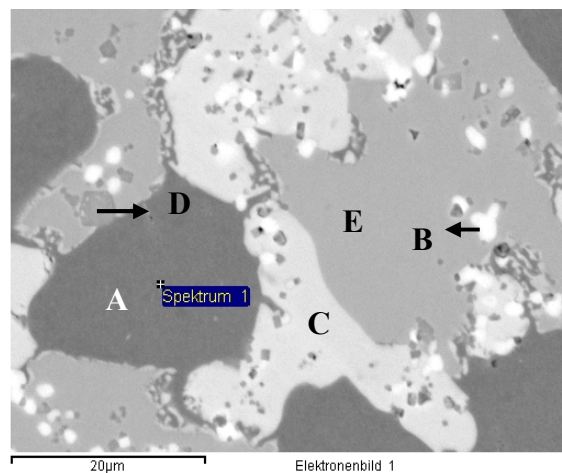


Figure 7.41 : BSE/EDX analyses of the F3-VSC samples.

The phase analyses on the determined phases of the F3-VSC parts are given in the Table 7.26.

Table 7.26 : EDX analyses of the sintered un-etched F3-VSC part.

	at%				
	A	B	C	D	E
Fe K	29.67			1.17	17.81
Co K	68.21	4.17	50.61	2.94	63.66
Cu K	1.83				7.63
Zr L		2.44		95.43	
Sm L	0.28	93.39	49.39	0.47	10.91

In Fig. 7.41, the marked area A, which had a similar structure as like the D phase in F2-VSC parts, had nearly $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ composition. Phase B also pointed out the oxide phase, where samarium was oxidized to Sm_2O_3 . Phase C had the same composition as the marked phase E of the F2-VSC parts. This phase had Sm_1Co_1 atomic formula.

The marked phase D, were also Zr platelet structure which had 95.43at% Zr. Phase E represents the matrix phase and had $\text{Sm}_{10.91}(\text{Co}, \text{Fe}, \text{Cu})_{89.09}$ shortly $\text{Sm}_2\text{Co}_{16.33}$ formula which was nearly 2:17 phase composition.

7.3.2.2 Samples prepared by SSC powder

$\text{Sm}_2\text{Co}_{17}$ isotropic powder which had 6 μm particle size was obtained commercially from MS-Schramberg™ (B30047E). The physical and magnetic properties of this powder are given in Table 7.27.

Table 7.27 : The properties of the starting SSC powder.

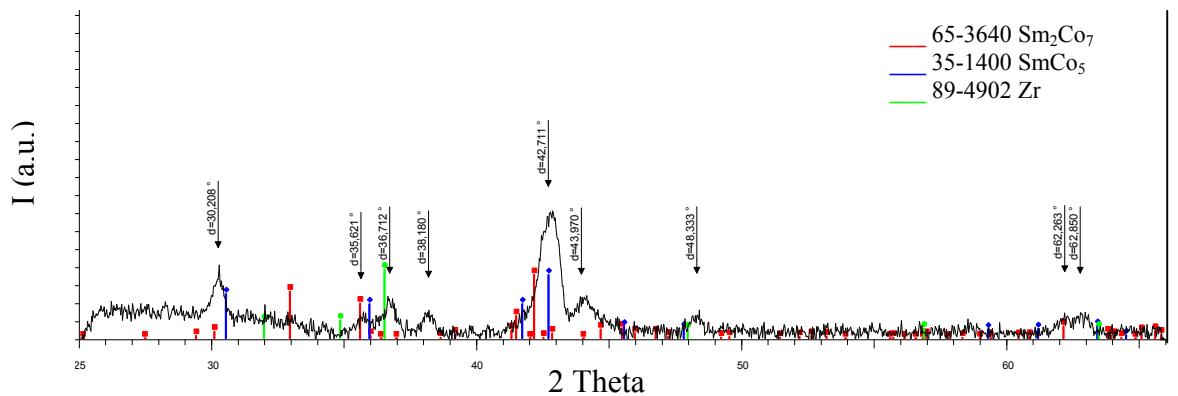
		wt%	Br (mT)	(BH) _{max} kJ/m ³	B _{Hc} (kA/m)	i _{Hc} (kA/m)	Density (g/cc)	O (ppm)	C (ppm)
Sm ₂ Co ₁₇	Fe K	15.85							
	Sm L	25.48							
	Cu K	4.91	997	177	700	1273	8.25	3000 - 4000	500 - 900
	Zr L	2.81							
	Co K	50.95							

Several elements were added during powder production of SmCo magnets in order to induce special magnetic properties. The addition of Fe increases the spontaneous magnetization; addition of Cu produces a desirable microstructure and Zr obtains favorable effect on coercivity [133]. Oxygen and Carbon level measurements were carried out in IFAM, and the values are given in Table 7.28.

Table 7.28 : Properties of the SSC powder.

