

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**SYNTHESIS AND CHARACTERIZATION OF VARIOUS TUNGSTEN CARBIDE POWDERS
FROM TUNGSTEN HEXACHLORIDE POWDERS VIA MECHANOCHEMICAL
REACTION AND AUTOCLAVE/PRESSURE VESSEL METHODS**



Ph. D. THESIS

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Department of Materials Science and Engineering

Materials Science and Engineering Programme

MARCH 2020

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METODLARIYLA TUNGSTEN HEKZAKLORÜR TOZUNDAN ÇEŞİTLİ
TUNGSTEN KARBÜR TOZLARININ SENTEZİ VE KARAKTERİZASYONU**

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To my spouse and my son ,



FOREWORD

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ABBREVIATIONS

BPR	: Ball-to-powder weight ratio
DSC	: Differential Scanning Calorimeter
DSC/TGA	: Differential Scanning Calorimeter/ Thermogravimetric Analyser
EDS	: Energy Dispersive Spectroscopy
EDX	: Energy-Dispersive X-Ray Spectrometer
eV	: Electron Volt
g	: Gram
GPa	: Gigapascal
h	: Hour
HR-TEM	: High Resolution Transmission Electron Microscope
ICDD	: International Center for Diffraction Data®
Kg	: Kilogram
Kj	: Kilojoule
m	: Metre
M	: Molarity
mA	: Miliampere
MA	: Mechanical Alloying
MAC'd	: Mechanical Activated
MA'd	: Mechanical Alloyed
MCS	: Mechanochemical Synthesis
mg	: Miligram
Min	: Minute
mm	: Milimeter
MPa	: Megapascal
µm	: Micrometer
N	: Newton
nm	: Nanometer
PCA	: Process Control Agent
PML	: ITU Particulate Materials Laboratories

PSA	: Particle Size Analyzer
rpm	: Rotations per minute
SEM	: Scanning Electron Microscope
SM	: Stereo Microscope
T_c	: Powder temperature
t_{ig}	: Ignition time
T_{ig}	: Ignition temperature
TGA	: Thermogravimetric Analyser
TEM	: Transmission Electron Microscope
XRD	: X-Ray Diffractometer
W	: Watt



SYMBOLS

a, b, c	: Lattice parameters
°C	: Degree Celcius
°K	: Degree Kelvin
ΔG	: Standart Gibbs free energy change
θ	: Diffraction angle
$\sim$	: Approximation



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SYNTHESIS AND CHARACTERIZATION OF VARIOUS TUNGSTEN CARBIDE POWDERS FROM TUNGSTEN HEXACHLORIDE POWDERS VIA MECHANOCHEMICAL REACTION AND AUTOCLAVE/PRESSURE VESSEL METHODS

SUMMARY

Transition metal carbides have been studied for approximately last half century due to their extraordinary characteristics that make them convenient to be utilized for industrial applications such as tool and structural materials under special conditions. Tungsten carbide has a special location amongst transition metal carbides because of its superior properties such as high hardness, high density, high melting temperature, high fracture toughness, good electrical and thermal conductivity and high elastic modulus etc. These attractive properties make it preferred to be used for tips for cutting and drilling tools, WC-Co hard metals, wear-resistant surfaces for machines, scratch-resistant jewelry materials, erosion-resistant coatings for aerospace elements, extrusion and pressing molds, wear resistant parts in wire drawing, platinum-like catalytic materials for polymer electrode membrane fuel cells and thin film diffusion barriers in microelectronics. In W-C binary system, two phases such as W_2C and WC exist. These two phases possess various polymorphic modifications that are stable in different temperature and composition ranges.

Many production techniques have been used in the synthesis of tungsten carbides. The production of WC was firstly achieved in a conventional way by high temperature. A solid state direct reaction occurred between W and C powders at a temperature range of 1200°C-2000°C under controlled atmosphere to synthesize WC. Also there are different high temperature methods such as carbothermal reduction, chemical vapour condensation, self propagating high-temperature synthesis, molten salt synthesis, calcining and thermal processing at high temperatures. In addition to these techniques there are relatively low temperature methods such as low temperature autoclave processing, combined process of calcination, nitridization and carburization at low temperatures, electrochemical synthesis from halide-oxide melts under pressure, mechanically alloying and mechanochemical synthesis. Especially mechanically alloying and mechanochemical synthesis are advantageous methods due to having simple and low-cost equipment and performing reactions at room temperatures in relatively short reaction times.

The main aim of this dissertation is to produce WC powders with an effective technique that overcomes the limitations of traditional production methods and provides advantages of time, energy saving, simplicity and low equipment cost. In order to achieve this aim, elemental W and C powders were first milled in a spex at different durations by mechanical alloying method to obtain tungsten carbide powders. The aim of the first stage is to obtain the tungsten carbide powders with the starting powders traditionally used, and to compare the results with the results of the

study in which tungsten carbide was synthesized with the alternative starting powders. In the second stage, mechanical chemical reaction was used to synthesize high purity and sub-micron sized WC powders using WCl_6 (as W source), Na_2CO_3 (as C source) and Mg (as a reducing agent) powders. In a very short time the chemical reaction started and the WC phase occurred. In a very short time chemical reaction started to form and WC phase occurred. Amounts of C source (Na_2CO_3) and reducing agent (Mg) were varied to optimize raw materials reacted and to obtain high-purity WC powders. After purification of the obtained powders, nano-sized tungsten carbide powders, which are the only WC phase, were achieved in high purity without any intermediate phase and impurity.

The other purpose of this dissertation is to use an alternative production technique in order to produce WC powders, and compare the products, especially those produced by mechanical alloying / mechanochemical synthesis and autoclave methods. Therefore in the third stage low temperature autoclave processing was employed for the fabrication of WC powders from the same raw materials. The autoclave processing was used with mechanical activation to reduce the reaction temperature by activating the reactive particles and to homogenize the distribution of the microstructure. In this method powder blends were placed in a hydrothermal reactor and the hydrothermal reactor was heated in a furnace. This autoclave processing was implemented by varying the temperature and the duration of synthesis, the type of excess carbon source, the amounts of carbon sources and reducing agent. High purity and nano-sized tungsten carbides were obtained by optimizing the production conditions. Furthermore, autoclave synthesis is accepted as an eco-friendly method due to carrying out in a closed / isolated system and saving energy.

The final powders of two different methods were characterized and compared each other using X-ray diffractometer (XRD), particle size analyzer (PSA), pycnometer, stereo microscope (SM), scanning electron microscope/energy dispersive spectrometer (SEM/EDS), transmission electron microscope (TEM) and differential scanning calorimetry/thermogravimetric analysis (DSC/TGA).

WC powders were produced from WCl_6 - Na_2CO_3 -Mg powder blends via mechanochemical synthesis for the first time in the literature. In this way the results of mechanochemical synthesis from new raw materials for WC powder production contributed the literature. Also, this thesis provides a comparison of mechanochemical method which is a simple, energy saving and room temperature method and autoclave method which is a more traditional method for producing tungsten carbide.

MEKANOKİMYASAL REAKSİYON VE OTOKLAV/BASINÇLI KAP METODLARIYLA TUNGSTEN HEKZAKLORÜR TOZUNDAN ÇEŞİTLİ TUNGSTEN KARBÜR TOZLARININ SENTEZİ VE KARAKTERİZASYONU

ÖZET

Geçiş metal karbürleri, özel koşullar altındaki çeşitli alet ve yapı malzemeleri gibi endüstriyel uygulamalar için kullanılmasını kolaylaştıran olağanüstü karakteristikleri nedeniyle yaklaşık son yarım yüzyıl boyunca incelenmektedir. Tungsten karbür, yüksek sertlik, yüksek yoğunluk, yüksek erime noktası, yüksek kırılma tokluğu, iyi elektriksel ve termal iletkenlik ve yüksek elastik modül vb. gibi benzersiz özellikleri nedeniyle geçiş metali karbürleri arasında özel bir konuma sahiptir. Bu çekme özellikleri, kesme ve delme takımları, WC-Co sert metaller, makinalar için aşınmaya dayanıklı yüzeyler, çizilmeye dayanıklı mücevher malzemeleri, havacılık bileşenleri için aşınmaya dayanıklı kaplamalar, tel çekme işleminde aşınmaya dayanıklı parçalar, ekstrüzyon ve pres kalıpları, polimer elektrot membran yakıt hücreleri için platin benzeri katalitik malzemeler ve mikroelektronikte ince film difüzyon bariyerleri için tercihen kullanılmasını sağlar. W-C ikili sisteminde, W_2C ve WC gibi iki faz vardır. Bu iki faz, farklı sıcaklık ve bileşim aralıklarında stabil olan çeşitli polimorfik modifikasyonlara sahiptir. Tungsten karbürlerin sentezinde birçok üretim tekniği kullanılmıştır. WC üretimi ilk olarak geleneksel olarak yüksek sıcaklıkta elde edildi. WC sentezlemek için kontrollü atmosfer altında 1200 °C-2000 °C sıcaklık aralığında W ve C tozları arasında bir katı hal doğrudan reaksiyonu meydana geldi. Ayrıca karbotermal indirgeme, kimyasal buhar yoğunlaşması, kendiliğinden yayılan yüksek sıcaklık sentezi, erimiş tuz sentezi, kalsine etme ve yüksek sıcaklıklarda termal işleme gibi farklı yüksek sıcaklık yöntemleri vardır. Bu tekniklere ek olarak, düşük sıcaklıkta otoklav işleme, düşük sıcaklıklarda kombine kalsinasyon, nitrürleme ve karbürizasyon işlemi, basınç altında halid oksit eriyiklerinden elektrokimyasal sentez, mekanik alaşımlama ve mekanokimyasal sentez gibi nispeten düşük sıcaklık yöntemleri vardır. Özellikle mekanik alaşımlama ve mekanik kimyasal sentez, basit ve düşük maliyetli ekipmanlara sahip olmasından ve oda sıcaklığında nispeten kısa reaksiyon sürelerinde reaksiyonları gerçekleştirmesinden dolayı avantajlı yöntemlerdir.

Bu tezin ana amacı, geleneksel üretim yöntemlerinin sahip olduğu kısıtlamaları aşan ve zaman, enerji tasarrufu, basitlik ve düşük ekipman maliyeti avantajları sağlayan etkili bir teknikle WC tozları üretmektir. Bu amaca ulaşmak için, ilk olarak elementel W ve C tozları, tungsten karbür tozu elde etmek için mekanik alaşımlama yöntemi ile farklı sürelerde bir öğütücüde öğütüldü.

İlk aşamanın amacı geleneksel olarak kullanılan başlangıç tozları ile tungsten karbür tozunu elde ederek, sonuçları alternatif başlangıç tozları ile tungsten karbür tozunu elde etme çalışmalarının sonuçları ile kıyaslamaktır. Mekanik alaşımlanmış ve tavlanmış tozların partikül boyut analizleri gerçekleştirilmiş, ayrıca bu tozların termal özellikleri diferansiyel taramalı kalorimetre/termogravimetri analiz cihazı (DSC/TGA) ile incelenmiş, ortalama yoğunluğu ise Quantachrome TM gaz piknometresi ile 15.1 g/cm³ olarak ölçülmüştür. Stokiyometrik oranda elementel tungsten ve karbon tozlarının 15 sa süreyle mekanik alaşımlanmasının ardından 1000° C’de 1 sa süreyle tavlanmasıyla ortalama partikül büyüklüğü 305 nm olan WC tozları elde edilmiştir. İkinci aşamada ise WCl₆ (W kaynağı olarak), Na₂CO₃ (C kaynağı olarak) ve Mg (bir indirgeme maddesi olarak) tozları kullanılarak yüksek saflıkta ve mikron altı boyutlu WC tozlarının sentezlenmesi için mekanik kimyasal reaksiyon kullanıldı. Çok kısa sürede kimyasal reaksiyon oluşmaya başladı ve WC fazı meydana geldi. Reaksiyona giren hammaddeleri optimize etmek ve yüksek saflıkta WC tozları elde etmek için C kaynağı (Na₂CO₃) ve indirgeme maddesi (Mg) miktarları değiştirildi. Elde edilen tozların saflaştırılmasından sonra, tek WC fazı olan nano boyutlu tungsten karbür tozları, herhangi bir ara faz ve safsızlık olmaksızın yüksek saflıkta elde edildi. Bu aşamada ise stokiyometrik veya ağırlıkça % 50 fazla Mg ilave edilen WCl₆-Na₂CO₃-Mg karışımları, mekanik alaşımlama ve liçten sonra WCl₆, WO₂Cl₂ ve W fazlarının bir miktarıyla hem WC hem de W₂C tozlarının oluşumuyla sonuçlandı. Bununla birlikte, ağırlıkça % 50 Na₂CO₃, WCl₆-Na₂CO₃-Mg karışımlarına ilave edildiğinde WCl₆ ve WO₂Cl₂ fazları ortadan kaybolarak sadece W₂C, WC ve W fazları elde edildi. En iyi sonuçlar ise ağırlıkça % 70 fazla Na₂CO₃ içeren WCl₆-Na₂CO₃-Mg karışımları için elde edildi. Bunun sonucunda 5 saat boyunca mekanik alaşımlama ve 7M HCl ile liç prosesi sonrası 191 nm ortalama partikül boyutuna sahip saf WC tozları sentezlendi. Bu tezin bir diğer amacı, WC tozları üretmek için alternatif bir üretim tekniği kullanmak ve özellikle mekanik alaşımlama / mekanokimyasal sentez ve otoklav yöntemleriyle meydana gelen ürünlerini karşılaştırmak olduğundan aynı ham maddelerden (WCl₆-Na₂CO₃-Mg karışımı) WC tozlarının üretilmesi için üçüncü aşama olarak düşük sıcaklıkta otoklav işlemi kullanıldı. Otoklav işleminde, reaktif parçacıkları aktive ederek reaksiyon sıcaklığını azaltmak ve mikro yapının dağılımını homojenleştirmek için mekanik aktivasyon kullanıldı. Bu yöntemde, toz karışımları bir hidrotermal reaktöre yerleştirildi ve hidrotermal reaktör bir fırında ısıtıldı. Bu otoklav işlemi, sıcaklık ve sentez süresi, fazla karbon kaynağının tipi, karbon kaynağı ve indirgeyici madde miktarları değiştirilerek gerçekleştirildi. Üretim koşullarının optimizasyonu sağlanarak yüksek saflıkta ve nano boyutlu tungsten karbür tozu elde edildi. Yüksek miktarda WC fazına, düşük miktarda ise W₂C fazına sahip tungsten karbür tozları ağırlıkça % 100 fazla aktif C ilave edilmiş WCl₆-Na₂CO₃-Mg tozlarının 8 saat boyunca 700 °C’de hidrotermal reaktörde otoklav yöntemiyle sentezlenmesi ve ardından 7M HCl ile liç uygulanmasıyla elde edilmiştir. Ağırlıkça % 100 fazla aktifleştirilmiş C ve 7M HCl ile liç uygulandıktan sonra otoklavlanmış tozların ortalama parçacık boyutu 200 ve 900 nm arasında bir boyut dağılımı ile 384 nm olarak ölçülmüştür. Ayrıca bu tozların TEM karakterizasyonunda kapalı WC tozları içinde grafitik tabakalar gözlenmiştir.

WC tozları, literatürde ilk kez mekanik-kimyasal sentez yoluyla WCl_6 - Na_2CO_3 -Mg toz karışımlarından üretildi. Bu şekilde, WC toz üretimi için yeni hammaddelerden elde edilen mekano-kimyasal sentez sonuçları literatüre katkıda bulunmuştur. Ayrıca, bu tez, basit, enerji tasarrufu ve oda sıcaklığı yöntemi olan mekanokimyasal yöntemin ve tungsten karbür üretmek için daha geleneksel bir yöntem olan otoklav yönteminin karşılaştırmasını sağlar.



1. INTRODUCTION

Transition metal carbides have been explored since 1950's due to their special characteristics which offer several advantages as tools and building materials used at high temperatures and in aggressive environments operating under high loading conditions (Williams, 1971; Toth, 1971; Oyama, 1996; Andrievski, 1999; Upadyaya, 2001). Through the all transition metal carbides, WC is an important material due to its superior properties related to strength and rigidity (Upadyaya, 2001; Kurlov and Gusev., 2006). The properties which make them attractive for many applications are high hardness, high rigidity, high melting point, good compressive strength, high fracture toughness, high density, high elastic modulus, high chemical and thermal stability, high Young's modulus and high thermal conductivity, heat and oxidation resistance, low thermal expansion coefficient, good electrical and thermal conductivity and good wear resistance (Schwarzkopf and Kieffer, 1953; Toth, 1971; Hugosson, 2003; Koc et al., 1999). There are two phases in the binary W-C system: WC and W_2C . These two phases possess various polymorphic modifications that are stable in different temperature and composition ranges. There exist three polymorphs of the W_2C phase above 1250 °C which are α - W_2C (primitive hexagonal, 29.5–32.5 at % C), β - W_2C (primitive orthorhombic, 29.5–33 at % C) and γ - W_2C (primitive hexagonal, 25.5–34 at % C) Besides, there are two polymorphs of the WC phase which are β -WC (face-centered cubic, 37.1–50 at % C) and α -WC (primitive hexagonal, 49–50 at % C) (Kurlov and Gusev, 2006; Sara, 1965; Okamoto, 2008). Tungsten carbides have been used in cutting tools, mining tools, milling cutters, machine tools, cement drills, saw blade tips, and wear resistant parts as a hard metal (Georgiev, 2006; Schwarzkopf and Kieffer, 1953, Toth, 1971; Kosolapova, 2012; Beardsley, 1992; Rieck, 1977). They are also used as a in the fabrication of high temperature furnace crucibles and other components (Georgiev, 2006). Moreover, they are used as a substitute some noble metals like Pt, Pd and Ir in catalysis industries (Lecleercq et al., 1989; Ledoux et al., 1992), erosion-resistant coatings for aerospace elements (Ledoux et al., 1989; Garg and Dyer, 1989) and thin diffusion

barrier in microelectronic industries (Ghaisas, 1991). Many production techniques have been utilized in the synthesis of tungsten carbides with different raw materials. For instance, elemental W and C powders were used to in solid-state direct reaction at a temperature between 1200°C and 2000°C under controlled atmosphere (Toth, 1971; Lassner and Schubert, 1999; Yih and Wang, 1979). WC powders have been synthesized by carbothermal reduction between high-energy ball-milled CaWO_4 carbon coated WO_3 or mechanically activated WO_3 powders at temperatures in the range of 600 °C-1600 °C under flowing Ar/H_2 atmosphere or vacuum (Polini et al., 2015; Singh and Pandey, 2013; Yih and Wang, 1979; Koc and Kodambaka, 2000, Ma and Zhu, 2010; Kim and Kang, 2014). Chemical vapor condensation (CVD) method is also used to produce WC. Kim and Kim (2004), used CVD method of $\text{W}(\text{CO}_6)$ precursor with CO carrier gas at 500 °C- 1000 °C under air, Ar and other vacuum atmosphere gases. Electric discharge machining of W rods and subsequent annealing at between 800°C–1600 °C under N_2/H_2 atmosphere was implemented to produce WC (Lin, 2005). Carburization of W_2N and WS_2 was carried out under CH_4/H_2 atmosphere in the temperature range of 777 °C–900 °C to produce WC powders (Hara et al., 2007). WO_3 and C powders were heated in the presence of KCl/Ni/Fe at 1800 °C and WC powders were synthesized (Rees et al., 2008). A mixture of W powders and activated/milled viscose rayon cloth was treated thermally at 1000°C under Ar gas flow for manufacturing WC (Lukovic et al., 2015). In addition to these methods, hydrothermal reaction of ammonium metatungstate (AMT)/corn starch blends at 200 °C followed by spray-drying (at 250 °C) and heating (at 980 °C under vacuum) treatments (Singh and Pandey, 2015), combustion synthesis of W and activated carbon powders under electric field (Jiang et al., 2004), self-propagating high-temperature synthesis of WO_3 , Mg, C, NaCl and Na_2CO_3 containing powder mixtures at temperatures below 1600 °C (Won et al., 2007), electrochemical synthesis from halide-oxide melts under excess CO_2 pressure (Malyshev et al., 2002), molten salt synthesis at 1000 °C from mechanically activated W-C-NaCl KCl powders (Yang et al., 2011), chemical synthesis (dissolving in water and spray-drying) and heating of ammonium paratungstate (APT), AMT and glycine containing precursors at 1300 °C under Ar/H_2 atmosphere (Kanerva et al., 2015), calcining and thermal processing of AMT and glucose mixtures up to 1300 °C (Jin et al., 2012), and (combined process of calcination (at 600 °C), nitridization (with ammonia at 680 °C) and carburization (under CH_4/H_2 gas

at 880 °C) starting from AMT (Thomas-Garcia et al., 2014) were utilized in the synthesis of WC. All these techniques mentioned above could be restricted by high reaction temperatures, long reaction time and the use of expensive and advanced equipment and technology. For this reason, an effective method that can come through these restrictions and provide advantages of time, simplicity and inexpensiveness of equipment and energy savings should be explored. Recently, mechanical alloying and mechanochemical techniques have been utilized for the direct synthesis of nanocrystalline WC powders at room temperature without the need of any external heat (El-Eskandarany, 2000a; Öveçoğlu and Özkal, 2004; Bolokang et al., 2010; Hoisenpur et al., 2013; El-Eskandarany, 2000b; 2005; Zhu et al., 2010; Sakaki et al., 2009; 2013; Stanciu et al., 2016; Tan and Wu, 1998; Tan, 2009). Further, mechanical alloying and mechanochemical methods can be employed to a precursor preparation method as a mechanical activation to enhance the activity of the raw materials and make ready them for subsequent heat treatments (Polini et al., 2015; Lukovic et al., 2015; Sing and Pandey, 2013; Koc and Kodambaka, 2000; Ma and Zhu, 2010; Kim and Kang, 2014; Yang et al., 2011). It makes the surface of reactant particles more active and the microstructure distribution of reactants more homogeneous (Akçamlı, 2016). Throughout the activation process, a large amount of energy from the ball or ball wall collisions is transformed into structural defects (such as vacancies, dislocations and stacking faults) stored in the particles (Akçamlı, 2016; Balaz, 2008; Boldryev and Tkacova, 2000; Butyagin, 1984; Mc Cormick and Froes, 1998; Murty and Raganathan; 1998; Sopicka-Lizer, 2010; Suryanarayana, 2001).

