

İSTANBUL TECHNICAL UNIVERSITY « INSTITUTE OF SCIENCE AND TECHNOLOGY

**DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF
MECHANICALLY ALLOYED AND SINTERED W – TiC – Ni
COMPOSITES**

**M.Sc. Thesis by
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Department : Advanced Technologies

Programme : Materials Science and Engineering

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JUNE 2009

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**Date of submission : 04 May 2009
Date of defence examination : 05 June 2009**

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JUNE 2009

İSTANBUL TEKNİK ÜNİVERSİTESİ « FEN BİLİMLERİ ENSTİTÜSÜ

**MEKANİK ALAŞIMLAMA YÖNTEMİYLE ÜRETİLMİŞ W – TiC – Ni
KOMPOZİTLERİNİN GELİŞTİRİLMESİ VE ÖZELLİKLERİNİN
İNCELENMESİ**

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Tezin Enstitüye Verildiği Tarih : 04 Mayıs 2009

Tezin Savunulduğu Tarih : 05 Haziran 2009

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HAZİRAN 2009

To my dearest mother,

*“Yaşamak şakaya gelmez,
büyük bir ciddiyetle yaşayacaksın
bir sincap gibi mesela,
yani, yaşamının dışında ve ötesinde hiçbir şey beklemeden,
yani bütün işin gücün yaşamak olacak.*

*Yaşamayı ciddiye alacaksın,
yani o derecede, öylesine ki,
mesela, kolların bağlı arkadan, sırtın duvarda,
yahut kocaman gözlüklerin,
beyaz gömleğinle bir laboratuarda
insanlar için ölebileceksin,
hem de yüzünü bile görmediğin insanlar için,
hem de hiç kimse seni buna zorlamamışken,
hem de en güzel en gerçek şeyin
yaşamak olduğunu bildiğin halde.*

*Yani, öylesine ciddiye alacaksın ki yaşamayı,
yetmişinde bile, mesela, zeytin dikeceksin,
hem de öyle çocuklara falan kalır diye değil,
ölmekten korktuğun halde ölüme inanmadığın için,
yaşamak yanı ağır bastığından.*

Nazım Hikmet”

FOREWORD

There are many people associated with this thesis deserving recognition. First of all I would like to thank my supervisor Prof. Dr. M. Lütü Öveçoğlu for his invaluable guidance, support and training during the course of my thesis and for my mentor throughout my graduate studies. I would also like to thank to Assist. Prof. Dr. Burak Özkal for his guidance and also for keeping his door open and always having an answer. I am also thankful to Res. Assist. Selim Coşkun for his supports and helps.

I would like to express thanks to the members of particulate materials laboratory, A. Umut Söyler, Hasan Gökçe, Demet Tatar, Cengiz Hamzaçebi, Alper Evirgen, H. Kübra Yumakgil, S. Seda Yakar, Şeyma Duman, Nida Yıldız, Mithat Cem Elbizim, Deniz Yılmaz for their support and help. A special thank goes to Çiğdem Çakır Konak for her help in SEM and TEM analyses.

I would also like to thank my friends and colleagues Canhan Şen, Nagihan Sezgin, Özgen Aydoğan, H. Doğa Özkaya, Berk Alkan, Ali Erçin Ersundu, Eren Seçkin, Övgü Genç, whose understanding and support made schooling relatively easier.

I am extremely grateful to my parents for their infinite support, help and motivation.

June, 2009

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Metallurgical and Materials Engineer

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MEKANİK ALAŞIMLAMA YÖNTEMİYLE ÜRETİLMİŞ W-TiC-Ni KOMPOZİTLERİNİN GELİŞTİRİLMESİ VE ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Volfram ve alaşımları yüksek ergime sıcaklıkları, yüksek elastik modülleri, termal şoka karşı dayanımları, düşük termal genleşme katsayıları ve yüksek sıcaklıklarda gösterdiği mukavemet ve direngenliklerinden dolayı yüksek sıcaklıklarda kullanılacak malzemelerin geliştirilmesinde matris malzemesi olarak öne çıkmaktadırlar. Yüksek ergime sıcaklığı ve düşük tokluğundan dolayı volfram üretmek çok zordur. Toz metalurjisi yöntemi kullanılması durumunda bile yüksek yoğunluklarda volfram üretmek için 2400 – 2800 °C sıcaklıklara ihtiyaç duyulmaktadır. Aftifleştirilmiş sinterleme adı verilen yöntem, Pd, Pt, Ni, Co ve Fe gibi bazı geçiş metallerinin düşük miktarlarda eklenmesinde dahi volframın sinterleme sıcaklığının büyük oranda düşürülmesini sağlamaktadır.

Volfram ve alaşımlarının mekanik özelliklerinin geliştirilmesi amacıyla TiC, ZrC, HfC, TiN, Y₂O₃, La₂O₃, Sm₂O₃, ThO₂, ZrO₂ gibi çeşitli refrakter karbürler, nitrürler ve oksit fazları takviye elemanı olarak kullanılmaktadır. Bu çalışmada, takviye elemanı olarak yüksek ergime derecesi, yüksek sertlik, yüksek sıcaklıklarda dayanım ve iyi korozyon direnci gibi mükemmel özelliklere sahip TiC, aktivasyon elemanı olarak Ni kullanılan W matrisli kompozitler düşük partikül boyutuna sahip ve homojen bir dağılım elde etmek amacıyla değişik sürelerde mekanik alaşımlandı. Mekanik alaşımlama sürelerinin yanı sıra aktifleştirilmiş sinterlemenin geliştirilen kompozit malzemenin yapısına ve özelliklerine etkisi incelendi. Mekanik alaşımlama sonucu elde edilen kompozit tozlarının partikül boyutları laser partikül boyut ölçüm cihazı ile ölçüldü. Kompozit tozlarının ve sinterlenmiş numunelerin mikroyapı ve faz analizleri taramalı elektron mikroskobu (SEM), geçirimli elektron mikroskobu (TEM) ve x ışınları kırınımı (XRD) teknikleri kullanılarak yapıldı. Preslenmiş numunelerin yoğunluğu boyutsal olarak, sinterlenmiş numunelerin yoğunluğu Arşimet tekniği kullanılarak ölçüldü. Ayrıca sinterlenmiş numunelerin sertlikleri Vicker's mikrosertlik cihazı ile tespit edildi.

DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF MECHANICALLY ALLOYED W-TiC-Ni COMPOSITES

SUMMARY

As interesting and appropriate matrix materials with their high melting point, high modulus, high resistance of thermal shock, low CTE and good high temperature strength and stiffness, in this last decade, tungsten and its alloys have received attention with a view of improving the high temperature mechanical properties.

Generally, it is very difficult to fabricate tungsten because of its high melting point, low ductility, and even using powder metallurgy techniques, processing requires very high sintering temperatures up to 2400 – 2800 °C to get near fully dense tungsten. The addition of small quantities of some transition metals such as Pd, Pt, Ni, Co, and Fe makes it possible to greatly reduce the sintering temperature of W.

As dispersion strengtheners, refractory carbide, nitride and oxide phases, such as TiC, VC, ZrC, HfC, TiN, Y₂O₃, La₂O₃, Sm₂O₃, ThO₂, ZrO₂, etc. have been mainly used to improve the mechanical properties of tungsten and its alloys. In this study, tungsten matrix composites reinforced with TiC particles or VC particles were mechanically alloyed (MA'd) for different times. Ni is used as sintering aid which is added before and after mechanical alloying. Furthermore, W and Ni mechanically alloyed together to investigate both effect of MA and activated sintering and TiC particles or VC particles were added after mechanical alloying for reinforcement. Microstructural and phase characterizations of composite powders and sintered samples were carried out via SEM, TEM and XRD analyses. Density and hardness measurements of sintered samples were carried out.

1. INTRODUCTION

Materials and the tools made from them play a crucial role in the history of human development. It is no accident that pivotal epochs such as the Stone, Bronze, and Iron Ages are named for materials. Materials are no less important today. Many of our modern technologies require materials with unusual combinations of properties which cannot be met by conventional metal alloys, ceramics, and polymeric materials. Since no single material could fulfill these rising requirements in the last 20 years, an increasing interest in developing new materials has been aroused to serve the need for new materials having unique properties for special applications (Song et al., 2003a; Tang et al., 2004). A composite material which is made by combining two or more materials to give a unique combination of properties can fulfill the requirements of the modern technology have been, and are yet being, extended (Mazumdar, 2002). Composite materials refers to materials having strong reinforcing fibers—continuous or noncontinuous—surrounded by a weaker matrix material. The matrix serves to distribute the reinforcements and also to transmit the load to the reinforcements. The reinforcements can be fibers, particulates, or whiskers, and the matrix materials can be metals, plastics, or ceramics (Mazumdar, 2002; Gay et al., 2003).

An easy way to classify composites is to separate the matrix and reinforcing phase constituents, and divide them into several groups. The first classification is based on the type of the matrix constituent: Polymer-Matrix, Metal-Matrix or Ceramic-Matrix Composites. Composites can also be classified based on the type of reinforcement used: fiber reinforced (continuous or discontinuous) or particulate reinforced (flakes, chopped fibers, shaped particles, and whiskers). However, the best way to classify the composites is to include both the reinforcement and matrix constituent, such as particle-reinforced-metal-matrix composites (PRMMC) (Schwartz, 1984; Coskun, 2006).

Metal matrix composites (MMCs), like all composites, consist of at least two chemically and physically distinct phases, suitably distributed to provide properties

not obtainable with either of the individual phases. Generally, there are two phases, e.g., a fibrous or particulate phase, distributed in a metallic matrix (Chawla and Chawla, 2006). The reinforcing constituent is in most cases a ceramic, although there are exceptions to this and MMCs can be taken to encompass materials “reinforced” with relatively soft and/or compliant phases, such as graphitic flakes, lead particles, or even gases. It is also possible to use refractory metals, inter-metallics, or semiconductors, rather than true ceramics (Clyne, 2000). The mechanical properties of the MMC’s highly depend on the volume fraction and the type of the reinforcement as well as the type of the matrix (Stjernstoft, 2004). On the other hand, while continuous fiber-reinforcement provides the most effective strengthening in a given direction, particle-reinforcement provides cost-effectiveness and especially isotropic properties to the composite (Chawla and Shen, 2001).

Beside all the attention that the composites received for the last 20 years, there is another group of materials which have found applications in various industries, such as defense and aerospace in recent years, namely nanostructured materials or nanomaterials (Cahn, 2001). These materials exhibit unique microstructures and superior mechanical properties (Han et al., 2005). Nanotechnology is regarded world-wide as one of the key technologies of the 21st Century, and nanotechnological products and processes hold an enormous economic potential for the markets of the future (Zweck and Luther, 2003). So, the combination of composite materials and nanostructured materials, namely “nanocomposites” with the appropriate matrix and reinforcing phase constituents would be candidate materials for industrial applications, such as defense, aerospace and as cutting tools materials (Coskun, 2006).

As interesting and appropriate matrix materials with their high melting point, high modulus, high resistance of thermal shock, low CTE and good high temperature strength and stiffness, in this last decade, tungsten and its alloys have received attention with a view of improving the high temperature mechanical properties (Song et. al., 2002). Generally, it is very difficult to fabricate tungsten because of its high melting point, low ductility, and even using powder metallurgy techniques, processing requires very high sintering temperatures up to 2400 – 2800 °C to get near fully dense tungsten (Li and German, 1983). The addition of small quantities of some transition metals such as Pd, Pt, Ni, Co, and Fe makes it possible to greatly reduce

the sintering temperature of W (Li and German, 1983; German and Munir, 1976; Vajek, 1959; Hayden and Brophy, 1963).

As dispersion strengtheners, refractory carbide, nitride and oxide phases, such as TiC, VC, ZrC, HfC, TiN, Y₂O₃, La₂O₃, Sm₂O₃, ThO₂, ZrO₂, etc. have been mainly used to improve the mechanical properties of tungsten and its alloys (Song et. al., 2002; Song et. al., 2003b; Lee et. al., 2004). Keeping the above concepts in mind, the aim of this study has been to develop and characterize nanostructured TiC particle-reinforced tungsten composite powders and their consolidated and sintered counterparts. Ni used as activation agent to investigate activated sintering of mechanically alloyed W-TiC

2. LITERATURE REVIEW

2.1. Metal Matrix Composites

Metal matrix composites (MMCs), like all composites, consist of at least two chemically and physically distinct phases, suitably distributed to provide properties not obtainable with either of the individual phases. Generally, there are two phases, e.g., a fibrous or particulate phase, distributed in a metallic matrix (Chawla and Chawla, 2006). Metals are chosen as the matrix material in MMC structures mainly because of the following characteristics: a) they have higher application temperature ranges, b) they have higher transverse stiffnesses and strengths, c) in general, they have high toughness values, d) when present in metal matrices, the moisture effects and the danger of flammability are absolutely absent and they have high radiation resistances, e) they have high electric and thermal conductivities, f) MMC have higher strength-to-density, stiffness-to-density ratios, as well as better fatigue resistances, lower coefficients of thermal expansion (CTE) and better wear resistances as compared with monolithic metals, and g) they can be fabricated with conventional metal working equipment (Akovali and Uyanik, 2001).

The reinforcing constituent is in most cases a ceramic, although there are exceptions to this and MMCs can be taken to encompass materials “reinforced” with relatively soft and/or compliant phases, such as graphitic flakes, lead particles, or even gases. It is also possible to use refractory metals, inter-metallics, or semiconductors, rather than true ceramics (Clyne, 2000). In general, there are three kinds of metal matrix composites (MMCs): particle reinforced MMCs, short fiber or whisker reinforced MMCs and continuous fiber or sheet reinforced MMCs (Chawla and Chawla, 2006). Fig. 2.1 shows the schematic representations of these three major types of metal matrix composites.

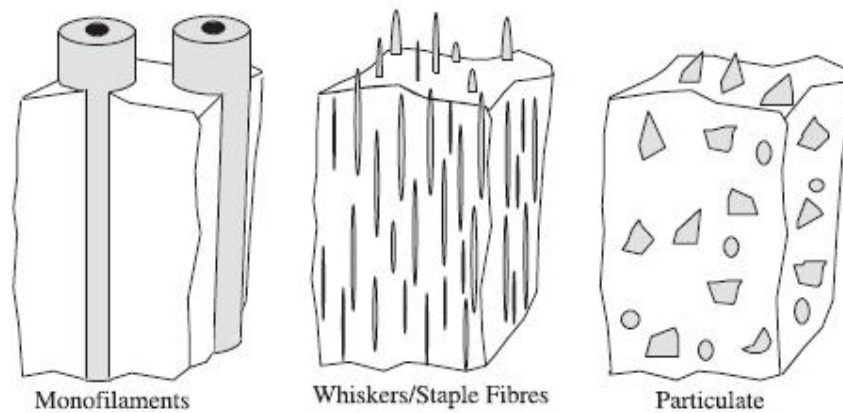


Figure 2.1 : Schematic representation of three shapes of metal matrix composite materials (Clyne and Withers, 1993).

2.1.1. Particulate Reinforced Metal Matrix Composites (PRMMC's)

Particulate reinforced metal matrix composites are comprised of the class of metals containing reinforcement phases exhibiting approximately equiaxed geometries, typically referred to as particles or particulates. These differ from composites containing higher aspect ratio reinforcements such as fibers or whiskers in significant and important ways (Hunt, 2000). More recently, PRMMC's have received an increasing attention because of their relatively low costs, good formability and machinability as well as characteristic isotropic properties (Ibrahim et al., 1991; Tjong and Ma, 2000; Sun et al., 2003).

Particle reinforced composite systems can be considered in two sub-classes: 'large particle' and 'dispersion' strengthened composites, by basing on the reinforcement or strengthening mechanisms.

2.1.1.1. Large particle composites

The term 'large' is used to denote that particle-matrix interactions can not be treated on atomic or molecular level and 'continuum mechanics' is used. For composites reinforced by large particles, the reinforcing component is usually harder and stiffer than the matrix and they tend to restrain movement of the matrix. The matrix transfers some of the applied stress to the particles. The efficiency of reinforcement depends strongly on interaction at the particle-matrix interface (Akovali and Uyanik, 2001). These composites are used widely as cutting tools for hardened steels. The hard carbide particles provide the cutting surface but, are not themselves capable of withstanding the cutting stresses because they are extremely brittle. Toughness is

enhanced by their inclusion in the ductile metal matrix, which isolates the carbide particles from one another and prevents particle-to-particle crack propagation. Both matrix and particulate phases are quite refractory, to withstand the high temperatures generated by the cutting action on materials that are extremely hard (Askeland, 1984; Schwartz, 1984).

2.1.1.2. Dispersion-strengthened composites

In dispersion-strengthened composites, the fine dispersions of oxide, carbide, or boride particles impede the motion of dislocations so that the matrix is strengthened in proportion to the effectiveness of the dispersions as a barrier to the motion of dislocations. For a dislocation to pass through a dispersion of fine particles, the applied stress must be sufficiently large to bend the dislocation line into a semicircular loop. Calculations show that interparticle separation for effective dispersion hardening should be between 0.01 and 0.3 μm (10 – 300 nm). To achieve this range of spacing between the dispersoid, the particle diameters should be less than 100 nm at volume fractions below 15% (Asthana et al., 2006). Of many dispersion-hardened alloy systems only a few have reached commercial significance, namely, aluminum, nickel, and tungsten; two others, copper and titanium, have proved successful in laboratory and developmental stages (Schwartz, 1984). The development of oxide dispersion-strengthened (ODS) composites (e.g., W-ThO₂, Ni-A12O₃, Cu-SiO₂, Cu-A12O₃, NiCrAlTi-Y2O₃, Ni-ThO₂, Ni-HfO₂, etc.) has led to considerable improvements in the elevated-temperature strength and creep-resistance of the matrix alloys. The ODS composites contain small (< 15%) amounts of fine second-phase particles, which resist recrystallization and grain coarsening, and act as a barrier to the motion of dislocations. Small quantities of fine oxide ceramics improve the strength without degrading the valuable matrix properties (Asthana et al., 2006).

2.2. Fabrication of PRMMC

There are various processing techniques used to fabricate PRMMC's. These fabrication methods can be grouped according to the temperature of the metal matrix during the process. So, there are liquid phase processes, solid state processes and two phase processes. Main liquid phase processes are molten metal mixing process, melt

infiltration process and melt oxidation process. On the other hand, major solid state processes are powder metallurgy and high-energy-high-rate process. Finally, two phase processes are Osprey deposition, rheocasting and variable co-deposition of multi-phase materials (VCM) process (Ibrahim et al., 1991; Coskun, 2006).

Various processing techniques have been developed over the last two decades which try to optimize the structure and properties of PRMMC's (Ibrahim et al., 1991; Schwartz, 1997). Among these techniques, there were some luxurious ones to enhance the wettability by, for instance, introducing some kind of surface coating to the particles before fabrication. However, this preprocessing of particles increased the cost of PRMMC's further, which in turn limited their commercial utilization. In addition, some recently developed PRMMC's, using state-of-the-art high performance materials, such as tungsten, molybdenum, niobium and tantalum as the matrix material, are difficult to fabricate by using conventional liquid metallurgy process because these materials have incredibly high melting temperatures (Liu et al., 1994). In these cases, powder metallurgy seems more attractive and has become the most important fabrication technique for this group of PRMMC's (Coskun, 2006).

2.2.1. Powder Metallurgy (PM)

By far the most widely used method for producing particulate reinforced MMCs by powder metallurgy processing is to combine the matrix and reinforcement powders together in the form of an intermediate billet which is then utilized for subsequent deformation processing to final product form (Hunt, 2000). When higher strength discontinuous MMCs are required, PM processes are often used because segregation, brittle reaction products, and high residual stresses from solidification shrinkage can be minimized. In addition, with the advent of rapid solidification and mechanical alloying technology, the matrix alloy can be produced as a prealloyed powder, rather than starting with elemental blends (Campbell, 2006).

Powder metallurgy route has been used widely to produce PRMMCs because;

- a) These materials are difficult to fabricate by the conventional liquid processing route owing to the high processing temperature involved.
- b) It offers the possibility of using a wide range of reinforcement volume fraction and size.

c) It also ensures a homogeneous distribution of reinforcements in the matrix material.

d) A high dislocation density, a small subgrain size and limited recrystallization can be obtained through a PM route, resulting in superior mechanical properties (Das et. al., 2002).

Also, porous products, such as bearings and filters with better properties can be produced by using the PM technique (Coskun, 2006).

Starting materials in powder metallurgy processes have a very important role for the success of the process. In addition to the chemistry and the purity of the powders, there are additional issues to concern, such as particle size, size distribution, particle shape as well as the surface texture of the particles (Newkirk and Kosher, 2004). The improvements of mechanical properties in PRMMC's depend on the strength, the shape and the volume fraction of particles, a particle–matrix interface, etc (Kim and Hahn, 2006). Considering the PRMMC's, mechanical behavior, chemical stability, thermal mismatch and the cost are another factors which play a significant role in the success of the end-product (Liu et al., 1994).

After a proper selection of the materials is ensured, the next step is blending or mixing. This step is very important, because it controls the final distribution of reinforcement particles and porosity in green compacts, which strongly affects the mechanical properties of the PM end-products. However, there are some problems, such as segregation and clustering, associated with the today's modern mixing or blending methods. The reasons of these problems include different flow characteristics between metal powder and reinforcement particles and the tendency of the agglomeration of particles to minimize their surface energy. However, these segregation and clustering problems can be overcome by a technique called “Mechanical Alloying (MA)” (Liu et al., 1994). This technique will be discussed in detail in the section 2.2.2.

The next step after blending or mixing operation, is the consolidation and pressing of the powder mixture to form the green compacts (Liu et al., 1994). This step is the one of the most critical steps in the PM process, because it sets the density of the powder and the uniformity of the density throughout the product. Because final properties

strongly depend on density, uniform properties require uniform density (Newkirk and Kosher, 2004). The compaction process has the following major functions:

1. To consolidate the powders into the desired shape
2. To impart, as much as possible, the desired final dimensions considering any dimensional changes resulting from sintering
3. To give the desired level of porosity
4. To provide sufficient strength for subsequent handling (Upadhyaya, 2000).

In the conventional compaction methods, schematic view showed in Fig. 2.2, the pressure is usually applied in one direction resulting in a non-uniform distribution of consolidation and even insufficient densities (Liu et al., 1994). Mostly, mechanical and hydraulic presses and rigid dies are used (Newkirk and Kosher, 2004).

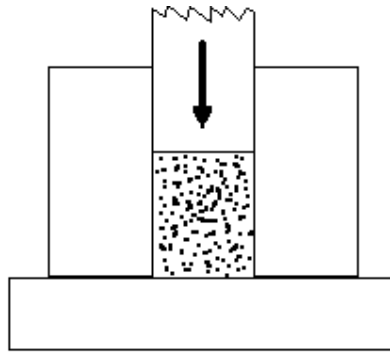


Figure 2.2 : Schematic view of a conventional one-directional press (Liu et al., 1994).

2.2.1.1. Sintering

Sintering is a processing technique used to produce density-controlled materials and components from metal or/and ceramic powders by applying thermal energy (Kang, 2005). In sintering, particles bond with one another by atomic diffusion. There are different variables which determine sinterability and the sintered microstructure of a powder compact which given in Table 2.1. All sintering equations contain a number of parameters such as diffusion coefficient, surface tension, particle size, initial pore volume, etc. One can divide these parameters into two classes:

1. Intrinsic — these specify the intrinsic properties of the materials being sintered, such as surface tension, diffusion coefficient, vapour pressure, viscosity, etc. These

properties change when the chemical composition, ambient atmosphere or temperature changes.

2. Extrinsic — these depend on the geometrical or topological details of a system. These include parameters, as average particle size, particle or pore or grain shape and size distribution, etc (Upadhyaya, 2001).

The driving force for sintering is the minimization of the solid-vapor interface area (i.e., the total area of the powders in contact with the surrounding vapor) and elimination of the regions of sharp curvature at powder contacts. In the initial stages of sintering, small necks form and grow between contacting particles by mass transfer via atomic diffusion. Fine powders increase the driving force for sintering because of a larger surface area per unit volume, which increases the total solid-vapor interfacial energy (Asthana et al., 2006).

Table 2.1: Variables affecting sinterability and microstructure (Kang, 2005).

Variables related to raw materials (material variables)	Powder; Shape, size, size distribution, agglomeration, etc. Chemistry; Composition, impurity, homogeneity, etc.
Variables related to sintering conditions (process variables)	Temperature, time, pressure, atmosphere, heating and cooling rate, etc.

Basically, sintering processes can be divided into two types: solid state sintering and liquid phase sintering. Solid state sintering occurs when the powder compact is densified wholly in a solid state at the sintering temperature, while liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering (Kang, 2005).

In addition to solid state and liquid phase sintering, other types of sintering, for example, transient liquid phase sintering and viscous flow sintering, can be utilized. Viscous flow sintering occurs when the volume fraction of liquid is sufficiently high, so that the full densification of the compact can be achieved by a viscous flow of grain-liquid mixture without having any grain shape change during densification. Transient liquid phase sintering is a combination of liquid phase sintering and solid state sintering. In this sintering technique a liquid phase forms in the compact at an early stage of sintering, but the liquid disappears as sintering proceeds and

densification is completed in the solid state (Kang, 2005). Moreover, activated sintering can be mentioned as another type of sintering which will be discussed in detail in this section (Upadhyaya, 2000).

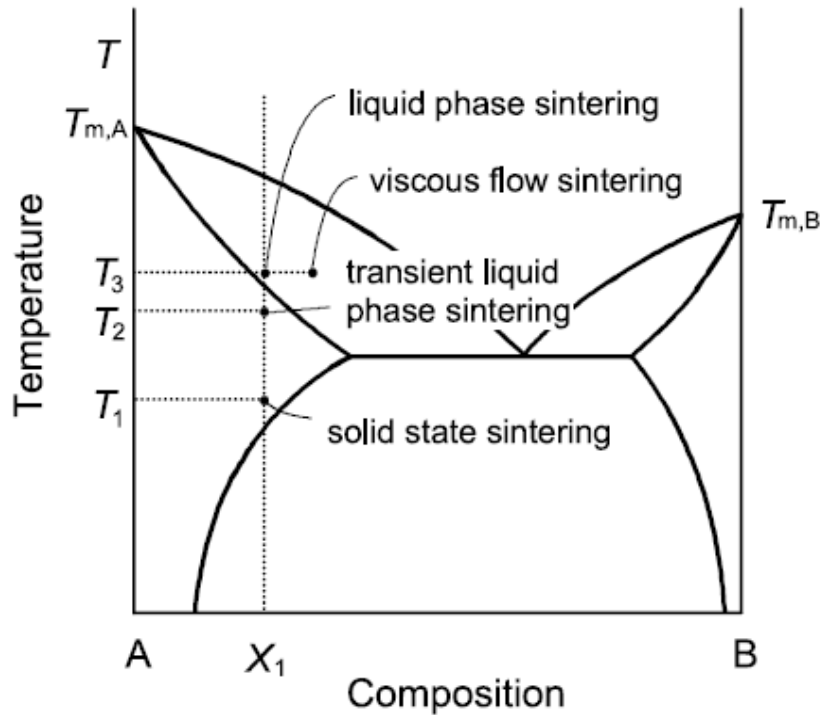


Figure 2.3 : Illustration of various types of sintering (Kang, 2005).

2.2.1.1.1. Solid-state sintering

The solid-state sintering is carried out in protective atmosphere within a furnace at a temperature below the melting point of the base metal. The process leads to a decrease in the surface area, an increase in compact strength and mostly shrinkage in the compact. Sintering longer at high temperature decreases the number of pores and makes the pore shape become smooth. Also, grain growth can be expected (Upadhyaya, 2000).

Various stages and mass transport mechanisms have been proposed to contribute sintering. The transport mechanisms detail the paths by which mass moves; for solid-state sintering the candidate processes include surface diffusion, volume diffusion, grain boundary diffusion, viscous flow, plastic flow, and even vapor transport from solid surfaces (German, 1996).

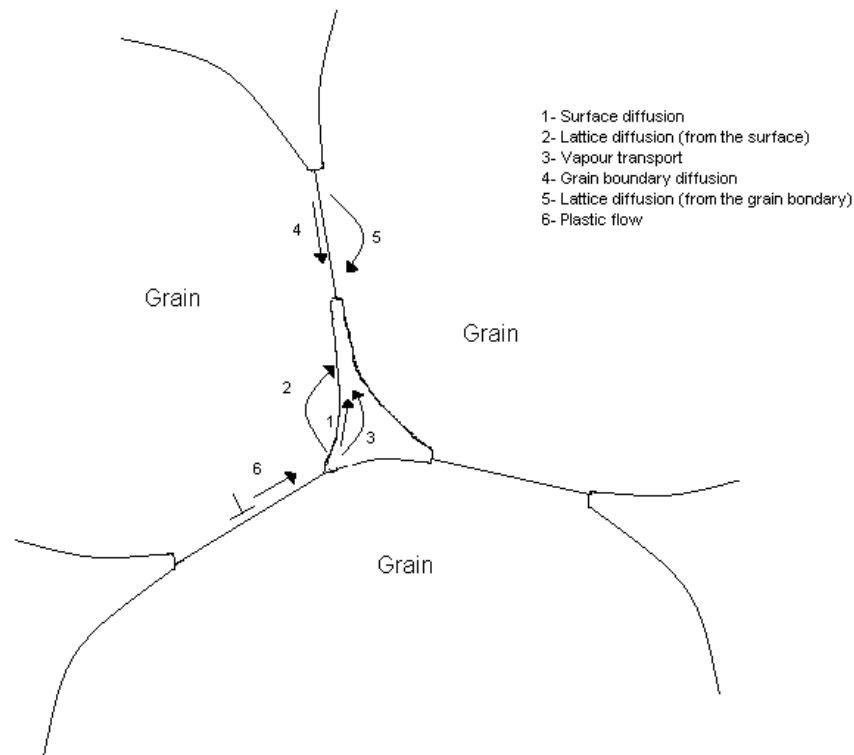


Figure 2.4 : Various sintering mechanisms (Upadhyaya, 2000).

The three stages of sintering and their schematic densification curve of a powder compact can be seen in Figure 2.5. In addition to these three stages, a very first stage occurs when particles come into contact, since there is a weak cohesive bond at the contacts. The initial sintering stage usually occurs during heating and is characterized by rapid grain growth of the interparticle neck. Although there is a considerable neck growth, the actual volume of the neck is small, so, it takes a small mass to form a neck. In the intermediate stage, the pore structure becomes smooth and develops an interconnected, approximately cylindrical nature. The appearance of isolated pores indicates the final stage of sintering and slow densification (German, 1995).

These three stages can be described with the highlights listed below:

Initial Stage: Particle surface smoothing and rounding of pores, grain boundaries form, neck formation and growth, homogenization of segregated material by diffusion, open pores and small porosity decreases <12%.

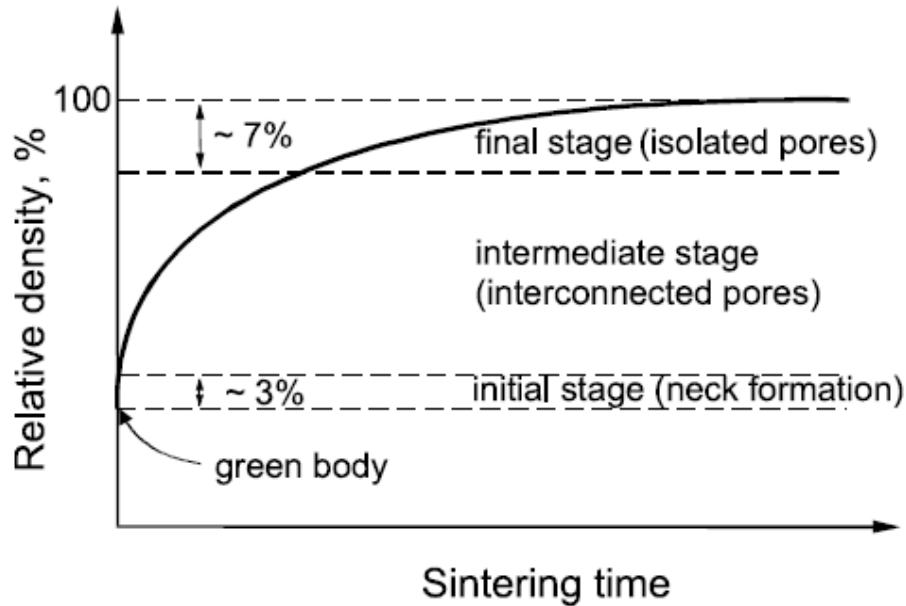


Figure 2.5 : Schematic showing the densification curve of a powder compact and the three sintering stages (Kang, 2005).

Intermediate Stage: Intersection of grain boundaries, shrinkage of open pores, porosity decreases substantially, slow grain growth and differential pore shrinkage and grain growth in heterogeneous material.

Final Stage: Closed pores--density >92%, closed pores intersect grain boundaries, pores shrink to a limiting size or disappear and pores larger than the grains shrink very slowly (Ring, 1996)

2.2.1.1.2. Liquid phase sintering

Liquid phase sintering 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. Unlike solid state sintering, the microstructure change during liquid phase sintering is fast because of fast material transport through the liquid (Kang, 2005). It is rare that sintering with liquid phase does not imply any chemical reactions, but in the simple case where these reactions do not have a marked influence, surface effects are predominant. The main parameters are therefore: i) quantity of liquid phase, ii) its viscosity, iii) its wettability with respect to the solid, and iv) the respective solubilities of the solid in the liquid and the liquid in the solid (Boch and Leriche, 2001).

There are two kinds of liquid phase sintering namely; heterogeneous systems and homogeneous systems. In heterogeneous systems, solid material is heated to sintering temperature and a liquid phase is formed which persists through out sintering and the liquid solidified during cooling. In case of homogeneous systems, as the consolidated powders are heated to sintering temperatures, a liquid phase is formed which gradually disappears as it is soluble in the matrix. Particle rearrangement stage, dissolution-precipitation stage, liquid assimilation and solid state grain growth stage are the four main stages of liquid phase sintering process (Ring, 1996).

2.2.1.1.3. Activated sintering

Activated sintering involves a small addition to the powder mix or, more rarely, to the sintering atmosphere in order to promote sintering kinetics. The action of the activator may be to remove the surface oxide from the powder particles or to facilitate more rapid diffusion of the metal's atoms (Upadhyaya, 2000). A high-melting-temperature materials material requires a high sintering temperature to induce significant diffusion. However, a lower-melting-temperature phase will have inherently faster diffusion rates. Activated sintering occurs when the high-melting-temperature material is soluble in the low-melting-temperature phase, resulting is a short-circuit sintering path. Some of the most dramatic examples of activated sintering occur with the refractory metals: molybdenum, tungsten, chromium, rhenium, and tantalum (German, 1996).