Powder	O wt%	C wt%
SSC-Powder	0.359 ± 0.003	0.053 ± 0.001

XRD analyses on the SSC powder which is given in the Fig. 7.42 indicated three phases such as; Sm₂Co₇, SmCo₅ and Zr present in this powder system.

**Figure 7.42** : XRD analyze of the SSC powder.

SEM/EDX analyses were realized on SSC commercial powders to control the particle size and phases. The particle size appeared to be around 10 µm however the

size distribution was not homogeneous. The particles were single grains. EDX analyze results of the SSC powder particle following to etching is given in Fig. 7.43.

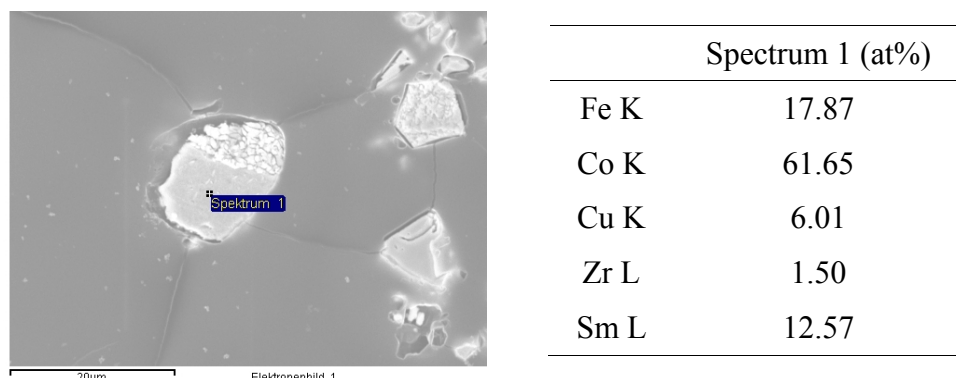


Figure 7.43 : BSE/EDX analyze of SSC powder particle.

The observation of the distribution of the elements on the SSC commercial powder is analyzed by mapping. The images are given in Fig. 7.44.

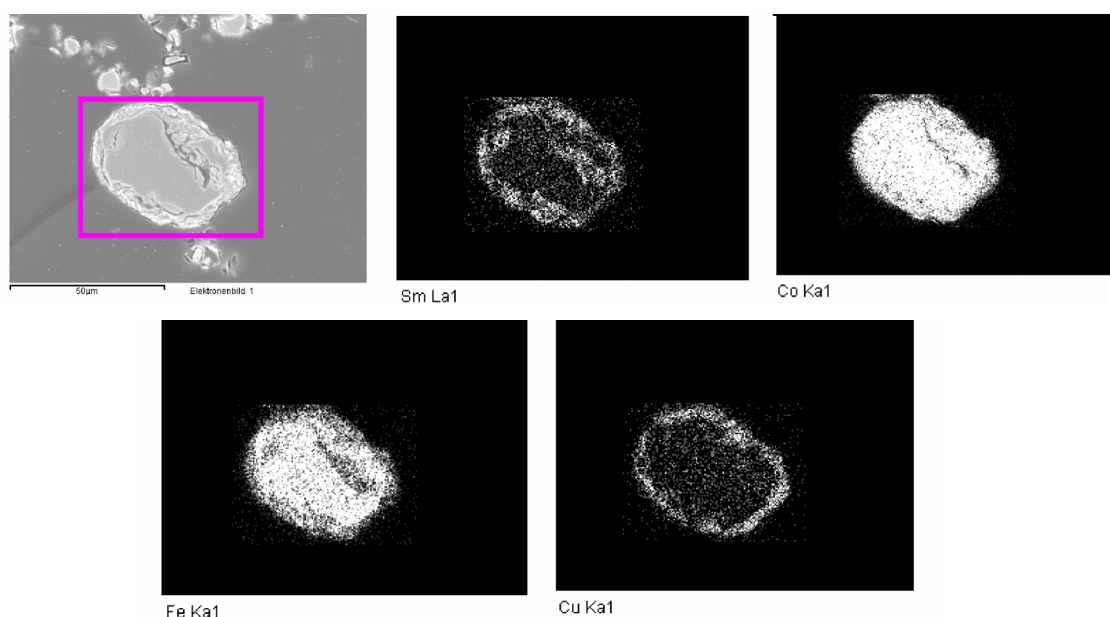


Figure 7.44 : Mapping images of the SSC powder particle.

Sm and Cu elements were mostly located on the surrounding of the SSC particles. Co and Fe elements however were distributed on the whole area of the powder particle. Gutfleisch et al. [83] observed also in their studies that cell boundary phase is rich in Cu and Sm, whereas matrix is rich in Fe and Co.

Injection molding of the F1-SSC feedstocks were performed via Hek™ machine without any injection problems. 5 bars injection pressure and 90° injection

temperature was used in order to produce isotropic and anisotropic F1-SSC green parts. Further information regarding the F1-SSC feedstock is given in Table 7.29.