In this dissertation two methods were utilized to obtain WC powders. These are mechanochemical synthesis and autoclave processing. Mechanochemical synthesis was used to express advantageous of this methods above-mentioned. On the other hand, low temperature autoclave processing for synthesis of WC powders was utilized as an alternative method with mechanical activation by high-energy ball milling to decrease the reaction temperature during the autoclave synthesis. Firstly WC powders were synthesized from WCl_6 -Mg- Na_2CO_3 powder blends by using high-energy ball milling. In this present study, mechanochemical synthesis of tungsten carbide was carried out using WCl_6 -Mg and Na_2CO_3 powder blends. To the best of our knowledge, this is a pioneering work in terms of utilizing the WCl_6 -Mg and Na_2CO_3 powder blends in the fabrication of WC. In other words, this will be the

first work of this nature which has not been universally attempted by any researcher. WCl_6 was used as tungsten source, Na_2CO_3 was utilized as C source and Mg was used as the metallic reducing agent. Milling durations and amounts of Mg and Na_2CO_3 were varied for optimization to produce the purest WC powder. Secondly low temperature autoclave processing assisted mechanical activation was employed for the synthesis of WC powders from the same raw materials in an alternative way. In this process, mechanical activation was conducted for 2 min and later mechanical activated powders were placed in hydrothermal reactor and the temperatures of reaction and amounts of reactant powders were varied. Different types of carbon sources were also used such as graphite and activated carbon to investigate the results of chemical reactions and conclude the optimal reactants for the synthesis of the purest WC powders. The detailed characterization investigations of synthesized powders were conducted using X-ray diffractometer (XRD), particle size analyzer (PSA), stereomicroscope (SM), scanning electron microscope/energy dispersive spectrometer (SEM/EDS), transmission electron microscope (TEM), pycnometer and differential scanning calorimetry/thermogravimetric analysis(DSC/TGA). The results were discussed regarding the effect of different production conditions such as amounts of reactant powders, temperatures and durations of processes

2. LITERATURE REVIEW

2.1 Powder Metallurgy

Powder metallurgy is a low cost process of manufacturing of tools and components from ceramic, metallic or composite powders. In fact, powder metallurgy is not a newly-introduced process and Egyptians used it to make their tools for preparing iron powder from “sponge iron” B.C. 3000 years ago (Turunen et. al, 2006). During that time, furnace work at high temperatures were not yet usable, so powder metallurgy was successfully accepted as a practical method that could be successfully utilized without the need for melting and casting processes for the close-to-net or net-shaped formation of metal oxides, cemented carbides and high melting point metals. Thus, growth of this process provided to manufacture high quality iron powders by grinding, next by ball milling and followed by heating to remove the oxides on the as-milled iron powders. In the second decade of the last century, tungsten carbide powders were produced on a large scale in the industry so that modern powder metallurgy was used with great success. Powder metallurgy became more popular between the 1920s and 1940s, particularly in the 1920s after mass production of bronze brushes for bearings. (Guilemany and Nin, 2006). II. Until World War II and the 1960s, a wide variety of new composites, ferrous and non-ferrous materials were developed. In the last 50 years, powder consolidation has developed at an incredible speed, such as cold / hot isostatic pressing, shock wave consolidation, spark plasma sintering and induction hot pressing were proposed as new techniques of powder pressing.

Consequently, powder metallurgy has grown rapidly due to large scale powders and consolidated precision and the ability to produce dense components close to the complex network. A typical powder metallurgical process shown in diagram form in Figure 2. Ball milling is a typical and basic example of the powder metallurgy technique to obtain advanced materials has fine particle size (El-Eskandarany;2015).

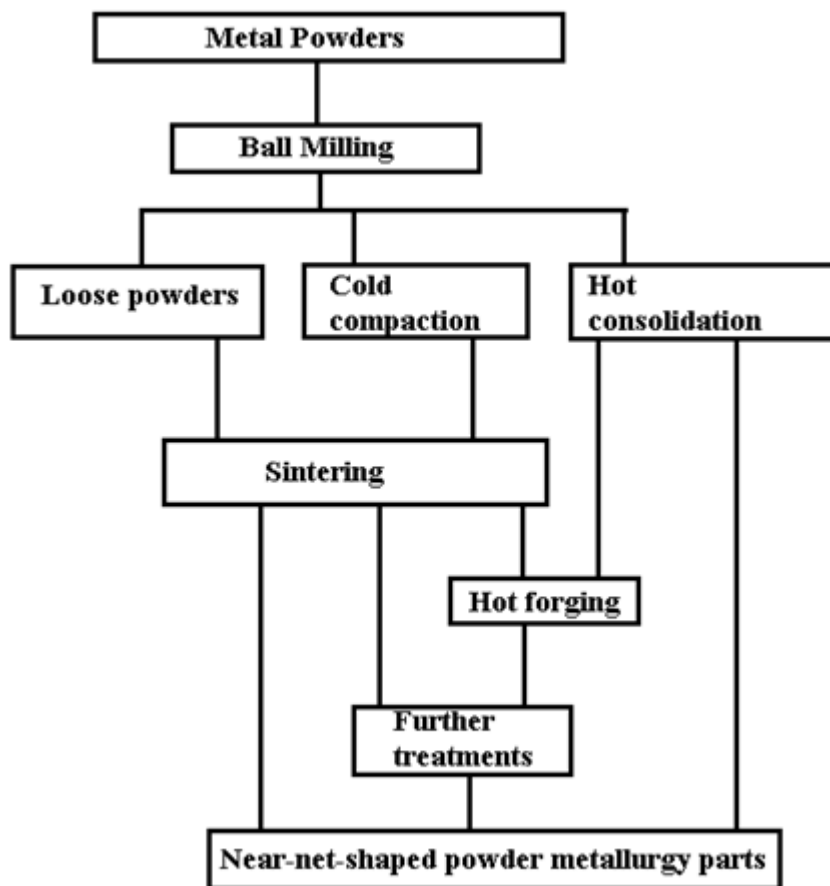


Figure 2.1 : The flowchart shows the mechanochemical methods of powder synthesis and its results on consolidation (El-Eskandarany, 2015).

2.2 Mechanical Alloying and Mechanochemical Process

2.2.1 Historical Perspective

The ophrastus of Eresus, student of Aristotle, published a book in which he described the mechanochemical process with the sentence....”native cinnabar was rubbed with vinegar in a copper mortar with a copper pestle yielding the liquid metal. For this mechanochemical process, equation 2.1 is given as reduction reaction (Balaz, 2008).



Carey Lea, (1882; 1883; 1884) the first mechanochemist, remarked in his investigations that mechanical energy can induce chemical reactions as well as electrical energy, heat, and light (Balaz,2000). Tamman (1929) probed the impact of mechanical energy on metals and claimed that this energy can provide to increase potential energy of materials. Ostwald (1887;1919) suggested to use the term of mechanochemistry for the first time in the synthesis of materials induced by mechanical forces. Ostwald's theoretical ideas about the relationship between mechanical and chemical energy led him to win the Nobel Prize in 1909. He realized mechanochemistry in a broader sense as part of physical chemistry such as thermochemistry, photochemistry and electrochemistry (Balaz, 2008). The definition asserted by Butjagin is: "Mechanochemistry is a science on acceleration and initiation of reactions in gases, liquids and solids by the effect of plastic energy" (Butjagin, 1971). Heinicke (1984) defined the mechanochemistry with chemical and physico-chemical transformations through mechanical energy and this definition was broadly accepted.

Initially, the basic applications of mechanochemical process were observed in the field of extraction metallurgy using extraction and leaching as a preliminary step of the process. The industrial requirement of developing an alloy combination oxide dispersion (ODS) by γ' -precipitation hardening in a nickel-based superalloy for applications of gas turbine has led this very simple technique to produce advanced materials. Benjamin and co-workers of the International Nickel Company (INCO) Paul D. Merica Research Laboratory (1970) proved that mechanical alloying (MA) should be used when normal distribution of oxide particles of liquid metals is impossible, and after a long study in 1966 developed a mechanical alloying process to produce nickel-based superalloys for applications of gas turbine. This technique was thought to compound the high temperature strength of gamma-prime precipitate. In this way, MA was first used as a technique to fabricate oxide dispersion strengthened (ODS) alloys in industry (Suryanarayana, 2001). Many researchers were interested in the process of MA to produce phases of novel alloy and ODS materials. Much of the subsequent work on the development and production of ODS superalloys for use in the aerospace industry was carried on INCO laboratories in USA (Ivanov and Suryanarayana, 2000). ODS materials are currently the main user of the MA process in the commercial manufacturing of iron-based or nickel high-

temperature alloys that can be utilized at higher temperatures than 1300°C in carburizing and sulfurizing environments (Benjamin, 1970). Öveçoğlu and Nix (1986) investigated a rapidly solidified and produced Al-Fe-Ce alloy of dispersion strengthened via MA. The INCO laboratories performed further researches about ODS superalloys to be utilized for aerospace industries. Another dramatic example of commercial application was using mechanochemically alloyed powders of Fe and Mg as heaters of meal-ready-to-eat (MRE) by USA during the Desert Storm Operation in 1996 (Ivanov and Suryanarayana, 2000)

Benjamin (1970) developed and named the process as “milling/mixing”, but Ewan C., a patent attorney worked for INCO changed it to “mechanical alloying” for the first patent application and this new name was begun to be used in the literature (Suryanarayana, 2001). In mid-1966, the ball milling process drew attention as a process that makes metal powders by its alloy in powder metallurgy, as it can coat hard phases (eg, ZrO₂ or WC) with a soft surplus (Co or Ni). It had been used for over 70 years to coat of tungsten carbide (El-Eskandarany, 2001; Koch et al., 1983; White, 1979).

The nickel-chromium-aluminum-titanium alloy consisting of thoria dispersoids was first synthesized via MA in a small shaker mill at high speed and then in a gallon mixed ball mill. Thus, MA was introduced as a technique for producing oxide dispersion-strengthened (ODS) alloys on an industrial scale. (Suryanarayana, 2001) Mechanical alloying is a high energy ball milling technique normally operated dry and is used to produce a wide variety of commercial and scientific materials. In 1981 an amorphous phase of an Y-Co intermetallic compound and in 1983 Ni-Nb system were synthesized by respectively mechanical grinding and ball milling (Ermakov et al., 1981; Koch et al., 1983; Suryanarayana, 2001). Thereafter, MA came to be known as a potential technique operating under nonequilibrium conditions. Since the mid-1980s, syntheses of various stable and metastable phases have been researched, included supersaturated solid solutions, amorphous alloys, crystalline and semi-crystalline intermediate phases. (Koch et al., 1993; Suryanarayana, 1995; Suryanarayana and Norton 1998; Lai and Lu, 1998; Murty and Ranganathan, 1998). Since the early 1990s, MA has continued its efforts to realize the fundamentals of the process by modeling. This method which is an uncomplicated but effective process

has been utilized for metals, polymers, ceramics and composite materials (Suryanarayana, 2001).

El-Eskarandy et al. (1991; 1992; El-Eskarandy 2000) fabricated nanocomposite WC-14% with the characteristics of fracture toughness and high hardness values in 1991 and 1992 and nanocrystalline WC and nanocomposite WC-Co that posses excellent morphological properties and has high values of hardness and elastic modulus in 2000 by the ball-stable and milling technique. Boldryev and Tkacova (2000) explained that mechanical activation is a multi stage process with changings in energetic parameters. This multi-step process consists respectively of storage of defects, amorphization, formation of metastable polymorphs and chemical reactions (Balaz, 2008).

Similarly, in addition to mechanical alloying process, mechanochemical methods have a considerable interest for the synthesis advanced materials. Considering developments of the mechanochemistry up to now, every year more than 1500 papers were published in this field. The mechanochemical process provides to synthesize of advanced materials which have unique characteristics and enlarges the application areas of the method (Sopicka-Lizer, 2010). Hydrogen storage materials such as metallic and or complex hydrides, photocatalysts and lithium ion batteries can be produced by mechanochemical process. Mechanochemistry is frequently researched in the field of hydrogen storage materials and hydrogen chemistry for example: metallic and complex hydrides (Ağaoğulları, 2014; Huot et al., 2013; Maltseva et al., 2001). Furthermore, in the last decade, mechanochemical synthesis has started to be used as one of the most preferred preparation techniques for electrode materials that are nanostructured for batteries of Li-ion. In this technique, low crystalline or fast amorphous precursors are formed throughout MA and then these structures are converted to nanostructured products under low temperature and short processing time. (Ağaoğulları, 2014; Yang et al., 2010; Ninga et al., 2004;). In addition, surface modifications using mechanical doping and photocatalyst production are among the research fields of mechanochemical processes. (Yine et al., 2010; Kim et al., 2005; Ağaoğulları, 2014; Komarov et al., 2010;). Moreover, intensive studies on the application of mechanical and chemical processes to large scale processes of minerals and waste have resulted in several practical applications, including

tungsten-containing ore treatment introduced at the Chirchik Factory or amalgam production for pediatric dentistry introduced at the Nikolsky Factory (Boldrev, 2006).

2.2.2 High-energy ball milling

High-energy ball milling is a method in which a powder blends placed in a ball mill is exposed to high-energy collisions between the balls and powder particles. It is a way of providing the formation of chemical reactions during milling by varying the reactivity of the ground solids and the conditions under which chemical reactions occur. (Rane et al., 2018). It was first advanced by John Benjamin (1970) and his colleagues at the International Nickel Company in the late 1960s. At that time, oxide particles (Y_2O_3 , Al_2O_3 , ThO_2) in nickel-based superalloys could not be produced by conventional powder metallurgy techniques. However, high-energy ball milling was discovered to be a technique that produces fine and uniform dispersions of oxide particles. The movements of the balls and the powder are shown in Figure 2.2. Because of the opposite direction of rotation of the bowls and balls, the centrifugal forces are synchronized alternately. In this way, friction is occurred by hardened milling balls and alternating rolling of the powder mixture in the inner wall of the container and hitting it against the opposite wall (Faraji and Kashi 2018).

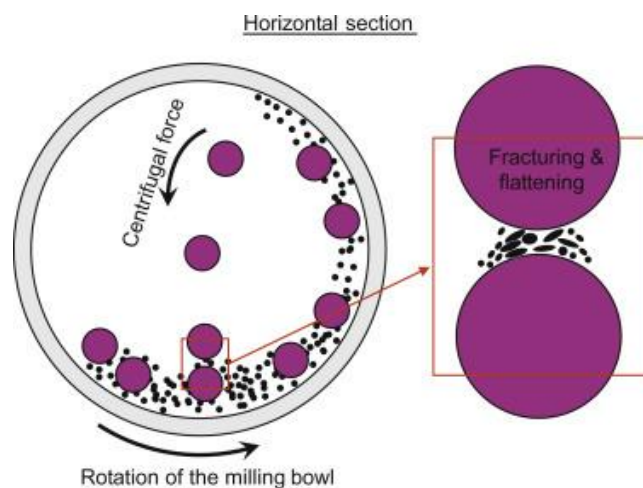


Figure 2.2 : The schema the movements of the balls and powders. (Faraji and Kashi 2018).

Throughout the high-energy ball milling process, the particles are exposed to high energetic effects. There are five steps in the mechanical alloying process: (1) initial powders, (2) flatterring, (3) welding, and (4) 3D welding and fracturing, (5) stable end

product. These five steps of MA process are schematically illustrated in Figure 2.3 (Balaz et al., 2013). In the first step of high-energy ball milling, the particles are flattened by the forces resulted by the pressure application of the balls. Microforging results in changes in the shape of clumps of particles due to repetitive forces from the grinding balls. However, such deformation of the powders does not show a clear change in mass. Following the flatenning step, a significant event occurs in the second step compared to the first step. At this step, cold welding becomes important. The forceful mixture of powder components reduces the distance of the diffusion. Fracture and cold welding are leading processes of milling at this stage. Although some decomposition occurs, there is still inhomogeneity in the chemical composition of the powder. In the final step of the mechanical alloying process, further purification and decrease in particle size occurs. The microstructure of the particle becomes more homogeneous than the previous steps. At the end step of mechanical alloying, the particles have a highly distorted metastable structure. Further milling (further mechanical alloying) after this step can not physically improve the distribution of dispersion. Thus forms a true alloy with a composition that resembles initial components (Faraji and KAshi, 2018).

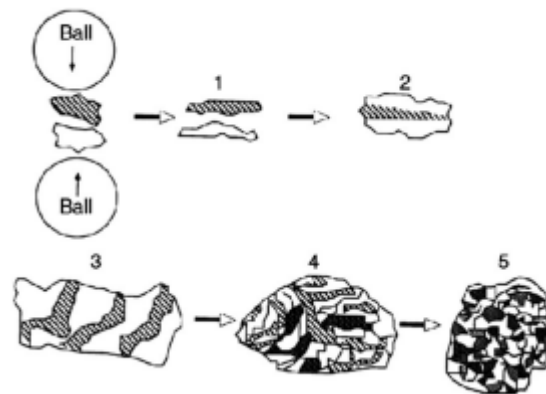


Figure 2.3 : Steps of mechanical alloying process: 1. initial powders, 2. flatenning, 3. welding, 4. 3D welding and fracturing, 5. stable end product (Balaz et al., 2013).

2.2.3 Mechanical alloying (MA)

Mechanical alloying (MA) is a type of high energy ball milling and mechanically generated solid state reaction that occurs between diffusion pairs and produces homogeneous materials from the reactive powders of materials in a ball mill which is a reactor work at room temperature (El-Eskandarany, 2015). In the MA process,

raw powders are mixed with the right proportion into the mill together with the grinding medium and then mechanically alloyed for desired length of prolonged time (Suryanarayana, 2001).

There are several types of high- energy mills which have various working principle such as compression, shear, impact. Types of mills which are the mostly utilized for high-energy milling are illustrated in Figure 2.4 (Balaz et al., 2013). They are classified in terms of capacity, milling efficiency and other settings such as heating, cooling, etc. (Suryanarayana 2001).

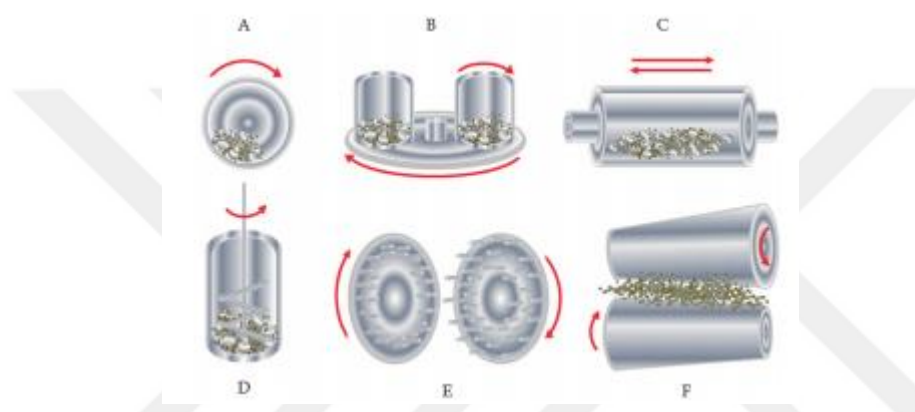


Figure 2.4 : Various types of mills utilized for mechanical alloying: A. ball mill, B. planetary ball mill, C. vibration mill, D. Attritor, E. pin mill, F. Rolling mill (Balaz et al., 2013).

2.2.3.1 SPEX™ mixer/mill

These mills are produced by SPEX™ Cert Prep, Metuchen, NJ especially to use for laboratory researchs. The designs of mills used today have two vials in which powders are fixated in the clamp with grinding balls and shaken back and forth with lateral movements of the vial. In Figure 2.5(a), a type of SPEX 8000 mixer/mill is shown as an example. SPEX mixer/mills can be regarded as high-energy mills because the velocity of the balls are on the order of 5 m/s and the speed and the amplitude of the clamp motion is respectively about 1200 rpm and 5 cm (Suryanarayana, 2001).

The materials for the vials of SPEX mills can be hardened steel, tungsten carbide, zirconia, alumina, stainless steel etc. A tungsten carbide vial, gasket and grinding balls are illustrated in Figure 2.5(b) (Suryanarayana, 2001).

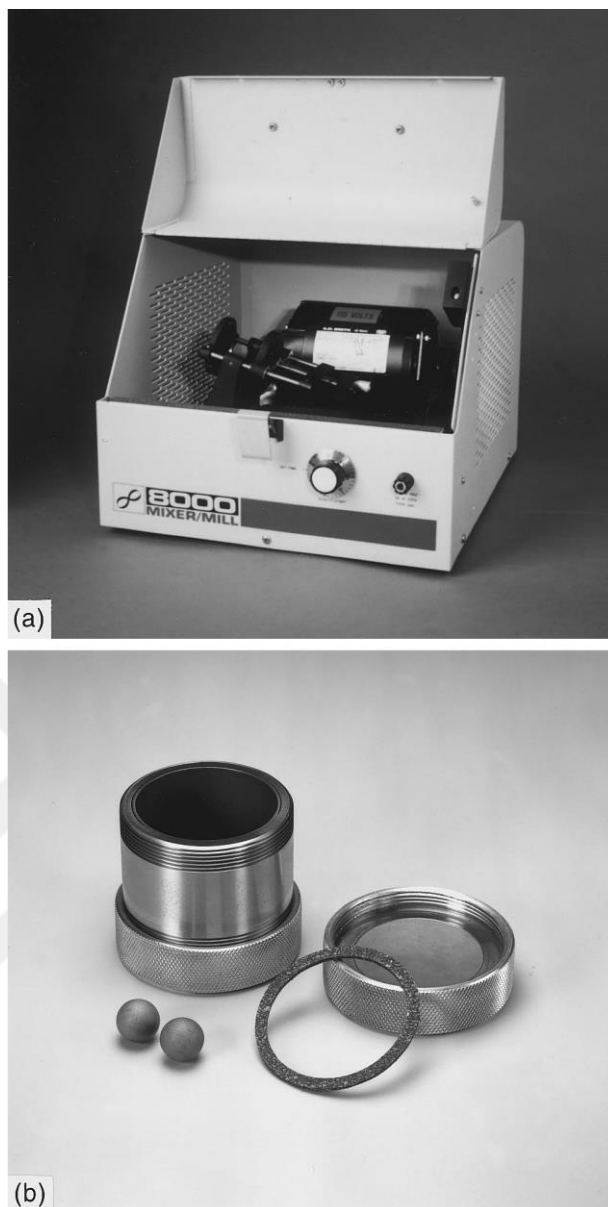


Figure 2.5 : (a) Spex 8000 mixer/mill. (b) Tungsten carbide vial, lid, gasket, and balls (Suryanarayana, 2001).