Generally, it is very difficult to fabricate tungsten because of its high melting point, low ductility. Even when the powder metallurgy techniques are used, processing of tungsten requires very high sintering temperatures up to 2400 – 2800 °C to get near fully dense structure (Li and German, 1983). The addition of small quantities of some transition metals such as Pd, Pt, Ni, Co, and Fe, provides a major reduce in the sintering temperature of W (Li and German, 1983; German and Munir, 1976; Vacek, 1959; Hayden and Brophy, 1963). This reduction of the sintering temperature is due the decrement of the activation energy between W particles. Activation energy for volume self-diffusion of tungsten, 135 kcal/mol, becomes 68 kcal/mol in the case of Ni activated W (Hayden and Brophy, 1963).

Hayden and Brophy interpreted the mechanism of the activated sintering in terms of three main stage in their study (Hayden and Brophy, 1963). After the appearance on the tungsten particle surface of a “supporting phase”, formed by activating agent, the dissolution of tungsten at the points of contact between particles takes place and the diffusion of tungsten atoms along the interface between the “supporting phase” and the particle provides densification. On this basis, the distance between the centers of adjacent particles decreases and consequently fuller shrinkage occurs (Hayden and Brophy, 1963; Samsonov and Yakovlev, 1967). Fig. 2.6. is the schematic representation of sintering nickel-coated tungsten powder which Brophy et. al., indicated during their project prepared in U.S. Navy in M.I.T. laboratories (Brophy et. al, 1963).

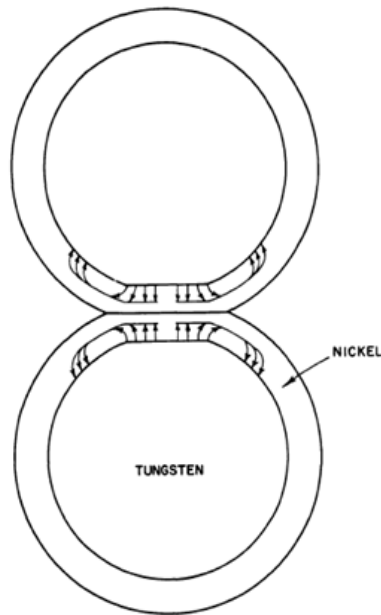


Figure 2.6 : Schematic representation of sintering nickel-coated tungsten powder (Brophy et. al., 1963).

Another elucidation of the activated sintering mechanism was accomplished in (Toth and Lockington, 1967) where dissolution of tungsten at the activator-tungsten interface is followed by volume diffusion outwards through the activator layer and subsequent surface diffusion. Diffusion through the activator layer to the contact point between adjacent particles results in the formation of sintering “necks” [Toth and Lockington, 1967; Corti, 1986).

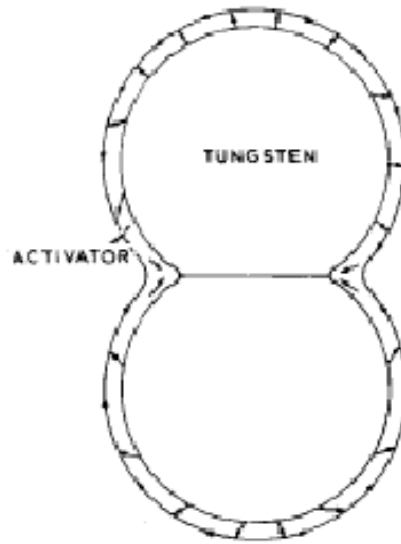


Figure 2.7 : Schematic representation of activated sintering of tungsten (Toth and Lockington, 1967).

Samsonov and Yakovlev stated activated sintering in terms of the electron structure of the activators and tungsten; an increase of the stable d-bonds in the system lowers the free energy, activating the sintering process in which diffusion is accelerated by the activators for which tungsten acts as an electron donor and this ease of electron transfer gives rise to the high solubility in the activating element (Samsonov and Yakovlev, 1969).

German and Munir reported that the activator has a role in providing enhanced grain boundary diffusion with the activator layer wetting the interparticle grain boundary. The relative solubility criterion is a prerequisite for enhanced diffusion of the refractory metal. Enhanced mass transport, and hence densification, results from the lowering of the activation energy for the refractory metal in the activator (German and Munir, 1982; Corti, 1986).

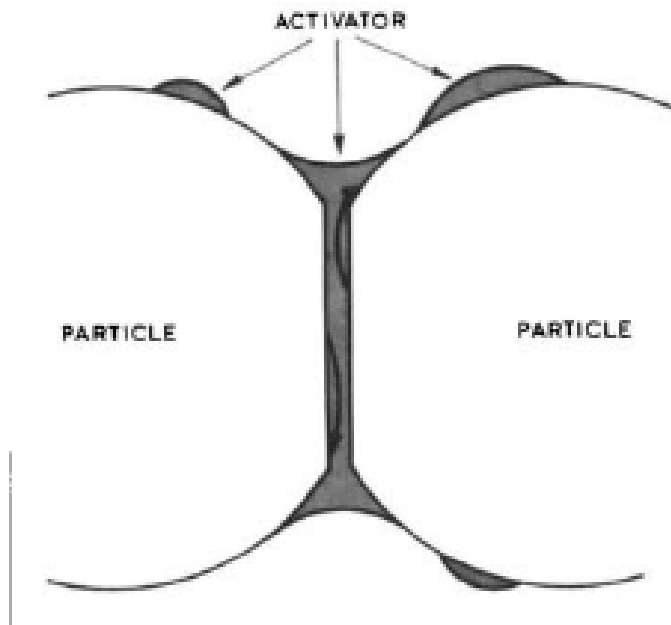


Figure 2.8 : Schematic representation of the activated sintering (German and Munir, 1982).

2.2.2. Mechanical Alloying (MA)

2.2.2.1. History and definition of mechanical alloying

The ever-increasing demands for properties and performance of materials have led to the design and development of advanced materials (Suryanarayana, 2001). As a result, non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials in comparison to conventional methods (Suryanarayana et al., 2001).

As mentioned above, the structure and constitution of advanced materials can be better controlled by processing them under non-equilibrium (or far-from-equilibrium) conditions and mechanical alloying (MA) is such a processing method that materials can be produced under non-equilibrium conditions (Suryanarayana, 2001). MA can be defined as a powder metallurgy process for producing composite metal powders with a controlled fine microstructure by repeated cold welding, fracturing and rewelding of powder particles in a high-energy ball mill (Öveçoğlu, 1987; Benjamin, 1992; Suryanarayana et al., 2001).

The mechanical alloying (MA) process is usually dated back to the pioneer work of Benjamin at the International Nickel Company's Paul D. Merica Research Laboratory in the late 1960's. It started as an industrial necessity to produce oxide-dispersion-strengthened nickel-based superalloys for gas turbine engine components (Öveçoğlu, 1987; Suryanarayana et al., 2001; Delogu et al., 2003). However, the subsequent discovery of metastable phase formation by MA opened the door to important applications in Materials Science (Delogu et al., 2003). In addition to the metastable phases, equilibrium phases of commercially useful and scientifically interesting materials can be synthesized by MA (Suryanarayana et al., 2001).

MA is a simple and versatile technique which includes economically feasible process with important technical advantages. One of the major advantages of MA is possibility of synthesizing of novel alloys, which normally immiscible elements. This synthesis is only possible with MA because MA is a completely solid-state processing technique, thus limitations imposed by phase diagrams do not apply for this process (Suryanarayana et al., 2001). Furthermore, MA holds an advantage over traditional ball milling processes which is to produce a material whose internal homogeneity is independent of the initial starting particle size. It is not uncommon to obtain mechanically-alloyed dispersions with less than 1 μm interparticle spacing from initial powder sizes of 50-100 μm average diameters (Goff, 2003).

2.2.2.2. Processing equipment and process variables

Different types of high-energy milling equipment are used to produce mechanically alloyed powders. These equipments include Spex Mixer/mills, planetary ball mills, attritor mills and commercial mills. They have different capacity, efficiency of milling and additional arrangements for cooling, heating, etc (Suryanarayana, 2001; Goff, 2003).

Spex Mixer/mills are most commonly used for laboratory investigations and they mill about 10 - 20 g powder at a time depending on the density of starting constituents (Goff, 2003). The common variety of these mills has one vial, containing the sample and grinding balls, secured in the clamp and shakes the milling container in three-mutually perpendicular directions at about 1200 rpm resulting in powder microstructural refinement with time (Suryanarayana, 2001; Goff, 2003). Ball-ball and ball-container collisions continually trap and refine the powder

constituents with time ultimately leading to an overall homogeneously dispersed microstructure (Goff, 2003). There are different vial materials available for the SPEX mixer/mills, which are hardened steel, alumina, tungsten carbide, zirconia, stainless steel, silicon nitride, agate, plastic, and methacrylate (Suryanarayana, 2001). Typical SPEX mill and tungsten carbide vial set can be seen in Fig. 2. 9.

Another popular mill for conducting MA experiments is the planetary ball mill in which a few hundred grams of the powder can be milled at a time. It is called the planetary ball because of its vial's planet-like movement. The centrifugal force produced by the vials rotating around their own axes act on the vial contents, consisting of material to be ground and the grinding balls. As result, powders are trapped between the rotating balls and the walls of the vial and refined. Even though the linear velocity of the balls in this type of mill is higher than that in the SPEX mills, the frequency of impacts is much more in the SPEX mills.

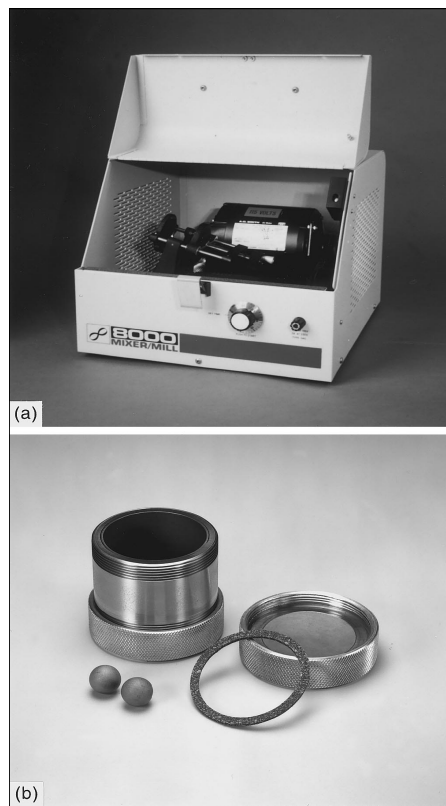


Figure 2.9 : a) A typical Spex shaker mill **b)** Tungsten carbide vial set consisting of the vial, lid, gasket, and balls (Suryanarayana, 2001).

Therefore, compared to SPEX mills, planetary ball mills can be considered lower energy mills (Suryanarayana, 2001). In Fig. 2.10, a schematic view of ball motion in a planetary ball mill can be seen.

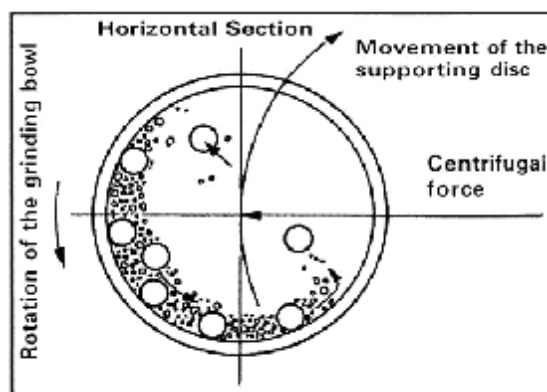


Figure 2.10 : A schematic view of ball motion in a planetary ball mill (Suryanarayana, 2001).

Another type of mills is the attritor mills which possible large quantities of powder (from about 0.5 to 40kg) can be milled at a time (Suryanarayana, 2001). It contains a vertical shaft with a series of impellers that rotates in the tank of about 250 rpm (Goff, 2003). As the shaft rotates, the balls drop on the metal powder that is being ground. The impellers energize the ball charge, causing powder size reduction because of impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers. The rate of grinding increases with the speed of rotation. However, at high speeds the centrifugal force acting on the balls exceeds the force of gravity, and the balls are pinned to the wall of the container. At this point the grinding action stops (Suryanarayana, 2001). Schematic view of an attritor mill is given in Fig. 2. 11.

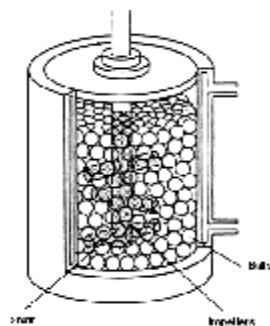


Figure 2.11 : A schematic view of an attritor mill (Goff, 2003).

Finally, commercial mills for MA are much larger in size than the mills described above and can grind several hundred kilograms of powders at a time. Mechanical alloying for commercial production is carried out in ball mills of up to about 1250 kg capacity (Suryanarayana, 2001). A picture of commercial-size ball mills can be seen in Figure 2.12.

The milling time decreases with an increase in the energy of the mill. Roughly, it can be estimated that a process that takes only a few minutes in the SPEX mill may take hours in an attritor and a few days in a commercial mill (Suryanarayana, 2001).

Besides the type of the mill, there are different variables that affect the result of the mechanical alloying process. These include the type (material) of the milling container and the milling medium, ball-to-powder ratio, milling atmosphere, milling time, use of a process control agent (PCA), etc. (Suryanarayana, 2001).

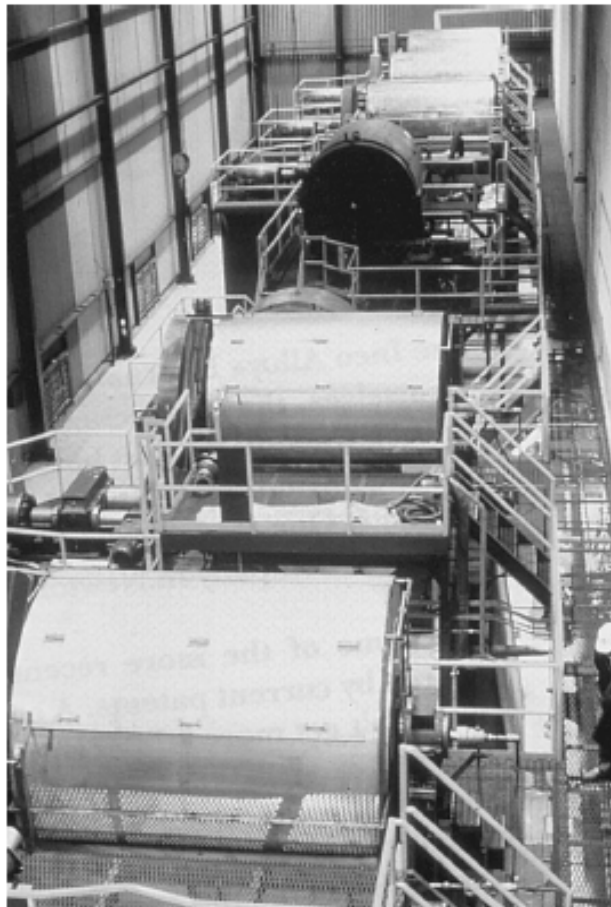


Figure 2.12 : Commercial production-size ball mills used for mechanical alloying (Suryanarayana, 2001).

The material used for the milling container (grinding vessel, vial) is important since the impact of the grinding medium on the inner walls of the container will result in tiny fractions of milling material that fracture off and disperse into the composite powder as contaminations. If the material of the grinding vessel is different from that of the powder, then the powder may be contaminated with the grinding vessel material, whereas if the two materials are the same, then the chemistry may be altered (Suryanarayana, 2001; Goff, 2003). Regardless of the type of mechanical alloying process, the most appropriate type of container and milling media for the given system should be chosen. Generally, milling media which is made of a similar material as that of the material to be processed is used to reduce contamination during processing (Goff, 2003). The density of the grinding medium should be high enough so that the balls create enough impact force on the powder (Suryanarayana, 2001).

Another important parameter is ball-to-powder ratio (BPR). This has been varied by different investigators from a value as low as 1:1 to as high as 220:1. Generally, a ratio of 10:1 is most commonly used while milling the powder in a small capacity mill such as a SPEX mixer/mill. The BPR has an important effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required (Suryanarayana, 2001).

Milling atmosphere is also an important variable for MA process. The major effect of the milling atmosphere is on the contamination of the powder. Therefore, the powders are milled in containers that have been either vacuumed or filled with an inert gas such as argon or helium. However, high-purity argon is the most common used gas to prevent oxidation and contamination of the powder (Suryanarayana, 2001). The presence of air in the vial cause to produce oxides and nitrides in the powder, especially if the powders are reactive in nature. Thus, the loading and unloading of the powders into the vial has to be carried out inside an atmosphere-controlled glove box (Suryanarayana, 2001; Fecht, 2002).

The time of milling is the most important parameter, where the rate of refinement of the internal structure (particle size, crystallite size, lamellar spacing, etc.) is roughly logarithmic with processing time (Fig. 2.13) and therefore the size of the starting particles is relatively unimportant. The lamellar spacing usually becomes smaller and the average crystallite size is refined to nanometer scale after milling. Normally, the

time is so chosen to achieve a steady state between the fracturing and cold welding of the powder particles. Furthermore, the times required depend on the type of mill used, the intensity of milling, the ball-to-powder ratio, and the temperature of milling. Milling time is a parameter to decide considering combinations of the above parameters and for the particular powder system. However, it should be realized that the level of contamination increases and some undesirable phases form if the powder is milled for times longer than required. Therefore, the powder has to be milled just for the required duration and not any longer (Suryanarayana, 2001).

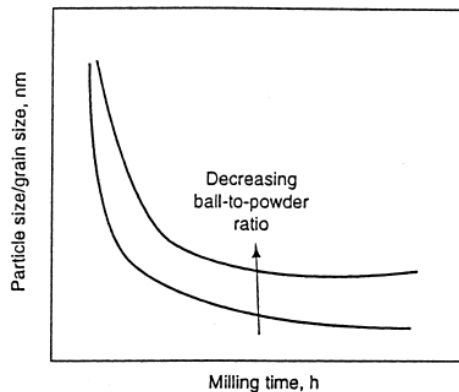


Figure 2.13 : Refinement of particle and grain sizes with milling time. Rate of refinement increases with higher milling energy, ball-to-powder weight ratio, lower temperature, etc. (Suryanarayana, 2001).

The use of process control agents (PCA) are another concern in the MA process. Generally, ductile powder particles get cold-welded to each other, due to the heavy plastic deformation during milling. However, true alloying among powder particles can occur only when a balance is maintained between cold welding and fracturing of particles, which require using a process control agent (PCA) during milling to reduce the cold welding (Öveçoğlu, 1987; Suryanarayana, 2001). The PCA's can be solids, liquids, or gases. They are mostly organic compounds, which act as surface-active agents by adsorbing on the surface of the powder particles and minimizing cold welding between powder particles and thereby inhibiting the agglomeration (Suryanarayana, 2001).

2.2.2.3. Science and mechanism of mechanical alloying

MA is an advanced fabrication process that can produce ultra-fine and homogenous powders (Ryu et al., 2000). Even, nanocrystalline materials (with a grain size of few nanometers, usually <100 nm) are also produced by MA of powder mixtures.

Additionally, it has been recognized that this technique can be used to induce chemical (displacement) reactions in powder mixtures at room temperature or at much lower temperatures than normally required to synthesize pure metals (Suryanarayana et al., 2001).

In any mechanical alloying process, starting powder constituents are first mixed or blended according to the required stoichiometry for desired composite batches. Then, they are put in the milling container with the appropriate ball charge and milled until a steady state of homogeneous dispersion is achieved (Goff, 2003). The central event of MA is the ball-powder collisions (Fecht, 2002). Microstructural refinement during the MA process occurs due to the repeated cold-welding, fracturing, and cold-welding of the dry powder constituents during their impact between ball-ball and/or ball-container collisions. Fig. 2.14. is a schematic representation of the collided balls. The force of the impact plastically deforms the powder particles leading to work hardening and fracture (Suryanarayana, 2001; Fecht, 2002).

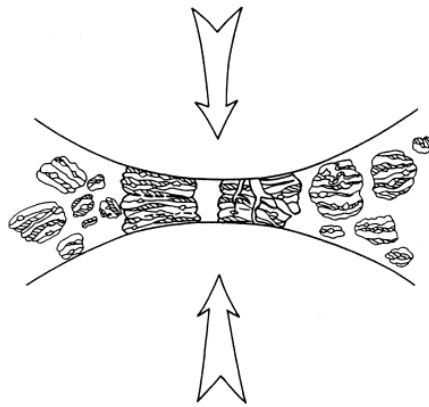


Figure 2.14 : Schematic view of a ball-powder-ball collision (Suryanarayana, 2001).

As a result, MA provides several strengthening mechanisms which are oxide dispersion strengthening, carbide dispersion strengthening, fine grain size strengthening, substructural strengthening and solid solution strengthening (Öveçoğlu, 1987).

In order to get better understanding about the physical phenomena that occur during MA processing, it is useful to divide the typical process into three or four stages (Öveçoğlu, 1987; Goff, 2003).

In the early stages of milling, the particles are soft (if we are using either ductile-ductile or ductile-brittle material combination), their tendency to weld together and

form large particles is high (Suryanarayana, 2001). A broad range of particle sizes develops, with some as large as three times bigger than the starting particles (Suryanarayana, 2001; Goff, 2003). The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents (Fig. 2.15.) (Öveçoğlu, 1987).

As the metallic phases are flattened and overlap during ball collisions, atomically clean surfaces are placed in contact with one another and subsequently cold-weld together, where brittle constituents (intermetallics and dispersoids) are occluded by the ductile constituents thus becoming trapped along cold-weld interfaces (Goff, 2003). Figure 2.16 shows early stage of processing in which particles are layered composites of starting constituents.

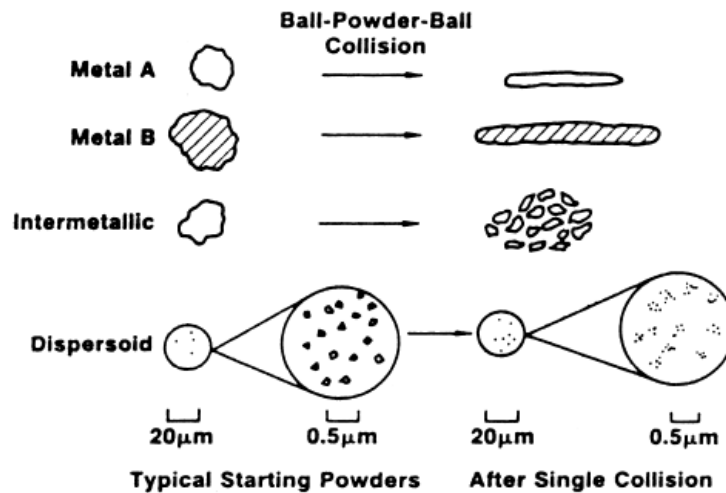


Figure 2.15 : Deformation characteristics of starting powders used in a typical MA process (Suryanarayana, 2001).

In the intermediate stage, the composite powder particles are further refined due to continual welding and fracturing of excessively work-hardened metallic phases and brittle intermetallics and/or dispersoids (Goff, 2003). At this stage the tendency to fracture predominates over cold welding (Suryanarayana, 2001). The particles consist of convoluted lamellae. The reduction in particle size, increased microstructural mixing, and elevated temperature of the powder constituents due to the adsorbed kinetic energy of milling balls all help to form areas of solute dissolution throughout the metallic powder matrix (Öveçoğlu, 1987). So, this potentially may lead to areas where new phases develop which is mainly due to an overall decrease in atomic diffusion distances between individual phases and

decreased activation energies for diffusion due to the increase in temperature (Öveçoğlu, 1987; Goff, 2003). Consequently, the inter-layer spacing decreases and the number of layers in a particle increase (Suryanarayana, 2001). Figure 2.17 is schematic view of the reduced lamellae thickness, solute dissolution, and formation of new phases in the intermediate stage of processing.

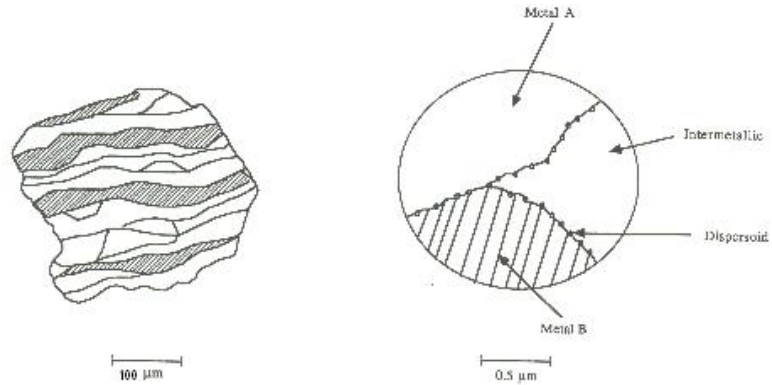


Figure 2.16 : Early stage of processing in which particles are layered composites of starting constituents (Öveçoğlu, 1987).

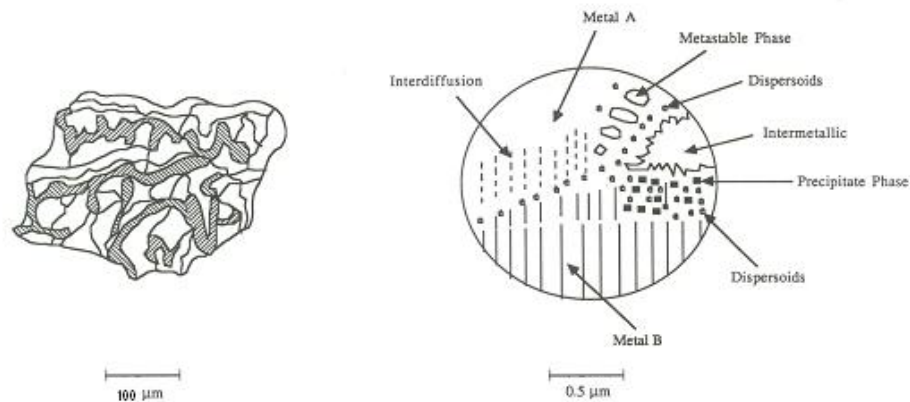


Figure 2.17 : Intermediate stage of processing showing reduced lamellae thickness, solute dissolution, and formation of new phases (Öveçoğlu, 1987).

In the final stage (Fig. 2.18.), steady-state equilibrium is attained when a balance is achieved between the rate of welding and the rate of fracturing. As a result smaller particles are able to withstand deformation without fracturing and tend to be welded into larger pieces, with an overall tendency to drive both very fine and very large particles towards an intermediate size (Suryanarayana, 2001).

Furthermore, individual particle compositions are equal to the starting powder blend composition; the lamellae are no longer optically resolvable; and the dispersoid spacing is equal to the distance between weld interfaces (Öveçoğlu, 1987). At this point, further processing would not improve the dispersoid distribution or serve to enhance the homogeneity of the composite microstructure (Öveçoğlu, 1987; Goff, 2003). The particle size distribution at this stage is narrow, because particles larger than average are reduced in size at the same rate that fragments smaller than average grow through agglomeration of smaller particles (Suryanarayana, 2001).

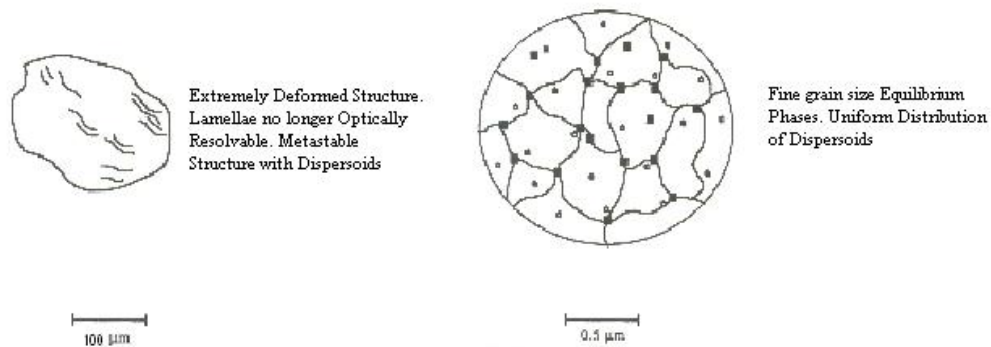


Figure 2.18 : The final stage of processing and consolidation (Öveçoğlu, 1987).

In order to complete the MA process and obtain a useable bulk composite form, the powders are heated to a temperature greater than half the melting temperature of the composite powder and consolidated. This serves to further homogenize the microstructure (Goff, 2003).

It is possible to conduct MA with three different combinations of metals and alloys, namely ductile-ductile, ductile-brittle and brittle-brittle systems. Therefore, it is convenient to discuss the mechanism of MA also under these categories (Fecht, 2002).

Ductile-ductile combination is thought to be the ideal combination for MA process. It is suggested that it was necessary to have at least 15% of a ductile component for achieving alloying. This was true because alloying occurs due to the repeated action of cold welding and fracturing of powder particles; cold welding cannot occur if the particles are not ductile. In the early stages of MA, the ductile components get flattened to platelet/pancake shapes. A small quantity of the powder, usually one or two particle thickness, also gets welded onto the ball surfaces. This coating of the powder on the grinding medium is advantageous since it prevents excessive wear of

the grinding medium; so, the contamination of the powder is prevented. However, the thickness of the powder layer on the grinding medium must be kept to a minimum to avoid forming a heterogeneous product (Suryanarayana, 2001). In the next stage, these flattened particles get cold welded together and form a composite lamellar structure of the constituent metals (Öveçoğlu, 1987). An increase in particle size is also observed at this stage (Suryanarayana, 2001). For instance, it has been found that during MA of Fe-Cu powder mixture, agglomerates of multilayers are formed leading to microstructures very similar to those obtained by cold-rolling (Fecht, 2002). With increasing MA time, the composite powder particles get work hardened, the hardness and consequently the brittleness increases, and the particles get fragmented resulting in particles with more equiaxed dimensions (Suryanarayana, 2001). With further milling, the elemental lamellae of the welded layer and both the coarse and fine powders become convoluted rather than being linear. Alloying begins to occur at this stage due to the combination of decreased diffusion distances (interlamellar spacing), increased lattice defect density, and any heating that may have occurred during the milling operation (Öveçoğlu, 1987). The hardness and particle size tend to reach a saturation value at this stage, called the steady-state processing stage. With further milling, true alloying occurs at the atomic level resulting in the formation of solid solutions, intermetallics, or even amorphous phases. The layer spacing becomes so fine or disappears at this stage that it is no longer visible under an optical microscope (Öveçoğlu, 1987; Suryanarayana, 2001).

Considering ductile-brittle combinations, in the initial stages of milling, the ductile metal powder particles get again flattened by the ball-powder-ball collisions, while the brittle oxide or intermetallic particles get fragmented. These fragmented brittle particles tend to become occluded by the ductile constituents and trapped in the ductile particles. The brittle constituent is closely spaced along the interlamellar spacings (Fig. 2.19a) (Öveçoğlu, 1987). With further milling, the ductile powder particles get work hardened, the lamellae get twisted, and refined (Fig. 2.19b). With continued milling, the lamellae get further refined, the interlamellar spacing decreases, and the brittle particles get uniformly dispersed, if they are insoluble, in the ductile matrix (Fig. 2.19c) (Öveçoğlu, 1987; Suryanarayana, 2001). On the other hand, if the brittle phase is soluble, alloying occurs between the ductile and brittle components also and chemical homogeneity is achieved (Suryanarayana, 2001).

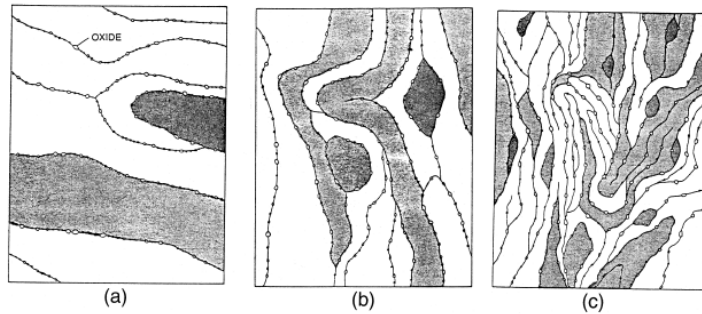


Figure 2.19 : Schematics of microstructural evolution during milling of a ductile-brittle combination of powders. This is typical for oxide dispersion strengthened case (Suryanarayana, 2001).

If a brittle-brittle combination is the case, it would appear that it is unlikely that alloying occurs in a system consisting of two or more brittle components. The reason for that is that the absence of a ductile component prevents any welding from occurring, and in its absence, alloying is not expected to occur. However, alloying has been reported to occur in brittle-brittle component systems such as Si-Ge and Mn-Bi or $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ (Suryanarayana, 2001; Fecht, 2002). Milling of mixtures of brittle intermetallics also produced amorphous phases. During milling, the brittle components get fragmented and their particle size gets reduced continuously. However, at very small particle sizes the powder particles behave in a ductile fashion, and further reduction in size is not possible; this is termed the limit of comminution. Furthermore, during milling of brittle-brittle component systems, it has been observed that the harder (more brittle) component gets fragmented and gets embedded in the softer (less brittle) component (Suryanarayana, 2001).

Nanostructured materials that are defined as materials with grain sizes less than 100 nm have received much attention as advanced engineering materials with improved physical and mechanical properties (El-Eskandarany, 2001). Because of the extremely small size of the grains, a large fraction of the atoms in these materials is located in the grain boundaries and as a result the material exhibits enhanced combinations of physical, mechanical, and magnetic properties (compared to material with a more conventional grain size, i.e., $>1\ \mu\text{m}$) (Fecht, 2002) (Suryanarayana, 2001). Nanostructured materials have increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction (Suryanarayana, 2001).