Table 7.29 : Properties of F1-SSC feedstock.

Feedstock	Powder Code	Binder	Solid Content vol%	Injection Machine	Injection Observations
F1-SSC	SSC	B27	55	Hek	No Problem

The viscosity of the F1-SSC feedstock was very low showing that 55vol% solid content was improper. SSC powder had smaller and homogeneous particle size distribution which let us the availability to increase the solid content.

F1-SSC parts sintered together with F3-VSC samples on the Y_2O_3 coated tungsten plates. The sintering conditions are given in Table 7.30. 3K/min debinding rate were applied for thermal debinding because during these experiments it was not yet discovered that 3 K/min actually a high rate which caused residual carbon in the sintered sample.

Table 7.30 : Sintering conditions of the injected F1-SSC feedstock.

Feedstock	Debinding				Sintering			Heat Treatment		
	R	T	Atm	P.P.	T	Atm	D.	T	D.	Cooling
F1-SSC	3	500	H ₂	800	1200	HV	0.5	850	8	400
					1220	Ar	1			(0.7 rate)
					1175	Ar	2			

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Sintered samples had net shapes meaning that sharp corners and homogeneous shrinkage. As mentioned above high debinding rate resulted in high carbon level. Oxygen level was also very high for to get an adequate remanence and coercivity. The magnetic properties of the sintered F1-SSC parts are given in Table 7.31.

Table 7.31 : Properties of the sintered F1-SSC feedstock.

	Rel. Den %	Shrinkage %	O level wt%	C level wt%	Br (T)	B_{Hc} (kA/m)	H_{c} (kA/m)	$(BH)_{max}$ (kJ/m ³)
F1-SSC	98	20	0.440	0.753	0.308	11.00	11.70	0.30

Although high relative density and shrinkage were obtained, the remanence and coercivity of the anisotropic sintered F1-SSC samples were very low. In addition to fast debinding rate, wrong binder choose could also be the problem for obtaining high amount of impurities.

Fig. 7.45 compares the cross section area of the sintered F2-VSC, F3-VSC and F1-SSC parts. It is visible that the shrinkage ratios were getting higher and porosity diminished as the particle size of the powder getting lower as in the F1-SSC sintered part.

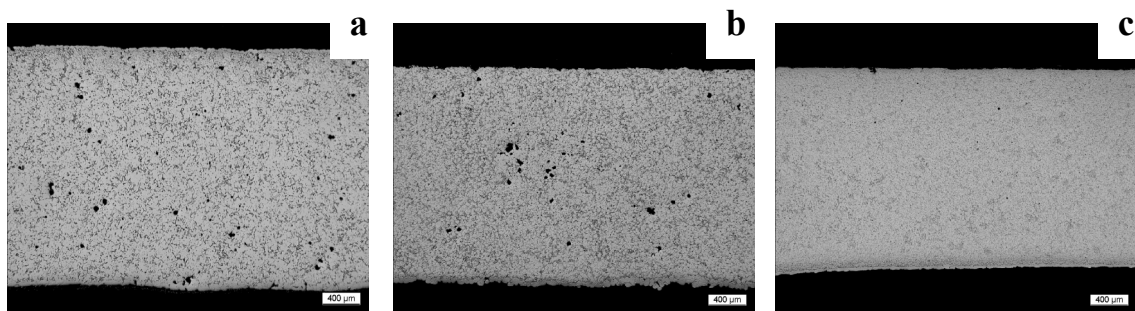


Figure 7.45 : Optical microscope view for the cross sectional areas of (a) F2-VSC, (b) F3-VSC and (c) F1-SSC.

SEM/EDX analyze of the F1-SSC sintered part reveals five different phases in the micro-structure. The observed phases are marked on the image given in Fig. 7.46.

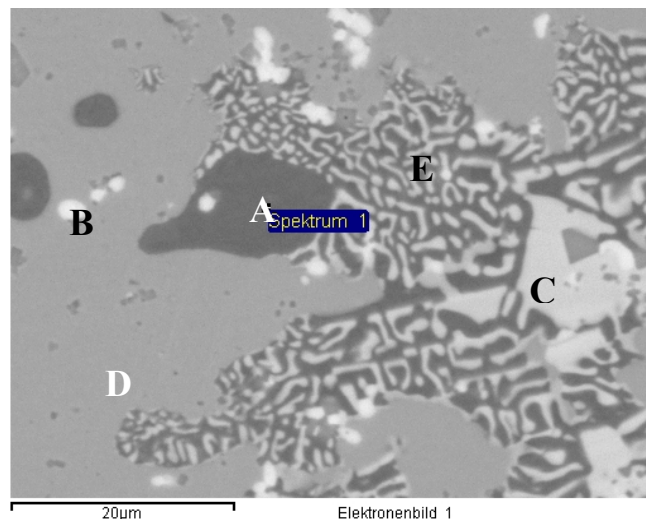


Figure 7.46 : SEM/EDX micrograph of un-etched sintered F1-SSC part.