2.2.3.2 Planetary ball mills

The principle of planet-like movement of the vials is used in planetary ball mills as the name suggests. These mills can be used to mill for much amount powders such as a few hundred grams of the powder. It has a rotating support disk and a special drive mechanism that provides it to rotate around its own axes (Suryanarayana, 2001). The planetary ball mills use the principle of centrifugal acceleration instead of gravitational acceleration (Balaz, 2008). Because the centrifugal force which is generated by the vials rotating around their own axes and by the special drive mechanism have an

impact on the vial contents. The vials and the support disc rotate in opposite directions causing two effects. The first effect is friction effect that is produced by striking of grinding balls inside wall of the vial. The second effect is the impact produced by the free removal of the grinding balls from the inner part of the vial and impacting the grinding balls opposite the wall.

Russian scientists studied planetary ball mills for mechanical activation (Golosov, 1971; Molcanov et. al., 1988; Malcanov and Jusupov, 1981; Avvakumov, 1986). They observed that these mills provide high mechanical activation energy by a relatively short milling time (Balaz, 2008).

In planetary ball mills, the linear speed of the balls is higher than in SPEX mills, but the impact frequency in SPEX mills is much higher than in planetary ball mills. For this reason, the planetary ball mills are established as lower energy mills (Suryanarayana, 2001).

2.2.3.3 Attritors

The attritors are comprised of a cylindrical milling chamber with a drive shaft having a plurality of impellers mounted on the rotary shafts. There are many types of impellers such as flat discs, discs with various geometric openings and concentric rings (Balaz, 2008). The impellers induce charging of the balls that reduces the powder size. Collisions occur amongst balls, amongst balls and container wall, and amongst impellers and agitator shaft result in reduced powder size (Balaz, 2000).

Attritors can be used to mill large amounts of powder (from 0.5 to 40 kg). The grinding tanks or containers can be either in stainless steel or stainless steel coated inside with, alumina, zirconia, silicon carbide, polyurethane, silicon nitride and rubber. Grinding media can also be tungsten carbide, stainless steel, zirconia, flint sand, steatite ceramic, glass, silicon carbide, silicon nitride, chrome steel and carbon steel. Figure 4 illustrates diagrammatic view of the attritor. The operation of the attritor is so uncomplicated. The powder is mounted to a stationary tank with grinding media. The powder mixture is rotated by a shaft whose arms rotate at about 250 rpm. This speed of the powders led to impact forces on the material (Suryanarayana, 2001).

2.2.3.4 New mill design

In recent years, special designs of several special purpose millers have been developed. Nishin Giken designed a mill which could check the temperature of milling from very low temperatures to a high temperature of 300°C (Url-1). Basset et al. (1993) and Kimura and Kimura (1990) used exceptional high-energy ball mills to synthesize amorphous alloys and nanocrystalline materials. Bakker et. al. (1995) developed a mill and a large ball was used in vials with the sample in this design of mill. This mill worked low efficiency because the sample was milled only throughout collisions with a long repeating time. Calka and Wexler (2002) developed magnetic mechanical milling and electric-discharge-assisted mechanical milling. Miani and Maurigh (2004) devised a new scalable concept of attrition mill to produce nanosize materials (Balaz, 2008).

2.2.3.5 Process variables

Mechanical alloying is a complicated synthesis method. Therefore, there are several important variables to acquire the required product phase and / or microstructure. Some parameters which are important and mentioned in this thesis are listed below:

a) Type of the mill, b) Material of milling media, c) Ball-to-powder ratio, d) Extent of filling of the milling chamber, f) Milling atmosphere, g) Milling speed, h) Milling time, i) Temperature of the milling, j) Process control agent and k) Type of mills

Several types of mills are used for mechanical alloying process. These mills are different in many characteristics such as capacity, speed of milling, control mechanism for temperature of milling and contamination of powders. SPEX mills are usually utilized for alloy screening. Planetary ball mills and attritors are utilized to synthesize large amount of powders. Mills which are specially designed are utilized for special purposes. Table 2.1 illustrates different capacities of various types of mills. Considering all variables of process such as type and quantity of the powder and the last desired product, the most appropriate type of mill can be chosen (Suryanarayana, 2001).

Table 2.1 : Different capacities of the various types of mills (Suryanarayana, 2001).

Mill type	Sample Weight
Mixer mills	Up to 2 x 20 g
Planetary mills	Up to 4 x 250 g
Attritors	0.5-100 kg
Uni-ball mill	Up to 4 x 2000 g

2.2.3.5.1 Materials of milling the media

The type of the materials of the milling media is important for mechanical alloying process because many collisions occur with milling balls and inner walls of the milling chamber. Commonly, materials used for milling media (milling chamber, vial and balls) are can be several steels (stainless, tungsten carbide lined, hardened chromium and bearing steel), alumina, silicon nitride, zirconia and tungsten carbide. (Ağaoğlu, 2014; Balaz, 2008)

The size and also the density has an important role for the milling efficiency. High density and the large size of the milling media should be preferred than low density and small size of the milling media. They provide greater impact energy for powders due to their larger balls, large weights and higher densities. In addition, the balls must be denser than the materials to be milled (Suryanarayana, 2001).

Although many investigators utilize solely one size of the milling medium, using different size balls is more advantageous. Because the higher collision energy can be gained by using different diameters of the balls than only one size of the balls (Balaz, 2008).

In the earlier stages of the milling process, the grinding medium can be coated with the powders being milled and can be cold welded that provides an advantageous situation. Because it avoids excessive wear of the milling medium and the contamination of the powders because of the reason of wear of the grinding medium. The difficulty of removing powders from milling medium provokes a disadvantageous situation that affects the efficiency of powder (Suryanarayana, 2001).

2.2.3.5.2 Ball-to-powder ratio (BPR)

Ball-to-powder ratio (BPR) is an significant method variable that describes the weight ratio of grinding balls to powder load. From values as low as 1:1 to as big as 220:1 BPR values have been used in a wide range by many investigators. When milling is conducted in a small capacity mill, a ratio of 10:1 is commonly used. But a higher value of BPR to 100:1 is used when milling is occurred in a large capacity mill, such as milling in an attritor. BPR also effect the time required for milling process to obtain a specific phase in the product. When the higher BPR is used, shorter times are demanded (Suryanarayana, 2001).

For a mechanical alloying process, if low BPR values and low speeds of rotations are used it is called as “soft” conditions. But when high values and high speed of rotations are used, named as “hard” conditions. Whereas soft conditions of MA compises metastable phases, hard conditions generate equilibrium phases as presented in the Zr-Co system (Gerasimov et al.,1991).

2.2.3.5.3 Extent of filling of the milling chamber

The extent of filling of the milling champer is a significant parameter for the mechanical process. If the amount of balls and powder particles are large, the area where the balls and dust will move becomes smaller and the energy from the impact is reduced. There must therefore be sufficient area for the balls and powder particles to move freely in the milling chamber. The extent of filling of the milling chamber relies on type of mill. Ordinarily empty space should be about 50% but in attritors this ratio can be decrease to 20-30% (Balaz, 2008).

2.2.3.5.4 Milling atmosphere

The milling atmosphere could cause the contamination of the powder. Milling should therefore be carried out in containers that are emptied or loaded with an inert gas such as helium or argon. Most commonly, high purity argon is utilized to prevent contamination or oxidation of the sample. Generally, atmosphere-controlled glove boxes discharged and refilled with argon gas are used only when loading into the vial. Occasionally, milling operation in mills are carried out in evacuated glove boxes (Suryanarayana, 2001).

Different types of atmosphere can be used for different effects. Nitrogen (N_2) and ammonia atmospheres (NH_3) can be used to synthesize nitrides. Similarly to synthesize hydrides, hydrogen atmospheres can be carried out (Ogino et al., 1993; Balaz, 2008; Calka and Radlinski, 1991). Also the nature of the final phase can be affected by the type of the atmosphere (Suryanarayana, 2001). For example Ogina et al. (1990) milled Cr-Fe powder mixtures in different type of atmosphere. If the powder was milled in an argon atmosphere, Cr peaks were detected but amorphous phase was not detected by X-ray diffraction. However, if the powder was milled in air comprising nitrogen or argon atmosphere, amorphous phases were detected in final product (Ogina et al., 1990).

2.2.3.5.5 Milling speed

Milling speed has a significant experimental parameter which can affect the mechanical alloying process. Because simply, when the mill rotates faster, the higher energy would arise. But there are some restrictions about the maximum velocity and energy due to the design of the mill. Higher than a specific velocity, the pellets do not apply any collision with the powder because the balls are fixed to the inner walls of the vial. To produce maximum impact energy, the velocity of the balls must be below this critical value maximum collision energy the speed of the balls should be below this critical value (Suryanarayana, 2001).

The other limitation about the maximum speed is the temperature of the vial. When the balls have maximum speed, the temperature of the vial would be a high value. Where diffusion helps to homogenate or alloy of powders, high value of speed can be beneficial for mechanical alloying process. However, high temperatures can not be desired where the temperature induces the decompositions of supersaturated solid solutions or occurring other metastable phases throughout milling process (Suryanarayana, 2001). As an example, Ni-Zr powder mixture was milled at different energy levels that induced different final products. At the highest energy level, a fully amorphous phase was occurred, at low and intermediate energy level, crystalline and as well as amorphous phases were occurred (Calka and Radlinski, 1991).

2.2.3.5.6 Temperature of the milling

The temperature can have a significant effect on the formation of the milled powder with diffusion processes. There are two types of temperature effects while the milling process. One of these is “local temperature resulting from ball collisions.. The other one is “the overall temperature“ in a vial. Milled powders consist of powders attached to vial walls, balls and free part moving in the milling chamber, have different temperatures. The diffusivity at defect concentration in the powders are affected by the temperature of the powders and this also influence the phase transformations (Suryanarayana, 2001; Balaz, 2008).

There have been limited number of investigations in which the temperature of the milled powder has been intentionally changed. Intentional change of temperature can be accomplished by dropping liquid nitrogen onto the mill container to lower the temperature and heating the mill bottle to increase the milling temperature.

2.2.3.5.7 Process control agent (PCA)

There are several materials which are called as process control agents, surfactants or lubricants, adsorb on the interfaces, minimize cold welding amongst powder particles and hence prevent agglomeration. Process control agents can be solids, liquids or gases. They are utilized in an amount of about 1-5% of the total powder. Hexane, stearic acid, ethanol and methanol are commonly used and important process agents. In addition didcyl dimethyl ammonium bromide (DDAB), sodium-1,2-bis-dodecloxy carbonyl sulfa diodecyl dimethyl ammonium acetate (DDAA), polyethylene glycol, trichlorotrifluoroethane, ethyl acetate, dodecane, oxalic acid, alumina, alumina nitrate, borax and boric acid are also used as other process control agents (Suryanarayana, 2001).

The type and amount of the process control agent and the type of starting powders determine the size, purity and shape of the milled powders. Usually using large amount of process control agent causes the reduction of the particle size by 2-3 orders of magnitude. When 1 wt % stearic acid was utilized with aluminium and milled for 5 hours, the particle size of 500 μm of final product was synthesized. Also when 3 % stearic acid was used, the particle size of the final product decreases to 10 μm (Balaz, 2008; Lai and Lu, 1998).

2.2.4 Mechanism of mechanical alloying

In mechanical alloying (MA) process, powders are enclosed in a container with steel balls or tungsten carbide coated balls and the container in the miller is shaken up (Fecht, 2002). In this process, particles are repeatedly flattened, cold welded, fractured and rewelded, respectively. Balls trapped in container collide with each other or with the reactor walls. In each collision about 1000 particles weighted around 0.2 mg are confined, as illustrated in Figure 2.6. Forces caused by impacts induce work hardening and fracture.

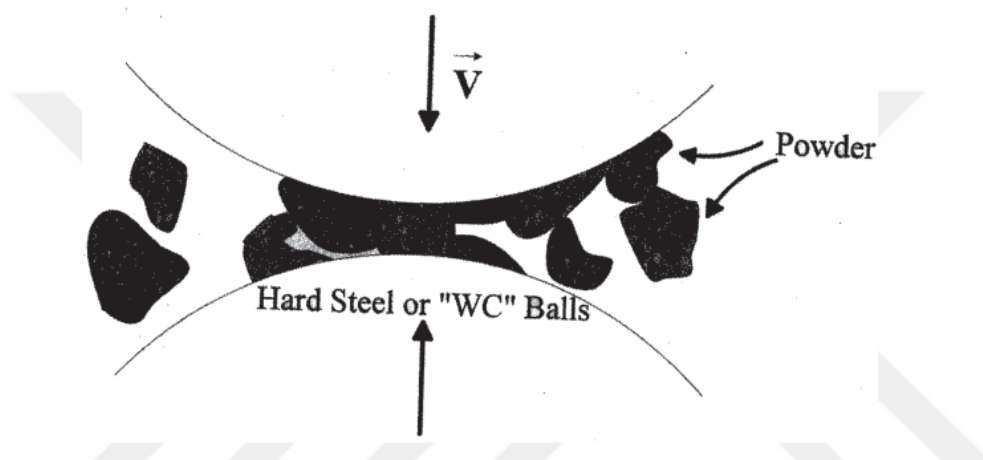


Figure 2.6 : Diagram of the process of mechanical attrition (mechanical alloying) of metal powders. Vector $\vec{v}$ point out the velocity of balls which are colliding (Fecht, 2002).

New and fresh surfaces created during mechanical alloying provide powders to weld together and this produce fine grain size. It can be said in the first steps of the milling process, particles are soft, their are large and they have an affinity to weld together. When the deformation continues, the particles work hardens and/or fractures. Fragments occurred by fracturing provides small grains without strong agglomerating forces. As the effect of grinding balls continue, the structure of particles improves but the sizes of particles do not change. As a result, as the interlayer declines, the number of layers in a particle enlarges. Also it must be noticed that the decrease in particle size is only about 0.1% during the conventional high energy milling process (Suryanarayana, 2001).

The milling time, initial particle size, starting partical size, characteristics of ingredients, equipment for the operation system and operating all parameters to produce a determined structure in mechanical alloying (MA) process. However, the

size of the initial particles is relatively insignificant. The lamellar spacing with particle / crystallite size are almost logarithmic with the milling time as shown in Figure 2.7. From one minute to one hour, the lamellar spacings shrink and crystallite or grain size reaches nanometer ranges. Therefore the advantage of MA is to be able to synthesize nanocrystallite materials (Suryanarayana, 2001; Suryanarayana, 1995; Benjamin, 1970).

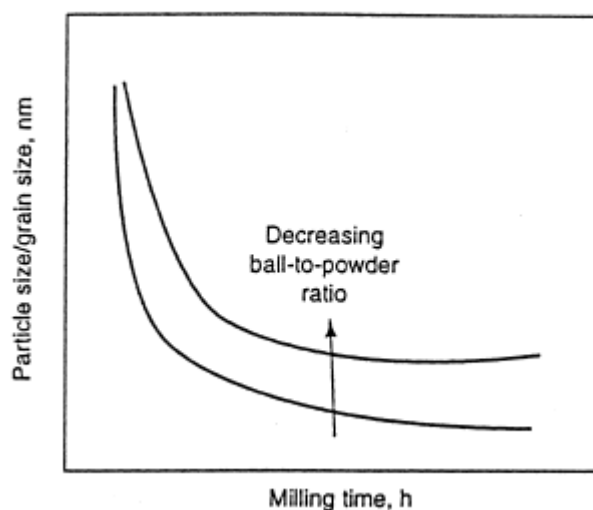


Figure 2.7 : Illustrative graph of alteration of particle/grain size with the milling time (Suryanarayana, 2001).

During mechanical alloying surface and interface contamination is a big problem especially for nanocrystalline materials. It can be minimized by reducing the milling time, preferring the purest and most ductile powders and coating of the milling tools as a thin layer of with the relevant powder materials. Whereas Fe contamination can be minimized to less than 1-2 at %, nitrogen and oxygen contamination can be reduced to less than 300 ppm. From this point of view, mechanical alloying method can be used to synthesize nanoscaled powder materials which have higher purity than other methods, such as inert-gas evaporation chemical processes or condensation (Fecht, 2002).

If refractory metals such as tungsten is mechanically alloyed in a shaker or planetary mill with high vibrational frequencies for extended durations (>30 hours), Fe contamination level can be more than 10 at %. Then again, contamination does not always have detrimental effects. Sometimes it can provide advantages for synthesizing

metal/ceramic nanocomposites with a metal which is highly reactive with the environment gas (Fecht, 2002).

2.2.5 Mechanism of mechanochemical alloying (MCA)

In 1989, a first statement was made about MA which could be utilized to induce solid-solid and liquid-solid chemical reactions (Schaffer and McCormick, 1989; McCormick et al., 1989). After that it was shown that the chemical reaction between Ca and CuO took place by the high-energy ball milling. Milling of CuO and ZnO together with Ca provided the production of β' -brass. (Suryanarayana, 2001). Actually in 1984, mechanical energy was converted into chemical energy to produce chemical reactions (McCormick; 1989). Thus, it was with this work that the terms “mechanosynthesis” or “mechanochemical synthesis” appeared for the first time in literature in mechanical alloying process.

Equation 2.2 illustrates a mechanosynthesis reaction which is named displacement reaction.



By means of a reactive metal (reductant, R) metal oxide (MO) is reduced to the pure metal. Metal chlorides and sulphides can also be reduced by this method (Suryanarayana, 2004). Figure 2.8 illustrates the chemical reaction existing between MO and R (reactants). As seen from the Figure 2.8, M and RO (product phases) formed at the interface can be described as a nominal boundary surface between the reactants. This boundary surface serves as a no reaction zone. Thus the reactants perform as a barrier and the kinetics are very slow. For this reason, elevated temperatures are needed to increase the reaction rates. It should be remarked that in mechanochemistry increasing the rate of solid-state reaction is a significant parameter with regard to the interaction between the reactants (Suryanarayana, 2004; Balci; 2015).

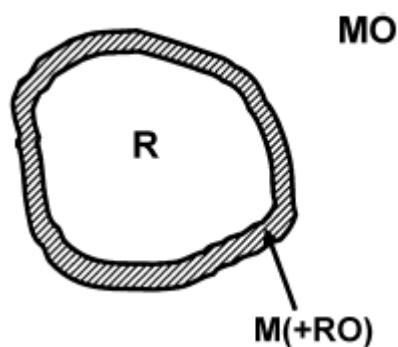


Figure 2.8 : Diagram of the chemical reaction occurring between metal oxide (M) and reductant (R) (Suryanarayana, 2004).

In the mechanochemical process, mechanical activation between the reagents are different from the process of MA (Heinicke, 1984; Gutman, 1998). Mechanical activation increases the surface area and by this way the reaction is accelerated. The energy acquired from plastic deformation, fracture and friction processes in MA are modified to other energy forms achieved from broken bonds and structural defects (Chen et al., 1997). Butyagin described mechanical activation as an increment in reaction ability on account of stable changings in solid structure. (Butyagin, 1984).

Crystal sizes decrease during high-energy milling and amorphization is induced by energy supply to these small size of crystals. In other words, a substantial amount of kinetic energy generated during high-energy milling is accumulated at the surface or in the volume of the crystals (Boldyrev and Tkacova, 2000). Small particles merge with each other to form larger particles leading to particle size increase. This particle size enlargement make the particle size reduction complicated. This phenomenon, which is closely associated agglomeration, is called as equilibrium state of milling (Balaz et al., 2013).

During the milling process, an effective gradual deterioration is detected. Three stages are observed: (a) the Rittinger stage in which the interactive relation of particles are ignored, (b) the aggregation stage in which particle interaction is present and the new surface area occurred is unproportional to the energy entried and (c) the agglomeration stage in which growing of dispersion decrease to insignificiant value and then stops. Mechanochemical reactions and all modifications in the crystal

structures take place in this stage. These stages are shown schematically in Figure 2.9 (Balaz et al., 2013; Opoczky, 1977).

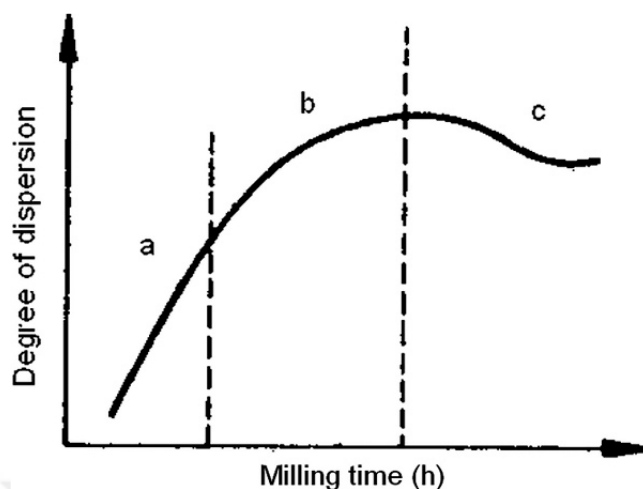


Figure 2.9 : Three-stages during high-energy milling (Opoczky, 1977).

In the mechanochemical process, there are two different kinetic mechanisms: 1. Gradual transformation: In this type of kinetic mechanism, the reaction occurs and develops slowly with each collision. 2. Self-propagating combustion reaction: In this second type of kinetic mechanism the reaction enthalpies reach very high values. Thus, critical milling time is required for self propagating combustion reaction to be initiated (Suryanarayana, 2004).