Recently, MA process has become a popular method to fabricate nanocrystalline materials due to its simplicity and relatively inexpensive equipment (El-Eskandarany et al., 2000; El-Eskandarany, 2001). The advantage of using MA for the synthesis of nanocrystalline materials lies in its ability to produce bulk quantities of material in the solid state using simple equipment and at room temperature (Suryanarayana, 2001). In this process, lattice defects are produced by pumping energy into powder particles of typically 50 μm particle diameter. This internal refining process with a reduction of the average grain size by a factor of 10^3 - 10^4 results from the creation and self organization small-angle and high-angle grain boundaries within the powder particles during the mechanical deformation process (Fecht, 2002). Grain sizes with nanometer dimensions have been observed in almost all mechanically alloyed pure metals, intermetallics, and alloys (Suryanarayana, 2001). The elemental processes leading to formation of nanostructures include three basic stages. Firstly, the deformation is localized in shear bands which contain a high dislocation density (Fecht, 2002). Their typical width is approximately 0,5-1 μm (Suryanarayana, 2001). At a certain level of strain within the high strained regions, these dislocations annihilate and recombine to small-angle grain boundaries separating the individual grains (Fecht, 2002). This results in a decrease of the lattice strain. With the continuing process, deformation occurs in shear bands located in previously unstrained parts of the material. The grain size decreases steadily and the shear bands unite. The small angle boundaries are replaced by higher angle grain boundaries and, consequently, dislocation-free nanostructured grains are formed (Suryanarayana, 2001).

2.3. Materials Selection

The matrix of the composites has to be chosen considering two main requirements, matrix has to bind and support the reinforcing phase and, secondly, to satisfy special properties based on the requirements in service. Binding strength between the matrix, whose main function is to transfer and distribute the load to the reinforcement, and the reinforcement depends on the type of matrix and reinforcement (Huda et al., 1995; Lindroos et al., 2004). Matrix-reinforcement interface has significant importance due to its role of determining load transfer and crack resistance of the composite during deformation. It is now widely known that in order to maximize

interfacial bond strength, it is necessary to promote wetting (when a liquid phase process is present), control chemical interactions and minimize oxide formation (Ibrahim et al., 1991).

On the other hand, the hardness of the matrix is the key factor in supporting the reinforcing phase. Furthermore, other considerations such as, cost, weight, fabricability and availability of the matrix materials should be made (Lindroos et al., 2004). Generally, Al, Ti, Mg, Ni, Cu, Pb, Fe, Ag, Zn, Sn and Si are used as the matrix materials (Huda et al., 1995). In addition to these, tungsten (W) has lately received some attention as a matrix material (Song et al., 2002; Song et al., 2003b).

Reinforcement phase in the composites are mainly used to increase the strength, stiffness, temperature resistance capacity and to lower the density. Generally, ceramics are used as the reinforcement phase, which are typically oxides, carbide and nitrides (Huda et al., 1995). Selection criteria for these ceramic reinforcements include elastic modulus, tensile strength, density, melting temperature, thermal stability, coefficient of thermal expansion, size and shape, compatibility with matrix material and cost (Ibrahim et al., 1991). Common reinforcement elements are TiC, ZrC, SiC, Y₂O₃, Al₂O₃, B₄C and Si₃N₄ (Huda et al., 1995).

2.3.1. Tungsten

The refractory metals are conveniently described as metals that melt at temperatures above 1850 °C, and for this consideration, twelve metals are in this group namely: W, Re, Os, Ta, Mo, Ir, Nb, Ru, Hf, Rh, V, Cr. Among these, due to their high melting point, high modulus, high resistance of thermal shock, low CTE and good high temperature strength and stiffness properties, tungsten alloys are potential candidates for service conditions which require high strength at elevated temperatures (Song et al., 2002). Properties of tungsten are listed in Table 2.2.

A large number of tungsten alloys and composites were investigated in literature before, whereas only some of them achieved technical importance. The aim of alloying tungsten is to improve its chemical, physical and mechanical properties at both ambient conditions and at elevated temperatures. However, alloying of tungsten (W) has been relatively less studied than of some of the other refractory metals. Tungsten is mainly used in aerospace applications in the unalloyed form which is much easier and cheaper to produce and fabricate. Also, it has been found that,

particularly at temperatures above 2200°C, the strengthening effects of many alloying agents decrease disproportionately (Lassner and Schubert, 1999).

Table 2.2: Properties of Tungsten (Lassner and Schubert, 1999).

Period	6
Atomic Number	74
Atomic Mass	183.85
Electronegativity	1.7
Space Group	Im3m
Lattice Parameter	3.16524 Å
Density	19.3 g/cm ³
Melting Point	3422 °C
Boiling Point	5663 °C
Specific Heat	0.0317 cal/gK
CTE	4.32-4.68x10 ⁻⁶ K ⁻¹ (25 °C)
Tensile Strength	172.4 MPa
Young's Modulus	390-410 GPa
Shear Modulus	156-177 GPa
Bulk Modulus	305-310 GPa
Poisson' Ratio	0.28-0.30
Hardness	350-450 kg/mm ²

Tungsten is mainly consumed in three forms, which are tungsten carbide, alloying additions and pure form. Tungsten carbide accounts for about 65% of tungsten consumption (Lassner and Schubert, 1999). It is combined with cobalt as a binder to form the so-called cemented carbides, which are used in cutting and wear applications because of their high hardness, good wear resistance, good fracture resistance and high temperature strength (Zhang et al., 2003) Cemented carbides such as WC-Co and WC-Co-TiC are the most widely used material for metalworking. As a consequence, a considerable amount of research effort has been spent to develop alternative cemented carbide systems in order to improve the microstructure and mechanical properties of these materials (Acchar et al., 2004). Characteristically, most of the carbides used in cermets have high hardness, good electrical and thermal conductivity, and high stability. The brittleness of carbides, however, has prevented their use as single-phase materials in highly stressed structural applications and has led to the development of metal-bonded composites (cemented carbides or cermets) (Coskun, 2006).

Metallic tungsten and tungsten alloy mill products account for about 16% of consumption. Tungsten and tungsten alloys dominate the market in applications for which a high-density material (19.3 g/cm^3) is required, such as kinetic energy penetrators, counterweights, flywheels, and governors. Other applications include radiation shields and x-ray targets. In wire form, tungsten is used extensively for lighting, electronic devices, and thermocouples (Lassner and Schubert, 1999).

The high melting point of tungsten makes it an obvious choice for structural applications exposed to very high temperatures. Tungsten is also used at lower temperatures for applications that can use its high elastic modulus, density, or shielding characteristics to advantage (Lassner and Schubert, 1999).

2.3.1.1. Tungsten composites

In order to improve properties of tungsten, dispersion-strengthened and precipitation hardened composites were developed. Its first application can be considered as non-sag tungsten (tungsten doped with potassium) which is used as filaments in lamps is one kind of dispersion-strengthened composites, which have excellent creep resistance. The term non-sag refers to the resistance of the material against deformation (sagging) under its own weight at incandescent temperatures (Lassner and Schubert, 1999).

Moreover, oxide-dispersion-strengthened tungsten composites were mainly used in literature. The addition of small amounts of finely dispersed oxides increases the mechanical properties of tungsten. The most common one is the W-ThO₂ alloy which contains a dispersed second phase of 1 to 2% thorium. The thorium dispersion enhances thermionic electron emission, which in turn improves the starting characteristics of gas tungsten arc welding electrodes. It also increases the efficiency of electron discharge tubes and imparts creep strength to wire at temperatures above one-half the absolute melting point of tungsten (Mabuchi et al., 1997; Lassner and Schubert, 1999; Chen et al., 2000). However, it is desirable to replace ThO₂ with non-radioactive activators because of the radioactive pollution of thorium during fabrication, service or handling. In the last decade, considerable efforts have been directed to develop new materials, especially to explore new activators. It has been found that tungsten electrodes activated with rare-earth metal oxides (such as La₂O₃, Y₂O₃, CeO₂, etc.) exhibit superior arc characteristics compared to pure W and W-

ThO₂ electrodes (Chen et al., 2000). Particularly, W- La₂O₃ composites exhibit good mechanical properties and have no radioactive potential (Mabuchi et al., 1997). Furthermore, there are studies about strengthening the WHA's by adding Y₂O₃. As a result, the strength of WHA's are improved with decreasing particle size which is proportional to the Y₂O₃ content (Ryu and Hong, 2003.).

There are also different refractory carbides, such as HfC, TiC, ZrC, TaC, and NbC used as dispersoids (Lassner and Schubert, 1999). Recently, mechanical and thermophysical and ablation properties of TiC/W and ZrC/W at elevated temperatures are studied. As a result, it is proved that both of them possess excellent high temperature strength and good thermophysical properties, which make them good candidates for high temperature applications (Song et al, 2002; Song et al, 2003a; Song et al, 2003b).

Table 2.3: Comparison of Young's modulus of some carbides (Shackelford, 2001).

Ceramic	Young's Modulus (GPa)	Temperature
Boron Carbide (B ₄ C)	290-450	Room temp.
Silicon Carbide (SiC) (pressureless sintered) (hot pressed)	303 440	Room temp. Room temp.
Tantalum Monocarbide (TaC)	285-629	Room temp.
Titanium Monocarbide (TiC)	439 310-379	Room temp. 1000 °C
Tungsten Monocarbide	669-714	Room temp.
Zirconium Monocarbide (ZrC)	195-480	Room temp.
Hafnium Monocarbide (HfC)	424	Room temp.

Table 2.4: Comparison of tensile strength of some carbides (Shackelford, 2001).

Ceramic	Tensile Strength (MPa)	Temperature
Boron Carbide (B ₄ C)	155	980 °C
Silicon Carbide (SiC) (hot pressed) (hot pressed)	34-138 200 40-150	25 °C 20 °C 1400 °C
Tantalum Monocarbide	14-290	1000 °C
Titanium Monocarbide	119	1000 °C
Tungsten Monocarbide	345	1000 °C
Zirconium Monocarbide	110 81-99 89-109	Room temp. 980 °C 1250 °C

Table 2.5: Comparison of hardness of some carbides (Shackelford, 2001).

Ceramic		Hardness
Boron Carbide (B_4C)		Knoop 100g: 2800 kg/mm ² Knoop 1000g: 2230 kg/mm ² Vickers : 2400 kg/mm ²
Silicon Carbide (SiC)		Vickers 25g : 3000-3500 kg/mm ² Knoop 100g : 2500-2550 kg/mm ²
Tantalum Monocarbide (TaC)		Knoop 50g: 1800-1952 kg/mm ² Knoop 100g: 825 kg/mm ² Vickers 50g: kg/mm ²
Titanium Monocarbide (TiC)		Knoop 100g: 2470 kg/mm ² Knoop 1000g: 1905 kg/mm ² Vickers 50g: 2900-3200 kg/mm ² Vickers 100g: 2850-3390 kg/mm ²
Tungsten Monocarbide (WC)		Knoop 100g: 1870-1880 kg/mm ² Vickers 50g: 2400 kg/mm ² Vickers 100g: 1730 kg/mm ²
Zirconium Monocarbide (ZrC)		Knoop : 2138 kg/mm ² Vickers 50g : 2600 kg/mm ² Vickers 100g : 2836-3840 kg/mm ²
Hafnium Monocarbide (HfC)		Knoop : 1790-1870 kg/mm ² Vickers 50g : 2533-3202 kg/mm ²

Tables 2.3 – 2.5 are comparison of mechanical properties of different refractory carbides. Among these refractory carbides TiC have received attraction due to its very high melting temperature (3067 °C), high hardness, good high temperature strength, and good corrosion resistance (Pierson, 1996). Summary of properties of TiC is given in Table 2.6.

Table 2.6: Summary of Properties of TiC (Pierson, 1996).

Atomic mass	51.91
Space group	Fm3m
Lattice parameter	4.328 Å
Density	4.54 or 4.91 g/cm ³
Melting Point	3067 °C
Specific Heat	33.8 J/mol*K
CTE	7.4x10 ⁻⁶ °C ⁻¹ (25 °C)
Young Modulus	410 – 510 GPa
Shear Modulus	186 GPa
Bulk Modulus	240 - 390 GPa
Poisson Ratio	0.191
Hardness	28-35 GPa

2.3.1.1.1. W-TiC system

TiC with its above mentioned excellent properties used as reinforcement in W matrix composites. In addition to its properties, no detrimental new phase will be formed except that W diffuses into the TiC lattice to form (Ti,W)C solid solution according to the TiC–W binary alloy diagram (Lipatnikov et al., 1997). A schematic of the solid-solution mechanism in TiC-W composite system is given in Fig. 2.20. The formation of a (Ti,W)C solid-solution, which has greater strength than that of TiC, should improve the strengthening effect of TiC (Liu et al., 1997).

Song et al. investigated TiC dispersion strengthened W composites with different TiC additions varying between 0 and 40 vol.% (Song et al., 2003b). They reported a relative density value of 97% and a microhardness value about 7 GPa for the W-20 vol%TiC composite fabricated by ball milling for 24 h followed by hot pressing at 2000 °C, and a maximum microhardness value 11 GPa and having 95.5% relative density with 40 vol.% TiC addition (Song et al., 2003b). More recently, Chen et al. reported a microhardness value of 8 GPa after hot pressing of 24 h ball milled W – 5 wt% TiC powders at 2100 °C for 90 min, where relative density value was about 94% (Chen et al., 2008).

These former studies indicated that W-TiC composites can be produced with high densities and high hardness values, which gave the motivation to do such an study about W – TiC composites.

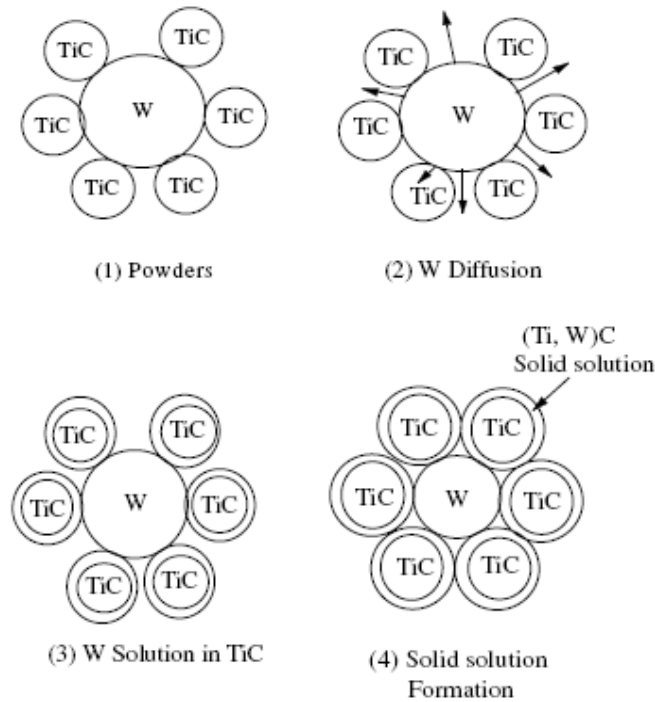


Figure 2.20 : A schematic of the solid-solution mechanism in the TiC-W composite system (Song et al., 2003b).

2.3.2. Ni Activated Sintering

Activated sintering mechanism is explained in detail in Session 2.2.1.1.3., stating that addition of small quantities of some transition metals such as Pd, Pt, Ni, Co, and Fe, enables major reductions in the sintering temperature of W. One of the activating agents, Ni, dissolves up to 38 wt% W in its solid solution and the solubility of W into Ni is only about 0.1 wt% which is negligible (Fig. 2. 21) (Massalski, 1990). Moreover, the volume diffusion of W into Ni is rather more rapid than that of Ni into W (Panichkina, 1967). Hayden and Brophy reported a value of 68 kcal/mole for the activation energy for volume self-diffusion of W in the case of activated sintering with Ni, a value much lower than 135 kcal/mole pertaining to pure W (Hayden and Brophy, 1963).

Activated sintering of W with different transition metal additions have mainly investigated in literature which mentioned above. German and Munir, reported that Pd is the best activator agent for W, and sequentially, Ni, Pt, Co, Fe, Cu addition provides activation (German and Munir, 1976). Even though Pd, reported as the best activator for W, its use is limited due to its very high price. Ni is proper activator

agent which can be used instead of Pd, specially at temperature ranges about 1400 °C (Fig. 2.22) (German and Munir, 1976).

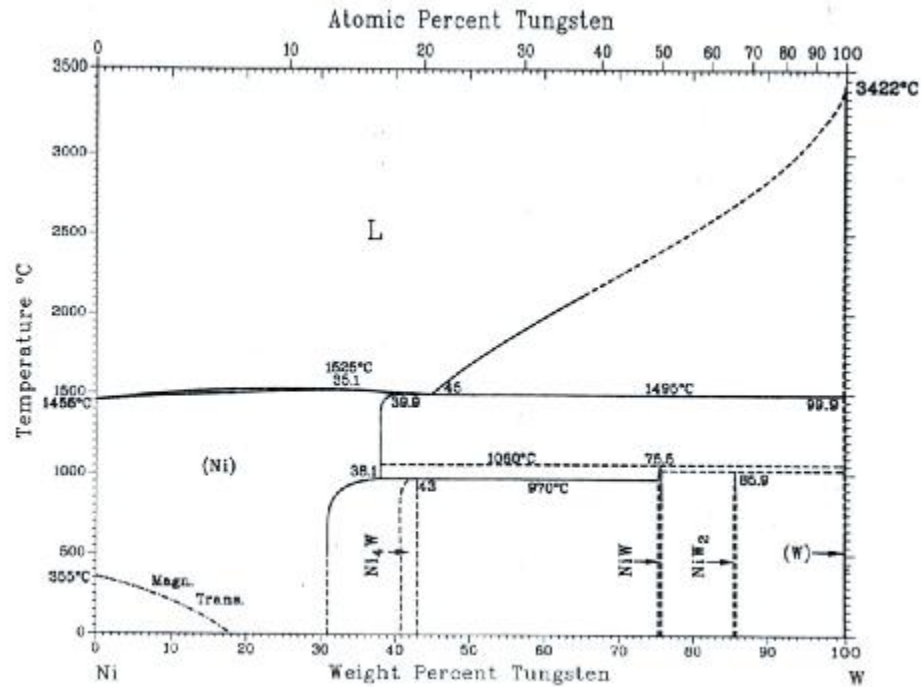


Figure 2.21 : Ni-W phase diagram (Massalski, 1990).

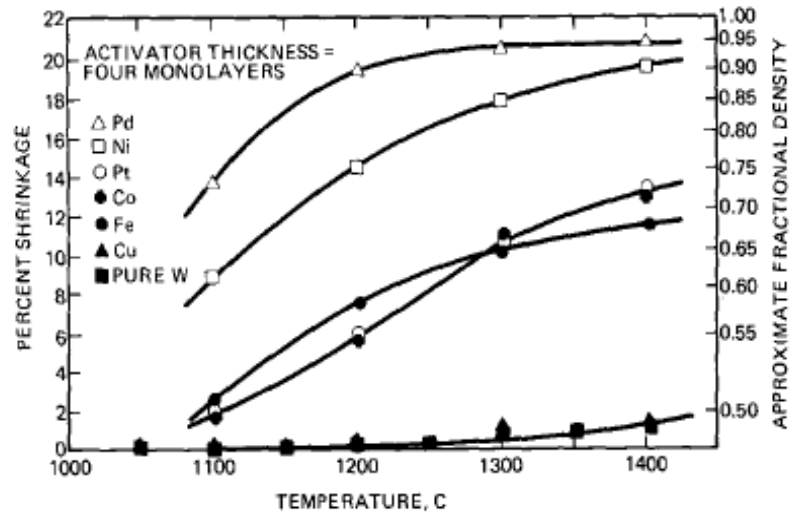


Figure 2.22 : Shrinkage dependence on activator type and temperature in activated sintering of W (German and Munir, 1976).

Above mentioned literature review represented the development of dispersion strengthened W matrix composites and activated sintering of W. However, there are no detailed studies about the sintering behaviour and microstructural properties of dispersion strengthened W-based composites sintered with the presence of a

transition metal constituent. This study aims to fulfill this gap with investigations of sintering behaviour and mechanical properties of mechanically alloyed and Ni activated sintered W-TiC composites. Thus, the objective of the present study is to report on the microstructural characterization and physical properties of mechanically alloyed and sintered W-2wt% TiC-1wt% Ni composites.

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3. EXPERIMENTAL PROCEDURE

The experimental studies was conducted in order to develop Ni activated sintered W-TiC composites produced via mechanical alloying and to get better understanding about sintering behavior, microstructural and mechanical properties of developed W-TiC-Ni composites.

The first part experiments deals with both effects of mechanical alloying and activated sintering together, having a composition batch W-2 weight(wt)%TiC-1 wt.% Ni powders. Duration of mechanical alloying and sintering regime were determined in this part, as well. Moreover, another series of experiments were conducted to understand the effects of Ni activated sintering on TiC dispersion strengthened W composites. Finally, strengthening of Ni activated W investigated.

The experimental procedure of the present study is summarized in the flow chart show in Figure 3.1.

3.1. Preparation of Green Compacts

3.1.1. Characterization of Powders

Elemental tungsten (W) powders (99.9% purity, 14 μm average particle size) as the matrix of the composite and titanium carbide (TiC) powders (99.5% purity, 2.7 μm average particle size) as reinforcement and 1 wt% Ni powders (99.9% purity, 8 μm average particle size) as activating agent are used in this study. Furthermore, 0.5 wt% graphite powders (99.9% purity, 21 μm average particle size) was used as a process control agent (PCA) to minimize cold welding between powder particles and thereby to inhibit agglomeration. Mechanical alloying (MA) experiments were carried out using a Spex™ Duo Mixer/Mill 8000D with a speed of 1200 rpm for 3 h, 6 h, 12 h and 24 h in a tungsten carbide (WC) vial with WC balls having a diameter of 6.35 mm ($\frac{1}{4}$ inches). The ball-to-powder (BPR) weight ratio was 7:1. W-2wt% TiC-1 wt% Ni (hereafter referred as W2TiC1Ni) were mixed and MA'd for 3 h, 6 h, 12 h and 24 h in first part of experiments where both effects of MA and activated sintering

investigated. Moreover, W-2 wt% TiC were mixed and MA'd for the same durations and 1 wt% Ni added after MA and further MA was conducted for 20 min with W-2 wt% TiC and 1 wt% Ni (hereafter referred as W2TiC+1Ni). In addition, W and 1 wt% Ni were mixed and MA'd for the same durations. 2 wt% TiC added to MA'd W-1 wt% Ni and MA'd together for 20 min (hereafter referred as W1Ni+2TiC).

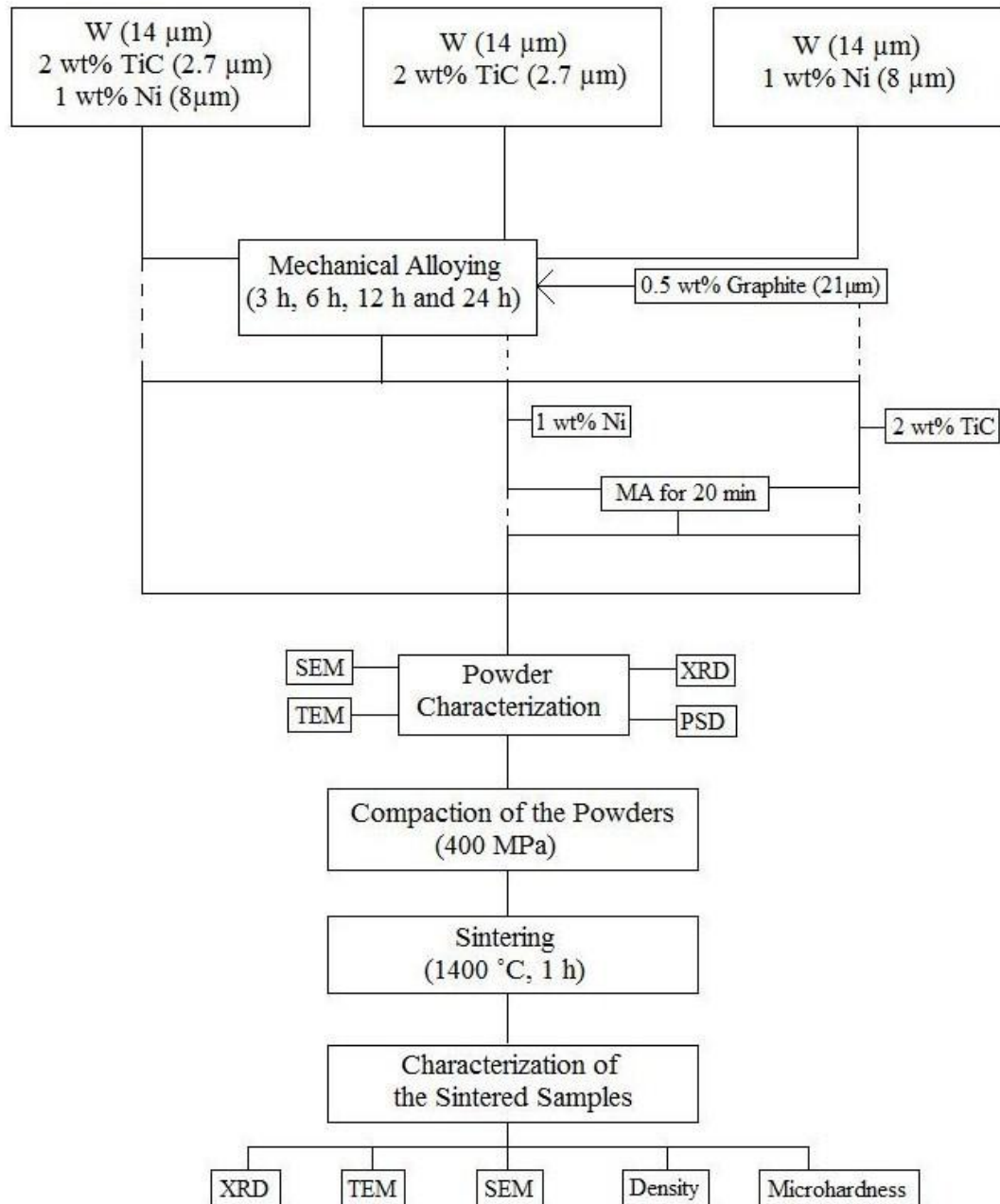
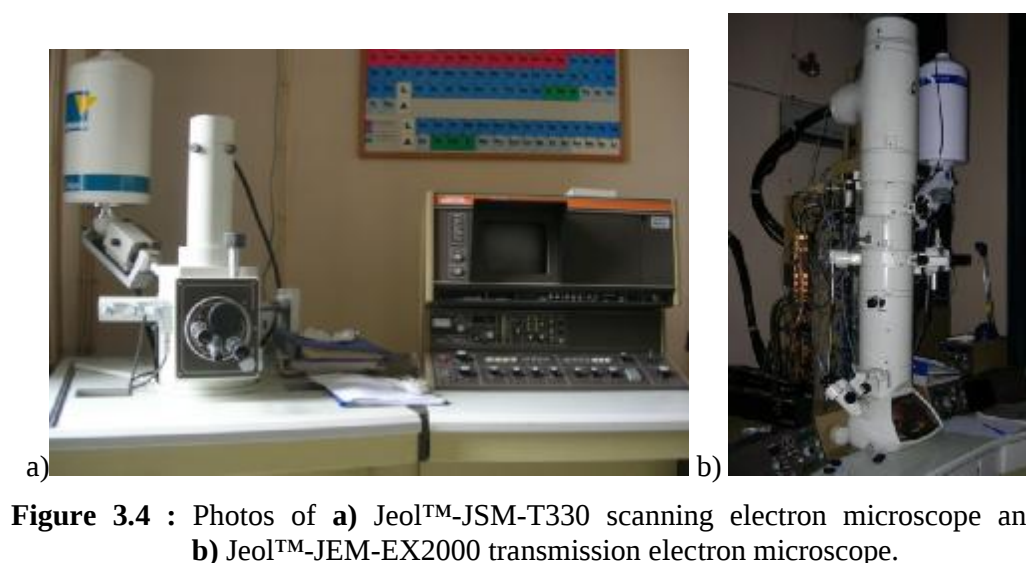
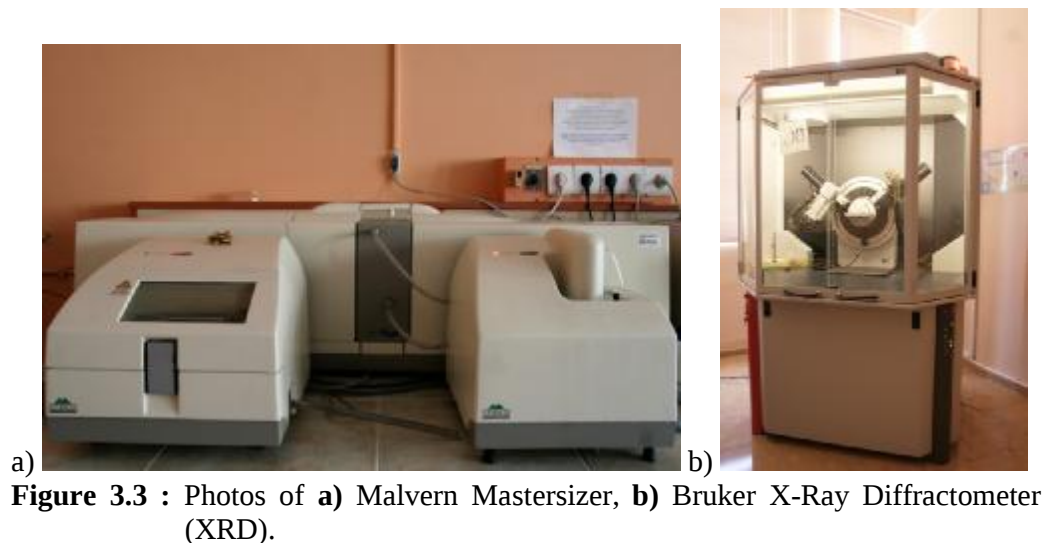


Figure 3.1 : The Flow Chart of the Experimental Procedure.

Powder particle size measurements were carried out in a MalvernTM Mastersizer Laser particle size analyzer. Microstructural characterization investigations of as-blended and MA'd powders were conducted using a JeolTM-JSM-T330 scanning electron microscope (SEM), JeolTM-JEM-EX2000 transmission electron microscope (TEM) and a BrukerTM X-Ray Diffractometer (XRD) (CuK_α radiation). TOPAS 3 (Bruker AXS) software (Kern and Coelho, 2006) was used to estimate crystallite sizes.



3.1.2. Compaction

The mechanically alloyed powders were compacted by cold pressing in a tool-steel die at a pressure of 400 MPa into cylinder shaped green compacts with a diameter of $\approx 12\text{mm}$ for 1 minute by using a 10 tons “APEXTM 3010/4” one-action hydraulic

press. Zinc Stearat was applied to the walls of the die to take the samples out of the die easily. As-blended powders could not be compacted, because of these reason there are no sintered sample of as-blended powders in this study.



Figure 3.5 : The photo of APEX™ 3010/4 one-action hydraulic press.

3.2. Sintering and Characterization of Sintered Samples

The compacts were sintered in an Anter™ Dilatometer at 1400 °C under both inert Ar and reducing H₂ gas flowing conditions for 1 h. The microstructural and phase characterizations of the sintered samples were carried out using the same XRD, SEM and TEM. Before the sintered samples were characterized, they were mounted in bakelite using the Struers™ Labopress-1 machine. After that the samples were polished on the Struers™ Tegrapol-15 automatic polishing machine.

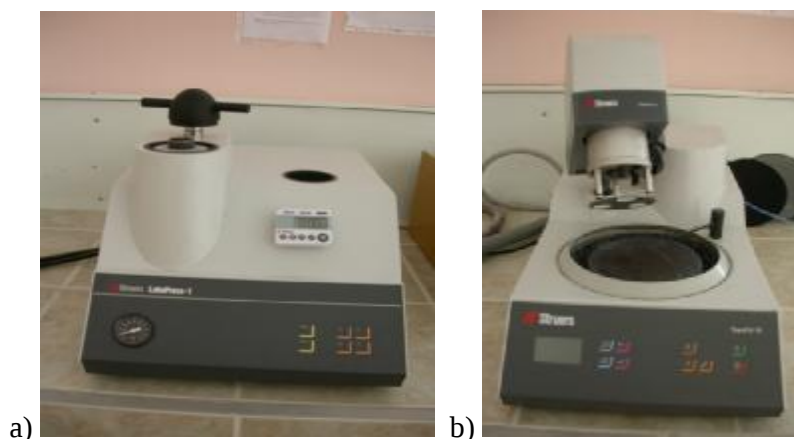


Figure 3.6 : Photos of **a)** Struers™ Labopress-1 machine and **b)** Struers™ Tegrapol-15 automatic polishing machine.

Sintered samples were grinded and polished to make thinner sample for TEM. Grinded samples were mechanically punched to 3 mm diameter, punching followed by standard dimpler and etching (HF:HNO₃) processes.

Sintered densities were measured by using the Archimedes method. Density results are the arithmetic mean of 5 measurements of the same sample. Vickers microhardness tests were conducted on the sintered samples using a Shimadzu™ microhardness tester under a load of 100 g for 15 seconds. Microhardness test result for each sample is the arithmetic mean of 10 successive indentations and standard deviations.

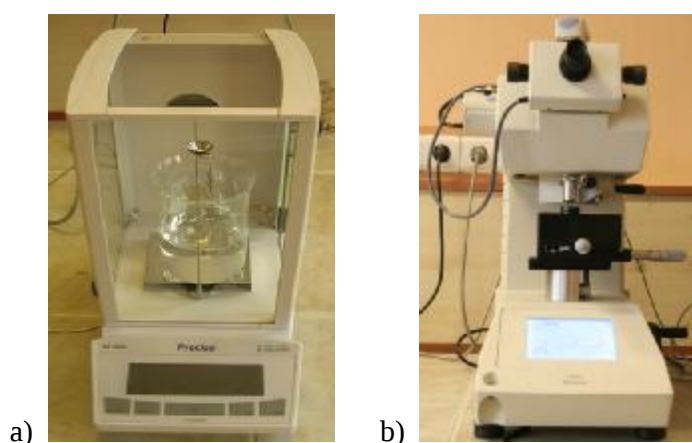


Figure 3.7 : Photos of **a)** Precisa™ XB220A weighing machine and **b)** Shimadzu™ micro hardness tester.

4. RESULTS

Experimental studies and results of the present study were conducted in there main routes an mentioned in Chapter 3 and if so, it is found convenient to present results in three main section.