The marked phase “A” had a similar composition as the previous identified phase however instead of having $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ composition, the Cu phase was slightly lower and formed $\text{Co}_{66}\text{Fe}_{33}\text{Cu}_{0.8}$ or shortly Co_2Fe composition.

White phase marked as B was the Sm_2O_3 oxide phase. Phase C was also present in the VSC parts and had the same Sm_1Co_1 composition. Additionally the matrix phase marked with D had $\text{Sm}_{10.15}\text{Co}_{63.20}\text{Fe}_{26.05}$ shortly $\text{Sm}_2(\text{Co}, \text{Fe})_{17}$ composition.

The zigzag shaped phase signed as E had bigger grain size than the other sintered parts and has $\text{Sm}_2(\text{Co}, \text{Fe})_{17}$ composition. EDX analyze results of the sintered un-etched F1-SSC parts are given in Table 7.32.

Table 7.32 : EDX analyze results of the sintered un-etched F1-SSC part.

	at%				
	A	B	C	D	E
O K		63.51			
Fe K	32.85			20.77	26.05
Co K	65.86	4.38	49.75	62.78	63.20
Cu K	0.77	0.41		5.78	0.60
Zr L		1.47			
Sm L	0.53	30.24	50.25	10.67	10.15

In literature, similar zigzag-shaped domain walls, which follow the 1:5 cell boundaries was observed by TEM characterizations as shown in Fig. 7.47 [202-204]. This observation was consistent with the domain walls being pinned at the cell boundaries of the prismatic cellular microstructure [37].

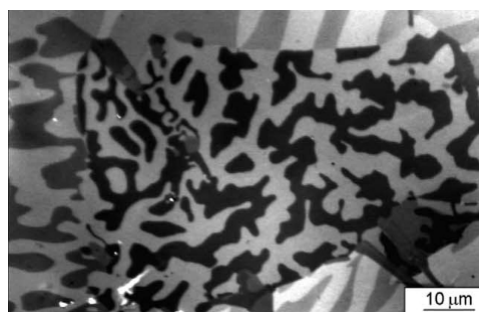


Figure 7.47 : Kerr microscopy image of $\text{Sm}(\text{Co}_{0.784}\text{Fe}_{0.100}\text{Cu}_{0.088}\text{Zr}_{0.028})_{7.19}$ [37].

The similar zig-zag shaped domains shown in the Fig. 7.47 was belong to solid solution treated $\text{Sm}(\text{Co}_{0.784}\text{Fe}_{0.100}\text{Cu}_{0.088}\text{Zr}_{0.028})_{7.19}$ reflecting a magnetic microstructure typical for coarse grained materials with easy axis type magnetic anisotropy [83].

The sizes and locations of the identified phases can be clearly compared with low magnified the optical and electron microscope micrographs of the F2-VSC, F3-VSC and F1-SSC sintered parts which are given entirely in Fig. 7.48.