In general ball milling parameters should be optimized to change the kinetics of mechanochemical reactions. Relative proportion of the reactions which is not mentioned before can be changed also to achieve better results from mechanocmechical process. Amount of reducing agent or other type of reactans can be increased. For example in several investigations, about 10-15% stoichometric excess of reducing agent has been used to compensate the decreasing amount of reductant powder which combines with the oxygen as forming surface oxidation (Suryanarayana, 2004).

2.2.5.1 Process Parameters

Similar to mechanical alloying processes, milling temperature, grinding ball diameter, ball-to-powder weight (charge) ratio, use of process control agent, and relative proportion of the constituents or the reactans in the powder batch affect the

nature of mechanochemical alloying and kinetics of the product phases resulting from the displacement reactions. For example, whereas the reduction of copper oxide by iron takes place by combustion, the same reaction proceeds slowly under dissimilar milling conditions (Suryanarayana, 2001).

Milling temperature

McCormick et al. explored the reduction of TiCl_4 with Mg both in liquid form at room temperature (20°C) and at solid state at -55°C . They stated that when milling was carried out at -55°C , the grinding time required to produce Ti was reduced by six fold, and this was due to the fact that solid-solid collision events were more effective during mechanochemical synthesis (MCS) (McCormick, 1995). However, if both reactants were solid at both temperatures, the increased diffusivity at high temperatures would enhance the reaction kinetics, and the time needed to synthesize TiCl_4 would be shorter.

Ball-to-powder weight ratio (BPR)

When the ball-to-powder-weight ratio (BPR) increases, the time needed for the reduction reaction decreases. For instance, the required time for the reduction reaction of TiCl_4 with Mg to form Ti at 20°C was 48 h at a BPR of 2:1 it whereas only 18 h at a BPR of 12:1 (McCormick, 1995). Furthermore, as stated by Xi et al. (1996), if the collision-induced energy is high, the reduction resulting in pure metal is possible. They observed that CuO was totally reduced to the pure Cu metal at a BPR of 80:1. However at lower BPR values, they found that CuO was reduced only not totally to Cu and Cu_2O or CuO was reduced only to Cu_2O and Cu phase was not detected.

Process control agent (PCA)

Process control agent, surfactant or lubricant, adsorb on the interfaces, minimize cold welding amongst powder particles and hence prevent agglomeration. However, for reduction reactions the components are generally brittle and therefore a process control agent (PCA) is not utilized (Suryanarayana, 2001). However, there are many studies that provide attractive results about using of PCA. For example, when CuO is

mechanically alloyed without PCA, a self-propagating combustion reaction took place after an incubation period. (Schaffer and McCormick, 1990a; 1990b).

PCA acts like a diluent and inhibits the combustion reaction. In addition, it suppresses inter-particle welding during collision, decelerates the reaction rate and it decreases the particle size. Therefore, it is possible to infer that PCA is to avoid combustion reaction and to produce nanocrystalline metals. During mechanochemical synthesis, a combustion reaction is undesirable since it causes partial melting and following solidification which leads to the occurrence of a coarse-grained structure (Suryanarayana, 2001).

Relative proportion of the reactants (Batch constituents)

It has become customary to utilize approximately 10-15 % stoichiometric excess of the reductant(s) in many mechanochemical synthesis investigations. The excess amount of the reductant is necessary to avoid the surface oxidation of the reactive reducing powders. In addition few studies have researched the effect of the proportion of constitutive reactants. For example, Takacs (1992) changed the amount of Al and investigated its effect on the mechanochemically synthesized with Al and Fe_3O_4 . They have shown that a small decreasing of amount of Al ended up occurrence of FeAl_2O_4 instead of Al_2O_3 and they concluded; excess Al inhibited the synthesis of metastable the $\gamma\text{-Al}_2\text{O}_3$ and FeAl_2O_4 and also caused the synthesis of random bcc $\alpha\text{-Fe(Al)}$ solid solution and $\alpha\text{-Al}_2\text{O}_3$.

Grinding Ball Diameter

Yang and McCormick (1993) researched how the grinding ball diameter changes the combustion reaction by milling TaCl_5 and Mg. They found that increasing the diameter of the ball reduces the ignition time (t_{ig}) for the combustion reaction.

Combustion takes place when powder mixture is reached the ignition temperature (T_{ig}), which depends on the microstructural properties. It has been determined that the T_{ig} decreases with a refinement in the microstructure (Suryanarayana, 2001). The collision between the powder particles increases the powder temperature (T_c) during milling. As a first estimate, it is assumed that the t_{ig} is identical to the milling time needed for T_{ig} to lower T_c (Schaffer and McCormick, 1991). Enhancing the ball size

enhance the collision energy and thus T_c . Therefore, t_{ig} should decrease with increasing of ball diameter (Suryanarayana, 2001).

2.3 Autoclave Processing

Autoclaves are closed and sealed containers that temperature, pressure and vacuum environment are implemented at the same time inside of the autoclave vessel. In autoclave processing, temperature, pressure and vacuum adjustments are allowed step by step. Autoclaves are produced in different sizes and mechanisms depending on the area to be used. Dimensions of autoclaves can vary from desktop dimensions to those sizes are produced inside which airplane wings (Çakıcı, 2017). The autoclave is a high temperature and pressure resistant device and was invented by Charles Chamberland in 1879. As shown in Figure 2.10, it consists of two main parts, which are tank and cover. It is very important to close the cover correctly and safely as it is performed under high pressure. In addition to main parts, an autoclave system also has a thermometer and a barometer to check the temperature and pressure values. In order to pressurize the autoclave tank, inert gases, usually nitrogen and argon, are utilized to avoid any explosion of the container by reacting any component in the autoclave with gas. Electric heater, oil bath or natural gas as different heaters can be used to heat the tank and according to the temperature value required for the process (Çakıcı, 2017).

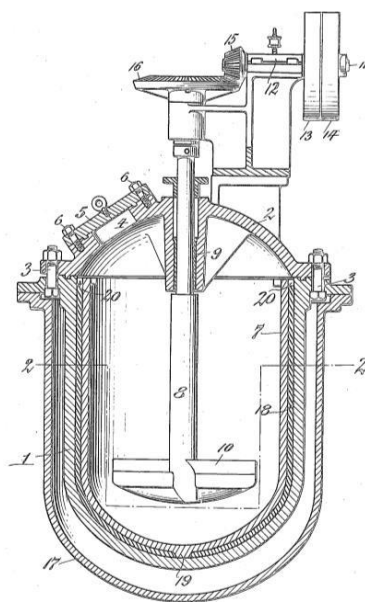


Figure 2.10 : Autoclave System (Çakıcı, 2017).

2.3.1 Historical Perspective

In 1450 B.C., the first health code, which included the purging of materials with fire and boiling water, was written in Leviticus, Numbers and Deuteronomy (Judelson, 2004). Afterwards, around, 460-377 B.C.E., Hippocrates used boiling water for surgical instruments for cleaning them. Denis Papin (1647-1712), a physicist and inventor of the steam engine, invented the steam pressure cooker which is an early version of the autoclave. An early pioneer in sterilization, Lazzaro Spallanzani (1729-1799), discovered that bacteria could be killed by heating them in closed glass bottles for 30 min. Then Pasteur discovered that in a pressure cooker when the pressure is 15 pounds/sqinch (1 atmosphere) above Standard pressure (760 mm Hg), the temperature at 121°C that water boils, kills all living things in 15 minutes or less. Here, these conditions have become the Standard for the sterilization apparatus. (Judelson, 2004). In the 1880s current design of the autoclave was largely completed by Charles Chamberland, a colleague of Pasteur (Judelson, 2004). This grew from his doctoral dissertation written by Chamberland in 1879.

With the discovery of autoclave, it has become a device with a wide range of applications from pressure cooker to advanced technology and industry. Autoclave systems are commonly used in synthesis of composites and numerous nanostructures of carbides, nitrides, oxides, phosphides, selenides, borides, sulfides and carbonaceous, sterilization, curing production and vulcanization processes, and also in many number of industrial areas. Leclercq et al. (1996) produced bulk tungsten carbides via carburization of W metal or W_2O_3 by CH_4 blends in hydrogen at different pressures. It was observed that W_2C was formed with 20% CH_4 - H_2 blends at atmospheric pressure at 650 °C and WC was formed only at higher temperatures. Also it was shown that the rate of reduction of W_2O_3 , amount of deposited free carbon, and carburization of W metal depended on partial pressures of hydrogen and CH_4 . Pol et al. (2008) produced carbon-enclosed SnS nanorods by the thermal decomposition of tetramethyltin where S powders exist in a autoclave at 700 °C for 40 min. They investigated SnS-C particles with ~12 nm thick carbon layer. Furthermore, the Mn-based II-VI compounds, semiconductor nanostructure of diluted magnetic, $Zn_{1-x}Mn_xTe$ nanosheets were manufactured via dry autoclaving synthesis (Erwin et al., 2005; Bhattacharyya et al., 2009). All obtained nanosheets are self-assembled and highly organized, similar to the steps of a stairs. Selvan et al. (2008) synthesized

hexaborides of La, Ce, Nd, Sm, Eu and Gd in a dry autoclave system that was carried out at 900°C for 3h with easily accessible metal acetates and NaBH₄ as raw materials. They obtained LaB₆ with a particle size from 200 nm to 20 μm. Carbon-supported PtP₂ nanoparticles were synthesized by dissociating (1000°C/3 h) of a precursor (single tetrakis triphenylphosphine platinum, (Pt(PPh₃)₄) in a sealed reactor without degassing (George et al., 2007). After the cooling the reactor and purification process, black colored PtP₂ product was obtained. Using dry autoclaving process, nanocrystals of TiN, TaN, and NbN are synthesized at 350°C for 12 h, by reacting of transition metal chlorides and sodium azide (George et al., 2009). After the thermal dissociation and transformations reactions, products of brownish-white powders were obtained. Pol et al. (2004) manufactured pure V₂O₃ nanoparticles evenly coated with a 15 nm thick carbon shell in a closed dry autoclave system at 700 °C under autogenic pressure. Then nanoparticles of V₂O₅ with a 4 nm thin carbon shell was obtained by heating of this V₂O₃ in air at 400°C for 30 min. Ma and Du (2006) synthesized WC nanoparticles with an average size of 20 nm via co-reduction of tungsten hexachloride and sodium carbonate with metallic magnesium in an autoclave at 600°C for 8 h.

The solvothermal process and different areas of application are described by Demazeau (2010). He defined the process as a “A solvo thermal process can be defined as a process in a closed reaction vessel inducing a decomposition or a chemical reaction(s) between precursor(s) in the presence of a solvent at a temperature higher than the boiling temperature of this solvent.” Also he studied the basic physico-chemical factors playing a key role in this process. In the autoclave process, the chemical composition of the starting materials has been shown to have a significant effect on the shape and morphology of the products. (Demazeau, 2008). For instance, CdSe and CeTe nanocrystals with different shape such as nanorods and nanodots were synthesized by the solvothermal synthesis changing the concentration of the precursors (Wang et al., 2006). The Fe- doped TiO₂ films were prepared with high visible photoactivity by autoclaved-sol process at low temperature (120°C) for 8 h (Lu et al., 2010). A series of borides (LaB₆, ZrB₂, TiB₂, CeB₆), carbides and nitrides were reproduced in a 20 ml capacity stainless steel autoclave by the help of metallic Na elemental S and related oxides and amorphous boron / activated carbon / NaN₃ by Chen et al. (2012). Kumar et al. (2008) used thermochemical reaction pathway in a specially designed stainless steel autoclave with a capacity of 50 ml to

produce WC nanoparticles by reducing WO_3 from two different carbon sources, ethanol and acetone. The results showed that reduction of WO_3 to WC was caused by adsorption of carbon on the surface of WO_3 , which was based on defects in the porous structure. When the concentration of adsorbed carbon increased, firstly nanotube was formed than converted to carbon-nanofibers. Lin et al. (2013) synthesized WC powders which has particle size between the range of 20-60 nm by carbothermal reduction using a novel core-shell structured precursor in a vacuum. Singh and Pandey (2015) manufactured nanocrystalline WC directly from the wolframite ore with activated charcoal and magnesium in an autoclave system heating at 800°C for 20 h. In the study of Akçamlı et al. (2016) studied the synthesis and consolidation of HfB_2 - HfO_2 ceramic powders by mechanical activation assisted autoclave processing and subsequent pressurized sintering or spark sintering. The autoclave synthesis was carried out mechanically for 5 hours and then mechanically with $HfCl_4$, B_2O_3 and Mg starting powders at a comparatively low temperature at 500 ° C for 6 hours or 12 hours.

2.3.2 Dry Autoclaving Synthesis

Currently, there exists several types of autoclave synthesis methods. Dry autoclaving synthesis is completely different the existent hydrothermal and solvothermal processes. The solvothermal process is implemented in a closed system in which chemical reaction takes place when a solvent (aqueous and non aqueous solution) existed in the system at a higher temperature than the boiling point of the solvent creating higher pressures (Demazeau, 2008). The term of “hydrothermal” is connected with the earth sciences and expresses high temperature and water pressure regime (Byrappa, 1991). In the hydrothermal synthesis, water is used both as a component of solid phases and as catalyst at high temperatures (>100°C) and high pressures (more than few atmospheres) during synthesis (Somiya and Roy, 2000). Practically, many numbers of compounds of all classes have been produced using hydrothermal synthesis, such as elements, carbides, simple and complex oxides, tungstates, carbonates and molybdates etc. The autoclave equipment for solvothermal and hydrothermal reactions should consist of steel cylinders with thick walls and hermetically sealed seals in order to have high temperatures and high pressures for long-term reactions. (Brinker et al., 1984).

In dry autoclaving synthesis, chemical reactions occur in a sealed reactor under autogenic pressure at high temperatures (above the decomposition temperatures of the chemical precursor / substances) without any solvent (Pol et al., 2008a). Pyrolyzed chemical precursors in a sealed system reach supercritical stages such as solid-liquid, liquid-gas, solid-gas or gas-gas interactions. These phases undergo nucleation and growth of individual components, which are predicated on kinetic and, thermodynamic stability resulting nanosized in materials (Pol et al., 2004). The reactor needs the capability of the decomposed chemical molecules to remain under autogenic pressure at high temperatures. The reactor requires the capacity of decomposed chemical molecules to remain under autogenic pressure at high temperatures. Using the newly-emerging dry autoclaving method, many of the nanosized carbide, boride, oxide, phosphide nitride, selenite, sulfur, and carbonaceous materials were produced in the core shell morphology. (Pol et al., 2007). The resulting nanostructures are used in many applications such as advanced anode or cathode materials in lithium ion batteries, hydrogen storage and catalyst supports, optical and luminescent devices (Kang et al., 2010; Odani et al., 2006; Pol et al.;2008b; Pol et al., 2006; Shanmugam and Gedanken, 2007).

2.3.2.1 Experimental system for the dry autoclaving

The main equipment for the dry autoclaving process is a reactor enclosed by a heater. The reactor also consists of an inner lining of quartz tube, piping for desired gases and a pressure gauge. Depending on final product requirements, the reactor capacity is varied. Assuming thermal decomposition over 13,79 MPa pressure typically, the precursor(s) occupies 35% volume of the reactor. During dry autoclaving operation, the reactor temperature is increased within the rate interval of 5-40°C/min and the maximum temperature is reached and held in a optimal duration. The decomposition and trasformation reactions take place under the autogenic pressure of the precursor at a high temperature and then the reactor is gradually cooled to the room temperature. After cooling process, the reactor is opened and the products are obtained followed by morphological and structural characterization (Pol et al., 2011). Figure 2.11 illustrates a basic instrumentation of an autoclave system.

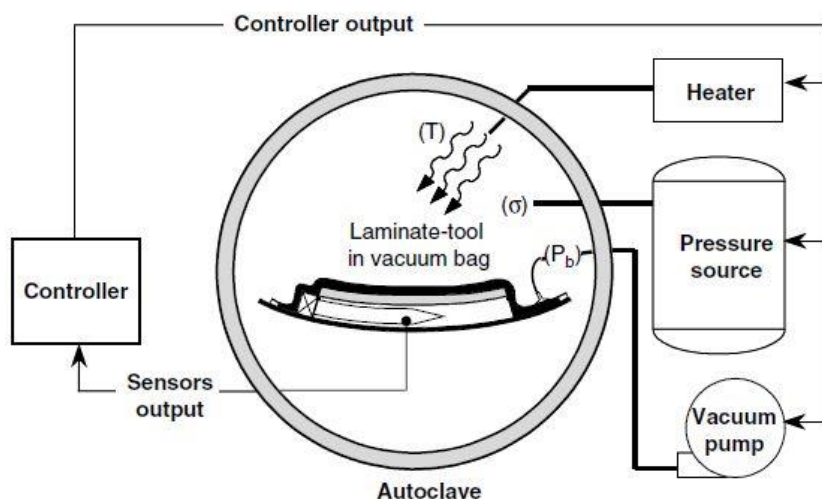


Figure 2.11 : A basic instrumentation of an autoclave system (Hubert et al., 2012).

The main characteristics for an ideal autoclave are:

- Mechanical strength for long time exposures to high temperature and pressures,
- Resistance to acidic, alkali and oxidant environments,
- Good sealing performance to achieve and retain required pressure,
- Appropriate size and shape to ensure a suitable temperature gradient (Akçamlı, 2016; Feng and Li, 2011),

2.3.2.2 Advantages of dry autoclaving synthesis

Main advantages of the dry autoclaving synthesis can be listed as follows:

- It is a nonaqueous, template-, surfactant-, and solvent-free method,
- Synthesis of pure crystalline dry products is possible,
- The products are displaced at the bottom of the reactor to achieve easy cycleability.
- It can be safely utilized in highly reactive, dangerous or carcinogenic precursors (e.g. carbonyls),
- Temperature used in dry autoclaving reaction reactor higher than (upto 1000 ° C) that obtained with commercial autoclaves limited to 650 ° C.
- The dry process is very versatile in the manufacture of a wide variety of nanomaterials, despite the different chemical and physical properties of the components of the reactant(s) (Pol et al., 2011).

2.4 Tungsten Carbides

Of all compounds, group V-VI transition metal carbides have the highest melting temperatures and hardness values. Due to these properties, they are commonly used as tool and structural materials that can operate at high temperatures, under aggressive environments and high loads. Considering the property as hardness, the compound WC is an extraordinary case. Even with temperature increases from room temperature (300K) to 1200-1300 K, the hardness of WC is adequately stable. Besides, WC has a smaller thermal expansion coefficient and high elastic modulus. Thus, owing to the combination of these properties, WC has been widely used in the production of wear-resistant hard alloys, which are the main components of all tool materials (Kurlov and Gusev, 2005). Approximately after 25 years the production of first WC by Moissan (1893), commercial-scale production of WC were begun. Therefore W-C phase diagram, structure and properties of W-C system has been studied since the discovery of WC to this days.

2.4.1 W-C phase diagram

The W-C system, besides tungsten (W) and carbon (C) phases, consists of WC and W_2C phases, each has a few structural modules that are stable at specific temperature and concentration ranges (Figure 2.12). Four modifications have been defined for lower tungsten carbide WC. Three of these are low-temperature β'' - W_2C , intermediate β' - W_2C and high-temperature β - W_2C , and in many of them they have been studied as α -, β - and γ - W_2C , respectively (Holleck H., 1984; Rudy, 1966; 1967). But structures of these modifications were determined using limited experimental data. Based on comprehensive neutron diffraction studies, another structural allotroph of the W_2C named as ϵ - W_2C was reported by Epicier et al. (1983; 1988). Atoms constitute an hcp metallic sublattice. In this lattice carbon atoms fill in one-half of octahedral interstitials. The atoms of lower carbide W_2C can occupy regular positions at low temperatures, based on the distributions of the C atoms. C atoms distributed in the lattice in various arrangements results in different structural modifications of W_2C . Higher carbide form of WC which has the hexagonal structure δ -WC or α -WC or simply WC (Sara, 1965; Ruddy, 1967; Holleck, 1984). Moreover, compositions between lower and higher tungsten carbides involve the cubic phase called γ - WC_{1-x} (also termed β -WC or α - WC_{1-x} or simply WC_{1-x}) (Sara, 1965; Ruddy,

1967; Holleck, 1984). Tungsten carbide has the cubic structure with a lattice constant of 0.416 nm. It was produced for the first time via the deposition process from $W(CO)_6$. Lander and Germen (1948) thought that they had discovered a W_2C carbide phase with the cubic structure. Afterwards, Lautz and Schneider synthesized cubic carbide which has a unit cell constant of 0.425 nm via spark discharge method which has the electrodes made of hexagonal WC carbide put into a petroleum bath. They identified that synthesized tungsten carbide was the lower W_2C tungsten carbide. Goldschmitt and Brand (1963) observed the cubic form of the tungsten carbide and named it a different high-temperature modification of W_2C . Currently, it is thought that cubic carbide $\gamma-WC_{1-x}$ is a structural modification of higher WC carbide. (Goldschmitt and Brand; 1963).

Tungsten(W) metal has the body-centered cubic (b.c.c.) Bravais lattice (Space group: $Im\bar{3}m$ (O_h^9)) which has the structural type of A2 (W -type) (Strukturbericht A2). The crystal lattice basis holds two atoms in positions 2(a) with equivalent coordinates of (0 0 0) and (1/2 1/2 1/2). Rudy et al. studied the W-C system and determined that the most high-temperature phase $\beta-W_2C$ has a hexagonal (space group $P6_3/mmc$ (D_{6h}^4)) which L'3-type structure shown in Figure 2.13. The lower tungsten carbide W_2C has the structure of L'3-type and was identified in a neutron diffraction study (Yvon et al., 1968). In that study, disordered W_2C phase was identified along with the ordered phase of this carbide. For entirely disordered W_2C at high temperature, the structure of L'3-type is quite acceptable by analogy with other lower carbides and nitrides. Especially, the hexagonal structure of L'3-type with the exception of V_2N is a characteristic example of most nonstoichiometric lower-carbides and nitrides M_2X_y ($M = V, Nb, Ta; X = C, N$).