4.1. Characterization Investigations of Mechanically Alloyed and Sintered W-2 wt% TiC-1 wt% Ni Composites

Abstract

Blended elemental W-2 wt% TiC-1 wt% Ni powders were mechanically alloyed (MA'd) for 3 h, 6 h, 12 h and 24 h in a Spex Mixer/mill at room temperature to investigate effects of both MA and activated sintering. MA'd powders were sintered at 1400 °C for 1 h under Ar, H₂ gas flowing conditions. Microstructural and phase characterizations of MA'd powders and sintered samples were carried out via SEM, TEM and XRD analyses. Whereas XRD investigations on MA'd powders revealed stable W and WC phases, those on sintered samples showed the presence of a new face-centered cubic W phase and Ni in addition to the matrix W phase. TEM investigations revealed the presence of Ni, TiC, W₂C, NiTi, rutile, TiO₂ and Ti₄O₇ phases existing in a W-matrix. Relative density values varied between 89 and 97%, and increased with increasing MA duration. Microhardness values of the sintered composites varied between 5 GPa and 5.6 GPa.

4.1.1. Characterization of Powders

XRD patterns of as-blended and mechanically alloyed (MA'd) for 3 h, 6 h, 12 h and 24 h W₂TiC₁Ni powders are shown in Figures 4.1a- 4.1e, respectively. As seen in these figures, the peaks of W which has a b.c.c. Bravais lattice and $Im\bar{3}m$ space group with the lattice parameter of $a = 0.316$ nm (ICDD, 04-0806,) can be identified in all samples. Additionally, the peak belonging to {111} reflections of Ni which has a f.c.c. Bravais lattice and $Fm\bar{3}m$ space group with the lattice parameter of $a = 0.352$ nm (ICDD, 65-2865) is identified in the as-blended sample (Fig. 4.1a). Peaks for TiC

are not seen, probably due to its small amount (2 wt%) in the powder blend and its small particle size (2.7 μm) compared to those of Ni (8 μm) and W (14 μm). Moreover, as seen in Figures 4.1d and 4.1e for samples MA'd for 12 h and 24 h, the presence of WC phase which has a hexagonal Bravais lattice and $P\bar{6}m2$ space group with the lattice parameters of $a = 0.290 \text{ nm}$ and $c = 0.283 \text{ nm}$ (ICDD, 51-0939) can be detected due to contamination during MA. Thus, it is clear that with increasing MA, peaks are broadened and peak heights are decreased, as a result of grain refinement and due to internal strain buildup during MA. Average grain size of the matrix W phase in the as-blended and MA'd W2TiC1Ni powders was calculated from Figures 4.1a – 4.1e using TOPAS 3 (Bruker AXS) software (Kern and Coelho, 2006) which decreased with increasing MA durations. Whereas the as-blended W2TiC+1Ni powders have a W grain size of 219 nm, those MA'd for 3 h, 6 h, 12 h and 24 h have average W grain sizes of 47.8 nm, 22.8 nm, 12.9 nm, 8.7 nm, respectively.

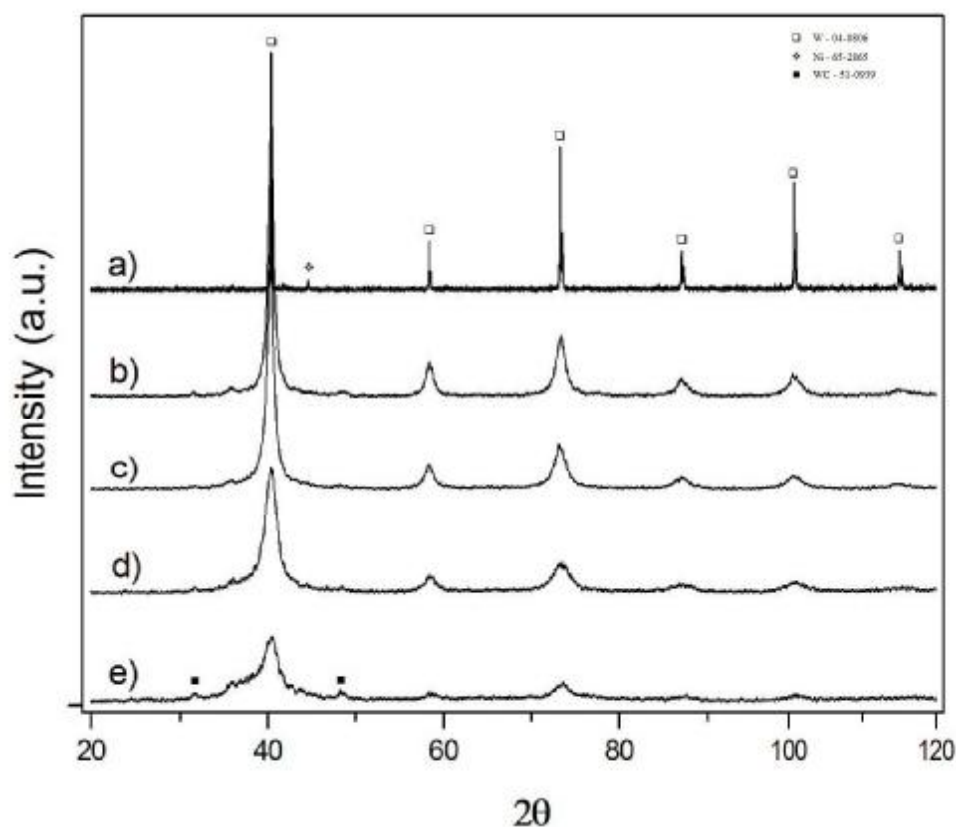


Figure 4.1 : XRD patterns of **a)** as-blended, **b)** MA'd for 3 h, **c)** MA'd for 6 h, **d)** MA'd for 12 h and **e)** MA'd for 24 h W2TiC1Ni powders.

Figures 4.2a and 4.2b are SEM micrographs taken from as-blended W2TiC+1Ni powders and from powders those MA'd for 24 h, respectively. Fig. 4.2c is a bright-field TEM micrograph of powders MA'd for 24 h. As seen in Figures 4.2a – 4.2c, microscale as-blended powders have diameters in nanoscale after MA. Moreover, TiC and Ni powders distributed homogeneously in W matrix after MA. Local agglomerations which are clearly seen in Fig. 4.2b, occur due to small particle size distributions of MA'd powders. Fig. 4.2c shows the equiaxed shaped particles varying in size between 100 and 200 nm.

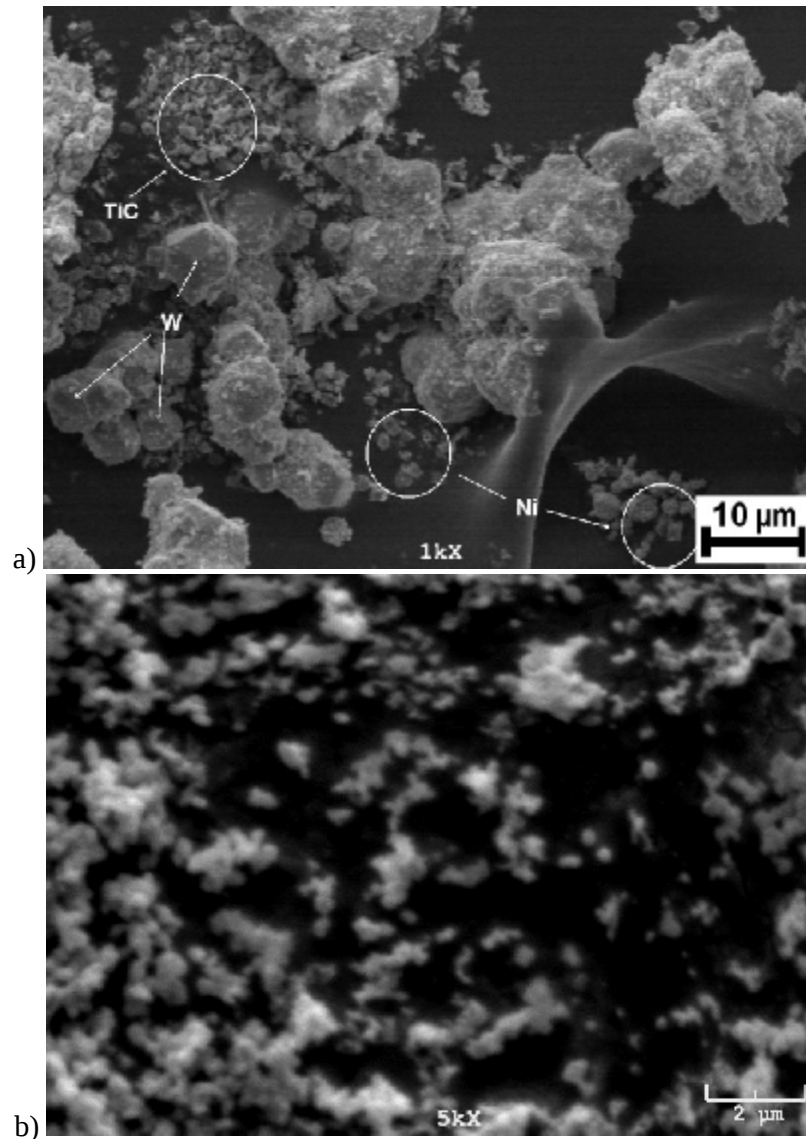


Figure 4.2 : Electron micrographs of as-blended and MA'd W2TiC1Ni powders. Representative SEM micrographs of: **a)** as-blended powders and **b)** those MA'd for 24 h. **c)** Bright-field (BF) TEM micrograph of powders MA'd for 24 h.

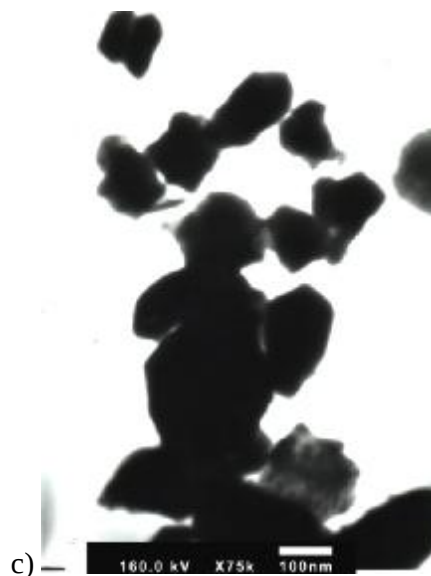


Figure 4.2 : Electron micrographs of as-blended and MA'd W₂TiC₁Ni powders. Representative SEM micrographs of: **a)** as-blended powders and **b)** those MA'd for 24 h. **c)** Bright-field (BF) TEM micrograph of powders MA'd for 24 h(**continued**).

Fig. 4.3. is particle size distributions of W₂TiC₁Ni powders MA'd for 3 h, 6 h, 12 h and 24 h. As seen in Fig. 4.3., average particles sizes are about 160 nm for W₂TiC₁Ni powders after 24 h MA. Furthermore, with MA, specific surface area of the powders drastically increases, which are less than 1 m²/g for as-blended W₂TiC₁Ni powders, become 44,5 m²/g for W₂TiC₁Ni powders MA'd for 24 h.

As explained in the Experimental Procedures, there are no pressed and sintered compacts prepared from as-blended powders used in this study. Relative green density values of the consolidated powders are 64%, 57%, 60% and 54% for MA for 3 h, 6 h, 12 h and 24 h, respectively.

4.1.2. Characterization of Sintered Samples

4.1.2.1. XRD and SEM Investigations

XRD patterns of W₂TiC₁Ni powders sintered at 1400 °C under both inert Ar and reducing H₂ gas flowing conditions for 1 h are shown in Figures 4.4a – 4.4d. As clearly seen in Figures 4.4a – 4.4d, stable b.c.c. W and f.c.c. Ni phases are identified in all sintered samples. Moreover, a second W phase which has a f.c.c. Bravais lattice with Fm $\bar{3}$ m space group and lattice parameter of $a = 4.06$ nm (ICDD, 88-2339) is present in W₂TiC₁Ni samples MA'd for 3 h and 6 h. On the other hand, in sintered

W2TiC1Ni sample MA'd for 3 h, other phases are identified, which are NiTi phase with hexagonal Bravais lattices having $P\bar{3}$ space group (ICDD, 72-3504), TiO phase with a base-centered monoclinic Bravais lattice having $A2/m$ space group (ICDD, 72-0020) and WO_2 phase with a orthorhombic Bravais lattice having $Pnma$ space group (ICDD, 48-1827). The reason of oxidation and thermal decomposition, which took place only in sintered W2TiC1Ni sample MA'd for 3 h, is not clearly understood.

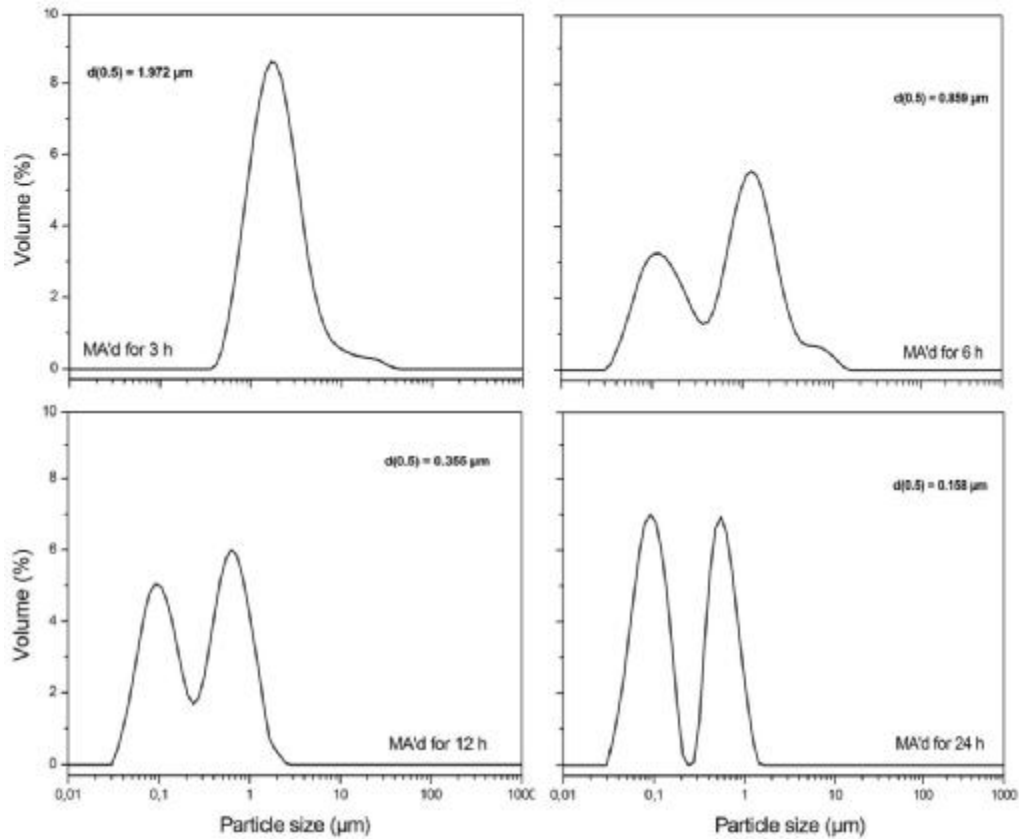


Figure 4.3 : Particle size distributions of MA'd W2TiC1Ni powders.

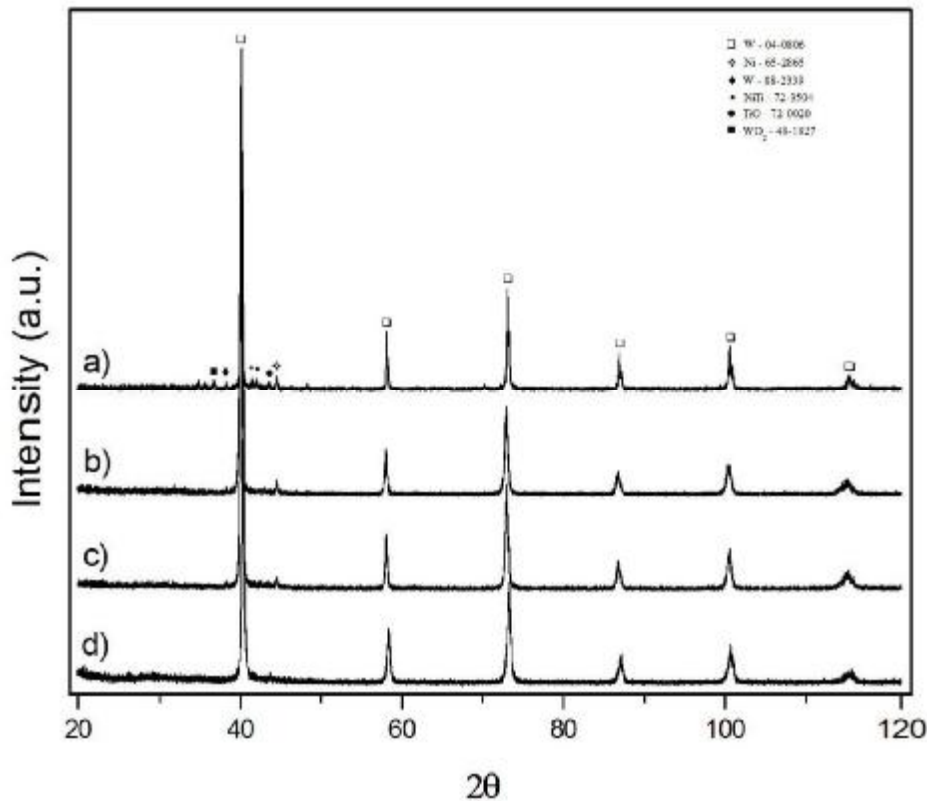


Figure 4.4 : XRD patterns of the sintered W₂TiC₁Ni samples which were **a)** MA'd for 3 h, **b)** MA'd for 6 h, **c)** MA'd for 12 h and **d)** MA'd for 24 h.

SEM micrographs taken from MA'd W₂TiC₁Ni samples are shown in Figures 4.5a – 4.5d. Since chemical etching (Murakami and H₂O₂) was ineffective, grain boundaries of the matrix W can not be observed. However, EDS spectra revealed that gray regions are matrix W, black dots are TiC and/or WC, porous like gray regions (Fig. 4.5d) are Ni rich areas surrounded by W matrix and white dots are dirtiness. As seen in Fig. 4.5a, sintering of the W₂TiC₁Ni sample MA'd for 3 h was not efficient. Moreover, no black dots (TiC and/or WC) can be seen in Fig. 4.5a, consisting with XRD results (Fig. 4.4a) where phases such as NiTi and TiO were formed during sintering as a result of thermal decomposition of TiC. As seen in Fig. 4.5d, TiC/WC particles distributed homogeneously in matrix W with a diameter range of 100 and 300 nm after MA for 24 h. A detailed EDS spectra analysis of these regions/phases can be shown in Table 4.1 (Page 73).

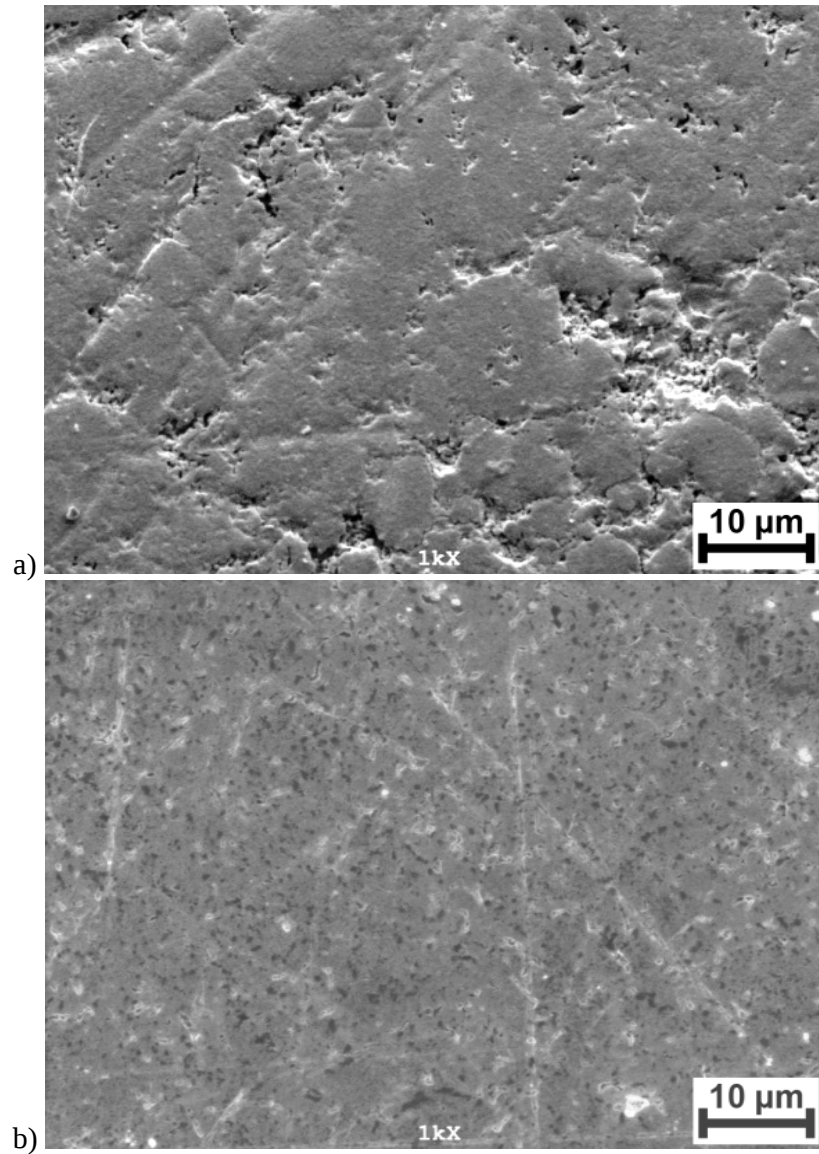


Figure 4.5 : SEM micrographs of sintered W₂TiC₁Ni samples which were **a)** MA'd for 3 h, **b)** MA'd for 6 h, **c)** MA'd for 12 h and **d)** MA'd for 24 h.

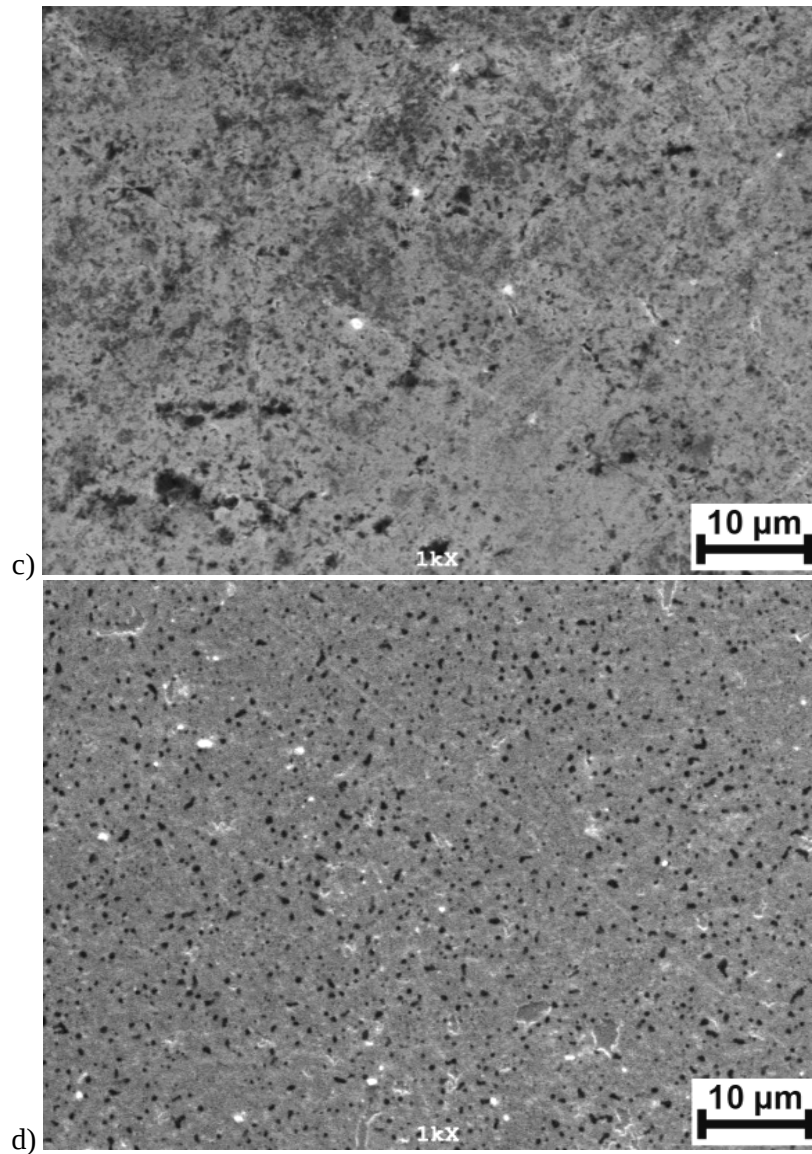


Figure 4.5 : SEM micrographs of sintered W₂TiC₁Ni samples which were **a)** MA'd for 3 h, **b)** MA'd for 6 h, **c)** MA'd for 12 h and **d)** MA'd for 24 h (**continued**).

4.1.2.2. TEM Investigations

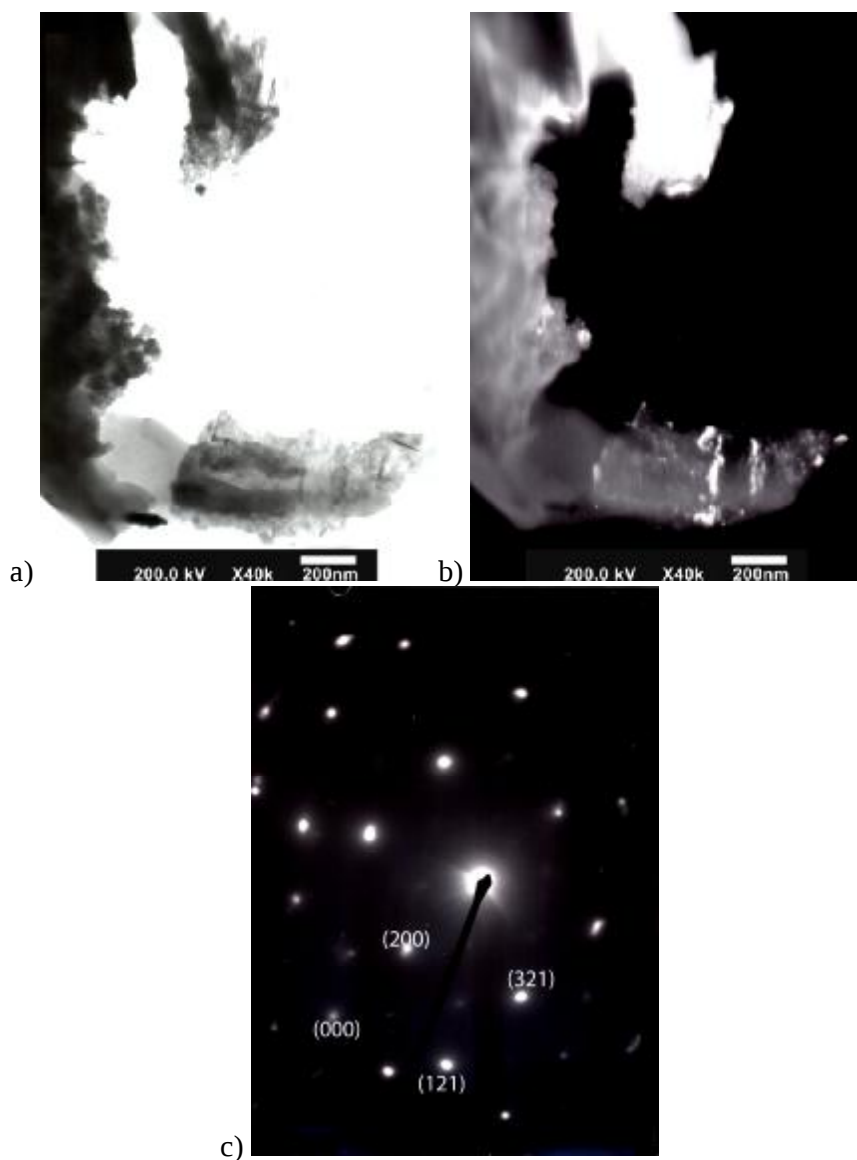


Figure 4.6: **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on (200) showing **b. c. c.** W regions and **c)** corresponding selected-area diffraction patterns of W (ICDD, 04-0806) in the W_2TiC_1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length, $L = 100$ cm, Zone axis is $[01\bar{2}]$).

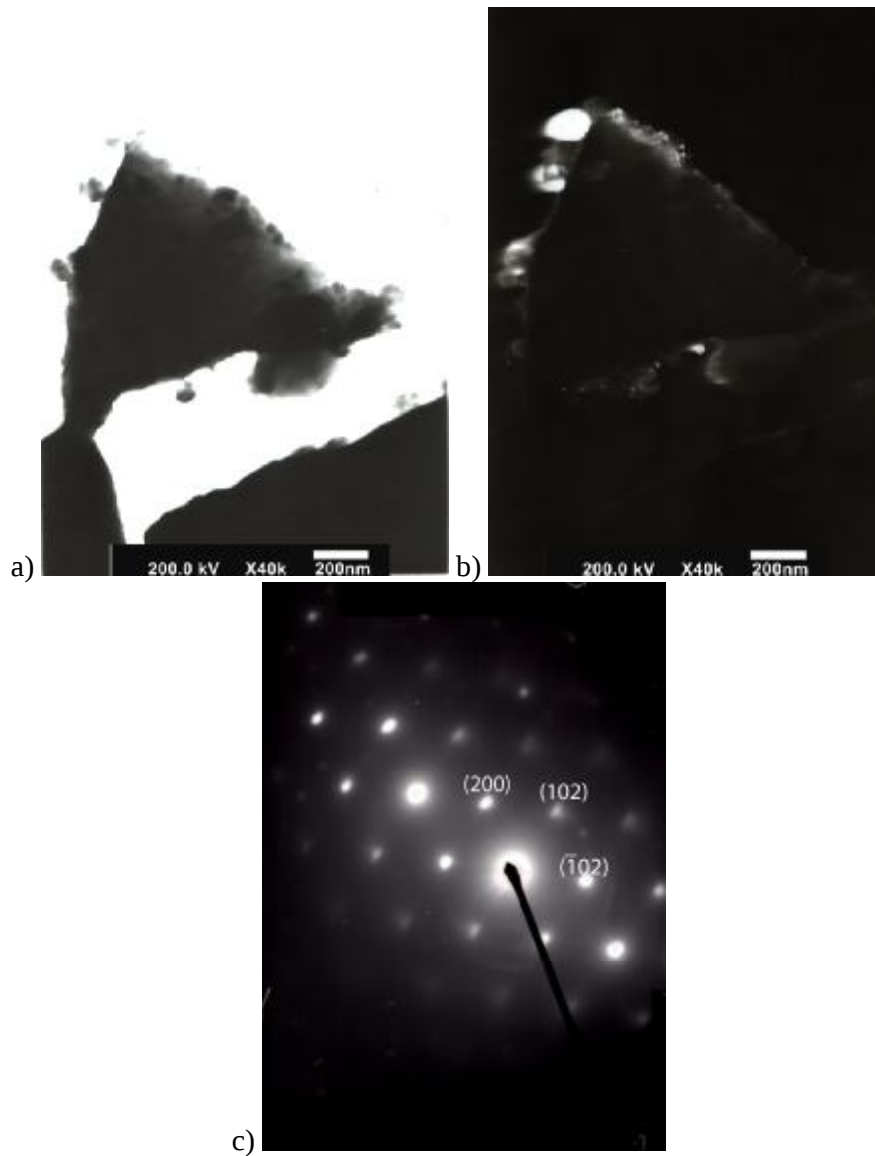


Figure 4.7 : a) Bright-field micrograph and b) dark-field electron micrograph with the objective aperture on $(\bar{1}0\bar{2})$ showing sphereoidal orthorhombic W_2C grains and c) corresponding selected-area diffraction patterns of W_2C (ICDD, 89-2371) in the W_2TiC_1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length, $L=100$ cm, Zone axis is $[010]$).

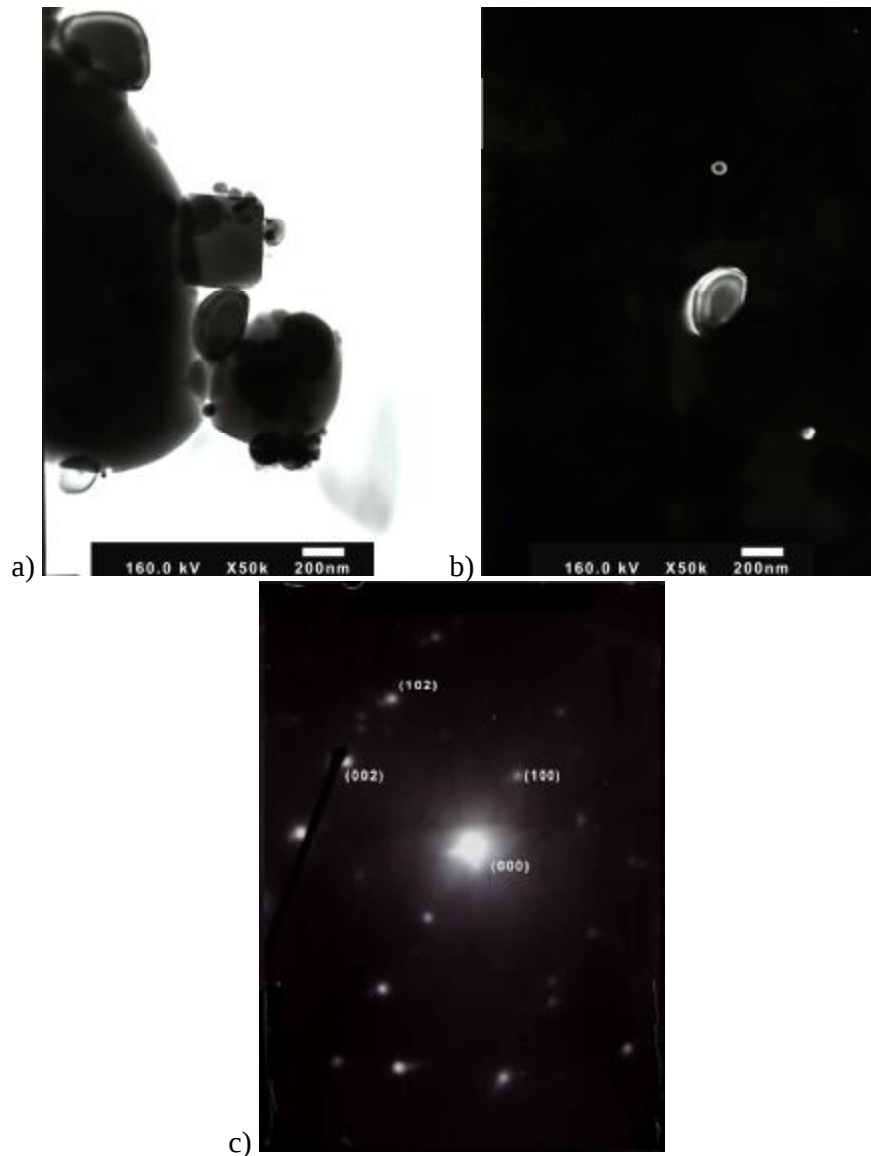


Figure 4.8 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(\bar{1}0\bar{2})$ showing spheroidal-shaped hexagonal W_2C (ICDD, 79-0743) particles in the W_2TiC_1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. **c)** Corresponding selected-area diffraction pattern. (Camera length: 100 cm; Zone axis: $[0\bar{1}10]$).