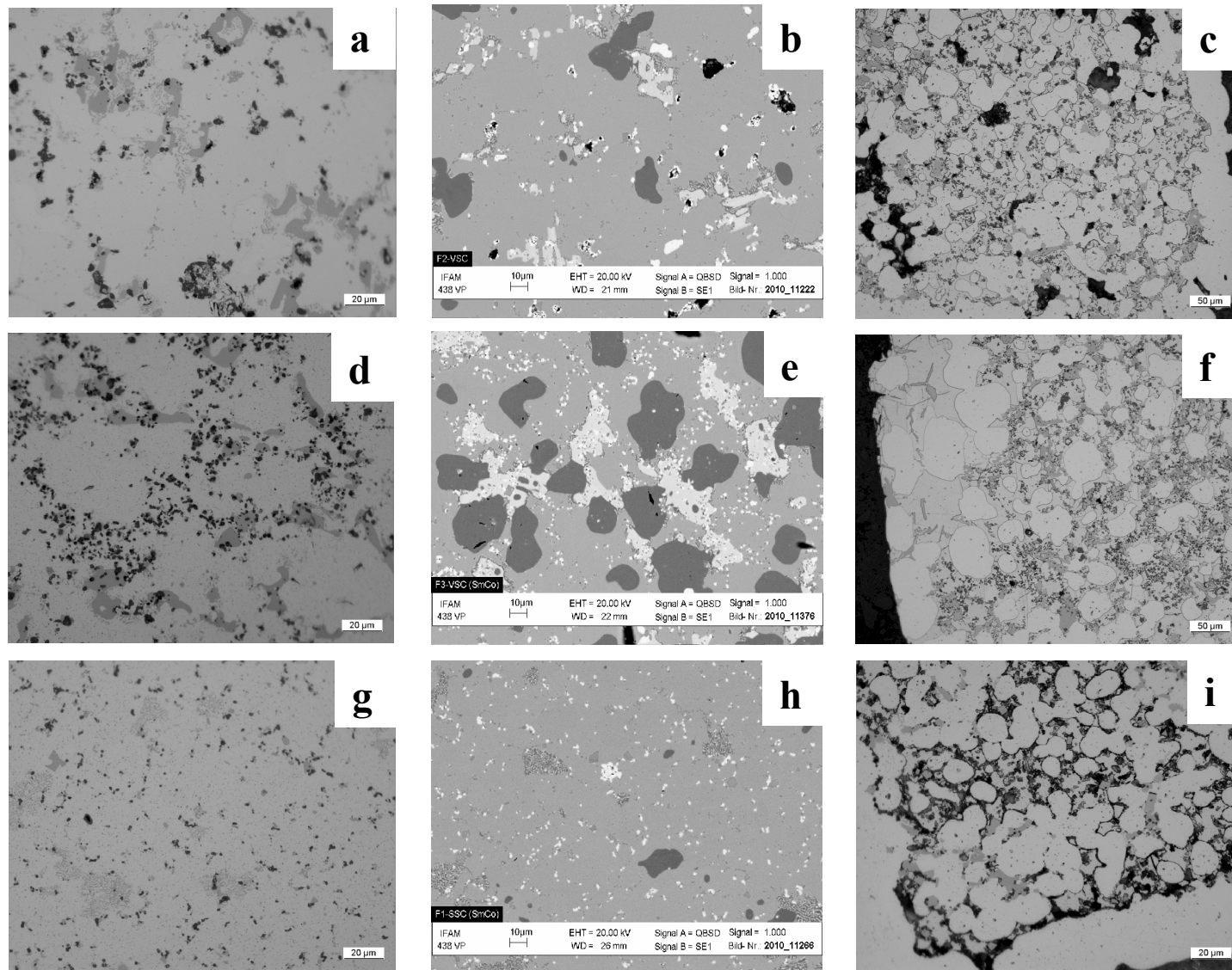


Figure 7.48 : Microstructure views of the sintered F2-VSC (a, b, c), F3-VSC (d, e, f) and F1-SSC (g, h, i) samples before (a, b, d, e, g, h) and after etching (c, f, i).

The optical microscope views of the unetched sintered F2-VSC, F3-VSC and F1-SSC are given in Fig. 7.48a, 7.48d and 7.48e respectively. In these pictures oxide phases were appeared as the darkest phase. On the other hand, in SEM images oxide phases had white color. As oxide phases were compared between the parts, it is clear that the F3-VSC sintered samples prepared from 5 hour milled VSC powders had the highest and largest Sm_2O_3 content.

Sm_2O_3 distribution in F1-SSC samples were homogeneous and having very small grain size. Moreover, low magnified SEM images revealed that grey phase which was analyzed as $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ phase was present mostly in the long milled sintered sample shown in Fig. 7.48e. F1-SSC sintered samples had the lowest amount of this phase. Therefore, $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ phase most probably formed during milling the powder. The longer milling, the higher amount of $\text{Co}_{68}\text{Fe}_{30}\text{Cu}_2$ phase appeared. As the SEM micrograph of F1-SSC sample analyzed, the zigzag phase could be seen as distributed big sized clusters.

F1-SSC sintered parts had the lowest grain size which was nearly 20 μm . On the other hand, F2-VSC and F3-VSC sintered parts had grain sizes around 40 μm , 50 μm ; respectively.

Optical microscope analyses given in Fig. 7.48c, 7.48f, 7.48i showed how serious oxidation had occurred on the surface of the parts.

XRD analyses which were carried out on the cross section area of the sintered un-etched F2-VSC, F3-VSC and F1-SSC parts are given in Fig. 7.49. All the parts had same phases with different amounts. In addition to Sm_2Co_7 , Sm_2Co_5 , Zr phases which were present in the starting powder; Fe, Zr and Sm_2O_3 phases were also observed following to sintering.