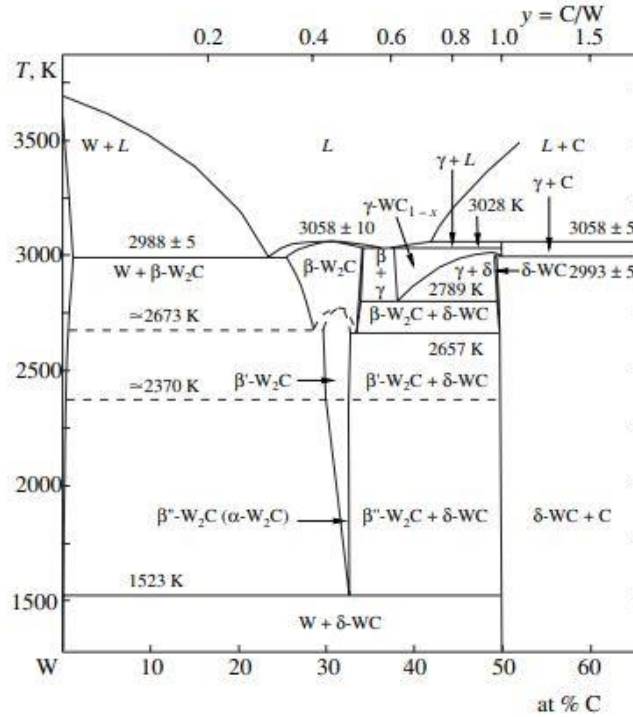


Figure 2.12 : Phase diagram of the W–C system (Kurlov and Gusev, 2013).

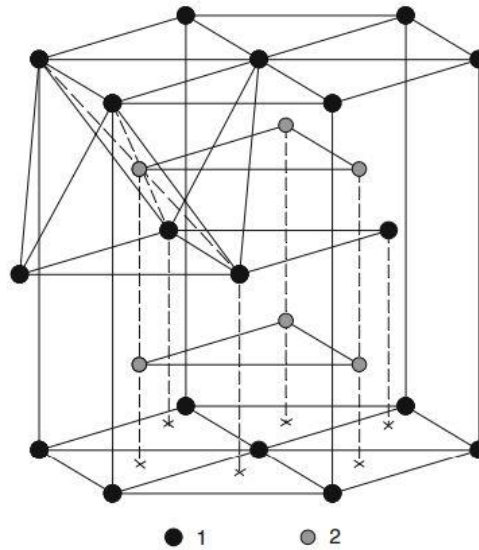


Figure 2.13 : Structure β -W₂C(L'3-type, space group P6₃/mmc) (Kurlov and Gusev, 2013).

The positions 2(c) with coordinates $(1/3 \ 2/3 \ 1/4)$ and $(2/3 \ 1/3 \ 3/4)$ are filled by two tungsten atoms and one C atom is arbitrarily dispersed among positions 2(a) with coordinates $(0 \ 0 \ 0)$ and $(0 \ 0 \ 1/2)$ in the unit cell of β -W₂C. Put it differently, the hexagonal β -W₂C phase is disordered, and its carbon atoms fill randomly one-half of all octahedral interstitials in the tungsten sublattice. For this reason, the occupancy ratio of the octahedral interstitials by any C atom is equal to 1/2. Nonmetallic lattice

sites form the AXBXAXBX stacking sequence with A and B layers alternating with the X layers perpendicularly to the c axis of the β -W₂C carbide. The hexagonal β -W₂C phase has a homogeneous solubility region between WC_{0.34} and WC_{0.52}. It is stable at temperatures ranging from 2670 to 2720 K to 3000–3050 K (Kurlov and Gusev, 2013). The constants of the unit cell of β -W₂C phase which has the composition WC_{0.52} are determined as: a = 0.2992 and c = 0.4722 nm (Storms, 1967). In reference to these data, constants of the unit cell of β -W₂C carbide are slightly higher and the values are a = 0.3002 and c = 0.475-0.476 nm. Constants of the unit cell of all phases are determined for samples quenched at room temperature (Rudy, 1966). These constants for the lower tungsten carbide W₂C, β -W₂C, β' -W₂C, β'' -W₂C and ϵ -W₂C are different only in the region of small angles 2 θ , in the XRD patterns. In accordance with calculations, only small-angle X-ray diffraction patterns are affected by the change in the distribution of carbon atoms in the W₂C lattice as shown in Figure 2.14 (Kurlov and Gusev, 2013).

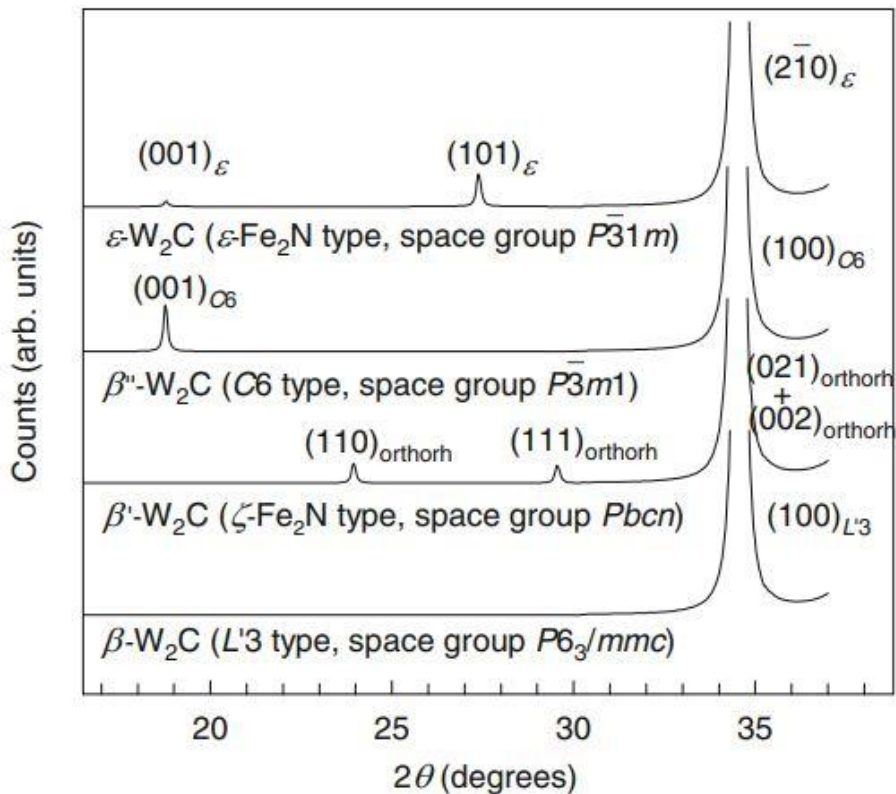


Figure 2.14 : XRD patterns of different β -W₂C, β' -W₂C, β'' -W₂C and ϵ -W₂C modifications of lower W₂C tungsten carbide (Kurlov and Gusev, 2013).

The modification of the lower tungsten carbide β' -W₂C forms the rhombic symmetry. However, the metallic sublattice has a hexagonal closely packed structure resembles to that of high temperature carbide β -W₂C the structure. Although the structure of orthorhombic lower tungsten carbide β -W₂C is still unknown, its space group is classified as Pbcn (D_{2h}^{14}) (Kurlov and Gusev, 2013). For this structure, the carbon atoms (C) have positions 4(c) with the coordinates (0 y 1/4) and the tungsten atoms (W) are at positions 8(d) with (xyz) coordinates. The lower carbide β' -W₂C isotypic with ordered Mo₂C and has the ζ -Fe₂N structure with space group being Pbc, namely has an orthorhombic (Parthe and Sadagopan, 1963; Rudy, 1967; Kurlov and Gusev, 2013). The hexagonal disordered, trigonal and orthorhombic modifications of the lower carbide W₂C which has the same unit cell constants of the basic disordered phase cannot be distinguished from XRD patterns at 2θ angles $>30^\circ$ (Figure 2.15). But, between the small angles between $2\theta < 30^\circ$, XRD patterns were slightly different (Figure 2.15).

Figure 2.15 illustrates the arrangements of C atoms in lower carbides β -W₂C, β' -W₂C, β'' -W₂C and ϵ -W₂C. Planes shown in Figure 2.15(a) are occupied by non-metallic sublattice and positioned perpendicularly to the c axis of the original disordered structure of the L' 3-type structure. W atoms are not illustrated, only C atoms and vacancies are illustrated in the structures. For instance, in Figure 2.15(a) random arrangement of carbon atoms with vacancies in the β -W₂C carbide phase with the structure of L'3-type are presented. The ordered distribution of C atoms and vacancies in the β' -W₂C phase with the structure of the Mo₂C (ζ -Fe₂N) are illustrated in Figure 2.15(b). Figure 2.15(c) demonstrates regularly alternating the layer of carbon atoms with the layer of structural vacancies in the C6-type structure of β'' -W₂C (α -WC) carbide. Figure 2.15(d) displays the ϵ -Fe₂N-type structure of the ϵ -W₂C carbide phase. Each vacancy is enclosed by six carbon atoms, or each carbon atom is enclosed by six vacancies which are alternative planes of the non-metallic substrate.

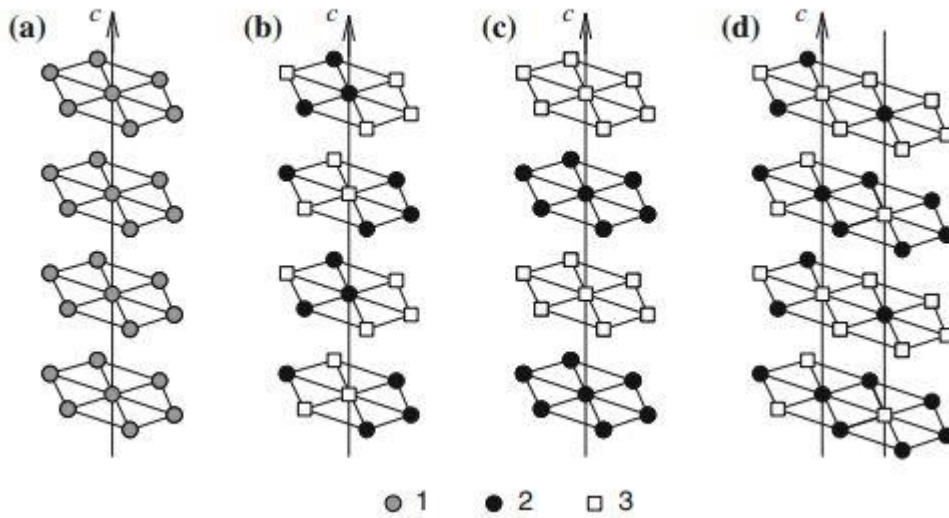


Figure 2.15 : Distribution of carbon atoms in lower carbides (a) β - W_2C , (b) β' - W_2C , (c) β'' - W_2C and (d) ϵ - W_2C (Kurlov and Gusev, 2013). 1 : Positions of nonmetallic interstitial atoms randomly filled by carbon atoms with a probability of 1/2; 2: the C atoms ; 3 : the vacancies.

Rudy and Windish (1967) determined the lattice constants of the orthorhombic β - W_2C as: $a=0.4728$ nm, $b=0.6009$ nm, and $c=0.5193$ nm. Kurlov and Gusev (2013) analyzed the dispersion of atoms in the orthorhombic unit cell, a derivative of the hexagonal unit cell which has the $L'3$ -type structure. Tungsten atoms have the $(1/4 \sim 1/8 \sim 1/12)$ coordinates of the 8(d) position and that the carbon atoms are in the 4(c) position with the coordinates $(0 \sim 3/8 \sim 1/4)$ was shown by analysis of Kurlov and Gusev (2013) and the calculation of XRD pattern the calculation of XRD pattern for β' - W_2C carbide with ζ - Fe_2N -type structure. When β' - W_2C with ζ - Fe_2N type structure phase was made comparison with the high-temperature hexagonal phase β - W_2C , it is ordered phase according to non-metallic sublattice is ordered as a regular phase. The orthorhombic carbide β' - W_2C is supposed to have a homogeneous solubility range of $WC_{0.34}$ to $WC_{0.49}$ and it exists at intermediate temperatures between ~ 2370 K range 2670–2750 K.

β'' - W_2C (α - W_2C) is an ordered low temperature phase, but its crystal structure and the temperature range where the phase exists have not been decided yet. Butorina and Pinsker (1960) synthesized tungsten carbide at low temperature by carburizing a thin metal tungsten film under an atmosphere of carbon monoxide at -1400 K for 5 min. They have stated that this lower temperature phase has the C6 (anti-CdI)-type structure with the space group No. 164, $P\bar{1}31m$ (D_{3d}^3). In the rhombohedral

(trigonal) structure with the C6-type, the carbon atom layer changes regularly with the structural vacancies layer normally oriented to the c axis. Only layers constituted by C atoms are located among pairs of layers AB located by W atoms. The layers of vacant interstitials are placed between the pairs of the metal layer BA (Figure 2.15 (c)). In the β'' -W₂C (α -W₂C) carbide having a perfect structure; two tungsten atoms with coordinates $(\frac{2}{3} \frac{1}{4})$ and $(\frac{2}{3} \frac{1}{3} \frac{3}{4})$ at positions 2(d) and a C atom with coordinate (0 0 0) at position 1(a) exist. Also there is a vacancy in position 1(b), which is with coordinate (0 0 $\frac{1}{2}$) (Kurlov and Gusev, 2013). Harsta et al. (1978) produced tungsten carbide with the composition $\sim \text{WC}_{0.43-0.45}$ via sintering process of pressed blends of tungsten and carbon black powders at 1920 K for 30–50 h. In this tungsten carbide phase, carbon atoms are ordered with respect to the ϵ -Fe₂N structure type. According to this study, the ϵ -W₂C phase forms a trigonal structure and has the space group No. 162, **P1 $\bar{3}$ 1m (D_{3d}¹)**. The unit cell constants of ϵ -W₂C carbide phase, $a = 0.5185$ and $c = 0.4723$ nm. In the perfect trigonal structure of this carbide, W atoms are positioned at 6(k) with coordinates $(\frac{1}{3} 0 \frac{1}{4})$ and C atoms fill 1(a) positions with coordinates (0 0 0) and 2(d) positions with coordinates $(\frac{1}{3} \frac{2}{3} \frac{1}{2})$, also positions 1(b) with coordinate (0 0 $\frac{1}{2}$) and positions 2(c) with coordinates $(\frac{1}{3} \frac{2}{3} 0)$ are filled by vacancies. The distribution of C atoms and vacancies in the nonmetallic sublattice of a perfect trigonal structure which has the space group **P1 $\bar{3}$ 1m** of ϵ -W₂C carbide phase is shown in Figure 2.15(d) (Kurlov and Gusev, 2013).

2.4.2 Properties and application areas of tungsten carbides

After the discovery of tungsten by Scheele in 1781, Moissan's synthesis of tungsten carbide (WC) in 1896 took more than a hundred years. Tungsten carbide developed faster than other transition metals after its discovery due to its extraordinary characteristics. These remarkable properties are high melting temperature (2600-2850°C), high density (15.25-15.88 mg/m³), high hardness (16-22 GPa at 500 g load Vickers), high rigidity, good compressive strength (5 GPa @ 20°C), high fracture toughness (28 MPa m^{1/2}), high elastic modulus (530-700 GPa), high chemical and thermal stability, good wear, heat and oxidation resistance, low thermal expansion coefficient and good electrical and thermal conductivity (Lassner and Schubert, 1999, Norgren et al., 2015; Polini et al., 2015; Ma and Du, 2008). The most

extraordinary characteristic of tungsten carbide is its high Young modulus (696 GPa) and this value is surpassed only by diamond. It has a low resistivity and high thermal conductivity of 145 W/mfC (Hugosson, 2003). Also it is the hardest binary carbide at high temperatures (1000 kg/mm² at 1000°C). Non-hexagonal centered symmetrical crystal structure of tungsten causes anisotropy in hardness (Exner, 1979; Engkvist et al., 1999). French and Thomas (1968) investigated that the hardness changes with the directions of the planes. In their study, Knoop hardness in both basal plane {0001} and in prism planes {1100} with the direction of {1120} were measured as about 2400 N/mm². Also, the hardness is about 1000 N/mm² on the prism planes with the long diagonal in the [0001] direction. By observing slip bands and dislocation networks, it was verified that WC could deform plastically on the slip plane family of {100} with [0001], [1120] and [1123] directions (Exner, 1979; Hugosson, 2003). By analyzing the wear debris caused by abrasion of WC by the use of TEM, the surface planes chosen by the debris were found to be the same as slip planes of the crystal (prismatic planes). Further, the direction of surface cracks and sliding steps adjacent to the grooves fit into one another of the crystal sliding planes, as shown in Figures 2.16 (a) and (b). The slip planes are also split planes during wear. For this reason, one way to increase the wear resistance for the WC is to reinforce the bonds among the prismatic planes (Hugosson, 2003). WC surface can be changed by creating different phase structures after suitable oxidation process in order to vary the surface electronic structure and catalytic properties (Santos, 2002 ;Wu, 2007). In this respect, WC having a high and stable catalytic activity is very similar to platinum (Pt). Hence it is used in many chemical reaction fields like Pt. In addition since catalytic activity is not affected by almost any CO and H₂S concentration, WC shows better resistance to types of poisoning and better stability for electrochemical oxidation (Houston, 1974; McIntyre, 2002). WC was mainly used as electrolysis for, water electrolysis, hydrogen evolution and methanol oxidation. Besides, WC is used as electrodes in fuel cell and electrochemical catalysis due to having good conductivity. For this reason, in these applications of areas, low-cost alternatives like WC and WC-composites are needed to be advanced (Papazov, 1990; Acres, 1997, Zeng et al., 2009).

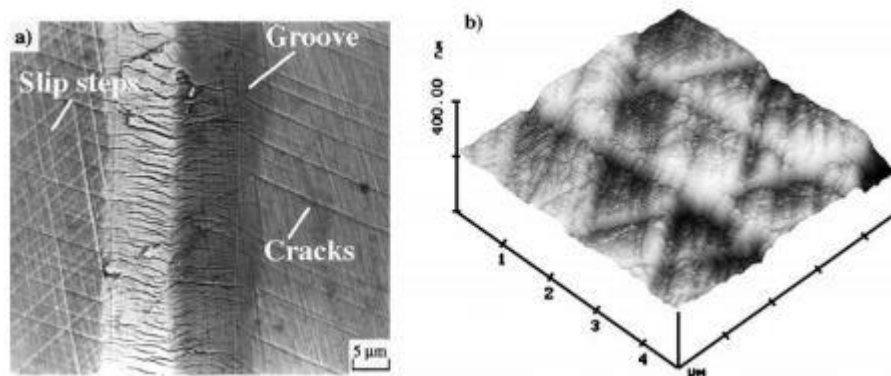


Figure 2.16 : Images of basal planes. (a) SEM image that shows slip steps, cracks and groove. (b) Atomic force microscope (AFM) image that shows high magnification of the slip steps on basal planes (Hugosson, 2003).

The application areas of WC can be stated as:

a) precursors for WC-Co hard metals, b) tips for cutting and drilling tools, c) inserts in valve stems sand blast nozzles, d) anvil material in high pressure instruments, e) wear-resistant surfaces for machines wire drawing and hot rolling mills, f) scratch-resistant jewelry materials, g) erosion-resistant coatings for aerospace components, h) extrusion and pressing dies, i) platinum-like catalytic materials for polymer electrode membrane fuel cells, j) thin film diffusion barriers in microelectronics (Ma and Du; 2008; Voevodin et al., 1999; Fang, 2005; Pansare et al., 2007; Kim and Kim, 2004; Lin, 2005; Hara et al., 2007; Rees et al., 2008; Luković et al., 2015; Singh and Pandey, 2015a; 2015b; 2013a; 2013b; Lin, 2005; Lin et al. 2013; Jiang et al., 2004).

2.4.3 Production techniques

Currently, there are various methods employed in the synthesis of tungsten carbides utilizing different raw materials. These methods can be listed and itemized as: (i) solid direct reaction of tungsten and carbon conventionally, at an elevated temperature under controlled atmosphere (1400-1600 °C), ii) carbothermal reduction of high-energy ball-milled CaWO_4 , carbon coated WO_3 or mechanically activated WO_3 powders at temperatures between 600-1600°C under flowing Ar/H_2 atmosphere or vacuum (Singh and Pandey, 2013; Polini et al., 2015; Koc and Kodambaka, 2000; Ma and Zhu, 2010; Kim and Kang, 2014), iii) co-reduction of WCl_6 and Na_2CO_3 with Mg in an autoclave at 600 °C (Ma and Du, 2008), iv) chemical vapor condensation of $\text{W}(\text{CO})_6$ precursor with CO carrier gas at 500-1000°C under air, Ar

and vacuum atmospheres (Kim and Kim, 2004), v) electric discharge machining of W rods and subsequent annealing at 800-1600 °C under N₂/H₂ atmosphere (Lin, 2005), vi) carburization of W₂N and WS₂ under CH₄/H₂ atmosphere at 777-900 °C (Hara, 2007), vii) heating a WO₃ and C powder blends in the presence of KCl/Ni/Fe at 1300 °C (Rees et al., 2008), viii) thermal treatment of a mixture of W powders and activated/milled viscose rayon cloth at 1000 °C under Ar gas flow (Luković et al., 2015), ix) autoclave synthesis of a mixture of wolframite or scheelite ores, activated charcoal and Mg at 800 °C (Singh and Pandey, 2013; 2015), x) hydrothermal reaction of ammonium metatungstate (AMT)/corn starch blends at 200°C followed by spray-drying (at 250 °C) and heating (at 980 °C under vacuum) treatments (Lin et al., 2013), xi) combustion synthesis of W and activated carbon powders under electric field (Jiang et al., 2004), xii) self-propagating high-temperature synthesis of WO₃, Mg, C, NaCl and Na₂CO₃ containing powder blends at temperatures below 1600 °C (Won et al., 2007), xiii) electrochemical synthesis from halide-oxide melts under excess CO₂ pressure (Malyshev et al.; 2002), xiv) molten salt synthesis at 1000°C from mechanically activated W-C-NaCl-KCl powders (Yang et al., 2011), xv) chemical synthesis (dissolving in water and spray-drying) and heating of ammonium paratungstate (APT), AMT and glycine containing precursors at 1300 °C under Ar/H₂ atmosphere (Kanerva et al.; 2015), xvi) calcining and thermal processing of AMT and glucose mixtures up to 1300 °C (Jin, 2012), and xvii) combined process of calcination (at 600 °C), nitridization (with ammonia at 680 °C) and carburization (under CH₄/H₂ gas at 880 °C) starting from AMT (Tomas-Garcia et al., 2014). Moreover, the nanocrystalline WC powders are produced from pure tungsten starting materials such as: (i) WO₃ (Hoisenpur et al., 2013; Aravinth et al., 2012; Kirokossyan et al., 2008), (ii) elemental W (Lin, 2005; Razavi et al., 2011), (iii) WCl₄ (Giordano et al., 2008), (iv) WCl₆ (Ma and Du; 2008) and (v) W(CO)₆ (Kim and Kang, 2004; Pol et al., 2006).