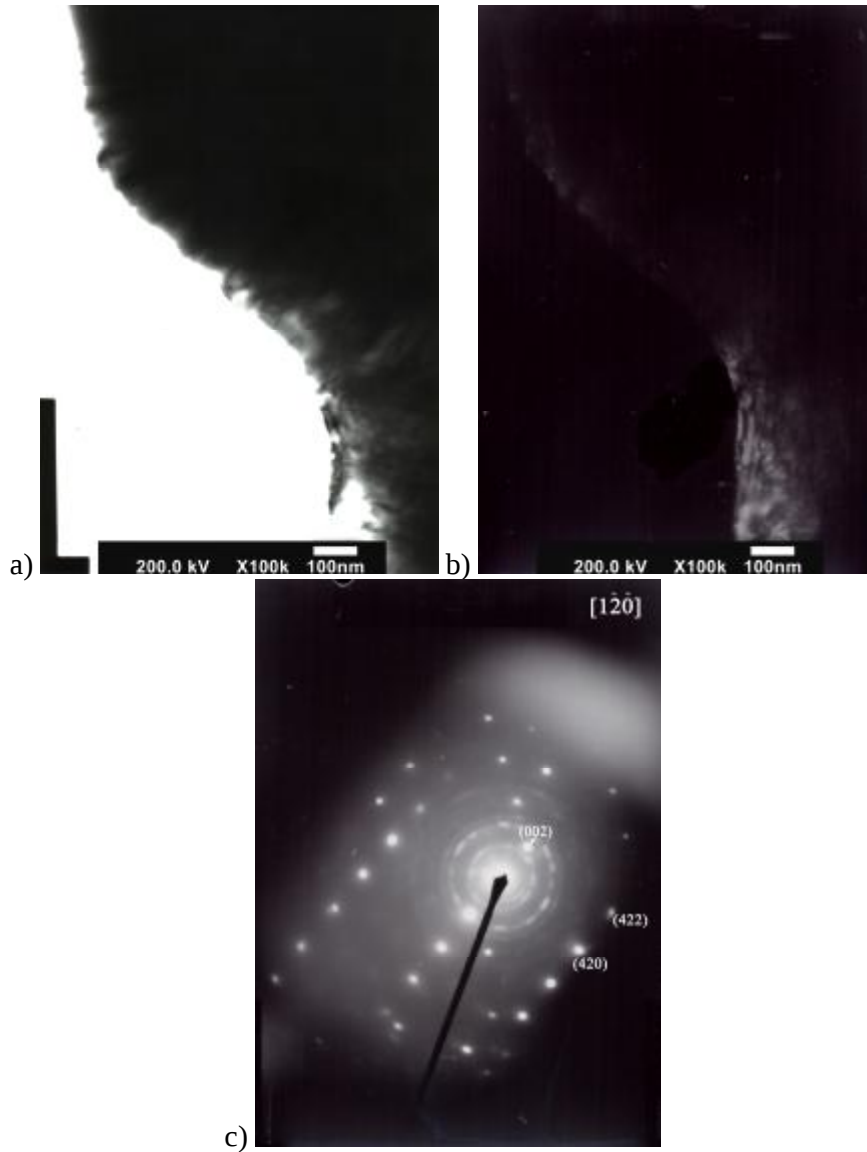


Figure 4.9 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(\bar{4} \bar{2} \bar{2})$ showing f. c. c. TiC region and **c)** corresponding selected-area diffraction patterns of TiC (ICDD, 65-0242) in the W_2TiC_1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length, $L = 100$ cm, Zone axis is $[1 \bar{2} 0]$).

Figures 4.10a and 4.10b are bright-field and dark-field TEM micrographs taken from the W_2TiC_1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h showing rectangular region with diameters of 100 nm width and 300 nm length. A selected electron diffraction pattern (SADP) taken from this rectangular region is shown in Fig. 4.10c. This rectangular region is unambiguously identified as being composed of the NiTi phase which has hexagonal Bravais lattice and $P\bar{3}$ space group with lattice parameters of $a = 0.735$ nm and $c = 0.528$ nm (ICDD, 72-3504). Thermodynamic

calculations using FACT-Sage software (Bale et al., 2002) confirmed that formation of NiTi out of Ni and TiC phases is not possible in the temperature range between 0 and 2000 °C. Identification of this intermetallic NiTi phase is self evident proof of decomposition of TiC in MA'd and sintered W2TiC1Ni composites where Ni and TiC powders added as starting materials.

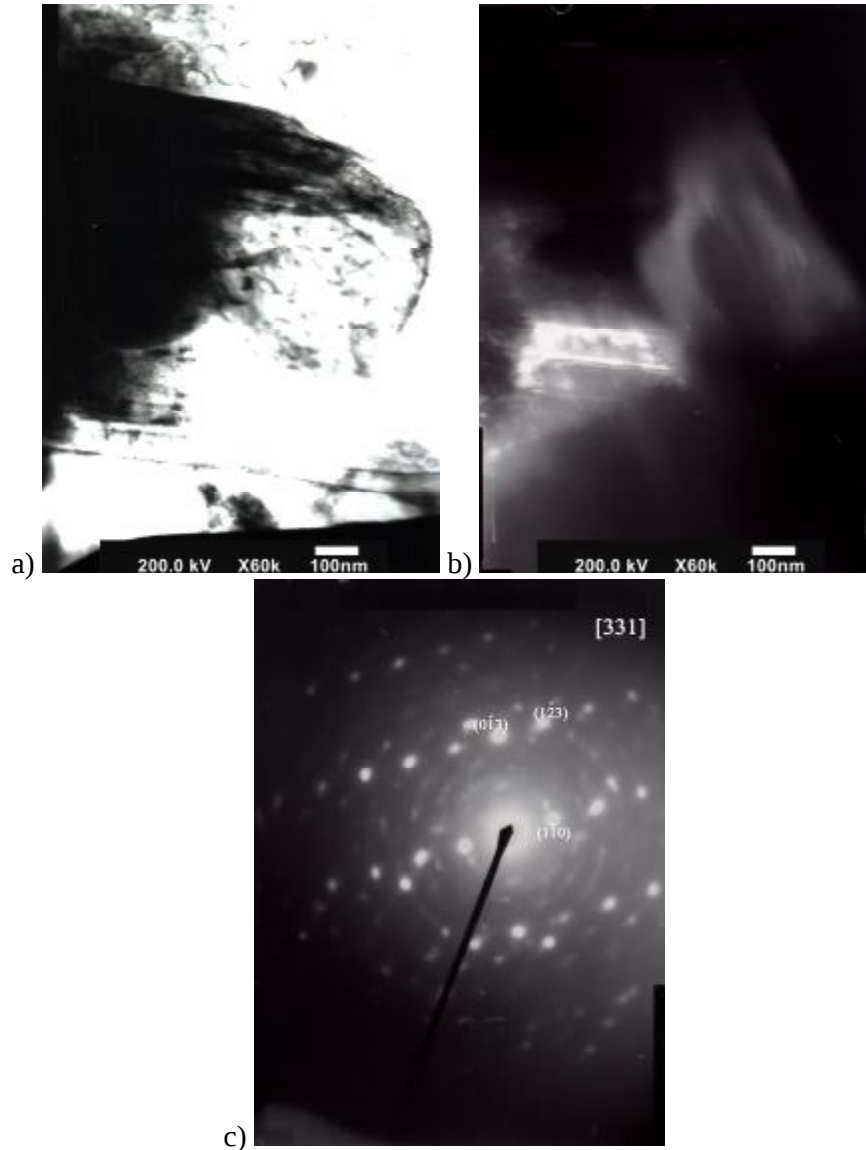


Figure 4.10 : **a)** Bright-field and **b)** dark-field electron micrographs with the objective aperture on $(01\bar{3})$ showing rectangular shaped region and **c)** corresponding selected-area diffraction pattern of hexagonal NiTi (ICDD, 72-3504) in the W2TiC1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length $L=100$ cm).

Figures 4.11a and 4.11b are bright-field and dark-field TEM micrographs taken from the W2TiC1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h showing

sphereoidal grains. A selected electron diffraction pattern (SADP) taken from the grain upper left of Fig. 4.11a is shown in Fig. 4.11c. suggesting that this grain is being composed of rutile (TiO_2) phase which has tetragonal Bravais lattice and $P4_2/mmm$ space group with lattice parameters of $a = 0.459 \text{ nm}$ and $c = 0.295 \text{ nm}$ (ICDD, 21-1276). As clearly seen in Fig. 4.11b, oxidation takes place at grain boundary which is a phenomena that Song et al. indicated as a result of TiC 's reaction with O_2 (Song et al., 2003a).

Figures 4.12a and 4.12b are bright-field and dark-field TEM micrographs taken from the $\text{W}_2\text{TiC}_1\text{Ni}$ sample MA'd for 24 h and sintered at 1400°C for 1 h. Fig. 4.12c is a selected electron diffraction pattern (SADP) taken from the spherical grain at Fig. 4.12a. This spherical grain is unambiguously identified as being composed of $\gamma\text{-TiO}_2$ phase which has orthorhombic Bravais lattice and $Pbnm$ space group with lattice parameters of $a = 0.483 \text{ nm}$, $b = 0.942 \text{ nm}$ and $c = 0.295 \text{ nm}$ (ICDD, 53-0619).

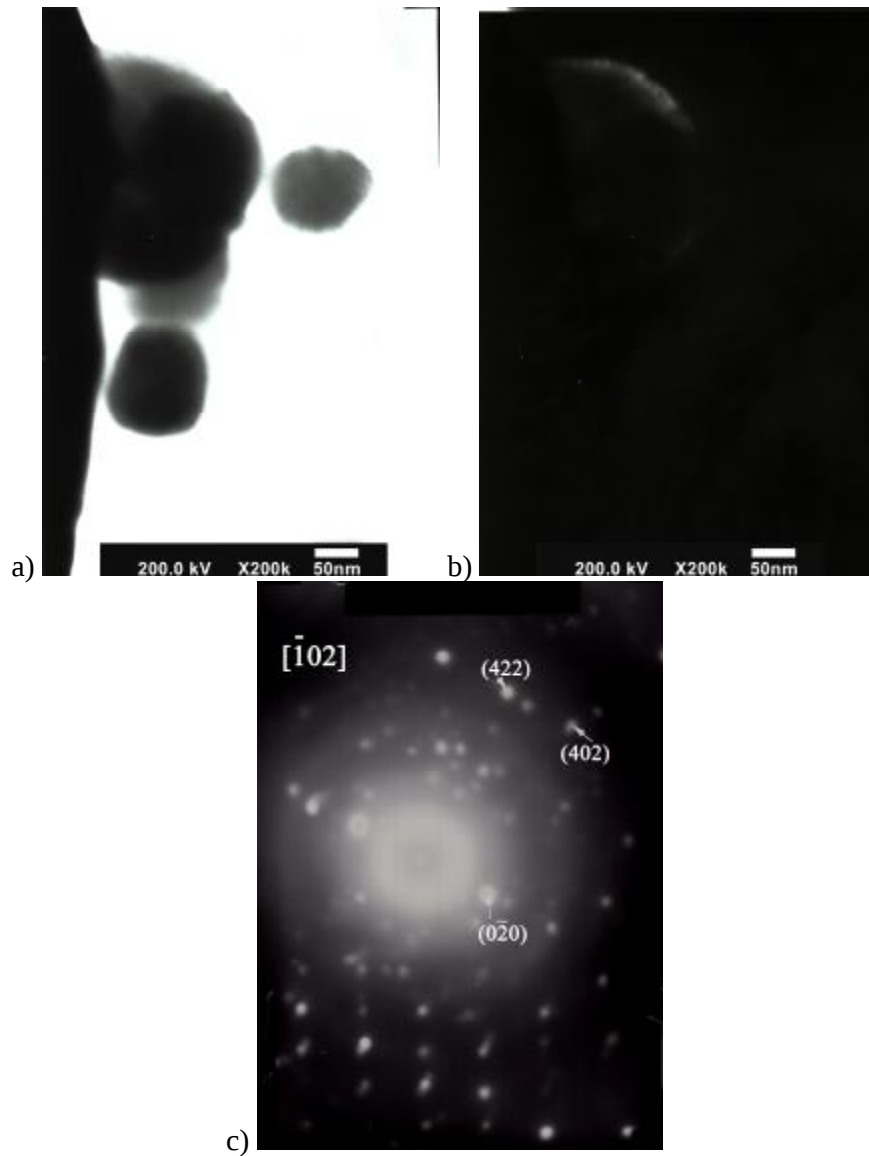


Figure 4.11 : **a)** Bright-field and **b)** dark-field electron micrographs with the objective aperture on (020) showing sphereoidal grain and **c)** corresponding selected-area diffraction pattern of Rutile (TiO_2) (ICDD, 21-1276) in the $\text{W}_2\text{TiC}_1\text{Ni}$ sample MA'd for 24 h and sintered at 1400°C for 1 h. (Camera length $L=100$ cm).

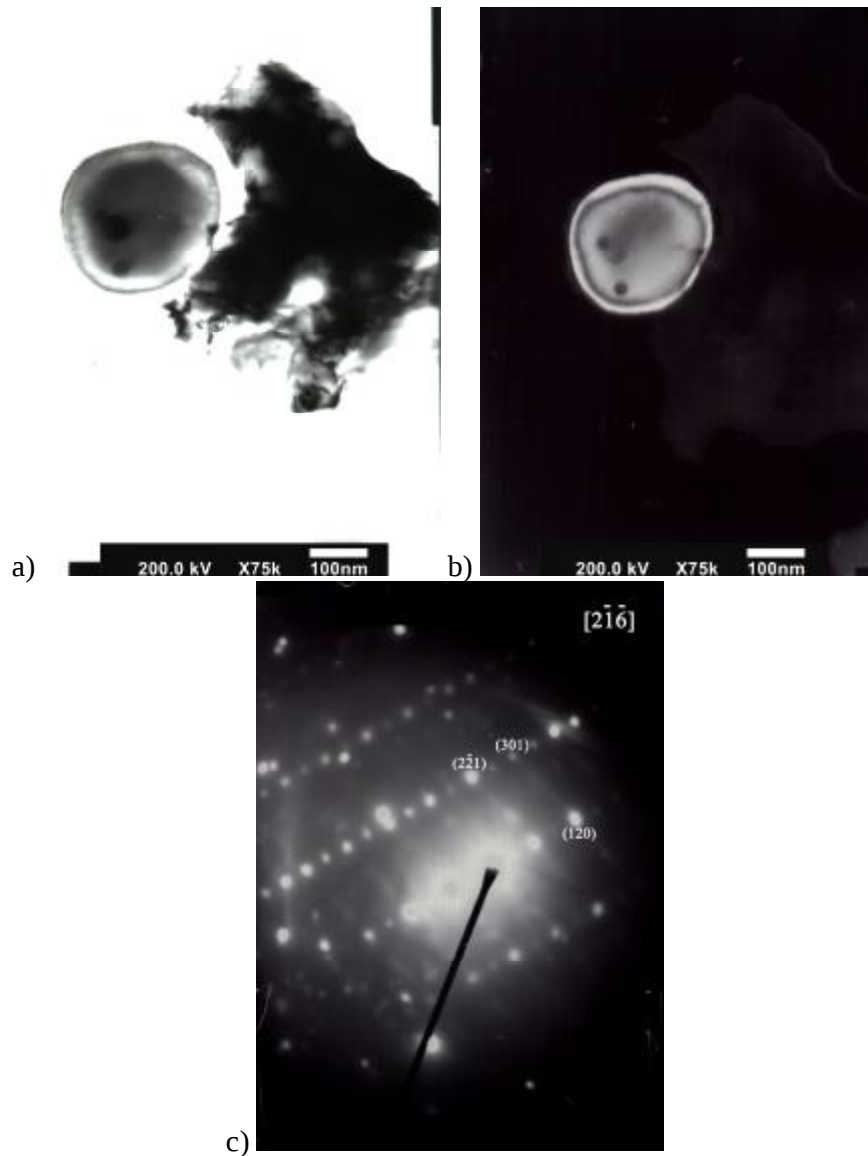


Figure 4.12 : **a)** Bright-field and **b)** dark-field electron micrographs with the objective aperture on $(\bar{1}\bar{2}0)$ showing sphereoidal grain and **c)** corresponding selected-area diffraction pattern of orthorhombic γ -TiO₂ (ICDD, 53-0619) in the W₂TiC₁Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length L= 100 cm).

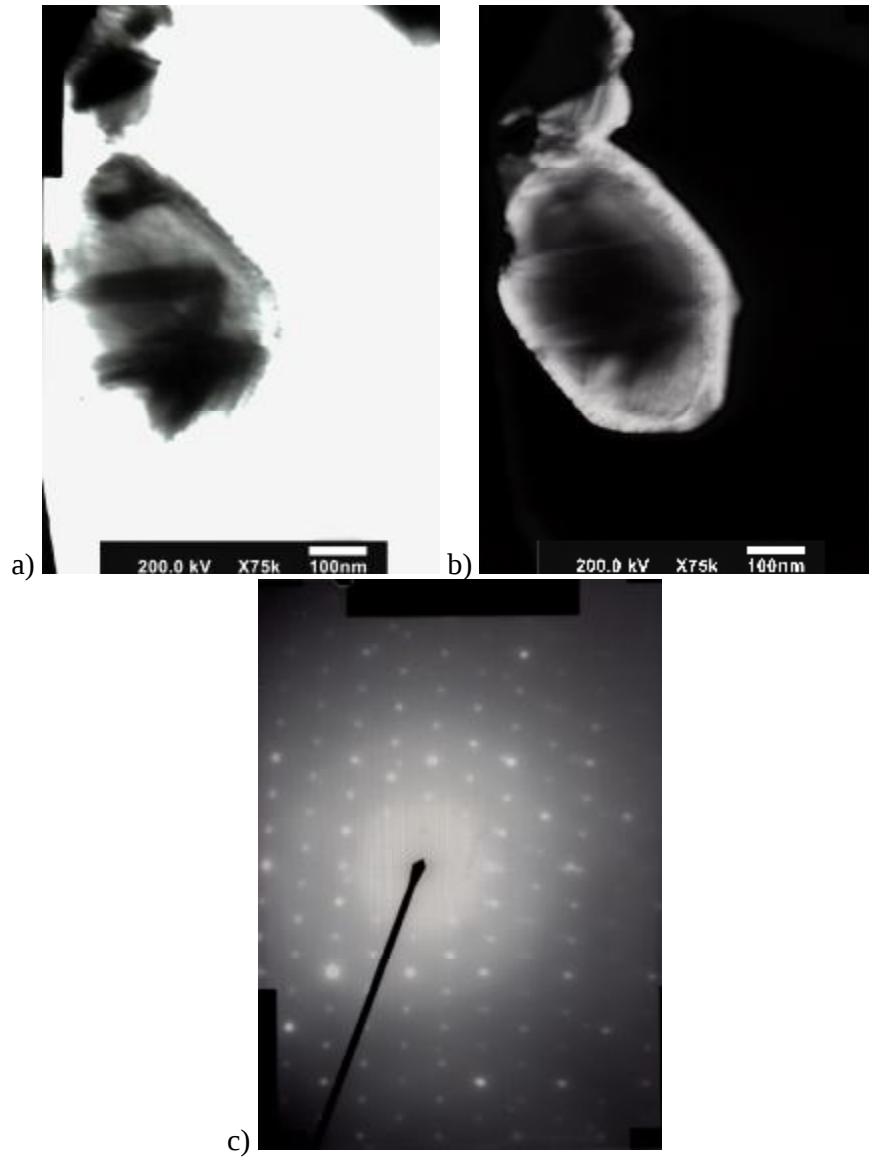


Figure 4.13 : a) Bright-field and b) dark-field electron micrograph with the objective aperture on $(\bar{2}\bar{1}\bar{1})$ showing sphereoidal triclinic Ti_4O_7 grains and c) corresponding selected-area diffraction patterns of Ti_4O_7 (ICDD, 72-4509) in the $\text{W}_2\text{TiC1Ni}$ sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length, $L = 100$ cm, Zone axis is $[23\bar{1}]$).

4.1.2.3. Density and Hardness Measurements

Relative densities were measured by using the Archimedes method and relative density results of the sintered $\text{W}_2\text{TiC1Ni}$ samples are given in Fig. 4.14. These results are the arithmetic mean of 5 successive measurements of the same sample and standard deviations. As seen in Fig. 4.14, relative density values vary between 88 and 97.5% and increase with increasing MA. Moreover, relative density value of

sintered W₂TiC1Ni sample MA'd for 3 h has very high standard deviation, which is due to its porous microstructure and uncompleted sintering (Fig. 4.5a).

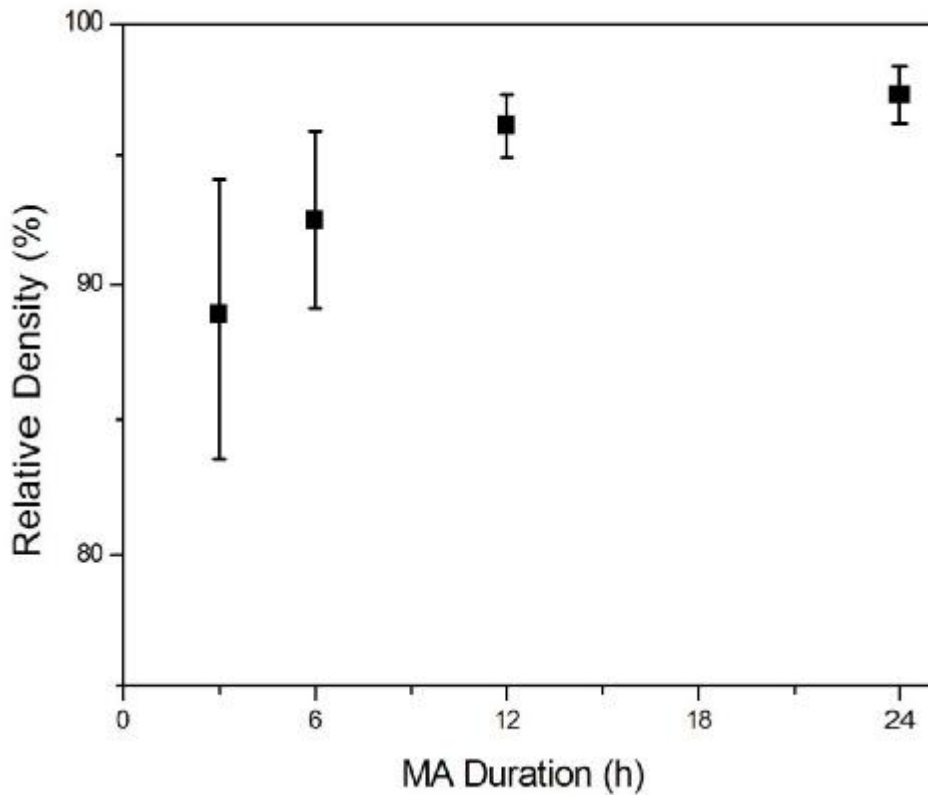


Figure 4.14 : Relative density values of the sintered W₂TiC1Ni composites MA'd for 3 h, 6 h, 12 h and 24 h.

Vickers microhardness results of sintered W₂TiC1Ni samples are given in Fig. 4.15. These microhardness test results for each sample are the arithmetic mean of 10 successive indentations and standard deviations. As seen in Fig. 4.15, microhardness values are between 5 and 5.6 GPa. Sintered W₂TiC1Ni sample MA'd for 3 h has a relatively high microhardness value of 5.4 GPa, this high value can be attributed to formation of new oxide and intermetallic phases (Fig. 4.4a). Sample MA'd for 6 h unexpectedly have higher hardness value (with higher standard deviation) from the sample MA'd for 12 h. Microstructures of these samples (Figures 4.5b and 4.5c, respectively) can give an idea about these microhardness results. As seen in Fig. 4.5b, sintered W₂TiC1Ni sample MA'd for 6 h, has better TiC distributions than the sample MA'd for 12 h (Fig. 4.5b). Moreover, it seems sample MA'd for 6 h has some cracks in microstructure.

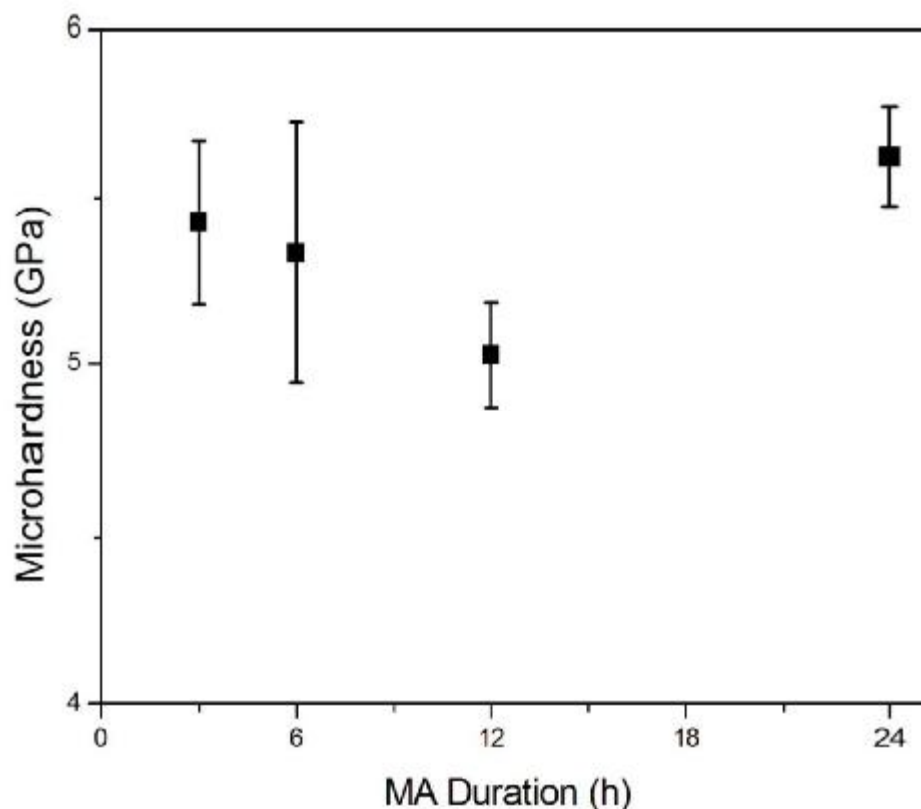


Figure 4.15 : Vickers microhardness values of the sintered W₂TiC₁Ni composites MA'd for 3 h, 6 h, 12 h and 24 h.

4.1.3. Conclusions

On the basis of the results of the present investigations, the following conclusions can be drawn:

- 1) XRD patterns of the as-blended and MA'd W₂TiC₁Ni powders revealed peaks belonging to the matrix W and Ni phases. Except the WC phase in the samples MA'd for 12 h and 24 h, there is no evidence of any intermetallic phase formation between W, TiC, C and Ni in the MA'd powders. Both average grain sizes and particle sizes of the MA'd W₂TiC₁Ni powders decrease with increasing MA duration. Minimum average grain size and particle sizes are achieved for the W₂TiC₁Ni powders MA'd for 24 h and these are 9 nm and 160 nm, respectively.
- 2) Due to Ni-activated sintering, MA'd W₂TiC₁Ni powders were sintered at a very low temperature of 1400°C. Relative density values varied between 88 and 97.5% and increased with increasing MA duration. Vickers microhardness values varied

between 5 and 5.6 GPa, where the highest value achieved in sintered W₂TiC₁Ni sample MA'd for 24 h.

3) XRD patterns of the MA'd and sintered W₂TiC₁Ni composites revealed the presence of the stable W and Ni phases and a small amount of a W phase which has a f.c.c Bravais lattice. New oxide and intermetallic phases, which thought to have detrimental effects on sintering, only formed in sintered W₂TiC₁Ni sample MA'd for 3 h.

4) SEM micrographs taken from MA'd and sintered W₂TiC₁Ni composites revealed the unefficient sintering of the sample MA'd for 3 h. TEM investigations confirmed the presence of the matrix W and Ni phases detected in the XRD patterns as well as the TiC, W₂C phases with hexagonal and orthorhombic Bravais lattice, NiTi, rutile, TiO₂ and Ti₄O₇ phases in the microstructures of the MA'd and sintered W₂TiC₁Ni composites.

4.2. Microstructural Characterizations of Ni Activated Sintered W-2wt% TiC Composites produced via Mechanical Alloying

Abstract

Blended elemental W-2 wt% TiC powders were mechanically alloyed (MA'd) for 3 h, 6 h, 12 h and 24 h in a Spex Mixer/mill at room temperature. 1 wt% Ni was added as a sintering aid after mechanical alloying to investigate the effects of MA and activated sintering. MA'd powders were sintered at 1400 °C for 1 h under Ar, H₂ gas flowing conditions. Microstructural and phase characterizations of MA'd powders and sintered samples were carried out via SEM, TEM and XRD analyses. Whereas XRD investigations on MA'd powders revealed stable W and WC phases, those on sintered samples showed the presence of a new face-centered cubic W phase and Ni in addition to the matrix W phase. TEM investigations on MA'd and sintered samples confirmed the presence of the matrix W and the f.c.c. W phase also detected in XRD patterns. TEM investigations also revealed the presence of TiC, Ni₄W and W₂C particles existing in a W-matrix. Relative density values were about 94% for all sintered composites which did not change with MA. Microhardness values of the sintered composites varied between 5.4 GPa for the 3 h MA'd sample and 6.0 GPa for the 24 h MA'd sample.

4.2.1. Characterization of Powders

XRD patterns of mechanically alloyed (MA'd) W₂TiC+1Ni powders are shown in Figures 4.16a – 4.16e. As seen in these figures, the peaks of W which has a b.c.c. Bravais lattice and $Im\bar{3}m$ space group with the lattice parameter of $a = 0.316$ nm (ICDD, 04-0806) can be identified in all samples. Additionally, the peak belonging to {111} reflections of Ni which has a f.c.c. Bravais lattice and $Fm\bar{3}m$ space group with the lattice parameter of $a = 0.352$ nm (ICDD, 65-2865) is identified in the as-blended sample (Fig. 4.16a). Peaks for TiC are not seen, probably due to its small amount (2 wt%) in the powder blend and its small particle size (2.7 μ m) compared to those of Ni (8 μ m) and W (14 μ m). Moreover, as seen in Figures 4.16c and 4.16d for samples MA'd for 6 h and 12 h, the presence of WC phase which has a hexagonal Bravais lattice and $P\bar{6}m2$ space group with the lattice parameters of $a = 0.290$ nm and $c = 0.283$ nm (ICDD, 51-0339) can be detected due to contamination during MA.

However, WC peaks can not be observed in the W₂TiC+1Ni powders MA'd for 24 h, probably due to peak broadening, which caused WC peaks to disappear in the background. Thus, it is clear that with increasing MA, peaks are broadened and peak heights are decreased, as a result of grain refinement and due to internal strain buildup during MA. Average grain size of the matrix W phase in the as-blended and MA'd W₂TiC+1Ni powders was calculated from Figures 4.16a – 4.16e using TOPAS 3 (Bruker AXS) software (Kern and Coelho, 2006) which decreased with increasing MA durations. Whereas the as-blended W₂TiC+1Ni powders have a W grain size of 219 nm, those MA'd for 3 h, 6 h, 12 h and 24 h have average W grain sizes of 47.8 nm, 21.1 nm, 10 nm and 5.2 nm, respectively.

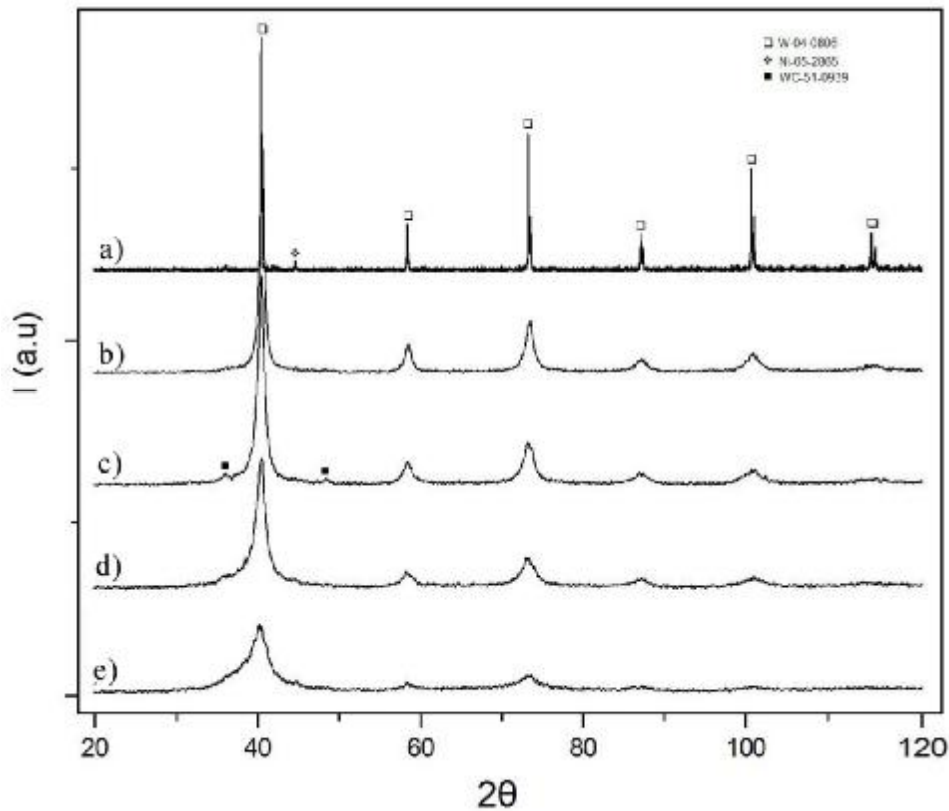


Figure 4.16 : XRD patterns of W₂TiC+1Ni powders: **a)** as-blended, **b)** MA'd for 3 h, **c)** MA'd for 6 h, **d)** MA'd for 12 h and **e)** MA'd for 24 h.