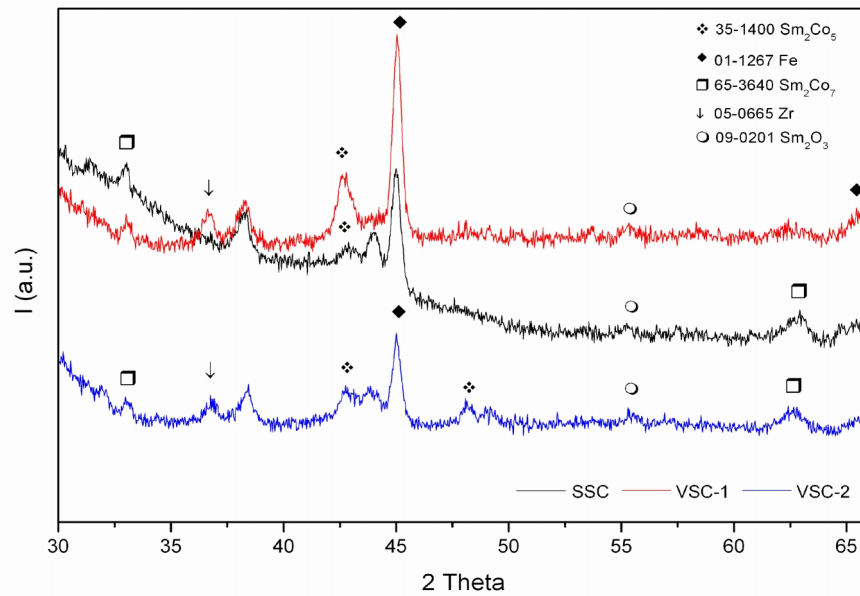


Figure 7.49 : XRD observation of the sintered F2-VSC, F3-VSC and F1-SSC parts. Vickers hardness measurements were applied on the cross-section area of the parts under 500gr load. The results are given in Table 7.33.

Table 7.33 : Hardness of the sintered parts.

Sintered Parts	Vickers Hardness (HV _{0.5})
F2-VSC	564 ± 166.36
F3-VSC	497 ± 88.77
F1-SSC	639 ± 68.79

In the literature, no additional data regarding mechanical properties of SmCo magnets could be found for comparison.

The image of the F2-VSC, F3-VSC and F1-SSC is given in the Fig. 7.50.



Figure 7.50 : The photo of isotropic injection molded and sintered parts, from left to right: F1-SSC, F2-VSC and F3-VSC.

7.3.2.3 Samples prepared by VSC2 Powder

Sm₂Co₁₇ anisotropic single crystalline powder was obtained from Vacuumschmelze™ (225/11255-A) which had 6μm particle size and 8.4 g/cc

theoretical density. The powder which was named hereafter as VSC2, was provided jet milled and had irregular particle shape.

VSC2 powder had "27%Sm, ... (Sm₂Co₁₇)" high amount of Sm phase which helps to enhance coercivity. 2:17 is the most tolerant composition to pick up carbon. This powder had 98% orientation and had remanence; Br = 1.1T.

If this powder fully heat treated following to sintering, the 25kOe (1989 kA/m) coercivity should be obtained. The level of impurities in the powder is given in the Table 7.34.

Table 7.34 : Oxygen and Carbon level measurement of VSC2 powder.

Powder	O wt%	C wt%
VSC2-Powder	0.240 ± 0.007	0.006 ± 0.000

VSC2 powders had lower oxygen and carbon levels compared to the previous studied SmCo powders.

XRD observations were performed on the VSC2 powder. Sm₂Co₁₇, SmCo₅, Zr and possible small amount of free Fe peaks were found and they are shown in Fig. 7.51.

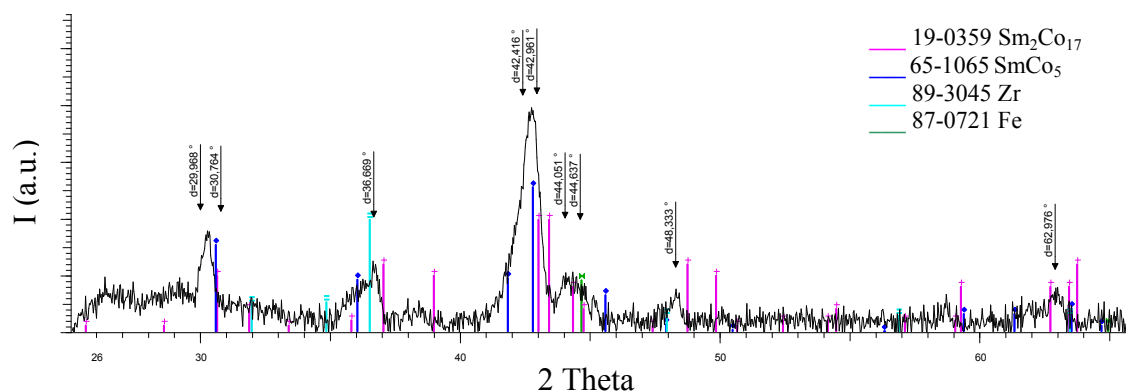


Figure 7.51 : XRD analyze of VSC2 powder.

F1-VSC2 feedstocks were prepared using B39 binder which had the lowest polyethylene content (15wt%). Injection molding was realized separately by Hek™ and Arburg™ machine.

The purpose of using two different injection molding machines was to observe and compare the oxygen content. Previous experiments showed an increase in oxidation when the NdFeB samples were molded by Hek™ machine. Since Hek™ machine does not have a screw; the feedstock amount coming out of the nozzle cannot be

digitally arrangeable. Therefore feedstock was recycled many times to process the machine. Anisotropic single and multi-pole F1-VSC2 parts were produced by Hek™ and Arburg™ machines using the same cavity dimensions (Table 7.35). Samples F1-VSC2-1 to F1-VSC2-3 were injected via Hek™ machine and F1-VSC2-4 were injected by means of Arburg™ machine.