All these above-mentioned techniques require high reaction temperatures, relatively long reaction times and advanced fabrication technology or equipment. For this reason, the use of simple, low-cost and low-temperature processes become necessary for the production of WC powders. Recently, mechanical alloying (MA) or mechanochemical synthesis (MCS) processes have been employed for obtaining nanocrystalline WC powders at ambient temperature without applying any external

heat (El-Eskandarany, 2000a; 2000b; 2005; Öveçoğlu and Özkal, 2004; Bolokong et al., 2010; Hoseinpur et al., 2013; Zhu et al., 2010; Sakaki et al., 2009; 2013; Stanciu et al.; 2016; Tan and Wu, 1998; Tan, 2009). Recently, high-energy ball-milling or mechanical activation has been utilized as a precursor preparation technique for WC reactions in order to increase the activity of the raw materials during the subsequent heat treatments (Polini et al., 2015; Luković et al.; 2015; Singh and Pandey, 2013; Koc and Kodambaka, 2000; Ma and Zhu, 2010; Kim and Kang, 2014; Yang et al., 2011). However, MA and MCS methods enable the direct synthesis of WC powders at room temperature in the presence of volatile or non-volatile by-products. For example, El-Eskandarany et al. (2000) produced single-phase nanocrystalline WC powders from elemental W and C powders via high-energy ball-milling for 432 kiloseconds. Öveçoğlu and Özkal (2004) investigated the synthesis of WC phase from elemental W and graphite powders after attritor milling for 30 h followed by high-energy ball milling for 6 h. Bolokanget al. (2010) produced WC and W₂C powders from elemental W and C by mechanical alloying (MA) at different carbon-rich and carbon-deficient compositions using different milling parameters (ball-to-powder weight ratio, milling speed and time). Hoseinpur et al. (2013) obtained WC nanoparticles after mechanochemical synthesis (MCS) of WO₃, Zn and C containing powders for 36 h and after HCl leaching of ZnO undesired phase. El-Eskandarany (2000a; 2005) prepared nanocrystalline WC powders by high-energy ball milling of WO₃ and graphite powders in the presence of Mg (for 173 kiloseconds) and Al (for 360 kiloseconds) reducing agents. Zhu et al. (2010) reported the impact of process control agent on the forming mechanism of WC powders prepared by MCS of WO₃, Mg and graphite blends in a planetary ball-mill. Sakaki et al. (2009; 2014) fabricated WC and W₂C powders by MCS of WO₃-C-2Al mixtures up to 8 h and also investigated the possibility of the conversion of W₂C to WC phase with the addition of excess carbon. Stanciu et al.(2016) studied the direct carburization of WO₃ by MCS and found that WO₃ was completely converted to WC phase after 30 h of milling. Tan and Wu (1998) produced nanocrystalline tungsten carbide powder mixtures of WC, W₂C and cubic WC_{1-z} by MCS from WO₃, Mg and graphite mixtures for 50 h followed by HCl leaching of undesired MgO. Besides, they obtained single-phase W₂C nanoparticles at a W-rich environment by using different W/C molar ratios and prolonged MCS time (Tan, 2009). Research studies about the preparation of tungsten carbides via MA and MCS present in the archival literature

reveal that elemental W and WO_3 starting powders were commonly used as tungsten sources whereas graphite was used as a carbon source.

As an alternative to mechanical alloying or mechanochemical synthesis, autoclave method i.e. the previously explained method was also used to obtain WC powders. In an investigation by Koc and Kodambaka (2000), WC powders were produced from novel carbon coated precursors with a method with two steps of coating and heating. They reduced the oxide powders with carbon decomposed from a hydrocarbon gas followed by mixing by-products with a significant amount of carbon black and heat treated in a temperature range between 600°C and 1400°C . Singh and Pandey (2013) used a single step synthesis of tungsten carbide particles from scheelite ore by heating in an autoclave system to 800°C for 8h. Singla et al. (2014) synthesized nanostructures of carbon encapsulated tungsten carbide ($\text{WC}@C$) by reaction between metallic magnesium (Mg), tungsten trioxide (WO_3) and acetone ($\text{C}_3\text{H}_6\text{O}$) in an autoclave system at 600°C . Ma and Du (2008) fabricated nanocrystalline tungsten carbide powders in an autoclave initiating a reaction of magnesium with sodium carbonate and tungsten hexachloride at 600°C for 8 h. They observed that for duration times less than 4h and temperatures lower than 600°C , the reaction was unfinished and the WC had lower crystallinity. There exists also some literature about combining mechanical alloying and chemical reaction by heating. Ha and Kim (2002) utilized mechanochemical process to manufacture WC/Co powders from water soluble salts involved W and Co components and they carried out heating treatments on these powders at 800°C under H_2 and N_2 atmospheres. Thus, in autoclave processes, external heat must be supplied to the system and extra time is required for chemical reactions. These requirements make the autoclave method an expensive method complicated with long duration times.

The aim of this dissertation is the preparation of tungsten carbide powders through MCS and autoclave synthesis as two different methods utilizing unconventional raw materials such as WCl_6 , Na_2CO_3 and Mg subsequent purification processes. The present study will make a contribution to the archival literature with its first results including the use of a chloride-based tungsten source for a room-temperature process, the need of shorter reaction time and the quality final products after simple purifying treatments and comparison of two different methods to achieve tungsten carbide powders. At the end of this study with the shortest duration processing time,

the cheapest and the simplest method of producing tungsten carbide powders which will have the best characteristics will be decided upon.





3. EXPERIMENTAL PROCEDURE

The experimental procedure section of this thesis gives information pertinent to every step of the production and characterization of tungsten carbide powders. This section consists of identification of raw materials, description of the production of WC powders by mechanical alloying, mechanochemical reaction and auto-clave processing methods and afterwards purification treatments of synthesized powders and finally characterization investigations carried out on the powders before and after purification.

3.1 Raw Materials

In most investigations, high purity precursors like WO_3 or W are utilized for the synthesis of tungsten carbide powders. (Tan, 2009; Wu et al; El-Eskandarany, 2000; Zhu et al, 2010; Öveçoğlu and Özkal, 2004). The major purpose of this dissertation work is to obtain tungsten carbide powders from different starting materials. Therefore, as an alternative material, tungsten hexachloride (WCl_6) was used as starting material in mechanochemical reaction and auto-clave methods. Mg powders were utilized as a strong reducing agent and Na_2CO_3 was used as the carbon source in both of methods. Graphite and activated carbon powders were alternatively used in excess amounts to achieve only formation of tungsten carbide (WC) phase in auto-clave method.

Experimental investigations of this dissertation were begun by preparing raw materials and carrying out pre-alloying experiments. Elemental tungsten and carbon (graphite) powders were utilized in the method of mechanical alloying to compare the outputs acquired in the case of using WCl_6 source. Table 3.1 illustrates characteristics of the starting materials used in all the experiment of this dissertation. Stereo microscope (SM) images of the raw materials are illustrated in Figure 3.1. These SM images of WCl_6 , Na_2CO_3 and Mg raw materials were captured by using a ZeissTM Discovery.V12 stereomicroscope (SM) coupled with a ZeissTM Axiocam ERc5s high resolution digital camera. SM images given in Figure 3.1 (a) through

3.1(f) shows WCl_6 powders with yellow region displaying partially hydrolized (3.1 (a)), white Na_2CO_3 salt (3.2 (b)), dark gray Mg particles 3.2(c)), almost black graphite and active carbon powders (3.2 (d) and 3.2 (e)) and gray tungsten powders with shiny particles (3.2 (f)), respectively.

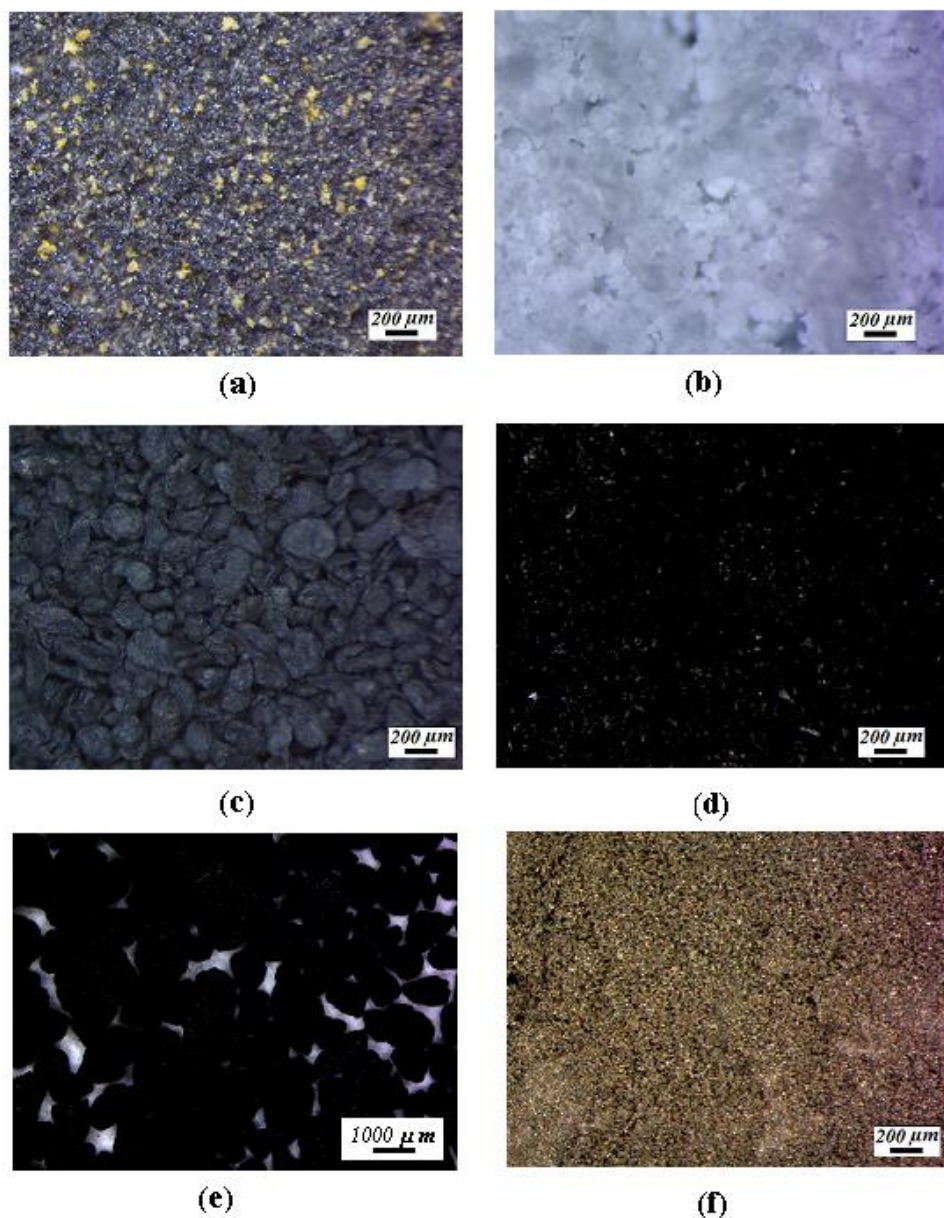


Figure 3.1 : SM images of the raw materials (a) WCl_6 (b) Na_2CO_3 (c) Mg (d) C (graphite) (e) C (active) and (f) W.

Table 3.1 : Characteristics of raw materials used in experiments.

Raw Materials	Supplier	Purity (%)	Average (μm)
W	Eurotungstene TM	99.99	3
WCl ₆	Acros Organics TM	99<841	
Na ₂ CO ₃	Alfea Aesar TM	98	
Mg	Alfea Aesar TM	99.71	42.7
Graphite	Alfea Aesar TM		
Activated carbon	Alfea Aesar TM		

The crystalline phases were identified by using a BrukerTM. D8 Advanced Series powder diffractometer (40 kV, 40 mA) with CuK α (0.154 nm) radiation in the 2 θ range of 10-120° with 0.02° steps at a rate of 5°/min. International Centre of Diffraction Data (ICDD) powder diffraction files were used to identify the crystalline phases of the raw materials. Figure 3.2(a), (b), (c), (d), (e) and (f) represent the X-ray diffraction (XRD) patterns of raw materials, WCl₆, NaCl, Mg, graphite, active carbon and W respectively. The XRD analysis of Mg, graphite and W have crystalline peaks with no trace of impurities. (Figure 3(c), 3(d) and 3(f)). However, 3.2 (e) shows the characteristic pattern of amorphous carbon. Since, WCl₆ and Na₂CO₃ powders are sensitive to humidity or oxygen in the air, the XRD analysis of WCl₆ reveals an amount of WO₂Cl₂ phase. Due to hygroscopic compound of WCl₆, the oxygen in the air hydrolyzes partially from these powders and transforms into tungsten oxychlorides (WO₂Cl₂, WOCl₄, WOCl₃ or WOCl₂) and/or tungsten oxides (WO₃, WO₂, etc.) (Figure 3.2 (a)). Moreover, Na₂CO₃.H₂O and NaHCO₃ phases are present in the XRD analysis of Na₂CO₃ because of the hygroscopic formation of Na₂CO₃ and absorbing moisture from the air as illustrated in Figure 3.2 (b).

3.2 Synthesis of the Powders and Their Purification

As expressed previously, the purpose of this dissertation is to produce tungsten carbide (W₂C and WC) powders using different methods, and to find out the effective method having some advantages such as time and energy savings, convenience and high purity of products. Tungsten carbide powders were synthesized using three different methods including mechanical alloying with elemental W and C

powders, mechanochemical sythesis and autoclave method with the same raw materials, WCl_6 , Na_2CO_3 and Mg . Purification process is implemented after the production of tungsten carbide powders by two methods, mechanochemical synthesis and autoclave process.

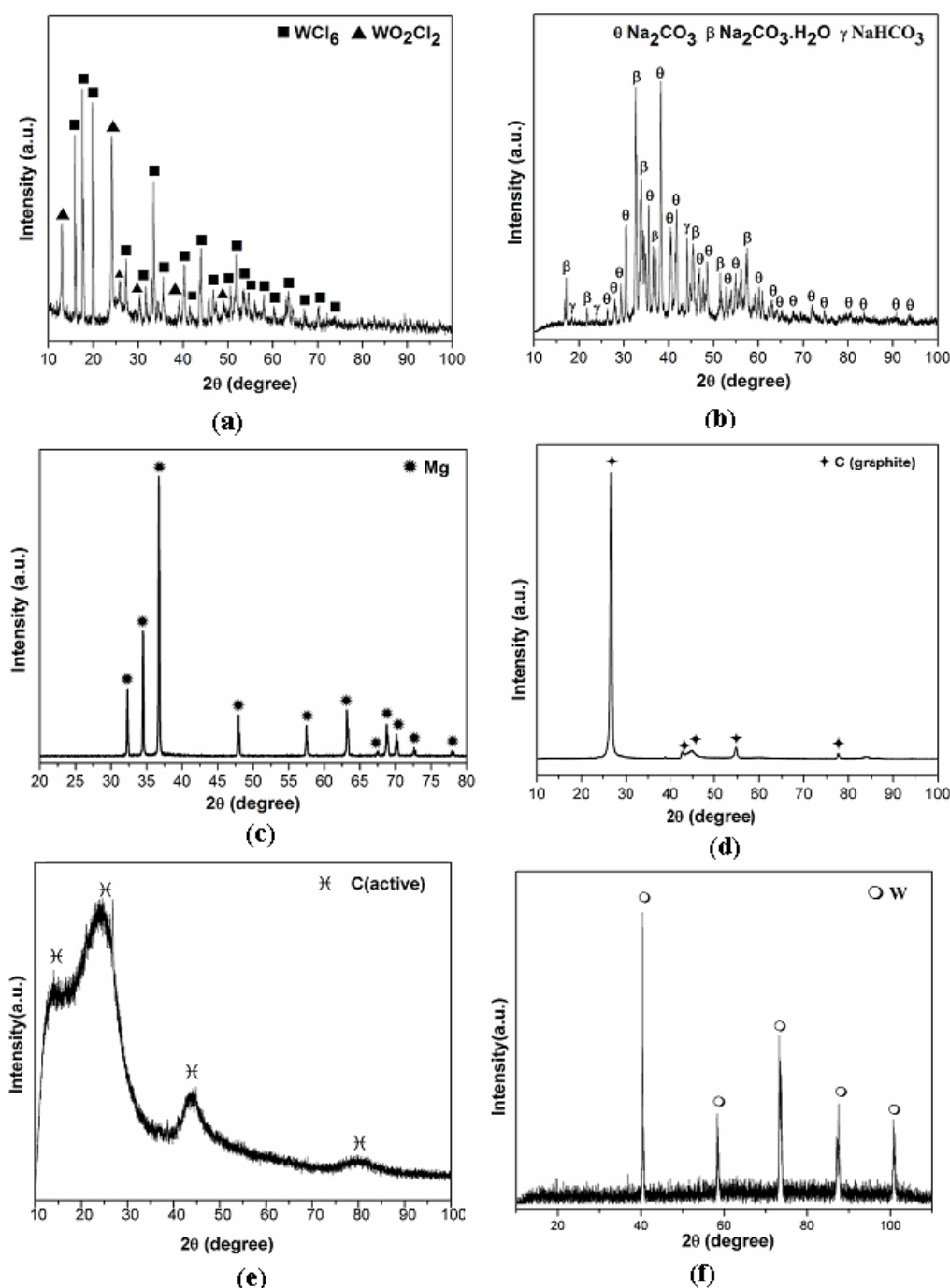


Figure 3.2 : XRD patterns of the raw materials (a) WCl_6 (b) Na_2CO_3 (c) Mg (d) C (graphite) (e) C (active) and (f) W .

3.2.1 Mechanical alloying (MA) investigations

In the beginning of this dissertation, W and C powders were used to compare the results when WCl_6 source was used. Stoichiometric powder blends of elemental W and C powders were homogenized in a WAB™ T2C Turbula blender for 1 h and these are hereafter referred to as as-blended powders. Elemental W and C powder batches of 9,8 g were milled in a high-energy ball mill with a milling rate of 1200 rpm with amilling duration times varied up to max. 15 h. The high-energy ball mill utilized in milling experiments, is Spex™ 8000 D Mixer/Mill shown in Figure 3.3 which is situated at the Particulate Materials Laboratories (PML). WC vials with a capacity of 50 ml and WC balls with a diameter of 6.5 mm shown in Figure 3.4 were used as the milling media with a ball-to-powder weight ratio of 10:1. The loading and unloading of the powders of the vials was performed in a glove box (Plas-Labs™) illustrated in Figure 3.5 and filled with purified Ar atmosphere (Linde™, in purity of 99.999 %). The milling vials were evacuated to about 10^{-2} Pa and back filled with Ar gas in the glove box to avoid surface oxidation and contamination of powder due to the presence of. Following mechanical alloying processes, powders were sintered for 1 h at 1000°C using MTI™ QTF-1200X tube furnace illustrated in Figure 3.6.



Figure 3.3 : Spex™ 8000 D Mixer/Mill in Particulate Materials Laboratories (PML)
(a) lid closed and (b) lid opened.



Figure 3.4 : WC vials and WC balls used in milling experiments.



Figure 3.5 : Plas-Labs[™] glove box used while loading and unloading of the powders in to the vials (ITU Particulate Materials Laboratories, PML).



Figure 3.6 : MTI[™]QTF-1200X tube furnace used in sintering process (ITU Particulate Materials Laboratories, PML).

The flowchart of mechanical alloying of WC powders summarizes the processes in Figure 3.7.

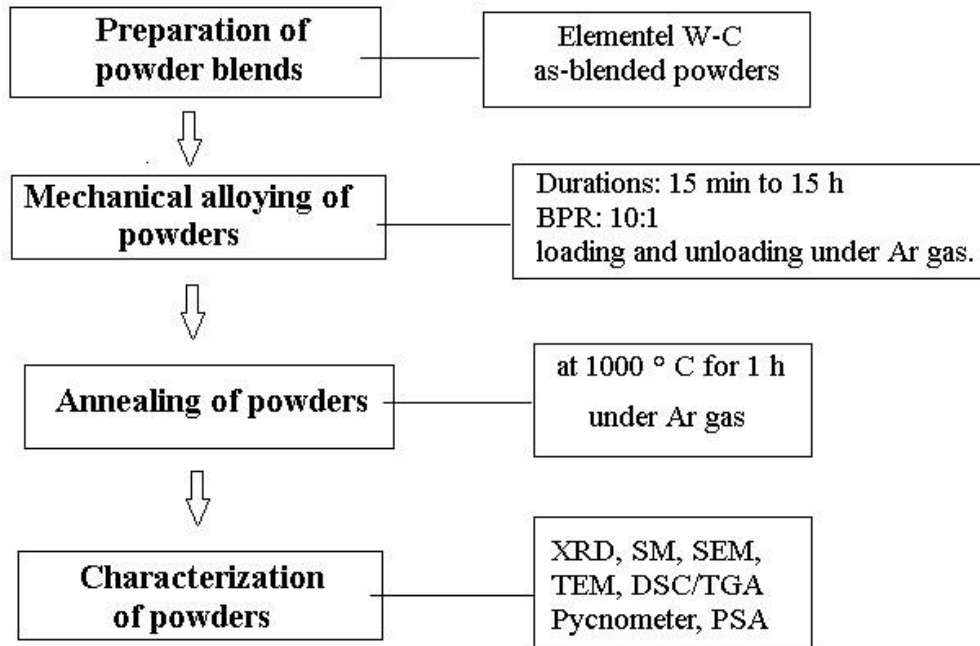
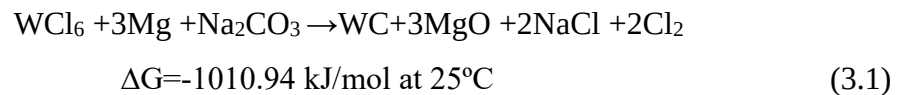


Figure 3.7 : The flowchart of mechanical alloying of WC powders.