Figures 4.17a and 4.17b are SEM micrographs taken from as-blended W₂TiC+1Ni powders and from powders those MA'd for 24 h, respectively. Fig. 4.17c is a bright-field TEM micrograph of powders MA'd for 24 h. As seen in Figures 4.17a – 4.17c, microscale as-blended powders have diameters in nanoscale after MA. Moreover, TiC and Ni powders distributed homogeneously in W matrix after MA. Local

agglomerations which are clearly seen in Fig. 4.17b, occur due to small particle size distributions of MA'd powders. Fig. 4.17c shows the equiaxed shaped particles varying in size between 100 and 150 nm.

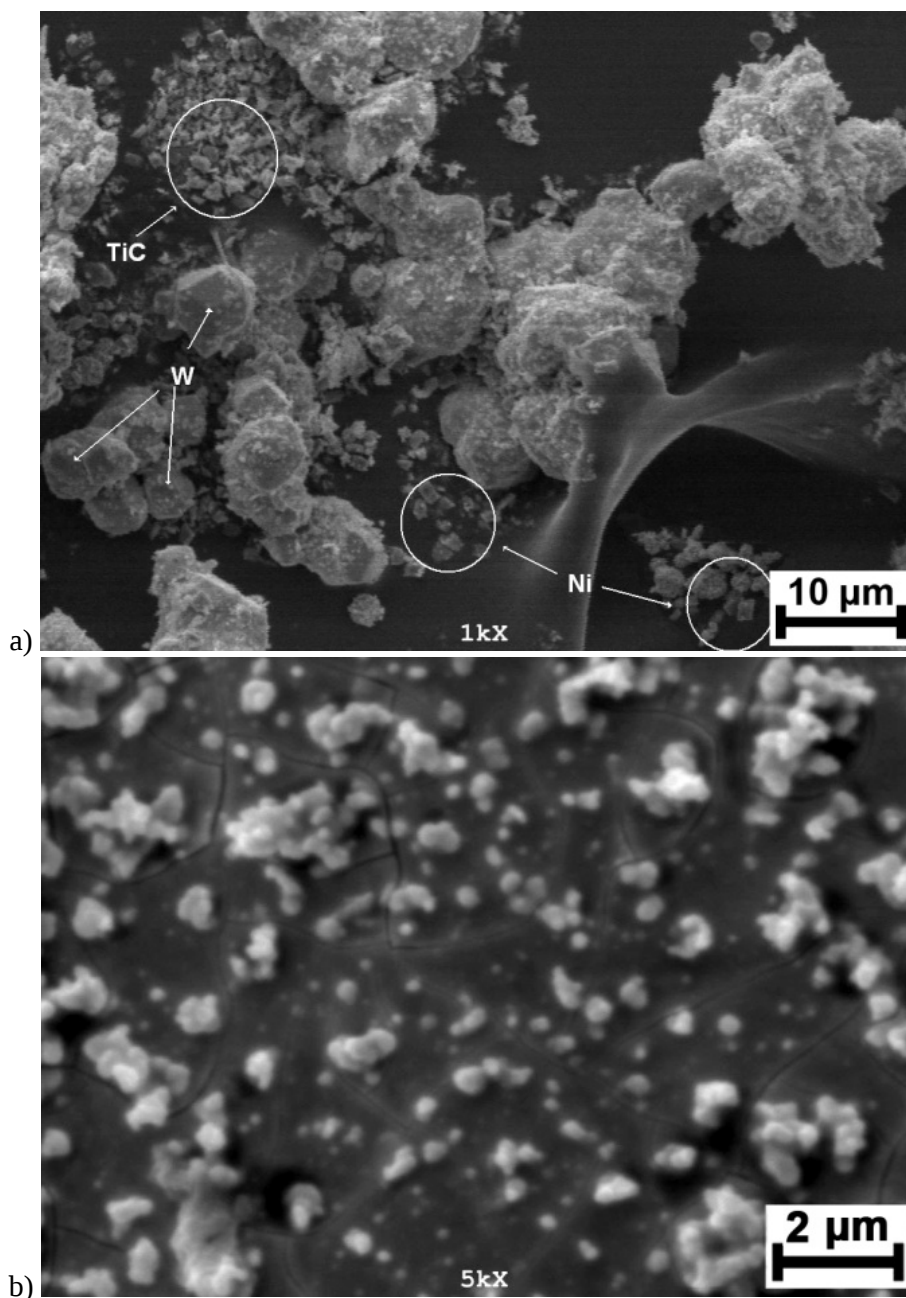


Figure 4.17 : Electron micrographs of as-blended and MA'd $W_2TiC+1Ni$ powders. Representative SEM micrographs of: **a)** as-blended powders and **b)** those MA'd for 24 h. **c)** Bright-field (BF) TEM micrograph of powders MA'd for 24 h.

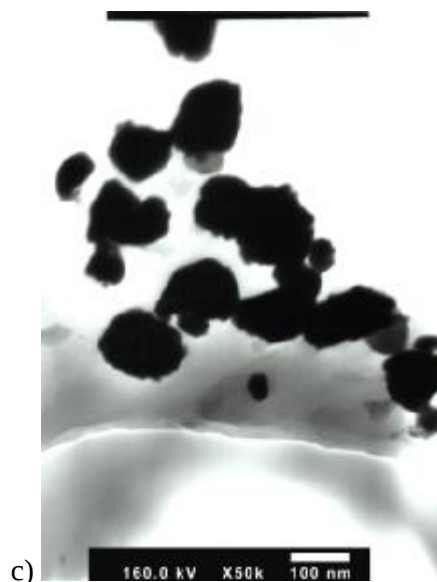


Figure 4.17 : Electron micrographs of as-blended and MA'd W₂TiC+1Ni powders. Representative SEM micrographs of: **a)** as-blended powders and **b)** those MA'd for 24 h. **c)** Bright-field (BF) TEM micrograph of powders MA'd for 24 h (**continued**).

Figures 4.18a – 4.18d are particle size distributions of as-blended W₂TiC+1Ni powders and those MA'd for 3 h, 12 h and 24 h, respectively. As-blended W₂TiC+1Ni powders have an average particle size of 33 μm (Fig. 4.18a), suggesting that agglomeration has taken place between the starting powders W (14 μm), Ni (8 μm) and TiC (2.7 μm). As seen in Figures 4.18b, 4.18c and 4.18d, drastic reductions in particle sizes are achieved with MA. Agglomeration peaks in Figures 4.18b – 4.18c can be attributed to addition of ductile Ni phase after MA of W – 2 wt% TiC. An average particle size of 1.4 μm is measured for the powder MA'd for 3 h (Fig. 4.18b). W₂TiC+1Ni powders have the final particle size distributions of 234 nm and 225 nm after MA for 12 h and 24 h, respectively. Furthermore, with increasing MA duration, specific surface area of the powders which is less than 1 m^2/g for as-blended W₂TiC+1Ni powders increases with MA and has the value of 36.5 m^2/g for the W₂TiC+1Ni powders MA'd for 24 h.

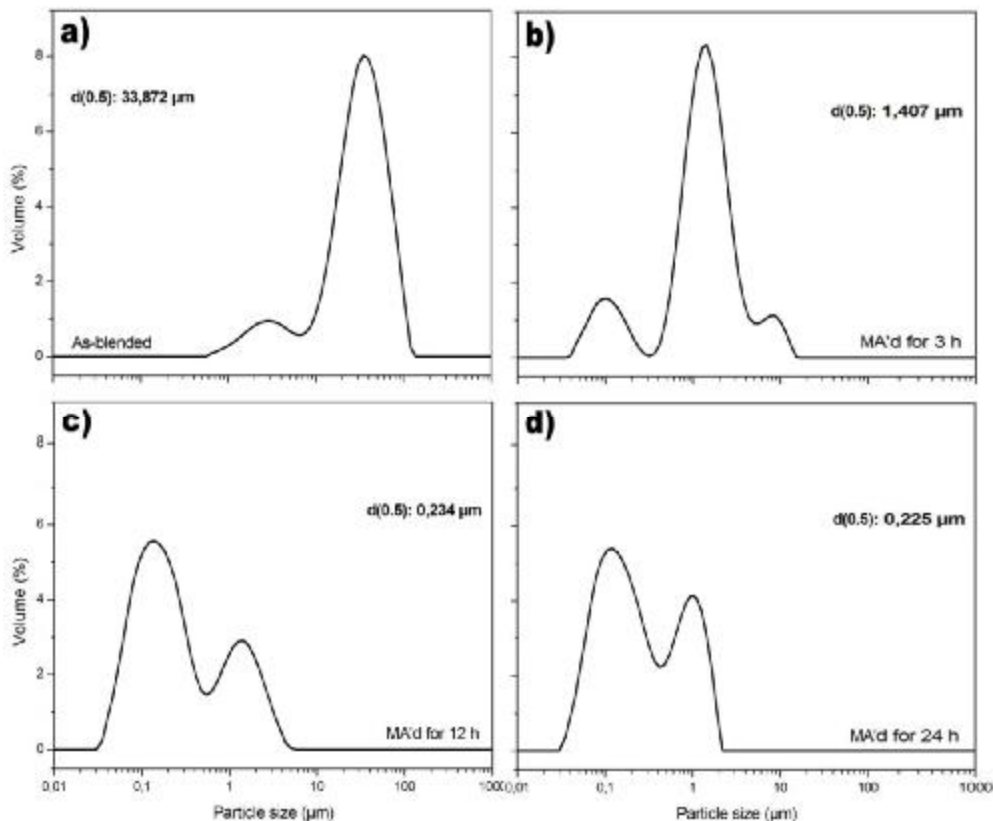


Figure 4.18 : Particle size distributions of **a)** as-blended W₂TiC+1Ni powders and those MA'd for: **b)** 3 h, **c)** 12 h, **d)** 24 h.

As explained in the Experimental Procedures, there are no pressed and sintered compacts prepared from as-blended powders used in this study. Relative green density values of the consolidated powders are 64%, 64.5%, 59% and 57% for MA for 3 h, 6 h, 12 h and 24 h, respectively. Green density values have tendency of decreasing with increasing MA duration.

4.2.2. Characterization of Sintered Samples

4.2.2.1. XRD and SEM Investigations

XRD patterns of W₂TiC+1Ni powders sintered at 1400 °C under both inert Ar and reducing H₂ gas flowing conditions for 1 h are shown in Figures 4.19a – 4.19d. As clearly seen in Figures 4.19a – 4.19d, stable b.c.c. W and f.c.c. Ni phases are identified in all sintered samples. Moreover, a second W phase which has a f.c.c. Bravais lattice with $Fm\bar{3}m$ space group and lattice parameter of $a = 4.06$ nm (ICDD,

88-2339) is present in all MA'd W₂TiC+1Ni samples and its major (111) peak is shown as an inset figure in Fig. 4.19.

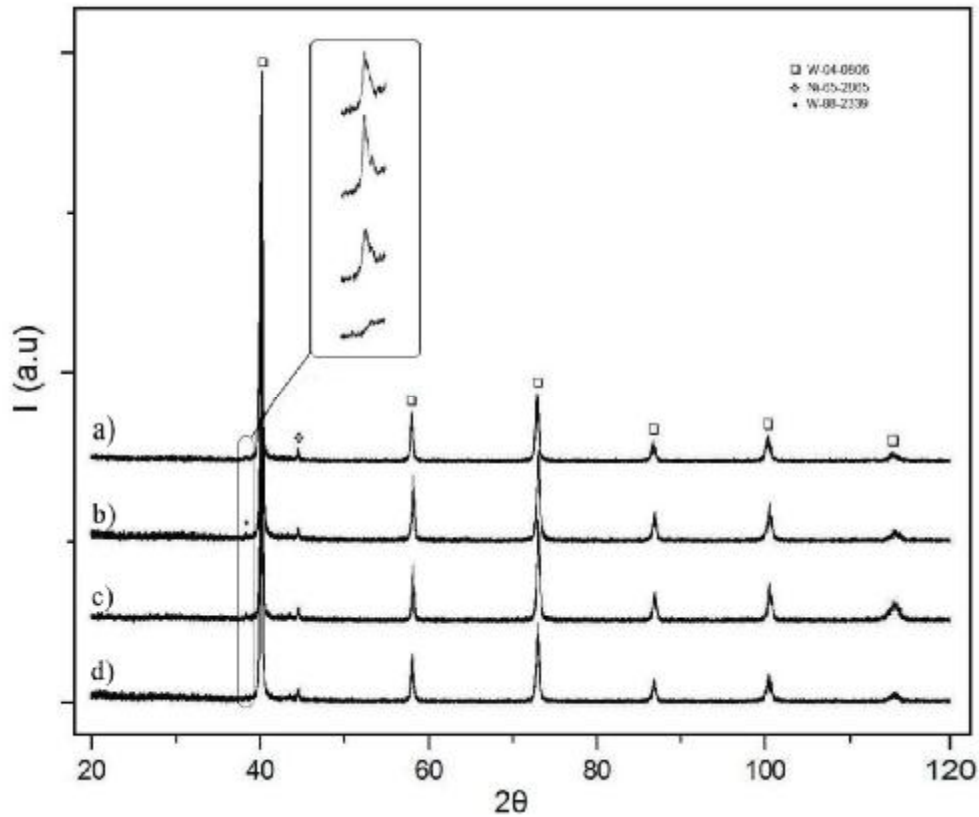


Figure 4.19 : XRD patterns of the sintered W₂TiC+1Ni samples which were **a)** MA'd for 3 h, **b)** MA'd for 6 h, **c)** MA'd for 12 h and **d)** MA'd for 24 h.

SEM micrographs taken from MA'd W₂TiC+1Ni samples revealed similar features in all sintered microstructures and almost no porosity. Fig. 4.20 is a representative SEM micrograph taken from sintered W₂TiC+1Ni sample MA'd for 12 h, showing three distinct regions indexed as A, B and C in the microstructure. Since chemical etching (Murakami and H₂O₂) was ineffective, grain boundaries of the matrix W can not be observed. However, EDS spectra taken from different locations have shown that regions indexed as A contained 84.41 ± 2.15 wt% W, 2 ± 1.12 wt% Ti, 13.04 ± 1.38 wt% C and 0.55 ± 0.54 wt% Ni, indicating that these regions are W matrix. EDS spectra taken from porous like gray grains (indexed as B) have shown that grains comprised 50.92 ± 11.04 wt% W, 0.95 ± 0.38 wt% Ti, 17.29 ± 2.75 wt% C and 30.78 ± 8.9 wt% Ni, inferring that these are Ni-rich grains surrounded by W matrix. In addition, black dots (indexed as C) varying in size between 0.1 μ m and 1 μ m are

also present in the microstructure. EDS spectra taken from these black dots revealed that they contained 36.38 ± 14.8 wt% W, 48.91 ± 15.32 wt% Ti, 13.77 ± 5.59 wt% C and 0.95 ± 1.22 wt% Ni. These EDS spectra results with almost equal content of W and Ti with high standard deviations indicate that black dots in the microstructure are TiC and/or WC particles.

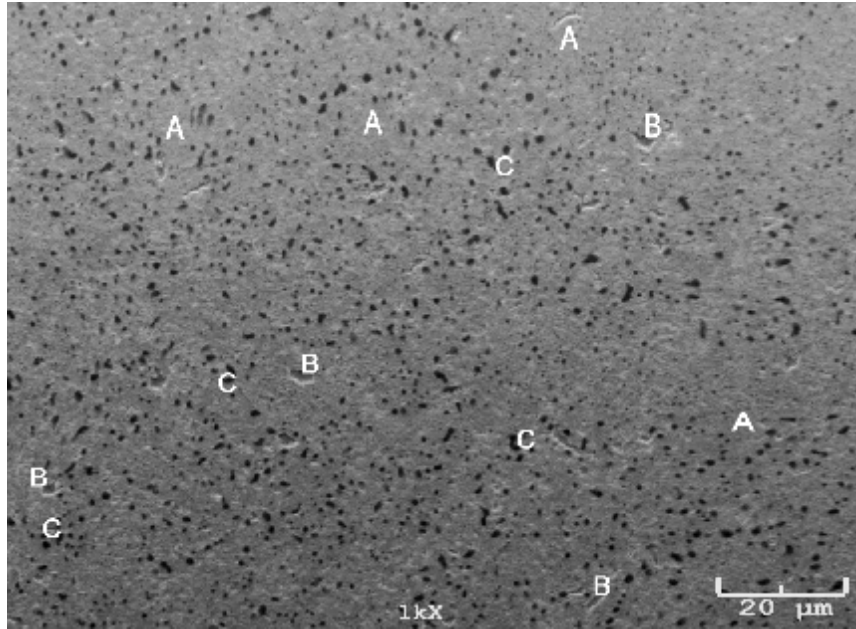


Figure 4.20 : Representative SEM micrograph taken from the W₂TiC+1Ni sample MA'd for 12 h and sintered at 1400 °C for 1 h.

Table 4.1: EDS spectra analysis

Region/ Elements	W	Ti	C	Ni
Region A	84.41 ± 2.15 wt%	2 ± 1.12 wt%	13.04 ± 1.38 wt%	0.55 ± 0.54 wt%
Region B	50.92 ± 11.04 wt%	0.95 ± 0.38 wt%	17.29 ± 2.75 wt%	30.78 ± 8.9 wt%
Region C	36.38 ± 14.8 wt%	48.91 ± 15.32 wt%	13.77 ± 5.59 wt%	0.95 ± 1.22 wt%

4.2.2.2. TEM Investigations

Figures 4.21a and 4.21b are bright-field and dark-field TEM micrographs taken from the sintered W₂TiC+1Ni sample MA'd for 24 h showing spheroidal grains (100 – 200 nm in size). A selected electron diffraction pattern (SADP) taken from the grain upper left of Fig. 4.21a is shown in Fig. 4.21c. Based on Figures 4.21b and 4.21c, these spheroidal grains are unambiguously identified as being composed of the matrix b.c.c. W (ICDD, 04-0806) phase. It is clear that sintering led to considerable grain growth from a 5 nm mean W grain size of the powders MA'd for 24 h to about 100 – 200 nm after sintering at 1400 °C for 1 h.

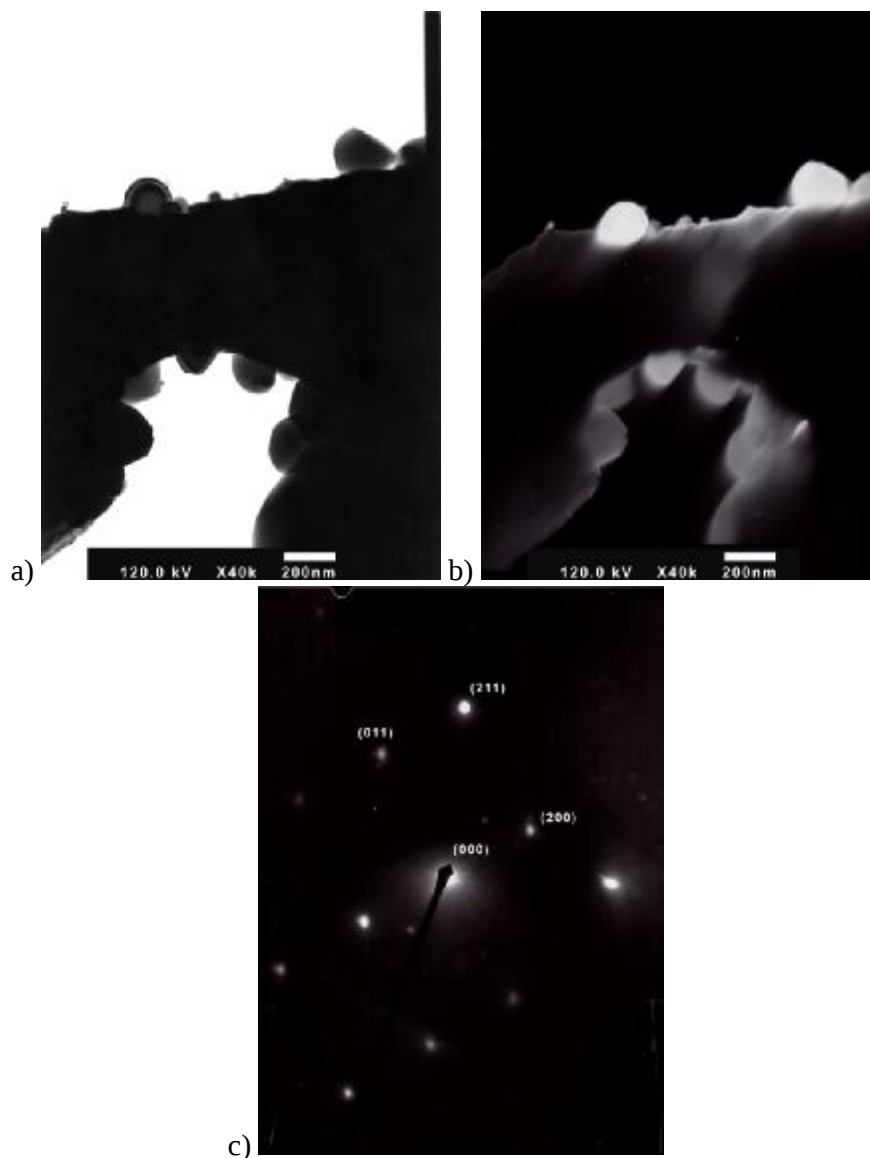


Figure 4.21 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(\bar{2} \bar{1} \bar{1})$ showing sphereoidal b. c. c. W grains and **c)** corresponding selected-area diffraction patterns of W (ICDD, 04-0806) in the W₂TiC+1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. (Camera length, L = 100 cm, Zone axis is $[0\bar{1}1]$).

Figures 4.22a and 4.22b are a pair of bright- and dark-field TEM micrographs taken from the sintered W₂TiC+1Ni sample MA'd for 24 h showing a rectangular-shaped region (indexed as A). An electron diffraction pattern from this rectangular region is shown in Fig. 4.21c. This region is unambiguously identified as the f.c.c. W which is also observed in the XRD pattern shown in Fig. 4.19 (ICDD, 88-2339). Thus, the existence of the fcc W phase which otherwise was reported in International Centre

for Diffraction Data (ICDD) as a calculated phase is confirmed by the TEM investigations of the present study (ICDD, 88-2339).

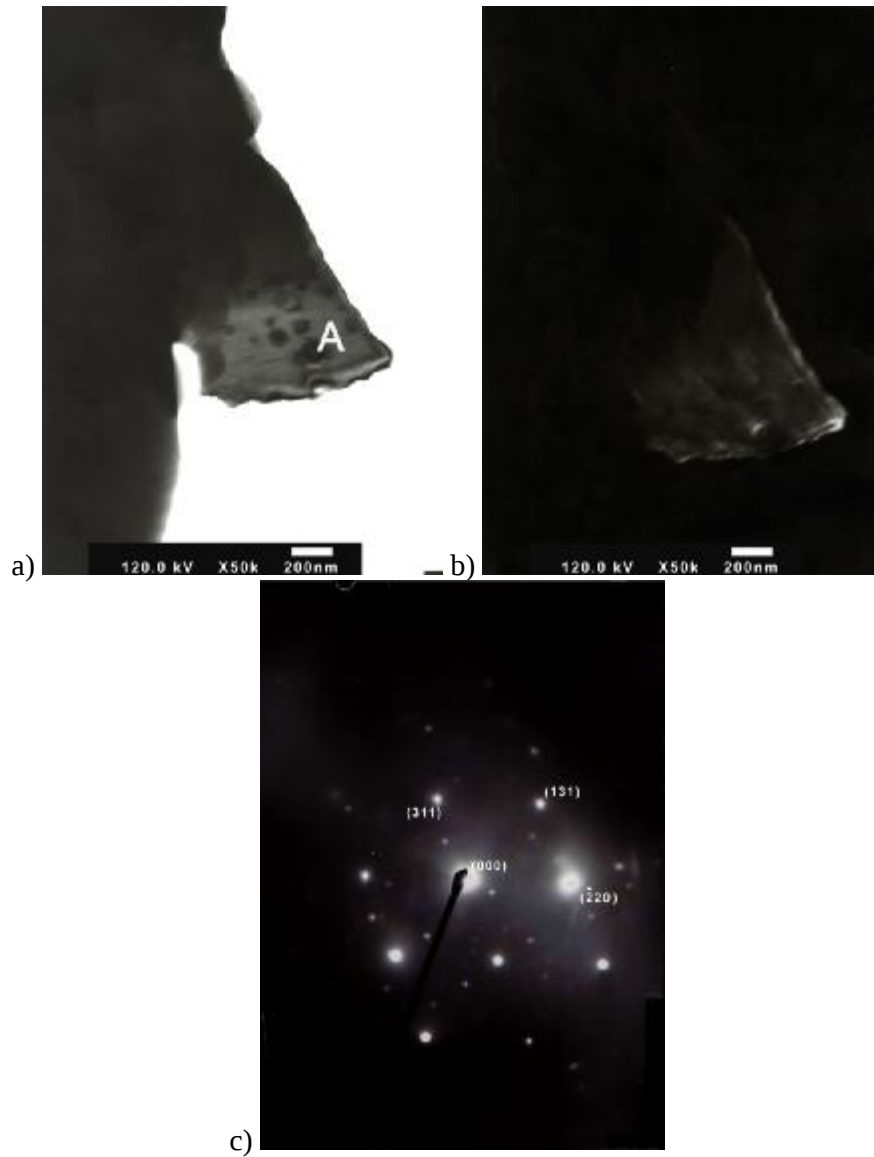


Figure 4.22 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(\bar{1}\bar{3}\bar{1})$ showing rectangular shaped (labeled as A) f. c. c. W grain (ICDD, 88-2339) in the W₂TiC+1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. **c)** Corresponding selected-area diffraction pattern. (Camera length, L= 60 cm; Zone axis is $[11\bar{4}]$).

Figures 4.23a and 4.23b are bright-field and dark-field TEM micrographs taken from spheroidal grains in the W₂TiC+1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h, respectively. Corresponding electron diffraction pattern from the spherical grain upper right of Fig. 4.23a is shown in Fig. 4.23c suggests that it is composed of

TiC with a face centered cubic Bravais lattice and with a lattice parameter of $a = 0.431$ nm (ICDD, 71-6256). Further, as clearly seen in Figures 4.23a and 4.23b, TiC particles which are not detected in the XRD patterns due to small amount (2 wt%) are distributed in the W matrix with diameters of 100 nm or smaller.

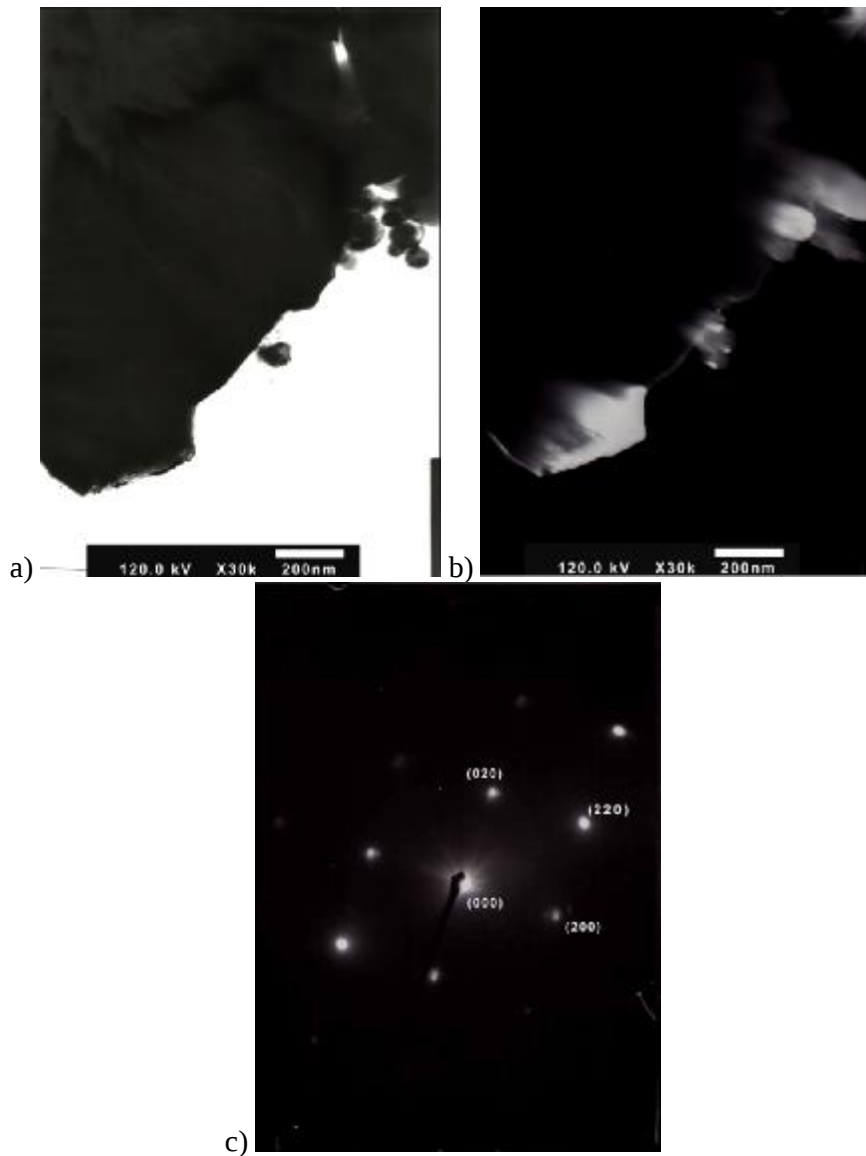


Figure 4.23 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(\bar{2} \bar{2} 0)$ showing several spherical-shaped TiC grains (ICDD, 71-6256) in the W₂TiC+1Ni sample MA'd for 24 h and sintered at 1400 °C for 1 h. **c)** Corresponding selected-area diffraction pattern. (Camera length, $L = 100$ cm; Zone axis is $[001]$).

Figures 4.24a and 4.24b are bright-field and dark-field TEM micrographs taken from the sintered W₂TiC+1Ni sample MA'd for 24 h showing spherical grains between 150 and 200 nm in size. Corresponding electron diffraction pattern from the lower

spherical grain at Fig. 4.24a is shown in Fig. 4.24c. These spherical particles are unambiguously identified as being composed of Ni_4W with a body centered tetragonal Bravais lattice and with lattice parameters of $a = 0.573 \text{ nm}$ and $c = 0.355 \text{ nm}$ (ICDD, 65-2673).

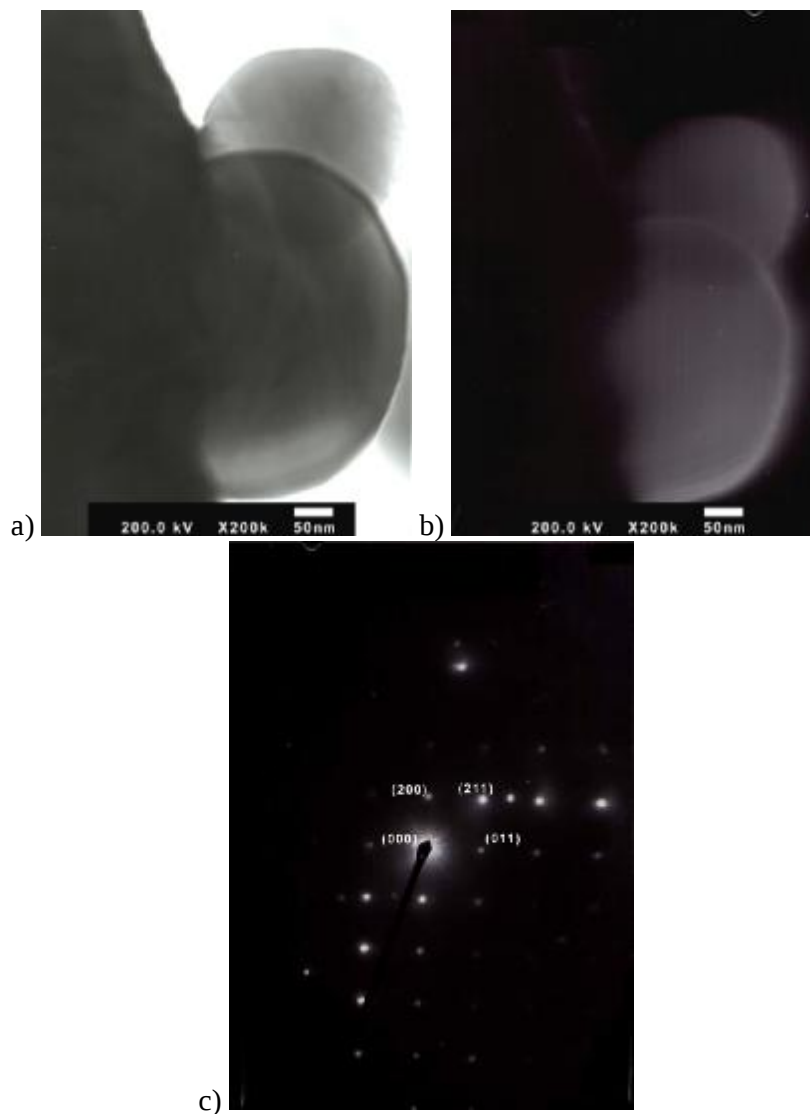


Figure 4.24 : a) Bright-field micrograph and b) dark-field electron micrograph with the objective aperture on $(\bar{2}\bar{1}1)$ showing spherical-shaped b. c. t. Ni_4W (ICDD, 65-2673) grains in the $\text{W}_2\text{TiC}+1\text{Ni}$ sample MA'd for 24 h and sintered at 1400°C for 1 h. c) Corresponding selected-area diffraction pattern. (Camera length: 100 cm; Zone axis: $[01\bar{1}]$).

Figures 4.25a and 4.25b are bright-field and-dark field TEM micrographs taken from the sintered $\text{W}_2\text{TiC}+1\text{Ni}$ sample MA'd for 24 h showing spheroidal shaped grains varying in size between 40 and 90 nm. Corresponding electron diffraction pattern from the spheroidal grains at the lower right of Fig. 4.25a is shown in Fig. 4.25c,

suggests that these grains are W_2C phase having a hexagonal Bravais lattice and with the lattice parameters $a = 0.519$ nm and $c = 0.472$ nm (ICDD, 79-0743).