Table 7.35 : Properties of F1-VSC2 feedstock.

Feedstock	Powder Code	Binder	Solid Content vol%	Injection Machine	Injection Observations
F1-VSC2	VSC2	B39	60	Hek™ Arburg™	No Problem

Sintering was processed separately for each cycle therefore there was no possible cross contamination. All the samples were place on Y₂O₃ coated tungsten plates with half closed lid, using Ti traps around the samples.

One additional step during sintering at 1170 °C was given due to the atmosphere change from high vacuum to argon. This change would increase the temperature of the atmosphere so this step was given in order to restrict the rise over 1190 °C. The sintering conditions are summarized in the Table 7.36.

Table 7.36 : Sintering conditions of the injected F1-VSC2 feedstocks.

Feedstock	Debinding						Sintering			Heat Treatment		
	R ₁	T ₁	R ₂	T ₂	Atm	P.P.	T	Atm	D.	T	D.	Cooling
F1-VSC2-1	3	250	0.5	500	H ₂	850	1170	HV	1			
							1190	Ar	2			
F1-VSC2-2	5	280	0.1	550	H ₂	850	1190	HV	0.5	1170	4	no
							1200	Ar	2			
F1-VSC2-3	3	250	1	500	H ₂	850	1170	V	1			
							1195	Ar	2			
F1-VSC2-4	3	250	1	500	H ₂	850	1190	HV	0.5	1170	4	no
							1200	Ar	2			

R(°C/min): Rate, T(°C): Temperature, Atm: Atmosphere, P.P(mbar): Partial Pressure, D(h): Dwell

Except F1-VSC2-2, all the other cycles resulted in distorted (concaved) shapes. All the parts had low oxygen and carbon level following to sintering however it did not make an impact on magnetic properties.

First two cycles resulted with better max energy product, so it is possible that slow debinding would be beneficial for these parts. The properties of the all sintering cycles are given in Table 7.37.

Table 7.37 : Properties of the sintered F1-VSC2 feedstocks.

	Rel. Den %	Shrinkage %	O level wt%	C level wt%	Br (T)	B_H (kA/m)	H_c (kA/m)	$(BH)_{max}$ (kJ/m ³)
F1-VSC2-1	90	concaved	0.278	0.029	0.80	112.76	123.24	28.22
F1-VSC2-2	95	17			0.80	104.60	115.70	23.05
F1-VSC2-3	82	8			0.62	67.34	81.49	9.15
F1-VSC2-4	96	14	0.257	0.007	0.47	126.80	181.57	15.49

A denser structure were obtained by injection molding in Arburg™ machine, however the oxygen level did not decrease in these samples (F1-VSC2-4) as it was expected. Therefore it can be highlighted that NdFeB alloy is more oxygen affinitive than SmCo to pick up the oxygen during injection molding.

No further micro-structural characterizations on F1-VSC2 parts were carried out following to sintering since the magnetic properties were not significantly enhanced. The photo belongs to F1-VSC2 sintered samples is given in Fig. 7.52.



Figure 7.52 : The image of the injection molded sintered anisotropic single-pole parts; from left to right: F1-VSC2-1 to F1-VSC2-4.

8. CONCLUDING REMARKS

Based on the results reported in the present investigations, the following conclusions can be drawn:

8.1 Conclusions for Hot Pressed ZrO₂/WC Composites

1. WC addition to the 3 mol% Y₂O₃ stabilized ZrO₂ matrix enhanced the indentation toughness values while hardness values remained constant. The 3Y-TZP reinforced with 32 vol% WC has the overall best mechanical and microstructural properties, i.e. the highest strength, Young's modulus and indentation toughness. WC reinforcements higher than 32 vol% WC resulted in the decline of the relative density values.
2. The main reason for the enhancement of indentation toughness with increasing WC content can be attributed to crack deflection, crack branching and bridging mechanisms incorporation with phase transformation toughening. Additionally, homogeneously distributed WC which has high modulus increased toughness significantly.
3. The optimized sintering temperature for the Y-TZP/WC composites was determined as 1450 °C. Higher temperatures led to a decline in flexural strength and indentation toughness due to increasing amount of the W₂C phase identified in the XRD patterns.
4. The tribological behavior of the 3Y-TZP matrix was enhanced significantly by the presence of homogeneously dispersed hard WC particles. The worn volume was reduced nearly 15 percent with 40 vol% WC addition. In addition, bimodal WC particle size distribution of nano-sized WC and coarse WC particles improved the relative density, Young's modulus, and indentation toughness considerably. Besides enhanced mechanical properties, superior wear resistance was obtained by nano-WC additions. Even with dry sliding conditions under relatively high normal load and long operation

conditions, the worn volume was 0.003 mm^3 for the 75 vol% nano-sized WC distributed 3Y-TZP/40WC composite.