3.2.2 Mechanochemical synthesis (MCS) of the powders and their purification

Raw materials (WCl_6 - Na_2CO_3 -Mg) powders were used to constitute WC as final product by MCS. Stoichiometric amounts of WCl_6 (2.046 g), Na_2CO_3 (0.578 g) and Mg (0.376 g) were weighed in a PrecisaTM XB320M sensitive balance to form powder batches of 3 g regarding Eq.(3.1) and homogenized in a blender for 1 h and hereafter referred to as-blended powders to make comparisons with the milled powders. For mechanochemical synthesis experiments, equipment and milling conditions were the same as in mechanical alloying experiments. In these experiments, the duration time of milling varied up to max. 8 h. They are referred to as mechanochemically (MCS'd) or milled WCl_6 - Na_2CO_3 -Mg powders.



Similar to mechanical alloying (mechanical milling) experiments, same equipment (SpexTM 8000 D Mixer/Mill and Plas-LabsTM) were utilized for the mechanochemical synthesis (MCS) experiments. In addition, 50 wt% excess of Mg,

50 wt% and 70 wt % excess of Na₂CO were utilized in the synthesis of WC powders along with stoichiometric amounts. WCl₆-Na₂CO₃ binary powders in stoichiometric amounts were MCS'd for 8 h to investigate the impact of Mg reductant in the reaction.

Following MCS, leaching experiments were implemented to remove MgO and NaCl from the system. MgO can be taken away from the system by reacting with the leaching solution in accordance with the following reactions. (3.2) and (3.3). NaCl and Mg(OH)₂ are dissolved by washing with distilled water at the end of the leaching experiments.



In leaching experiments, 4M and 7 M HCl solutions were utilized with a 1g/10 cm³ solid/ leachant ratio by the effect of ultrasonic stirring and heating (Bandelin TM Sonorex shown in Figure 3.8). The molarity of HCl solution in concentration of 37% is calculated as shown below. The molecular weight of HCl is 36.46 g/mol. The density of HCl is 1,19 g/mL..

$$\text{Molarity of HCl solution} = \frac{1 \text{ mol}}{36.46 \text{ g}} \times \frac{37 \text{ g}}{100 \text{ g}} \times \frac{1.19 \text{ g}}{1 \text{ ml}} \times \frac{1000 \text{ ml}}{1 \text{ L}} = 12.076 \text{ mol/L} \quad (3.4)$$

Thus, in order to prepare 1L of 1M HCl, $1/12.076 = 0.083 \text{ L} = 83 \text{ ml}$ of HCl should be added to 917 ml of distilled water. 5M and 7M HCl solution was prepared accordingly.

Hereafter, the solution was centrifuged in a Hettich TM Rotofix 32A centrifuge illustrated in Figure 3.9 with a rotation speed of 3500 rpm for 15 min. The decantation step was implemented to separate supernatant liquids from the insoluble solids. Decanting and washing with distilled water for several times were repeated and finally the solids were dried in a HeraeusTM FN 500 stove at 100°C for 24 h in air (ambient condition) shown in Figure 3.10. Leached solutions decanted from the solids were collected into a volumetric flask for the later instrumental analyses.

Figure 3.11 illustrates the flowchart of mechanochemical synthesis processes in brief.



Figure 3.8 : Bandelin TM Sonorex ultrasonic bath (ITU Particulate Materials Laboratories, PML).



Figure 3.9 : Hettich TM Rotofix 32A centrifuge (ITU Particulate Materials Laboratories, PML).



Figure 3.10 : Heraeus™ FN 500 stove (ITU Particulate Materials Laboratories, PML).

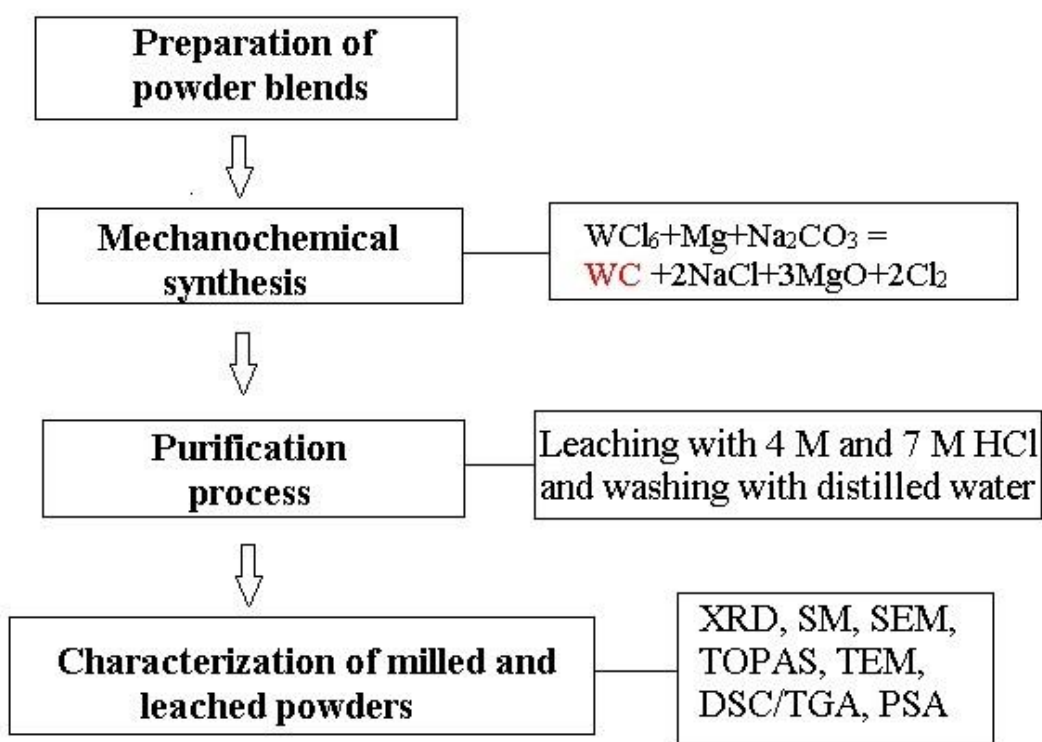


Figure 3.11 : The flowchart of mechanochemical synthesis of WC powders.

3.2.3 Autoclave synthesis investigations

Powder blends of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ with stoichiometric amounts were homogenized in a Turbula blender for 1 h prior to and for the for autoclave processing. The powder batches of 3 g were prepared according to Eq. (3.1) consistent with mechanochemical sythesis. The as-blended powders were mechanically activated for

2 min. in the Spex Mixer/Mill using the same milling conditions described in sections 3.2.1 and 3.2. These powders are referred to as the MAC'd stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders

The autoclave synthesis process was performed using two processing routes. In the first route, as-blended and mechanically-activated powder blends were loaded into the autoclave vessel. After that, the vessel was placed into a hastelloy autoclave (AmarTM) with 400 ml capacity illustrated in Figure 3.12.. The autoclave was purged and sealed under Ar atmosphere and initial dose of Ar pressure implemented to the system. This initial Ar pressure amount was changed from 1 bar to 50 bar to decide optimization conditions of experiment. Also the autoclave system was heated to 500°C which was kept constant at different durations.

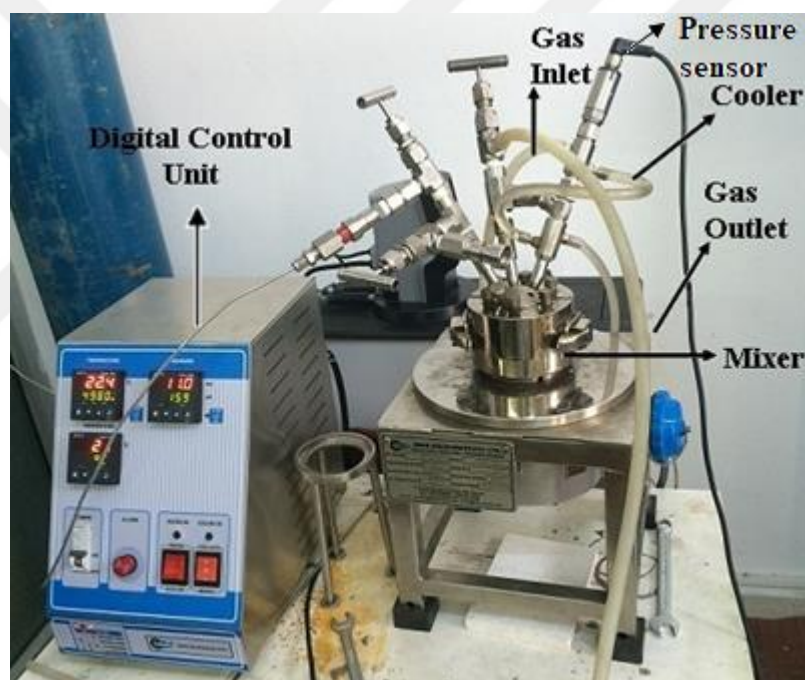


Figure 3.12 : The AMARTM autoclave system (ITU Particulate Materials Laboratories, PML).

In the second route autoclave processing experiments were implemented in hydrothermal reactor shown in Figure 3.13. As-blended and mechanically activated powders were transferred into a hydrothermal reactor with a capacity of 50 ml in the glove box under Ar atmosphere. After that, the hydrothermal reactor was placed into the ProthermTM binder removal furnace shown in Figure 3.14 and heated to different temperatures (400°C to 700°C) with a heating and cooling rate of 2°C/min and kept at these temperatures at different durations. Binary $\text{WCl}_6\text{-Na}_2\text{CO}_3$ powders were

autoclaved to observe the effect of Mg. Also binary WCl_6 -Mg were autoclaved to explore the effect of Na_2CO_3 . Moreover; 5, 10 and 100 wt % excess graphite (0.2, 0.5, 1 g and 2 g) and active 5, 10 and 100 wt % excess carbon powders (0.2, 0.5, 1 g and 2 g) are utilized as carbon source in this type of autoclave processing method. In addition, 100 wt % excess Na_2CO_3 and Mg were used respectively in the autoclave processing synthesis.



Figure 3.13 : The hydrothermal reactor.

Following the chemical reactions during two types of autoclave processing methods, purification process was employed by leaching the powders with 7 M HCl and washing with distilled water using the same leaching conditions in mechanochemical synthesis described in the sections 3.2.

After the autoclave and purification processes, the WCl_6 - Na_2CO_3 -Mg-activated C blends were annealed at 700°C for 1 h in alumina boats with a heating rate of $7^\circ\text{C}/\text{min}$ and cooling rate of $10^\circ\text{C}/\text{min}$ under Ar gas flow.



Figure 3.14 : Prothermal™ binder removal furnace into which hydrothermal reactor was placed (ITU Particulate Materials Laboratories, PML).

The flowchart shown in Figure 3.15 represents all operations of autoclave processing synthesis of WC powders.

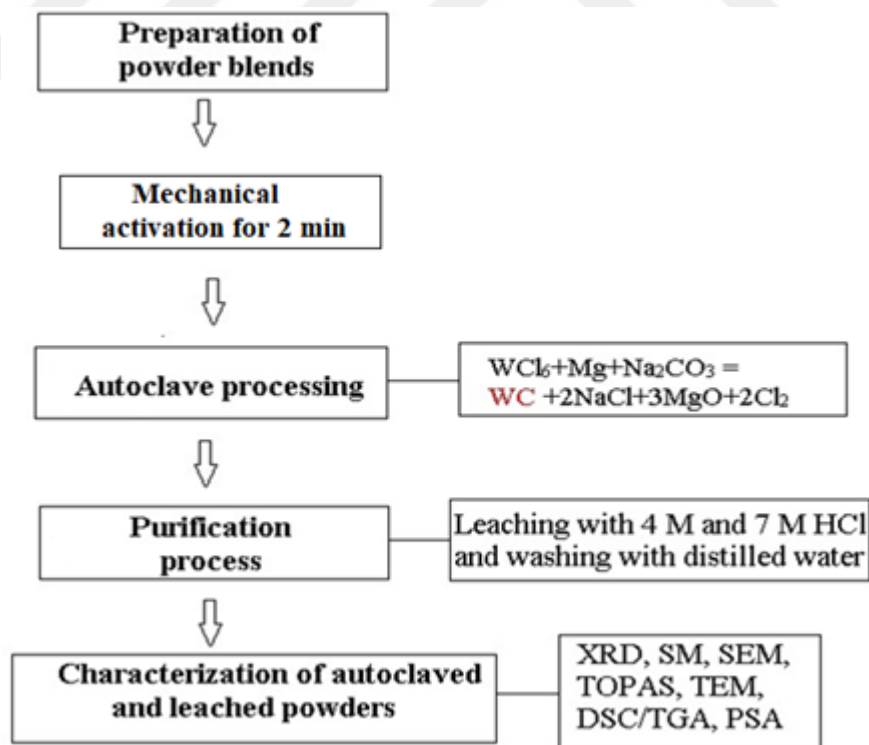


Figure 3.15 : The flowchart of autoclave processing synthesis of WC powders.

3.3 Characterization investigations of the powders

Phase analyses of the as-blended, mechanically alloyed, mechanochemically synthesized and purified powders were conducted in a BrukerTM D8 Advanced Series X-ray diffractometer (XRD) (Figure 3.16) with CuK α radiation ($\lambda=0.154$ nm, 40 kV and 40 mA). Crystalline phases were identified by using the International Center for Diffraction Data[®] (ICDD) powder diffraction files. Bruker-AXSTM TOPAS V3.0 software was utilized to calculate the average crystallite sizes and lattice strains of the mechanochemically synthesized powders based on the modified Scherrer's Formula (Suryanarayana and Norton, 1998). The amounts of different phases of mechanochemically synthesized powders were determined by the semi-quantitative Rietveld method. ZeissTM Discovery.V12 Stereomicroscope (SM) (Figure 3.17) coupled with a ZeissTM AxioCam ERc5s high resolution digital camera was used to take images of as-blended, milled and leached powders. Thermal analyses of milled and leached powders were conducted using a TATM Instruments SDT Q600 DTA/DSC/TGA (Figure 3.18). DSC/TGA experiments were carried out in an alumina crucible and heated to 1000°C with a heating and cooling rate of 10°C under Ar atmosphere.

Microstructural characterizations were performed in a JEOLTM JCM-6000 Benchtop Scanning Electron Microscope (SEM) (Figure 3.19) equipped with an energy-dispersive spectrometer (EDS) in a JEOL JEM-2100 (UHR) Transmission Electron Microscope (TEM) and also (Figure 3.20). For SEM characterization powders were dissolved in ethanol (C₂H₅OH, MerckTM, 99.9 % purity), the solution was syringed onto a base plate, suspension was dried in air and lastly their surface of the specimen was coated with a thin layer of gold with a PolaronTM SC7620 Sputter Coater (3.21) to increase conductivities of the specimens. For TEM characterization, powder specimens were prepared by dispersing in ethanol, taking on a porous carbon film on a copper grid and drying in a oven under vacuum.

Particle sizes of milled and leached powders were measured using MicrotracTM Nano-flex particle size analyzer (PSA) shown in Figure 3.22. Before particle size measurements, Bandelin SonopulsTM ultrasonic homogenizer (Figure 3.8) was used for 15 min to homogenize for powders in distilled water. Densities of the milled and leached powders were measured by in a MicromeriticsTM AccuPyc II 1340 gas pycnometer (Figure 3.23) with a sample chamber having a volume of 1cm³ at room

temperature using He gas (Linde™, in purity of 99.996 %) as the displacement medium.



Figure 3.16 : Bruker™ D8 Advanced Series X-ray diffractometer (XRD) (ITU Particulate Materials Laboratories, PML).



Figure 3.17 : Zeiss™ Discovery.V12 Stereomicroscope (SM) (ITU Particulate Materials Laboratories, PML).



Figure 3.18 : Instruments SDT Q600 Differential Scanning Calorimeter (DSC)/Thermogravimetric Analyser (TGA) (ITU Particulate Materials Laboratories, PML).



Figure 3.19 : JEOL™ JCM-6000 Benchtop Scanning Electron Microscope (SEM)
(ITU Particulate Materials Laboratories, PML).



Figure 3.20 : JEOL™ JEM-2100 (UHR) Transmission Electron Microscope (TEM)
(Selçuk University Advanced Technology Research and Application Center).



Figure 3.21 : Polaron™ SC7620 Sputter Coater (ITU Particulate Materials Laboratories, PML).



Figure 3.22 : Microtrac™ Nano-flex particle size analyzer (PSA) (ITU Particulate Materials Laboratories, PML).



Figure 3.23 : Micromeritics™ AccuPyc II 1340 gas pycnometer (ITU Particulate Materials Laboratories, PML).



4. RESULTS AND DISCUSSION

This chapter of the dissertation comprises three sections which express and analyze the experimental results of synthesis of the tungsten carbide powders by the detailed characterization investigations. The first section explains results of the synthesis and the production of tungsten carbon powders from elemental tungsten and carbide powders. These are preliminary investigations. In the second section, tungsten hexachloride powders as tungsten source was used via mechanochemical synthesis to produce various type of tungsten carbides. Different quantities of the carbon source were utilized during the synthesis of mechanochemical reaction to examine effects on the synthesis of tungsten carbide powders. In the last section, autoclave method was utilized for the production of various tungsten carbide powders. In addition to the quantity of carbon sources, different types of carbon sources were used in the autoclave method to find out the effects of carbon sources of different amounts and types on the production of carbide powders.

4.1 Mechanical Alloying (MA) of the Tungsten Carbide Powders from Elemental Tungsten and Carbon Powders

This section brings out results of a detailed phase analyses on the as-blended, milled and annealed powders with stoichiometric amounts. Also microstructure, some physical and thermodynamic properties of milled powders were explored using XRD, SM, SEM/EDX, TEM, DSC, density and particle size measurements. Figure 4.1 illustrates XRD patterns of as-blended of W and C powders and milled mechanically alloyed at various times (15 min, 1, 2, 3, 5, 7, 10, 12 and 15h) in Spex Miller. After 7 h of mechanical milling, WC incubation starts in their structure with the decrease in the W peak. It can be clearly observed that there is no evidence of metastable WC_x peaks. At 5 h, the major peak of WC (Bravais lattice: simple hexagonal, $a=b=0.291$ nm, $c=0.284$ nm, ICDD Card No:51-0939) bears the highest intensity than those of WC for the powders mechanically alloyed duration at the time range of 15 min and 15 h. Comparing with other milling durations it was evidently

observed that WC phase has the highest intensity peak after milling with the duration of 5 h. At milling duration of 15 h tungsten (W) phase was still detected simply meaning that more milling time is required for completion of WC synthesis as also observed in the literature (Öveçoğlu and Özkal, 2004). The intensity of peaks of C phase observed were not high due to amorphization of C phase. Also this experiment reveals that excess amount of carbon source or alternatively other W sources should be used to synthesize WC powders.

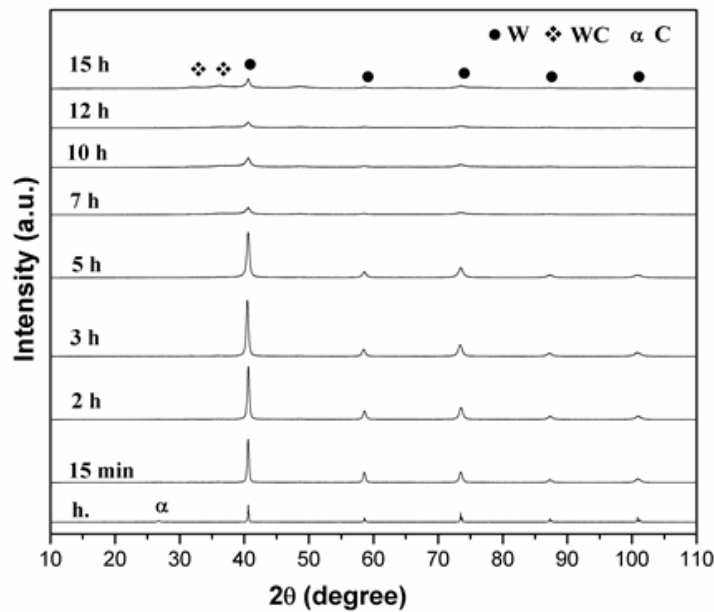


Figure 4.1 : XRD patterns of as-blended W and C powders and those mechanically alloyed (MA'd) at various milling time from 15 min to 15 h.

SEM images of powders MA'd for 15 h using elementer W and C with stoichiometric amounts are illustrated in Figure 4.2 (a) and (b) at different magnifications. The general appearance of the particles is spherical or equiaxed. Also, small particles in some regions have agglomerated to form larger particles. While the size of the agglomerates increases up to 10 μm , it observed that the small particles trapped in the agglomerates are less than 1 μm .