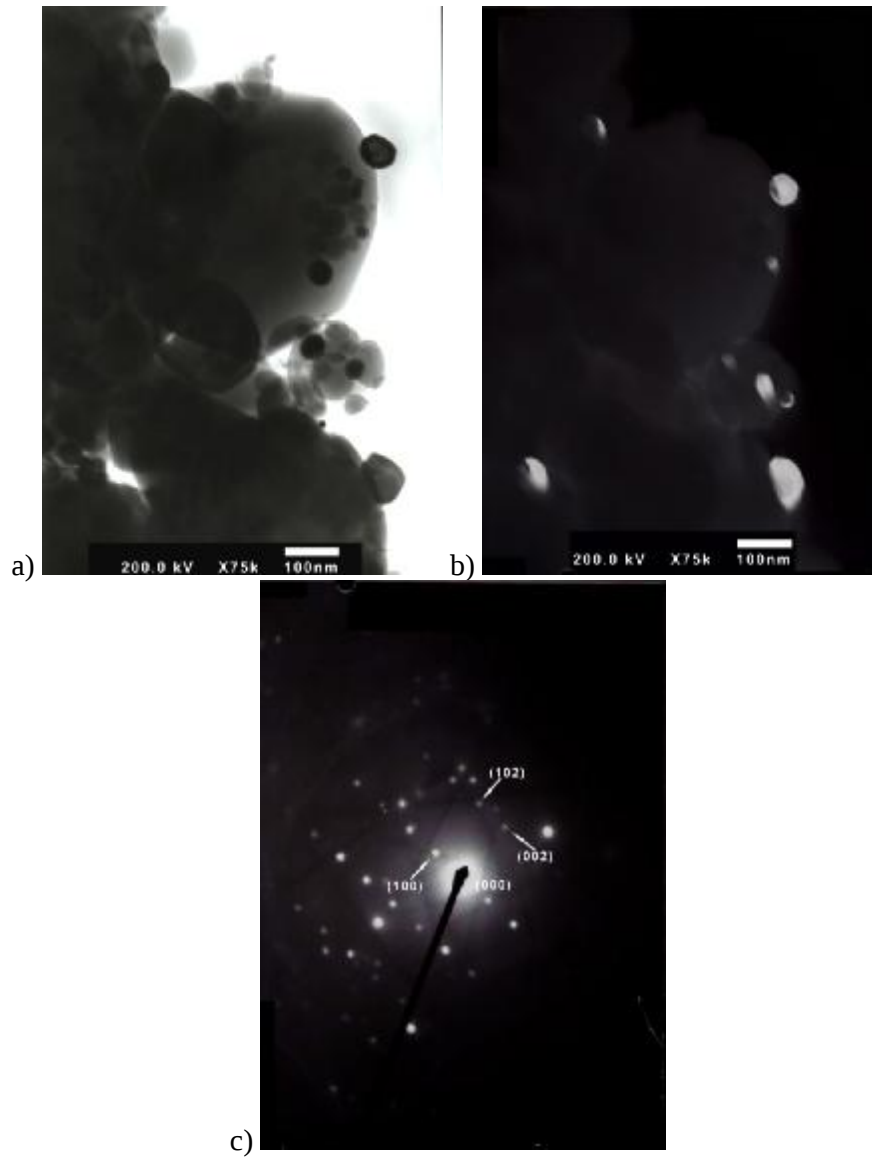


Figure 4.25 : **a)** Bright-field micrograph and **b)** dark-field electron micrograph with the objective aperture on $(10\bar{2})$ showing spheroidal-shaped hexagonal W_2C (ICDD, 79-0743) particles in the $W_2TiC+1Ni$ sample MA'd for 24 h and sintered at 1400 °C for 1 h. **c)** Corresponding selected-area diffraction pattern. (Camera length: 100 cm; Zone axis: $[01\bar{1}0]$).

4.2.2.3. Density and Hardness Measurements

Relative densities were measured by using the Archimedes method and relative density results of the sintered W2TiC+1Ni samples are given in Fig. 4.26. These results are the arithmetic mean of 5 successive measurements of the same sample and standard deviations. As seen in Fig. 4.26, relative densities are about 94.2 % for all the sintered W2TiC+1Ni. Moreover, relative density results of all the samples have almost the same standard deviation values which is about ± 0.9 %.

Vickers microhardness results of sintered W2TiC+1Ni samples are given in Fig. 4.27. These microhardness test results for each sample are the arithmetic mean of 10 successive indentations and standard deviations. As seen in Fig. 4.27, microhardness values are between 5.4 GPa and 6.0 GPa and they increase with increasing MA duration for all W2TiC+1Ni samples. Since all sintered samples have the same relative densities about 94%, this increase can be attributed to grain refinement during MA. Vickers microhardness values of the W2TiC+1Ni samples MA'd for 3 h, 6 h and 24 h have the standard deviations about $\pm 0.15 - 0.2$ GPa where the sample MA'd for 12 h has the highest standard deviation with a value of ± 0.26 GPa.

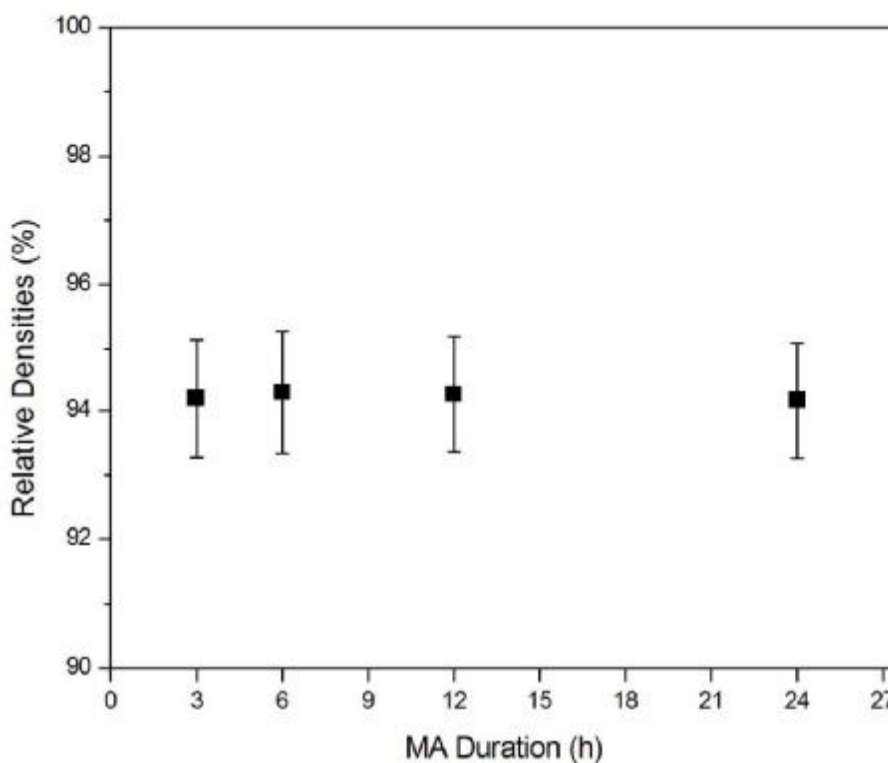


Figure 4.26 : Relative density values of the sintered W2TiC + 1Ni composites MA'd for 3 h, 6 h, 12 h and 24 h.

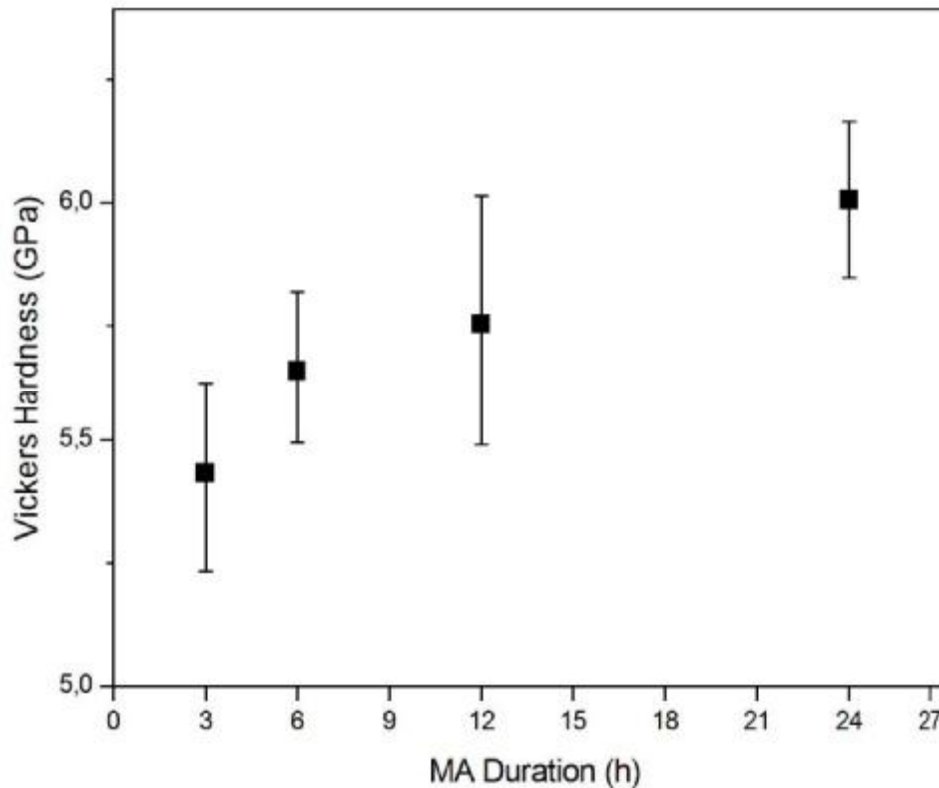


Figure 4.27 : Vickers microhardness values of the sintered W₂TiC + 1Ni composites MA'd for 3 h, 6 h, 12 h and 24 h.

4.2.3. Conclusions

On the basis of the results of the present investigations, the following conclusions can be drawn:

1) XRD patterns of the as-blended and MA'd W₂TiC+1Ni powders revealed peaks belonging to the matrix W and Ni phases. Except the WC phase in the samples MA'd for 6 h, there is no evidence of any intermetallic phase formation between W, TiC, C and Ni in the MA'd powders. Both average grain sizes and particle sizes of the MA'd W₂TiC+1Ni powders decrease with increasing MA duration. Minimum average grain size and particle sizes are achieved for the W₂TiC+1Ni powders MA'd for 24 h and these are 5 nm and 225 nm, respectively.

2) Due to Ni-activated sintering, MA'd W₂TiC+1Ni powders were sintered at a very low temperature of 1400°C. Whereas all MA'd and sintered compacts have the same relative sinter density of 94%, their microhardness values vary between 5.42 GPa and 6.00 GPa.

3) XRD patterns of the MA'd and sintered W₂TiC+1Ni composites revealed the presence of the stable W and Ni phases and a small amount of a W phase which has a f.c.c Bravais lattice. SEM micrographs taken from MA'd and sintered W₂TiC+1Ni composites revealed similar microstructural features with no porosity in the sintered microstructures. TEM investigations confirmed the presence of the matrix W and the f.c.c. W phases detected in the XRD patterns as well as the TiC, Ni₄W and W₂C phases in the microstructures of the MA'd and sintered W₂TiC+1Ni composites.

4.3. Characterization Investigations TiC Dispersion Strengthened W-Ni Composites produced via Mechanical Alloying

Abstract

Blended elemental W-1 wt% Ni powders were mechanically alloyed (MA'd) for 3 h, 6 h, 12 h and 24 h in a Spex Mixer/mill at room temperature to investigate the effects of MA and activated sintering. 2 wt% TiC was added as reinforcement after mechanical alloying. MA'd powders were sintered at 1400 °C for 1 h under Ar, H₂ gas flowing conditions. Microstructural and phase characterizations of MA'd powders and sintered samples were carried out via SEM and XRD analyses. Whereas XRD investigations on MA'd powders revealed stable W and WC phases, those on sintered samples showed the presence of a new face-centered cubic W phase and Ni in addition to the matrix W phase. Relative density values varied between 94 and 98.5% and increased with increasing MA duration. Microhardness values of the sintered composites varied between 4.8 GPa for the 3 h MA'd sample and 5.1 GPa for the 24 h MA'd sample.

4.3.1. Characterization of Powders

XRD patterns of mechanically alloyed (MA'd) W₁Ni₂TiC powders are shown in Figures 4.28a – 4.28e. As seen in these figures, the peaks of W which has a b.c.c. Bravais lattice and $\text{Im}\bar{3}\text{m}$ space group with the lattice parameter of $a = 0.316$ nm (ICDD, 04-0806) can be identified in all samples. Additionally, the peak belonging to {111} reflections of Ni which has a f.c.c. Bravais lattice and $\text{Fm}\bar{3}\text{m}$ space group with the lattice parameter of $a = 0.352$ nm (ICDD, 65-2865) is identified in the as-blended sample (Fig. 4.28a). Peaks for TiC are not seen, probably due to its small amount (2 wt%) in the powder blend and its small particle size (2.7 μm) compared to those of Ni (8 μm) and W (14 μm). Moreover, as seen in Figures 4.28b – 4.28d for samples MA'd for 3 h, 6 h and 12 h, the presence of WC phase which has a hexagonal Bravais lattice and $\text{P}\bar{6}\text{m}2$ space group with the lattice parameters of $a = 0.290$ nm and $c = 0.283$ nm (ICDD, 51-0339) can be detected due to contamination during MA. However, WC peaks can not be observed in the W₂TiC+1Ni powders MA'd for 24 h, probably due to peak broadening, which caused WC peaks to disappear in the background. Thus, it is clear that with increasing MA, peaks are

broadened and peak heights are decreased, as a result of grain refinement and due to internal strain buildup during MA. Average grain size of the matrix W phase in the as-blended and MA'd W2TiC+1Ni powders was calculated from Figures 4.28a – 4.28e using TOPAS 3 (Bruker AXS) software (Kern and Coelho, 2006) which decreased with increasing MA durations. Whereas the as-blended W1Ni+2TiC powders have a W grain size of 219 nm, those MA'd for 3 h, 6 h, 12 h and 24 h have average W grain sizes of 74.8 nm, 31.8 nm, 12.5 nm and 8.1 nm, respectively.

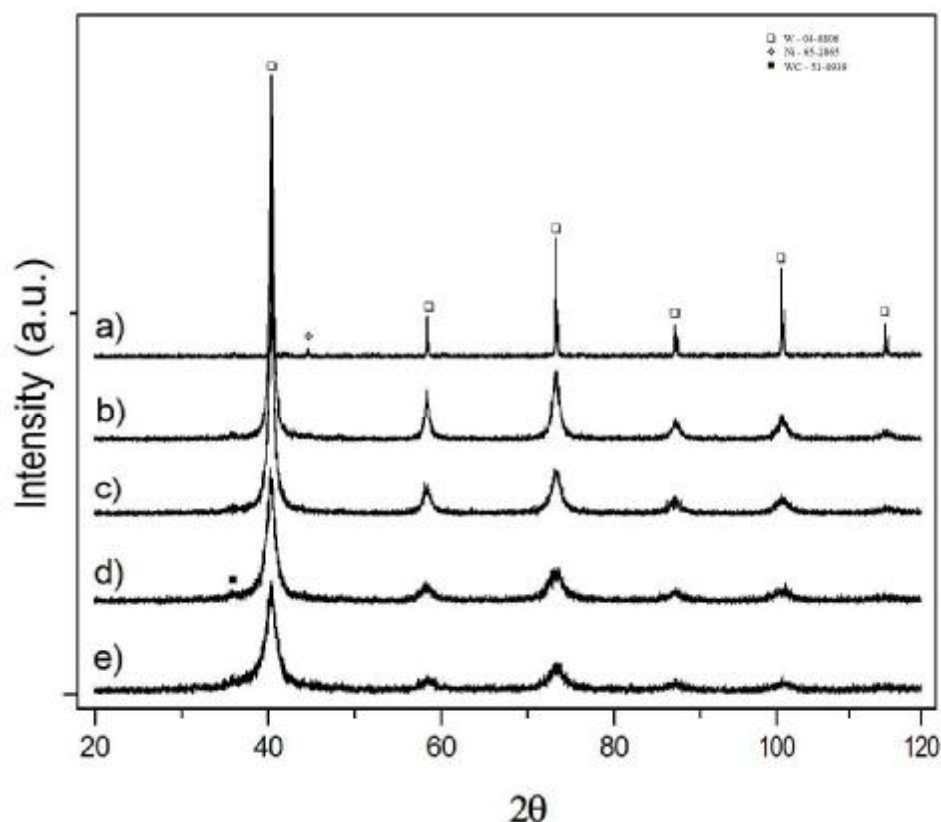


Figure 4.28 : XRD patterns of W1Ni+2TiC powders: **a)** as-blended, **b)** MA'd for 3 h, **c)** MA'd for 6 h, **d)** MA'd for 12 h and **e)** MA'd for 24 h.

Figures 4.29a and 4.29b are SEM micrographs taken from as-blended W1Ni+2TiC powders and from powders those MA'd for 24 h, respectively. As seen in Figures 4.29a and 4.29b, microscale as-blended powders have diameters in nanoscale after MA. Moreover, TiC and Ni powders distributed homogeneously in W matrix after MA. Local agglomerations which are clearly seen in Fig. 4.29b, occur due to small particle size distributions of MA'd powders.

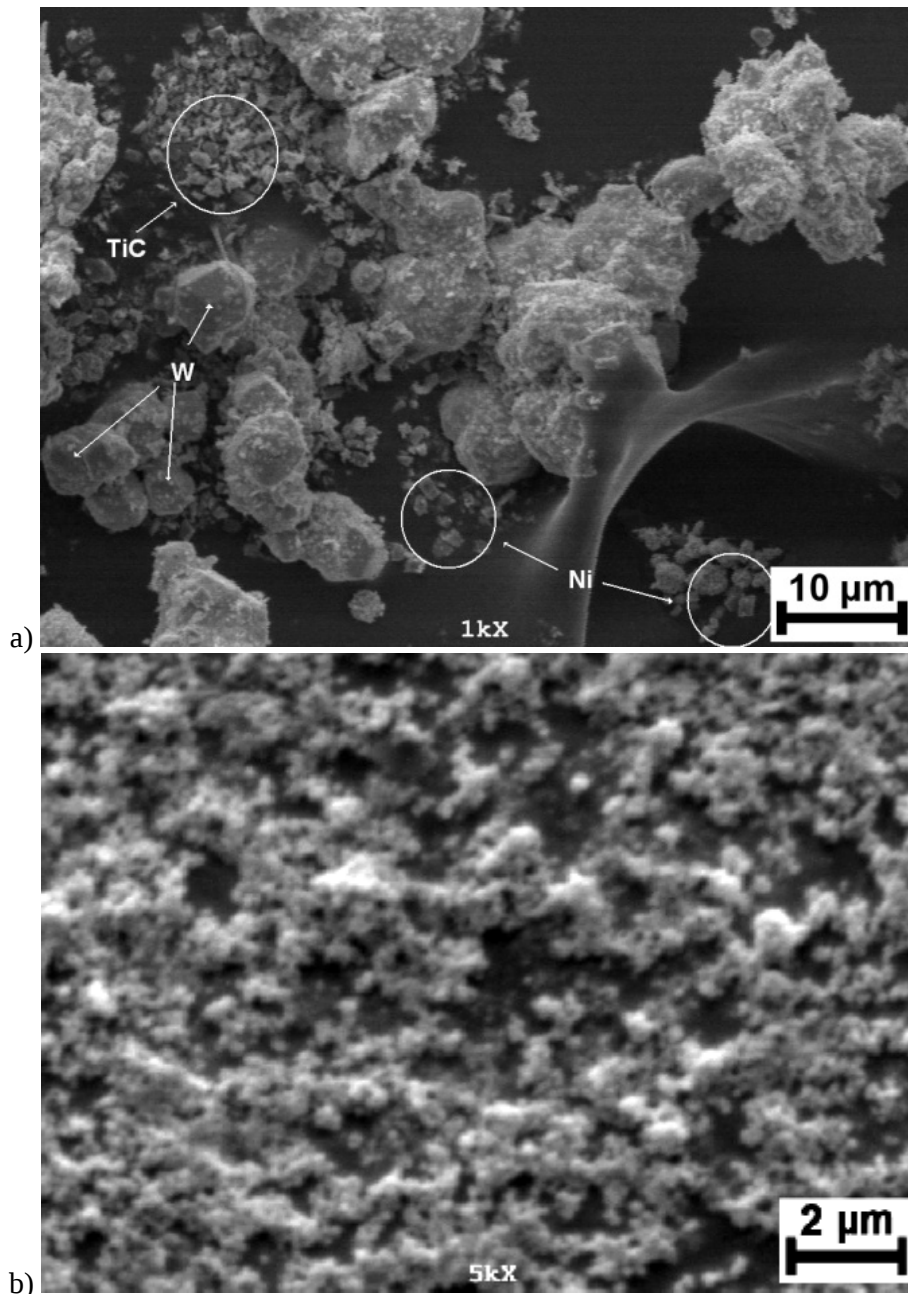


Figure 4.29 : Electron micrographs of as-blended and MA'd W₂TiC+1Ni powders. Representative SEM micrographs of: **a)** as-blended powders and **b)** those MA'd for 24 h.

Figures 4.30a – 4.30d are particle size distributions of as-blended W₁Ni+2TiC powders and those MA'd for 3 h, 6 h and 24 h, respectively. As-blended W₁Ni+2TiC powders have an average particle size of 33 µm (Fig. 4.30a), suggesting that agglomeration has taken place between the starting powders W (14 µm), Ni (8 µm) and TiC (2.7 µm). As seen in Figures 4.30b, 4.30c and 4.30d, drastic reductions in particle sizes are achieved with MA. W₁Ni+2TiC powders have the final particle

size distributions of 177 nm and 121 nm after MA for 6 h and 24 h, respectively. Furthermore, with increasing MA duration, specific surface area of the powders which is less than 1 m²/g for as-blended W1Ni+2TiC powders increases with MA and has the value of 52,2 m²/g for the W1Ni+2TiC powders MA'd for 24 h.

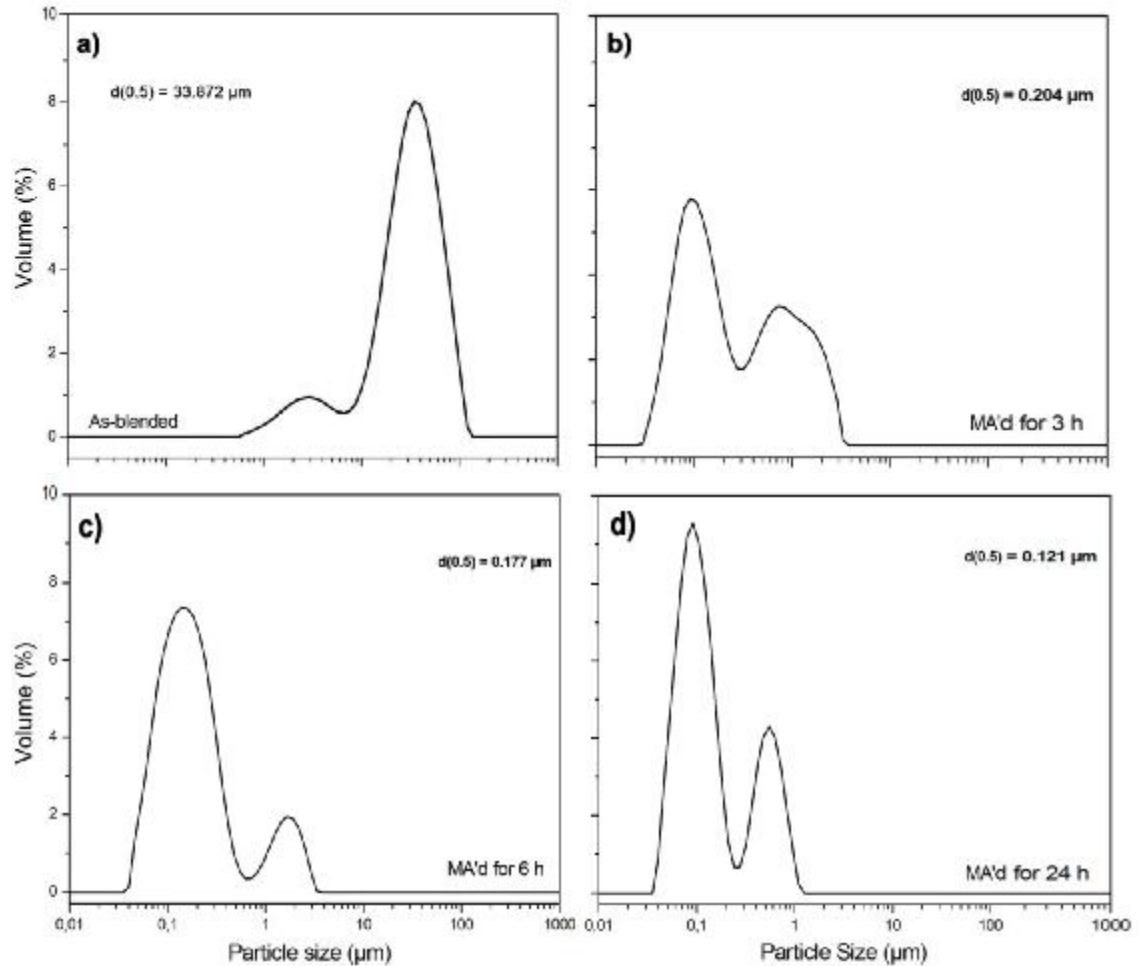


Figure 4.30 : Particle size distributions of **a)** as-blended W1Ni+2TiC powders and those MA'd for: **b)** 3 h, **c)** 6 h, **d)** 24 h.

There are no pressed and sintered compacts prepared from as-blended powders used in this study. Relative green density values of the consolidated powders are 64.8%, 64.8%, 60.9% and 56.6% for MA for 3 h, 6 h, 12 h and 24 h, respectively. Green density values have tendency of decreasing with increasing MA duration.

4.3.2. Characterization of Sintered Samples

4.3.2.1. XRD and SEM Investigations

XRD patterns of W1Ni+2TiC powders sintered at 1400 °C under both inert Ar and reducing H₂ gas flowing conditions for 1 h are shown in Figures 4.31a – 4.31d. As clearly seen in Figures 4.31a – 4.31d, stable b.c.c. W and f.c.c. Ni phases are identified in all sintered samples. Moreover, a second W phase which has a f.c.c. Bravais lattice with $Fm\bar{3}m$ space group and lattice parameter of $a = 4.06$ nm (ICDD, 88-2339) is present in all MA'd W1Ni+2TiC samples.

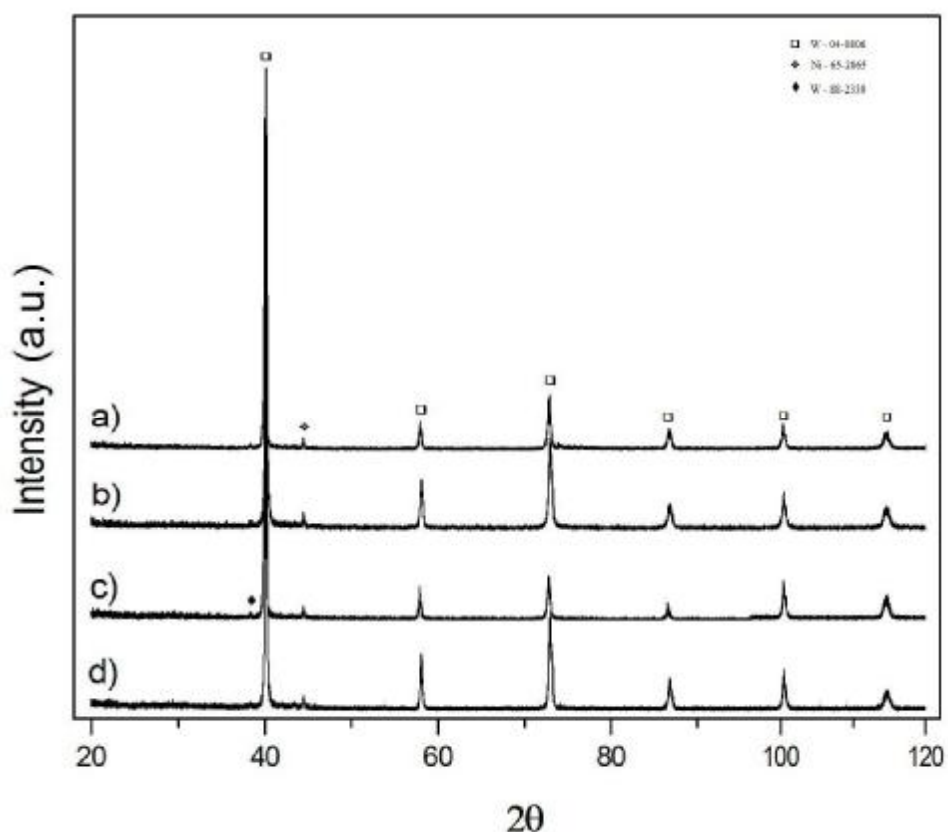


Figure 4.31 : XRD patterns of the sintered W1Ni+2TiC samples which were MA'd for **a)** 3 h, **b)** 6 h, **c)** 12 h and **d)** 24 h.

SEM micrographs taken from MA'd W1Ni+2TiC samples revealed two similar features first in 3 h and 6 h, and second in 12 h and 24 h and almost no porosity. Figures 4.32a and 4.32b are representative SEM micrograph taken from sintered W1Ni+2TiC sample MA'd for 3 h and 12 h, respectively. Since chemical etching (Murakami and H₂O₂) was ineffective, grain boundaries of the matrix W can not be observed. However, EDS spectra analysis have shown that gray regions are being

composed of matrix W, black dots are TiC and/or WC particles and white areas are dirtiness. As seen in Fig. 4.32a, distribution of TiC/WC particle is not homogeneous. Thus, with increasing MA duration TiC distributed more homogeneously, as seen in Fig.4.32b. Bigger black dots in Fig. 4.32b, which have size range between 200 nm and 1 μm , are TiC particles which added after MA of W-1Ni and further MA'd for 20 min, and smaller black dots are WC particles which contaminated during MA.

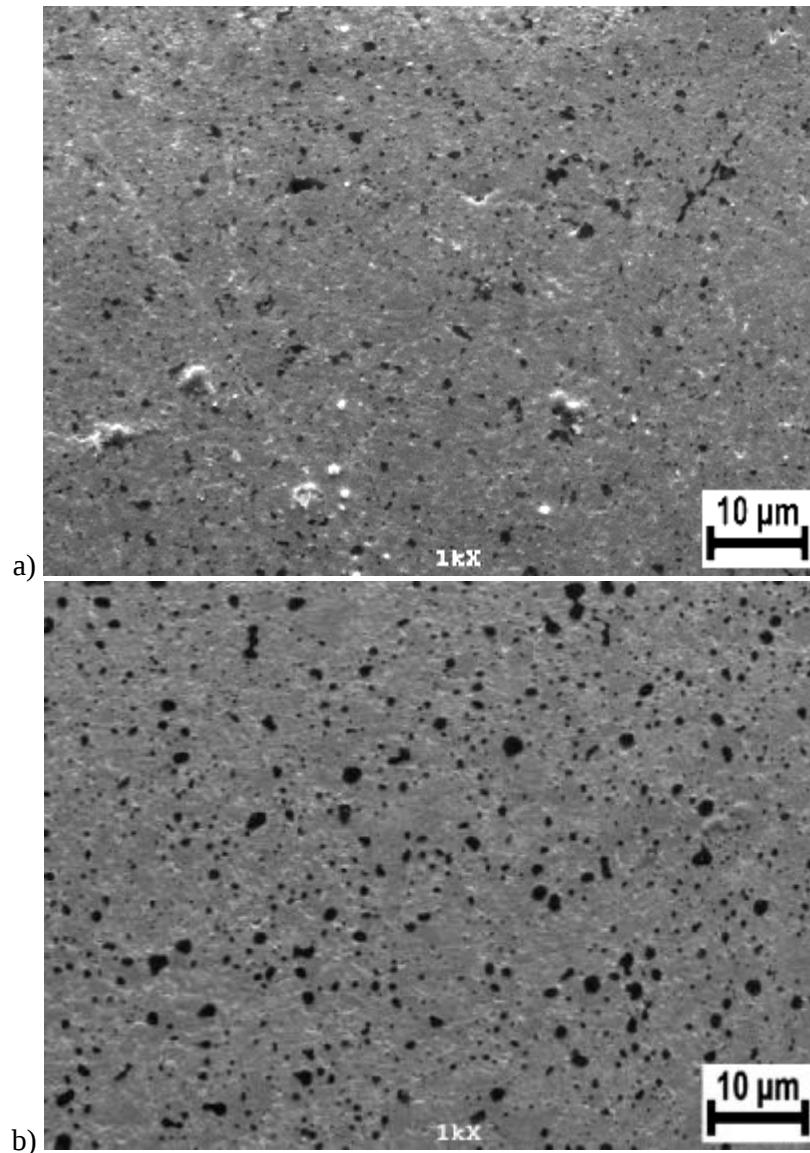


Figure 4.32 : Representative SEM micrographs taken from sintered W1Ni+2TiC samples MA'd for **a)** 3 h and **b)** 12 h.

4.3.2. Density and Hardness Measurements

Relative densities were measured by using the Archimedes method and relative density results of the sintered W1Ni+2TiC samples are given in Fig. 4.33. These results are the arithmetic mean of 5 successive measurements of the same sample and standard deviations. As seen in Fig. 4.33, relative density values vary between 94 and 98.5% and increase with increasing MA duration, where a value of 98.5% achieved in the sintered W1Ni+2TiC sample MA'd for 24 h. Moreover, relative density results of all the samples have almost the same standard deviation values which is about ± 1 %.