8.2 Conclusions for Ceramic Injection Molded and Sintered ZrO₂/WC Composites

1. In general, more than 20 vol% WC additions to the 3Y-TZP matrix cause problems during processing and sintering. In the injection molding step, higher injection pressures and lower speed were needed for processing of the 3Y-TZP/40WC feedstock which caused further jetting problems resulting poor surface quality. On the other hand, with 20 vol% WC dispersed feedstock the obtained surface quality was satisfactory.
2. Sintering process was carried out partly in H₂ atmosphere till 1550 °C. At higher sintering temperatures, secondary porosities were observed. Additionally, sintering at longer times caused bending and cracking. Thus, 1550 °C was determined as the optimum sintering temperature for the 3Y-TZP/10WC and 3Y-TZP/20WC composites.
3. Isotropic shrinkage was obtained in all the injection molded parts after sintering at 1550 °C for 4 and 6 hours. Mechanical properties varied due to WC addition and dwelling time. Relative density and further mechanical properties enhanced with lower secondary hard phase addition. Highest strength and hardness was obtained with 6 hours sintered 3Y-TZP/10WC composite. On the other hand, significant enhancement in fracture toughness was obtained by 3Y-TZP/20WC composite which had $9.2 \text{ MPa.m}^{1/2}$ toughness. This increase can be attributed to combination of martensitic phase transformation and crack deflection, crack branching and bridging mechanisms. Agglomeration problem of the fine WC powder restricted the enhancement of the mechanical properties of 3Y-TZP/10WC (75% coarse) composite therefore no positive effect of bimodal particle size distribution could be observed.
4. The tribology results indicate that the parts had low wear rate in the unlubricated environment even with long operation conditions under relatively high normal load. The friction coefficient values were almost similar in every composite, therefore WC amount, dwelling time and bi-

modal WC particle size distribution did not have much influence on the wear resistance.

8.3 Conclusions for NdFeB and SmCo Sintered Isotropic and Anisotropic Permanent Magnets Formed by Metal Injection Molding

1. Although different debinding and sintering parameters were used, H₂ debinding atmosphere was decided as the only way to reduce the carbon into a proper level. Binder composition had a major role on the residual carbon amount. In order to obtain good magnetic properties, the carbon level of the sintered samples should not exceed 0.1wt%. Slightly sintering temperature rise decreased the magnetic properties but could not enhance the density.
2. The phenomenon of getting concaved (distorted) sintered products had not been yet clearly understood. It is expected that the surface contact during the first vacuuming stage and also with the contact of the furnace atmosphere resulted in surface contaminations (oxidations) which inhibit sintering rate on the surface of the samples. Some further examinations in the laboratory were performed with a austenitic stainless steel lid, and the samples had lower distortion, higher density and mostly higher coercivity.
3. For the anisotropic single-pole disc parts (i.e. F3-SNFB-3), the best magnetic properties were obtained by 0.1 K/min debinding rate and 1080 °C sintering temperature. For bigger parts 1100 °C sintering temperature was required. Pressed - sintered parts (i.e. C-SNFB-2) were resulted in remarkably higher density, which had around 0.15wt% C amount and relatively high intrinsic coercivity (~400 μ Hc) than the injected sample (F3-SNFB-3) which had around 0.045wt% C and ~150 μ Hc intrinsic coercivity.
4. Although feedstock preparation was applied under protective Argon atmosphere in the glove box, oxidation took place during injection molding of the parts. The parts should be injected using high capacity injection molding machine, and possibly without recycling of the sprue and runners. As the excessive oxidation would be inhibited, the green density of the parts would be improved which results in high density and less distortion problems following to sintering. The oxygen levels in the sintered part should be lower than 0.5wt% in order to obtain high coercivity and energy product.

5. Prior to sintering stage, before the temperature reaches to 650 °C, all the hydrogen should be removed from the furnace atmosphere and also should be desorbed from the parts totally by high vacuum stage. Otherwise, the excessive hydrogen in the structure would react starting around at 650 °C with $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic phase which results in destruction of the magnetic phase.

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List of Publications and Patents:

- **N. Ünal**, M. L. Öveçoğlu, 2009. Effects of wet and dry milling conditions on properties of mechanically alloyed and sintered W–C and W–B₄C–C composites, *Powder Metallurgy*, **52**, 3, pp. 254-265 (12).
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- **N. Ünal**, F. Kern, M.L. Öveçoğlu, R. Gadow, 2011. Influence of WC Particles on the Microstructural and Mechanical Properties of 3 mol% Y₂O₃ stabilized ZrO₂ Matrix Composites Produced by Hot Pressing, *Journal of European Ceramic Society*, **31**, 13, pp. 2267-2275.
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- **N. Ünal**, F. Kern, M. L. Öveçoğlu, R. Gadow, 2009. Properties of Zirconia – Tungsten Carbide Composites Produced by Hot Pressing, *EURO PM2009 Proceedings* 3: 47–53.