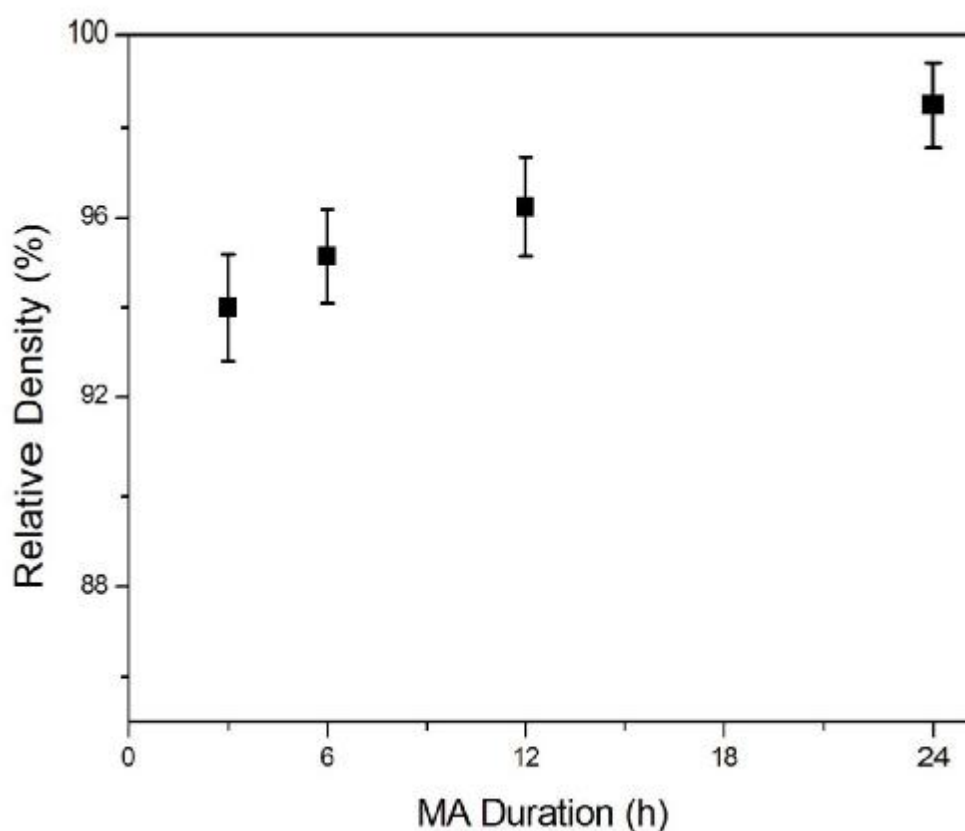


Figure 4.33 : Relative density values of the sintered W1Ni+2TiC composites MA'd for 3 h, 6 h, 12 h and 24 h.

Vickers microhardness results of sintered W1Ni+2TiC samples are given in Fig. 4.34. These microhardness test results for each sample are the arithmetic mean of 10 successive indentations and standard deviations. As seen in Fig. 4.34, microhardness values are between 4.8 GPa and 5.1 GPa and they increase with increasing MA duration for all sintered W1Ni+2TiC samples.

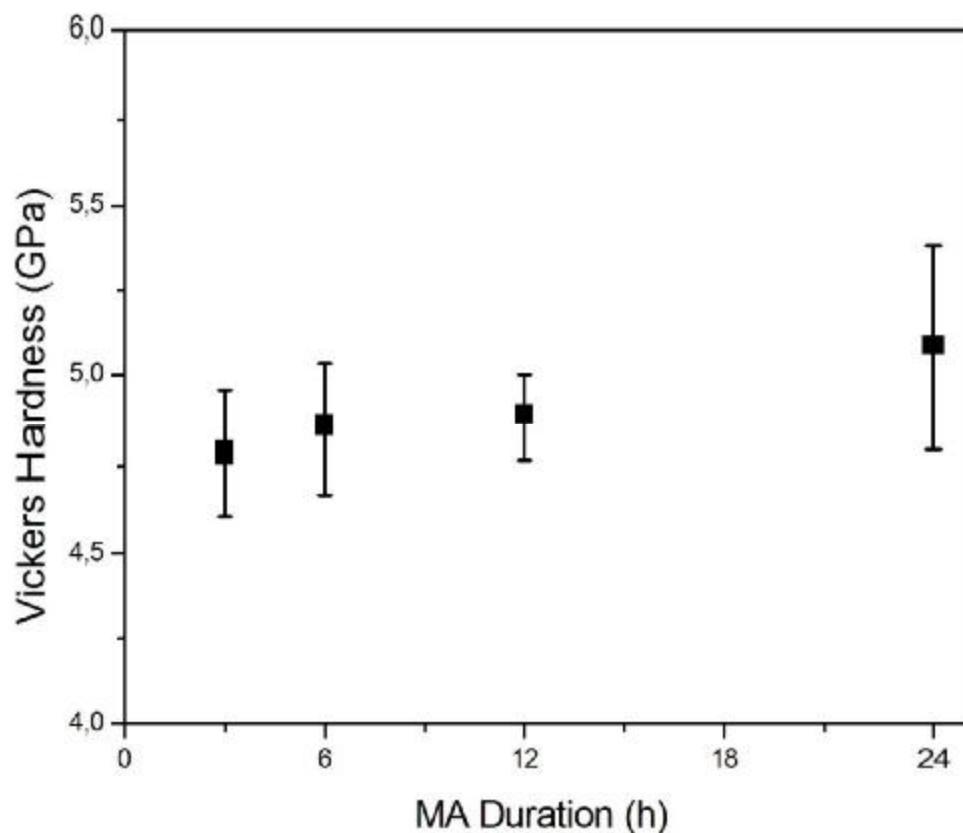


Figure 4.34 : Vickers microhardness values of the sintered W1Ni+2TiC composites MA'd for 3 h, 6 h, 12 h and 24 h.

4.3.3. Conclusions

On the basis of the results of the present investigations, the following conclusions can be drawn:

- 1) XRD patterns of the as-blended and MA'd W1Ni+2TiC powders revealed peaks belonging to the matrix W and Ni phases. Except the WC phase contaminated during MA, there is no evidence of any intermetallic phase formation between W, TiC, C and Ni in the MA'd powders. Both average grain sizes and particle sizes of the MA'd W1Ni+2TiC powders decrease with increasing MA duration. Minimum average grain size and particle sizes are achieved for the W1Ni+2TiC powders MA'd for 24 h and these are 8 nm and 121 nm, respectively.
- 2) Due to Ni-activated sintering, MA'd W1Ni+2TiC powders were sintered at a very low temperature of 1400°C for 1 h with a relative density value as high as 98.5% achieved in sintered W1Ni+2TiC sample MA'd for 24 h. Relative density values varied between 94 and 98.5% and increased with increasing MA duration. Whereas,

Vickers microhardness values were 4.8 GPa for the sample MA'd for 3 h and 5.1 GPa for the sample MA'd for 24 h.

3) XRD patterns of the MA'd and sintered W1Ni+2TiC composites revealed the presence of the stable W and Ni phases and a small amount of a W phase which has a f.c.c Bravais lattice. SEM micrographs taken from MA'd and sintered W1Ni+2TiC composites revealed two different microstructural features with no porosity in the sintered microstructures.

5. DISCUSSION

The present study has shown that dispersion strengthened W matrix composites can be successfully sintered using Ni activated sintering technique at high relative sinter densities and at high hardness values using a sintering temperature of as low as 1400°C and sintering duration of 1 h. Ni activated sintering of W has been investigated by several researchers who reported relative sinter density values varying between 88 and 95% for different amounts of Ni additions at sintering temperatures in the vicinity of 1400 °C (Vacek, 1959; Hayden and Brophy, 1963; Panichkina, 1967; Samsonov and Yakovlev, 1967; Toth and Lockington, 1967; Samsonov and Yakovlev, 1969; German and Munir, 1976; German and Munir, 1982; Li and German, 1983; Corti, 1986; Gupta et al., 2007). Samsonov and Yakovlev measured relative density values between 90 and 95% after sintering at 1400 °C for 1 h with 0.5 wt% Ni additions (Samsonov and Yakovlev, 1967). More recently, Gupta et al. (Gupta et al., 2007) investigated solid-state activated sintering of W with different Ni additions at different sintering temperatures. They explained the activated sintering mechanism on the basis of grain boundary diffusion and achieved a relative sinter density value of 89% for 1 at% Ni doped W sintered at 1400 °C. However, mechanisms of dispersion strengthening and activated sintering of W were not combined in none of these studies. Thus, the main contribution of the present investigation is the reduction of the sintering temperature of a TiC dispersed W composite by the addition of Ni. In the present study, after sintering in solid state well below the bulk eutectic temperature of 1495 °C (Fig. 2.20) (Massalski, 1990), a maximum relative density value of 98.5% were achieved for sintered W1Ni+2TiC sample MA'd for 24 h, where 2 wt% TiC added after MA of W-1Ni and further MA'd for 20 min. Relative density results measured in this study have shown that Ni distribution has the dominant role in densification of MA'd W2TiC composites. Thus, relative density values varied between 88 and 97.5% for W2TiC1Ni samples and 94 and 98.5% for W1Ni+2TiC samples and increased with increasing MA duration. Whereas, relative density values of 94% were achieved for all W2TiC+1Ni

samples where 1 wt% Ni added after MA of W2TiC and further MA for 20 min for all samples.

Moreover, ball milled W-TiC composites investigated by Song. et. al. (Song et al., 2003b) who found microhardness values about 5.5 GPa for the case of W-10 vol.% TiC after hot pressing at 2000 °C. Chen et al. reported a microhardness value of 8 GPa after the hot pressing of 24 h ball milled W – 5 wt% TiC powders at 2100 °C for 90 min, where relative density value was about 94% (Chen et al., 2008). Present study have measured a maximum Vickers microhardness value of 6 GPa for the sintered W2TiC+1Ni sample MA'd for 24 h which has a relative density of 94% which is comparable with Song et al.'s study where microhardness value of 5.5 GPa measured for the case of W-10 vol.% TiC after hot pressing at 2000 °C (Song et al., 2003b). A comparison can be done with three different experimental routes of this study which presented in detail in Chapter 4. In case of blended W-2 wt% TiC-1 wt% Ni powders MA'd together for different durations such as 3 h, 6 h, 12 h and 24 h, maximum microhardness value of 5.6 GPa achieved in the sample MA'd for 24 h, which had relative density value of 97.5%. Second route was MA of W-2 wt% TiC for same duration and addition of 1 wt% Ni as sintering aid which further MA'd together for 20 min, where relative density values were 94% for all sintered samples and did not change with MA duration and a maximum microhardness value of 6 GPa achieved in the sample MA'd for 24 h. Third route was MA of W-1 wt% Ni for 3 h, 6 h, 12 h and 24 h and addition of 2 wt% TiC as reinforcing agent which further MA'd together for 20 min. In this route, a maximum relative density value of 98.5% achieved in the sample MA'd for 24 h which had a microhardness value of 5.1 GPa.

Another important contribution of this work is the identification of face centered cubic W phase during characterization investigations via XRD (Fig. 4.19) and TEM (Fig. 4.22). Thus, the existence of the f.c.c. W phase which otherwise was reported in International Centre for Diffraction Data (ICDD) as a calculated phase (ICDD, 88-2339) is confirmed by the TEM investigations of the present study. Although, the formation mechanism of this phase is not known, since it is identified in all sintered samples, it is predicted that it somehow forms during sintering via diffusion and/or rearrangement of W atoms in the as-MA'd microstructures. Moreover, a Ni₄W with a body centered tetragonal Bravais lattice (ICDD, 65-2673) is identified via TEM investigations. It is expected that the stable intermetallic Ni₄W phase is precipitated

at the W-grain boundaries after activated sintering process (Kim et al., 2003). In addition to Ni_4W , other W-Ni intermetallics such as NiW and NiW_2 can be formed well below the bulk eutectic temperature of 1495°C (Fig. 2.20) (Massalski, 1990). These phases could reversely be decomposed at the high temperatures as seen in equilibrium diagram. The present study shows that with the TEM observations (Figures 4.24a – 4.24c) conducted at room temperatures, Ni_4W intermetallic compound exists after sintering at 1400°C for 1 h. Further, a W_2C phase having a hexagonal Bravais lattice (ICDD, 79-0743) which could not be observed in the XRD patterns, was detected during TEM investigations. This phase might be formed due to the decomposition of contaminated WC during sintering or directly due to contamination during MA.

Present study has also shown the solid state decomposition of TiC in $\text{W}_2\text{TiC1Ni}$ composites via XRD (Fig. 4.1a) and TEM (Figures 4.10 – 4.14). TiC, which oxidizes slowly in air at 800°C , but can be heated till its melting point without decomposition under hydrogen atmosphere, is isomorphous with TiN and TiO, thus oxygen and nitrogen can substitute for carbon to form binary and ternary solid solutions over a wide range of homogeneity (Pierson, 1996; Jung et al., 1999). Lo'pez et al. investigated thermal stability of TiC in Al-Si systems (Lo'pez et al., 2003). They found no evidence of solid-state reactions, whereas in liquid phase, between 600°C and 800°C , Ti-Al-Si intermetallics, with a wide noninteger stoichiometric composition, and Al_4C_3 layers were observed, which both formed at the TiC particle-matrix interface due to decomposition of TiC. At 850°C and above, reproduction of TiC out of intermetallics was observed with the constitution of Kennedy et al.'s (Kennedy et al., 2000) previous work on Al-Ti-C composites who reported a similar endothermic reaction between Al_4C_3 and Al_3Ti in Al to produce TiC at 890°C . Kennedy et al. (Kennedy et al., 2001) also stated that TiC was found to be stable at 900°C and above. Solid-state stoichiometric changes and displacement reactions of TiC in composite systems mainly investigated in literature (Wanjara et al., 2000; Yang et al., 2003; Li et al., 2004). However there are no detailed studies about solid-state decomposition of TiC except Song et al. (Song et al., 2003a) where high temperature ablation properties of W-TiC composites investigated, they stated formation of TiO layer as protector formed on the surface of TiC as a result of minor reaction of TiC with CO. Formation of intermetallic NiTi phase (Figures 4.10a –

4.10c) is self evident proof of decomposition of TiC in W2TiC1Ni composites according to FACT-Sage software (Bale et al., 2002) which revealed that formation of NiTi out of Ni and TiC phases is not possible in the temperature range between 0 and 2000 °C. Figures 4.11 – 4.14 are TEM observations showing Rutile, γ -TiO₂ and Ti₄O₇ phases, respectively and indicating oxidation of TiC or decomposed Ti in MA'd and sintered W2TiC1Ni composites. Since sintering was conducted in solid state, at a temperature of 1400 °C which is well below of bulk eutectic temperature of W-Ni (1495 °C) and melting point of TiC (3067 °C) under both inert Ar and reducing H₂ atmosphere, where TiC should be stable due to above mentioned literature (Pierson, 1996; Kennedy et al., 2001; Lo'pez et al., 2003). Song et al. reported oxidation of TiC as a result of ablation of TiC/W composites at high temperatures with main reaction given in Eq. 1 (Song et al., 2003a).



Song et al. investigated the ablation properties of TiC/W composites with a standard ablation experimental setup which involves a flame and temperatures as high as 3000 °C (Song et al., 2003a). They used far out parameters during processing of TiC/W composites in comparison with the present study and so oxidation mechanism was not thought to be same. However since they observed oxide phases grow out of decomposition of TiC, it should be mentioned in such a study. Sun et al. made a study of in-situ production of morph-genetic TiC/C ceramic out of tetrabutyl titanate which was firstly decomposed to anatase TiO₂, and then reacted with carbon to form TiC as seen in Eq. 2 which is reverse mechanism of Eq. 1 (Sun et al., 2004).



Conversion of C and TiO₂ to TiC as revealed in Eq. 2 took place at 1400 °C during sintering under Ar atmosphere (Sun et al., 2004). They conducted experiments almost same conditions with this study but came out with the direct opposite results about formation and/or composition behavior of TiC. These conflicted results predicted as effects of mechanical alloying (MA) which can be defined as a processing under non-equilibrium (or far-from-equilibrium) conditions (Suryanarayana, 2001). Additionally, it has been recognized that by using this technique chemical (displacement) reactions in powder mixtures can be induced at room temperature or at much lower temperatures than normally required to synthesize (Suryanarayana, 2001; Fecht, 2002). It is believed that, formation of these

oxide and intermetallic phases and so decomposition of TiC take place during MA and sintering at a temperature of 1400 °C.

General Conclusions

On the basis of the results of the present investigations, the following conclusions can be drawn:

- 1) XRD patterns of the as-blended and MA'd W-TiC-Ni powders revealed peaks belonging to the matrix W and Ni phases. Except the WC phase contaminated during MA, there is no evidence of any intermetallic phase formation between W, TiC, C and Ni in the MA'd powders. Both average grain sizes and particle sizes of the MA'd W1Ni+2TiC powders decrease with increasing MA duration
- 2) Due to Ni-activated sintering, MA'd W-TiC-Ni composite powders were sintered at a very low temperature of 1400°C for 1 h with a relative density value as high as 98.5% achieved in sintered W1Ni+2TiC sample MA'd for 24 h. Relative density values varied between 88% and 98.5% and increased with increasing MA duration. Whereas, Vickers microhardness values varied between 4.8 GPa and 6 GPa, maximum value achieved in the sintered W2TiC+1Ni sample MA'd for 24 h.
- 3) XRD patterns of the MA'd and sintered W-TiC-Ni composites revealed the presence of the stable W and Ni phases and a small amount of a W phase which has a f.c.c Bravais lattice.
- 4) TEM investigations confirmed the presence of the matrix W and Ni phases detected in the XRD patterns as well as the TiC, W₂C phases with hexagonal and orthorhombic Bravais lattice, NiTi, rutile, TiO₂ and Ti₄O₇ phases in the microstructures of the MA'd and sintered W2TiC1Ni composites. Moreover, TEM investigations confirmed the presence of the matrix W and the f.c.c. W phases detected in the XRD patterns as well as the TiC, Ni₄W and W₂C phases in the microstructures of the MA'd and sintered W2TiC+1Ni composites.

All above mentioned results have shown that dispersion strengthened W matrix composites can be successfully sintered using Ni activated sintering technique at high relative sinter densities (98.5%) and at high hardness values (6 GPa) using a sintering temperature of as low as 1400 °C and sintering duration of 1 h.

REFERENCES

- Acchar, W., Zollfrank, C. and Greil, P.,** 2004: Microstructure and Mechanical Properties of WC-Co Reinforced With NbC, *Materials Research*, **7**, 445-450.
- Akovali, G. and Uyanik, N.,** 2001: Introduction in Handbook of Composite Manufacturing, Ed. G. Akovali, Rapra Technology Ltd.
- Askeland, D.R.,** 1984: The Science and Engineering of Materials, Brooks/Cole Engineering Division, CA.
- Asthana, R., Kumar, A., and Dahotre, N.B.,** 2006: Composite Materials in Materials Processing and Manufacturing Science, 397-484.
- Asthana, R., Kumar, A., and Dahotre, N.B.,** 2006: Powder Metallurgy and Ceramic Forming in Materials Processing and Manufacturing Science: 167-245.
- Benjamin, J.S.,** 1992: Fundamentals of mechanical alloying. *Materials Science Forum*, **88-90**, 1-18.
- Boch, P. and Leriche, A.,** 2001: Sintering and Microstructure of Ceramics in Ceramic Materials Edited by Philippe Boch and Jean-Claude Niepce, HERMES Science Europe Ltd.
- Brophy, J.H., Hayden, H.W., Prill, A.L. and Wulff, J.,** 1963: The Investigation of the Activated Sintering of Tungsten Powder, Final Report, Prepared under U.S. Navy, Bureau of Naval Weapons Contract NO w 61-0326-d, Massachusetts Institute of Technology, Cambridge, Massachusetts.
- Cahn, R.W.,** 2001: The Coming of Materials Science, Pergamon, Amsterdam.
- Campbell, F.C.,** 2006: Metal Matrix Composites in Manufacturing Technology for Aerospace Structural Materials, 419-457.
- Chawla, N. and Chawla, K.K.,** 2006: Metal Matrix Composites, Springer, New York.

- Chawla, N. and Shen, Y.L.**, 2001: Mechanical behavior of particle reinforced metal matrix composites, *Advanced Engineering Materials*, **3**, 357-370.
- Chen, Z., Zhou, M. and Zuo, T.**, 2000: Morphological evolution of second-phase particles during thermomechanical processing of W-La₂O₃ alloy, *Scripta mater.*, **43**, 291–297.
- Chen, Y., Wu, Y.C., Yu, F.W. and Chen, J.L.**, 2008: Microstructure and mechanical properties of tungsten composites co-strengthened by dispersed TiC and La₂O₃ particles, *International Journal of Refractory Metals&Hard Materials*, **26**, 525-529.
- Clyne, T.W.**, 2000: An Introductory Overview of MMC Systems, Types, and Developments in Vol.3 Metal Matrix Composites of Comprehensive Composite Materials, Elsevier.
- Clyne, T.W. and Withers, P.J.**, 1993: Introduction to Metal Matrix Composites, Cambridge University Press, Cambridge.
- Corti, C.W.**, 1986: The Role of the Platinum Metals in the Activated Sintering of Refractory Metals, *Platinum Metals Rev.*, **30**, 184-195.
- Coskun, S.**, 2006: Development and Characterization Investigations of Mechanically Alloyed W-SiC and W-SiC-Y₂O₃ Composites, *M.Sc. Thesis*, I.T.U. Institute of Science and Technology, Istanbul.
- Das, K., Bandyopadhyay, T.K., and Das, S.**, 2002: A Review on the various synthesis routes of TiC reinforced ferrous based composites, *Journal of Materials Science*, **37**, 3881-3892.
- Delogu, F., Orrù, R. and Cao, G.**, 2003: A novel macrokinetic approach for mechanochemical reactions, *Chemical Engineering Science*, **58**, 815-821.
- El-Eskandarany, M.S.**, 2001: Mechanical Alloying for Fabrication of Advanced Engineering Materials, Noyes Publications, New York.
- El-Eskandarany, M.S., Mahday, A.A., Ahmed, H.A and Amer, A.H.**, 2000: Synthesis and characterizations of ball-milled nanocrystalline WC and nanocomposite WC–Co powders and subsequent consolidations, *Journal of Alloys and Compounds*, **312**, 315–325.

- Fecht, H.J.**, 2002: Nanostructured materials and composites prepared by solid state processing, in *Nanostructured Materials: Processing, Properties and Potential Applications*, Ed. Koch, C.C., Noyes Publications, New York.
- Flinn, R.A. and Trojan, P.K.**, 1995: Engineering Materials and Their Applications, Wiley, New York.
- Gay, D., Hoa, S.V., and Tsai, S.W.**, 2003: Composite Materials Design and Applications, CRC Press LLC, Florida.
- German, R.M.**, 1996: Sintering Theory and Practice, John Wiley & Sons, Inc., New York.
- German, R.M and Munir, Z.A.**, 1976: Enhanced Low-Temperature Sintering of Tungsten, *Metallurgical Transactions A*, **7A**, 1873-1877.
- German, R.M and Munir, Z.A.**, 1982: Activated Sintering of Refractory Metals by Transition Metal Additions, *Rev. Powder Metall. Phys. Ceram.*, **2**, 9-43.
- Goff, A.**, 2003: Modeling and synthesis of a piezoelectric ceramic-reinforced metal matrix composites, *MS Thesis*, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- Gupta, V.K., Yoon D-H., Meyer III, H.M., and Luo, J.**, 2007: Thin intergranular films and solid-state activated sintering in nickel-doped tungsten, *Acta Materialia*, **55**, 3131-3142.
- Hayden, H.W. and Brophy, J.H.**, 1963: The Activated Sintering of Tungsten with Group VIII Elements, *Journal of Electrochemical Society*, **110**, 805-810.
- Huda, M.D., Hashmi, M.S.J. and El-Baradie, M.A.**, 1995: MMCs: materials, manufacturing and mechanical properties, *Key Engineering Materials*, **104-107**, 37-64.
- Hunt, W.H. JR.**, 2000: Particulate Reinforced MMCs in Vol.3 Metal Matrix Composites of Comprehensive Composite Materials, Elsevier, New York.
- Ibrahim, I.A., Mohamed, F.A. and Lavernia, E.J.**, 1991: Particulate reinforced metal matrix composites – a review, *Journal of Materials Science*, **26**, 1137-1156.

- Jung, I-J, Kang, S., Jhi, S-H. and Ihm, J.,** 1999: A study of the formation of Ti(CN) solid solutions, *Acta Materialia* **47 (11)**, 3241-3245.
- Kang, S-J.L.,** 2005: Sintering Densification, Grain Growth and Microstructure, Elsevier, New York.
- Kennedy, A.R., Westoni D.P., Jones, M.I. and Enel, C.,** 2000: Reaction in Ti-Al-C powders and its relation to the formation and stability of TiC in Al at high temperatures, *Scripta Materialia*, **42**, 1187-1992.
- Kennedy, A.R., Westoni D.P. and Jones, M.I.,** 2001: Reaction in Al-TiC metal matrix composites, *Materials Science and Engineering A*, **316**, 32-38.
- Kern, A.A. and Coelho, A.A.,** 2006: TOPAS 3 (BRUKER AXS), www.brukeraxs.com
- Kim, S.H. and Hahn, H.T.,** 2006: Size effect in particulate metal matrix composites: an analytical approach, *Advanced Composite Materials*, **15**, 175-191.
- Kim, S-W., Lee, S-I., Kim, Y.D. and Moon, I-H.,** 2003: High temperature compressive deformation and fracture characteristics of the activated sintered W-Ni compacts, *International Journal of Refractory Metals&Hard Materials*, **21**, 183-192.
- Lassner, E. and Schubert, W.D.,** 1999: Tungsten: Properties, Chemistry, Technology of the Element, Alloys and Chemical Compounds, Kluwer Academic, New York.
- Lee, K.H., Yoon, J.K., Lee, J.K., Doh, J.M., Hong, K.T. and Yoon, W.Y.,** 2004: Growth Kinetics of W₅Si₃ Layer in WSi₂/W System, *Surface & Coatings Technology*, **187**, 146– 153.
- Li, C. and German, R.M.,** 1983, The Properties of Tungsten Processed by Chemically Activated Sintering, *Metallurgical Transactions A*, **14A**, 2031-2041.
- Li, S-B., Xie, J-X., Zhang, L-T. and Cheng, L-F.,** 2004: In situ synthesis of Ti₃SiC₂/SiC composite by displacement reaction of Si and TiC, *Materials Science and Engineering A*, **381**, 51-56.

- Lindroos, V.K., Hellman, J.T., Lou, D., Nowak, R., Pagounis, E., Liu, X.W. and Penttinen, I.M.**, 2004: Designing with metal matrix composites, in *Handbook of Mechanical Alloy Design*, Eds. Totten, G.E., Xie, L. and Funatani, K, M. Dekker, New York.
- Lipatnikov, V.N., Rempel, A.A., and Gusev, A.L.**, 1997: Atomic ordering and hardness of nonstoichiometric titanium carbide, *International Journal of Refractory Metals&Hard Materials*, **15**, 61-64.
- Liu, N., Hu, Z.H., and Cui, K.**, 1997: Valance electron structure and eigen properties of (Ti,W)C ceramic phase, *Journal of Chinese Ceramic Society*, **25(4)**, 420-425.
- Liu, Y.B., Lim, S.C., Lu, L. and Lai, M.O.**, 1994: Recent development in the fabrication of metal matrix particulate composites using powder metallurgy techniques. *Journal of Materials Science*, **29**, 1999-2007.
- Lo'pez, V.H., Scoles, A. and Kennedy, A.R.**, 2003: The thermal stability of TiC particles in an Al7wt.%Si alloy, *Materials Science and Engineering A*, **356**, 316-325.
- Mabuchi, M., Okamoto, K., Saito, N., Asahina, T. and Igarashi, T.**, 1997: Deformation behavior and strengthening mechanisms at intermediate temperatures in W-La₂O₃, *Materials Science & Engineering A*, **237**, 241-249.
- Massalski, T.B.**, 1990. Binary alloy phase diagrams, 2nd ed., ASM, Metals Park, OH, USA.
- Mazumdar, S.K.**, 2002: Composite Manufacturing, Materials, Product and Process Engineering, CRC Press LLC, Florida.
- Ovecoglu, M.L.**, 1987: Development of a dispersion-strengthened Al-Fe-Ce alloy by mechanical alloying and related theoretical modeling of dislocations in composite materials, *PhD Thesis*, Stanford University, Los Angeles, CA .
- Panichkina, V.V.**, 1967: Activated sintering of tungsten with small additions of nickel, Poroshkovaya Metallurgiya (In Russian), **2**, 1-5.
- Pierson, H.O.**, 1996: Handbook of Refractory Carbides and Nitrides Properties, Characteristics, Processing and Applications, Noyes Publications, USA.

Powder Diffraction Files: Card No. 04-0806, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 21-1276, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 48-1827, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 51-0939, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 53-0619, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 65-0242, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 65-2673, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 65-2865, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 71-6256, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 72-0020, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 72-3504, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 72-3504, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 72-4509, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 88-2339, Database Edition, The International Centre for Diffraction Data (ICDD).

Powder Diffraction Files: Card No. 89-2371, Database Edition, The International Centre for Diffraction Data (ICDD).

- Ring, T.A.**, 1996: Sintering in Fundamentals of Ceramic Powder Processing and Synthesis, 781-874.
- Ryu, H.J. and Hong, S.H.**, 2003: Fabrication and properties of mechanically alloyed oxide-dispersed tungsten heavy alloys, *Materials Science and Engineering A*, **363**, 179–184.
- Ryu, H.J., Hong, S.H. and Baek, W.H.**, 2000: Microstructure and mechanical properties of mechanically alloyed and solid-state sintered tungsten heavy alloys, *Materials Science and Engineering A*, **291**, 91–96.
- Samsonov, G.V. and Yakovlev, V.I.**, 1967: Activated Sintering of Tungsten with Nickel Additions, *Poroshkovaya Metallurgiya* (In Russian), **8**, 10-16.
- Samsonov, G.V. and Yakovlev, V.I.**, 1969: Activation of the Sintering of Tungsten by the Iron-Group Metals. *Poroshkovaya Metallurgiya* (In Russian), **10**, 32-38.
- Schwartz, M.M.**, 1984: *Composite Materials Handbook*, McGraw-Hill, New York.
- Schwartz, M.M.**, 1997: *Composite Materials-Vol.1*, McGraw-Hill, New York.
- Shackelford, J.F.**, 2001: *Materials Science and Engineering Handbook*, CRC Press LLC, Florida.
- Song, G.M., Wang, Y.J. and Zhou, Y.**, 2002: The mechanical and thermophysical properties of ZrC/W composites at elevated temperature, *Materials Science and Engineering A*, **334**, 223–232.
- Song, G.M., Zhou, Y. and Wang, Y.J.**, 2003a: Effect of carbide articles on the ablation properties of tungsten composites, *Materials Characterization*, **50**, 293–303.
- Song, G.M., Wang, Y.J. and Zhou, Y.**, 2003b: Thermomechanical properties of TiC particle-reinforced tungsten composites for high temperature applications, *International Journal of Refractory Metals & Hard Materials*, **21**, 1–12.
- Stjernstoft, T.**, 2004: Machining of some difficult-to-cut materials with rotary cutting tools, *PhD Thesis*, K.T.H., Stockholm.

- Sun, B., Fan, T. and Zhang, D.,** 2004: Production of morph-genetic TiC/C ceramic, *Materials Letters*, **58**, 798-801.
- Sun, L.Z., Liu, H.T. and Ju, J.W.,** 2003: Effect of particle cracking on elastoplastic behaviour of metal matrix composites, *Int. J. Numer. Meth. Eng*, **56**, 2183–2198.
- Suryanarayana, C.,** 2001: Mechanical alloying and milling, *Progress in Materials and Science*, **46**, 1-184.
- Suryanarayana, C., Ivanov, E. and Boldyrev, V.V.,** 2001: The science and technology of mechanical alloying, *Materials Science and Engineering A*, **304–306**, 151–158.
- Tang, H.G., Ma, X.F., Zhao, W., Yan, X.W., Yan, J.M. and Zhu, C.J.,** 2004: Crystallization of mechanically alloyed amorphous W–Mg alloy under high pressure, *Solid State Communications*, **129**, 147–150.
- Tjong, S.C. and Ma, Z.Y.,** 2000: Microstructural and mechanical characteristics of in situ metal matrix composites, *Materials Science and Engineering*, **29**, 49-113.
- Toth, I.J. and Lockington, N.A.,** 1967: The Kinetics of Metallic Activation Sintering of Tungsten, *J. Less-Common Met.*, **12**, 353-365.
- Upadhyaya, G.S.,** 2000: Sintered Metallic and Ceramic Materials: Preparation, Properties, and Applications, Wiley, New York.
- Upadhyaya, G.S.,** 2001: Some issues in sintering science and technology, *Materials Chemistry and Physics*, **67**, 1-5.
- Vacek, J.,** 1959: On Influencing the Sintering Behavior of Tungsten, *Planseeberichte fur Pulvermetallurgie*, **7**, 6-17.
- Wanjara, P., Drew, R.A.L., Root, J. and Yue, S.,** 2000: Evidence for stable stoichiometric Ti₂C at the interface in TiC particulate reinforced Ti alloy composites, *Acta Materialia*, **48**, 1443-1450.
- Yang, S., Sun, Z-M. and Hashimoto, H.,** 2003: Formation of Ti₃SiC₂ from Ti-Si-TiC powders by pulse discharge sintering (PDS) technique, *Materials Research Innovations*, **7**, 225-230.

Zhang, F.L., Wang, C.Y. and Zhu, M., 2003: Nanostructured WC/Co composite powder prepared by high energy ball milling, *Scripta Materialia*, **49**, 1123–1128.

Zweck, A., and Luther, W., 2003: Applications of Nanotechnology in Space Developments and Systems. Technological Analysis, VDI Technology Center Future Technologies Division, Duesseldorf.

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Publications:

1. **Genç, A., Coşkun, S., Öveçoğlu, M.L.**, 2009. “Microstructural Characterizations of Ni Activated Sintered W-2 wt% TiC Composites”, *Journal of Alloys and Compounds (submitted)*.
2. **Genç, A., Coşkun, S., Öveçoğlu, M.L.**, 2009: Development and Characterization Investigations of Mechanically Alloyed W-VC-Ni Composites. In PowderMet 2009, International Conference on Powder Metallurgy and Particulate Materials, Las Vegas, Nevada, USA, June 28 – July 1 (*Proceeding In Publication*).
3. **Coşkun, S., Genç, A., Öveçoğlu, M.L.**, 2009: Development and Characterization Investigations of Mechanically Alloyed WMn-VC Composites. In PowderMet 2009, International Conference on Powder Metallurgy and Particulate Materials, Las Vegas, Nevada, USA, June 28 – July 1 (*Proceeding In Publication*).
4. **Coşkun, S., Genç, A., Öveçoğlu, M.L.**, 2009: Development and Characterization Investigations of Mechanically Alloyed W-Ni/TiC Composites. In TMS 2009 Annual Meeting and Exhibition, Characterization of Microstructure of Properties of Materials Division, San Francisco, California, USA, 15-19 February, pp. 183 – 190 (CD-ROM).