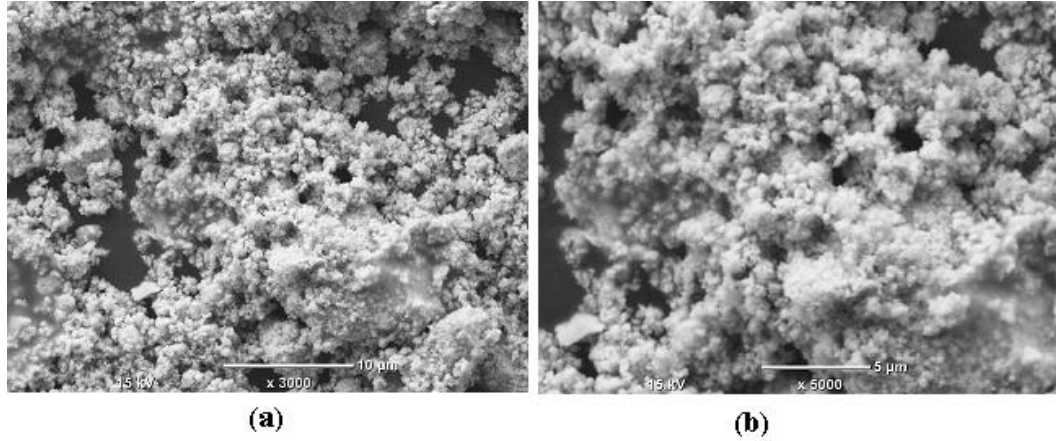


Figure 4.2 : SEM images of the powders MA'd for 15 h using W and C powders (a) at 3000X and (b) at 5000 X.

Figure 4.2 (a)-(d) represent the SEM images and corresponding elemental W and C mappings taken from the powders synthesized by MA using elemental W and C powders with stoichiometric amounts. Figures 4.2 (b)-(d) taken from the SEM image in Figure 4.2 (a) illustrates the distribution of W and C elements. The map of W (Figure 4 (b)) substantially coincides with the map of C (Figure 4 (c)). This indicates the presence of the WC phase. Furthermore, in Figure 4(d), the presence of oxygen is clearly observed. This is thought to be due to oxidation of the sample due to handling in laboratory conditions or treatment during analysis.

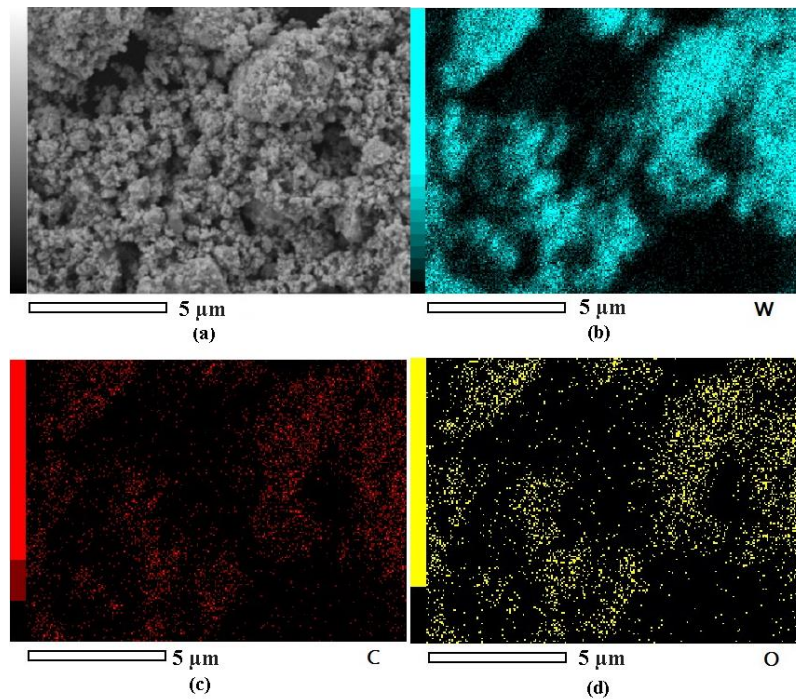


Figure 4.3 : (a) SEM image of synthesized powders by mechanical alloying for 15 h using elemental W and C with stoichiometric amounts, EDS mapping of (b) W, (c) C and (d) O.

Table 4.1 represents quantitatively the phase distributions of the regions marked on the SEM images (shown in Figure 4.4) of the mechanically alloyed elemental W and C powders. These results obtained in the SEM/EDS spectral analysis show the phase distributions of the remarked points on SEM images in Figure 4.4. According to the results obtained, the microstructure consisting of white and bright regions mainly comprise the W element (especially B and D regions). The composition of the stoichiometric WC phase contains about 93 wt% W and 7 wt% C. Regions B and D are consistent with the stoichiometric composition of the WC phase. The other light gray regions A, C and E have a relatively higher carbon and oxygen content than the other regions. Thus, in the microstructure, there are also different elemental regions that are rich in W and C phases.

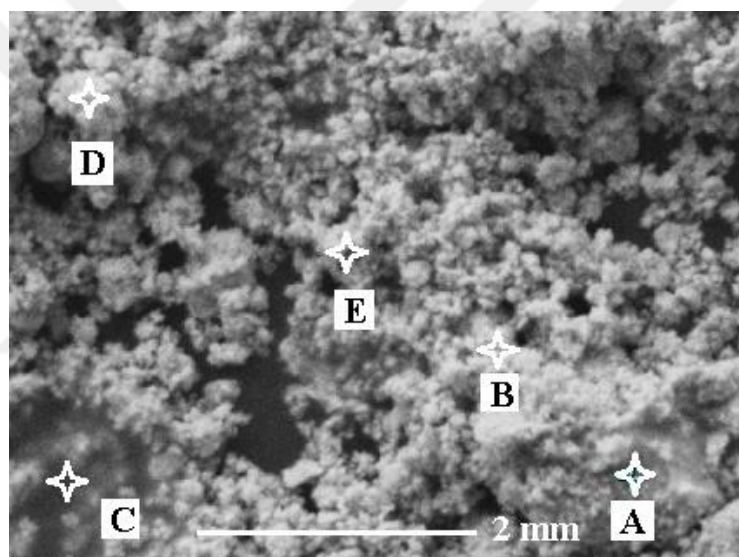


Figure 4.4 : SEM image of the blended W and C elemental powders MA'd for 15 h different regions are marked for EDS analysis.

Table 4.1: EDS analysis results of different regions indicating in Figure 4.4.

Elements (wt %)	A	B	C	D	E
W	57.97	92.52	53.40	92.54	83.30
C	36.34	4.52	37.42	5.55	11.41
O	5.69	2.96	14.13	1.91	5.29

Figure 4.5 shows the XRD graph of powders annealed for 1 h at 1000 ° C after 15 h mechanical alloying of elemental W and C powders in stoichiometric ratio.

According to this graph, the only phase after annealing is the WC phase. This shows that the kinetic energy generated during milling was not sufficient for the complete transformation into the WC phase. However, heating the sample to 1000 °C induced necessary displacement reactions to synthesize completely the WC phase from elementary powders W and C. This indicates that the kinetic energy, which causes necessary displacement reactions required to completely synthesize the WC phase from the basic powders of W and C and which could not be provided during milling. Nevertheless, milling caused the nucleation and formation of some amount of the WC phase in the powders, contributing to the complete synthesis of WC after annealing at 1000 °C.

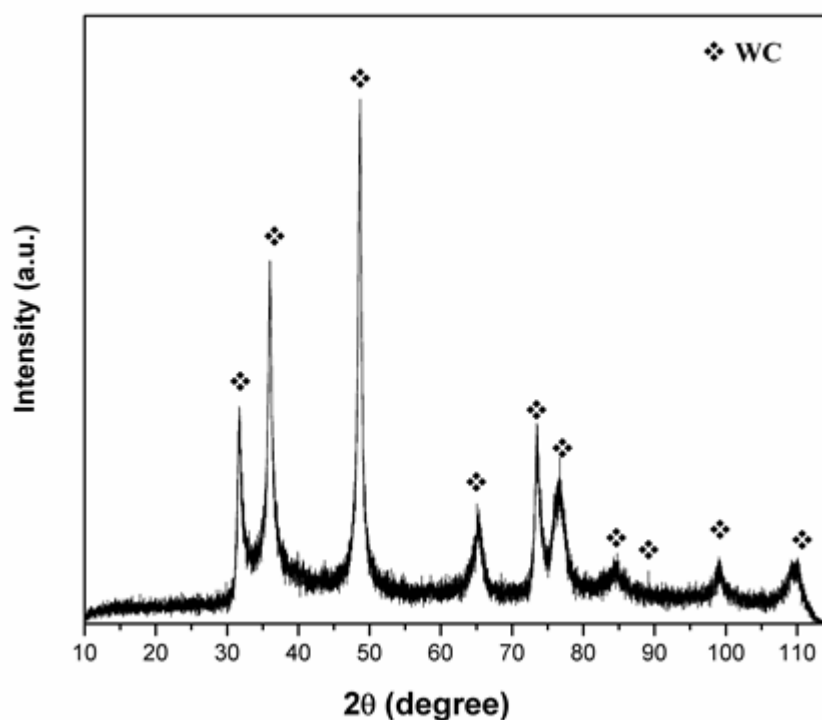


Figure 4.5 : XRD analysis of 15 h MA'd elemental W and C powders annealed for 1 h at 1000 °C.

Figures 4.6(a) and (b) show a particle size graph and SM image of powders mechanically alloyed for 15 h using elemental W and C powders in stoichiometric ratio, respectively. The average particle size distribution of these powders was measured between 50 nm and 500 nm and the average particle size was measured as 75 nm. The average particle size of the powders increased during annealing. The particle size was measured as 305 nm with an average particle size range between 90 to 900 nm. Also, it is remarkable that the color of the annealed powders is darker

than only mechanically alloyed powders in SM images. Since only the WC phase is present in the structure of powders annealed at 1000 °C for 1 h (Figure 9), it is expected that the color of the powders would be black in the SM image. The density of the powders mechanically alloyed for 15 h and followed annealed at 1000 °C for 1 h was measured as an average of 15.1 g/cm³ by QuantachromeTM gas pycnometer. This is an approximate value to the actual density value of tungsten carbide (15.63 g/cm³) (Url-2).

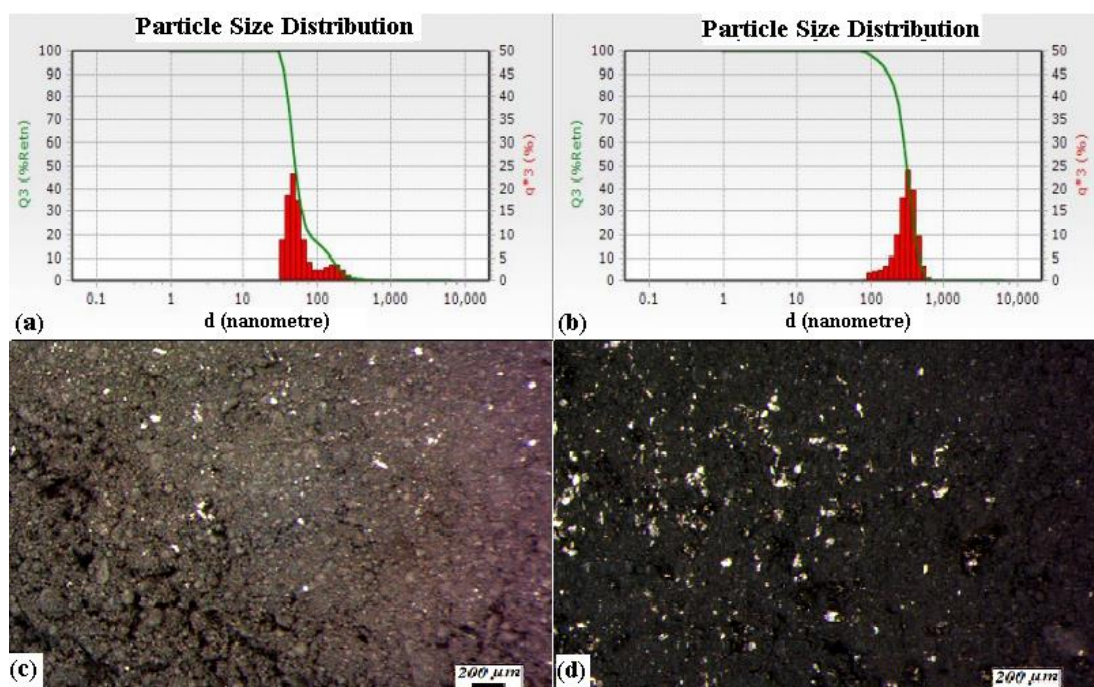


Figure 4.6 : (a) Particle size distribution graph and (c) SM image of the powders mechanically alloyed for 15 h using elemental W and C powders with stoichiometric ratio (b) Particle size distribution graph and (d) SM image of the powders annealed for 1h at 1000°C after mechanically alloyed for 15 h.

Temperature-weight gain curves obtained after DSC / TGA analysis of mechanically alloyed for 15 h and annealed for 1 h at 1000°C powders are given in Figure 4.7. Due to the WC and W phases in the structure of mechanically alloyed powders (Figure 4.1), during the heating process up to 1100 °C, weight gain decreased after 700°C. XRD analysis of those powders revealed the presence of WO₂ and W phases in the powder structure. Thus, the small amount of WC obtained by mechanical alloying for 15 h is not stable up to 1100°C. A part amount of powder has W phase transformed to lower oxide as a result of oxidation of W and WC is decomposed into WO₂ or W (Figure 4.8 (a)). The carbon content of WC is converted to volatile CO_x gas according to Boudouard reaction. Only WC phase was observed in the powders

mechanically alloyed for 15 h and annealed for 1 h at 1000°C (Figure 4.5). After heating to this powder up to 1000°C, the weight gain of the powder decreases only at a temperature close to 1000°C. This clearly shows that, unlike the only mechanically alloyed powders whose weight gain is reduced at 700°C, there is no free C phase in the annealed WC powder. In addition, it can be said that the WC powders produced by mechanical alloying decomposes at approximately 1000°C. XRD analysis of the powders after DSC / TGA analysis revealed the presence of W₂C (Bravais lattice: simple hexagonal, a = b = 0.518, c = 0.472 nm) and W phases (Figure 4.8(b)).

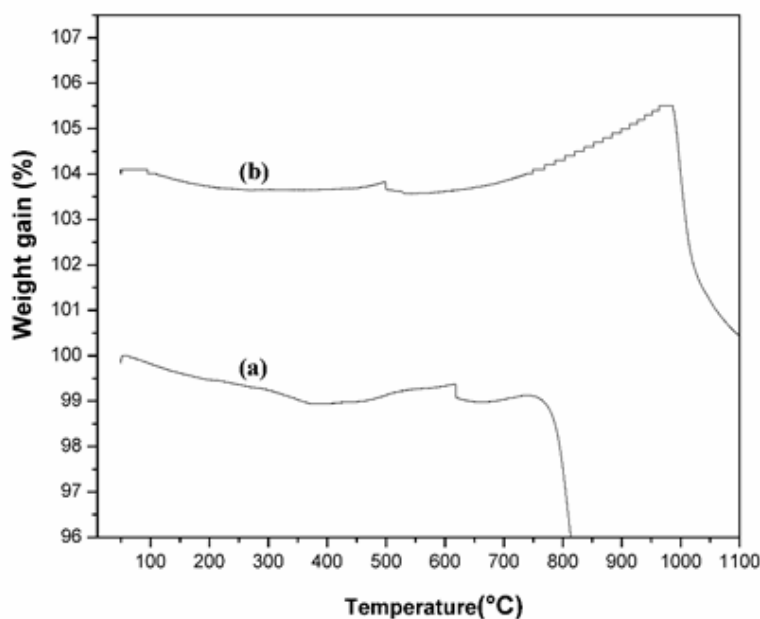


Figure 4.7 : Weight gain- temperature curves of powders (a) mechanically alloyed for 15h (b) followed annealed for 1 h at 1000°C obtained by DSC/TGA analysis.

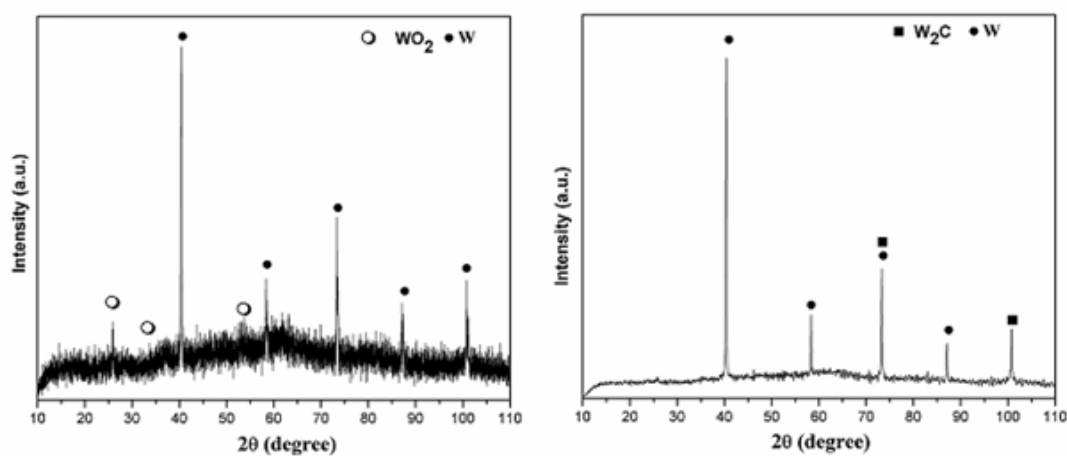


Figure 4.8 : (a) XRD analysis of the powders mechanically alloyed for 15 h and (b) followed annealed for 1 h at 1000° after DSC / TGA analysis.

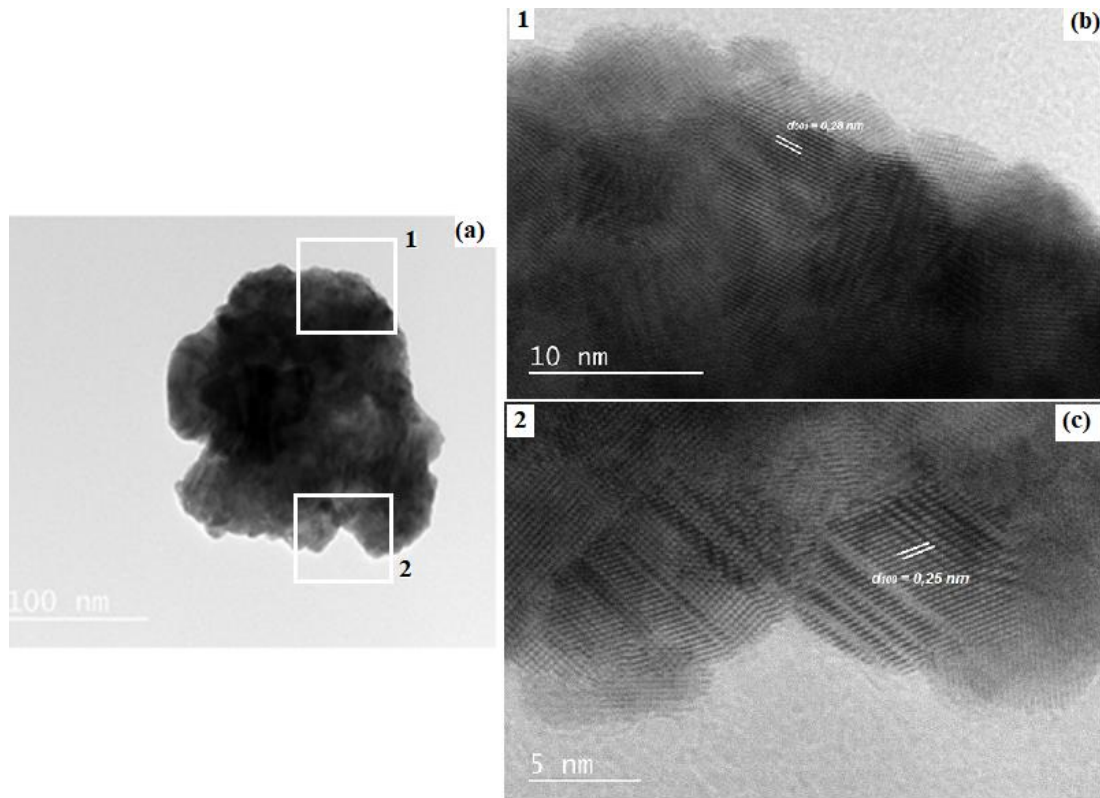


Figure 4.9 : (a) TEM image of powders mechanically for 15 h and followed by annealing for 1 h at 1000°C, (b) higher magnification of the image from the region indicated in (a) as 1 showing an interplanar spacing of 0,28 nm between graphite sheets, (c) higher magnification of the image from the region indicated in (a) as 2.

Figure 4.9 illustrates TEM images of powders mechanically for 15 h and followed by annealing for 1 h at 1000°C. These TEM images show that WC particles are surrounded by graphitic shells with different thicknesses. In the Figure 4.9 (a) two regions are remarked as 1 and 2. Figure 4.9 (b) shows higher magnification of the image from the region indicated in (a) as 1 showing an interplanar spacing of 0,28 nm between graphite sheets which indicates this particle is hexagonal WC in the [100] zone axis orientation. Another higher magnification image from the region indicated in (a) as 2 is illustrated in Figure 4.9 (b). An interplanar spacing of 0,25 nm between graphite sheets is measured in this image. This shows also this particle is hexagonal WC in the [100] zone axis orientation.

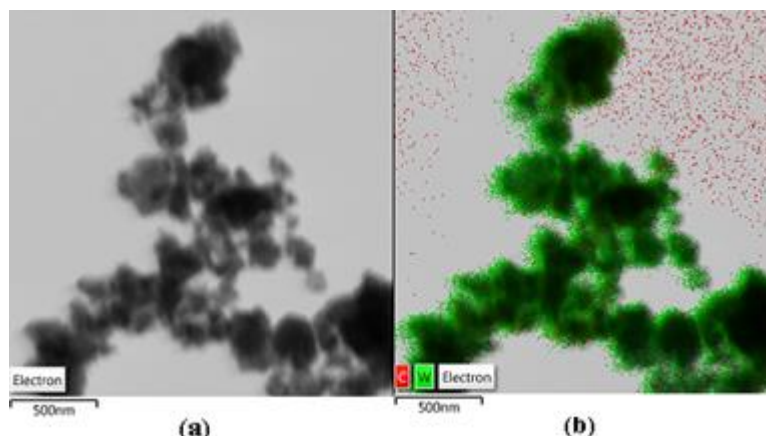


Figure 4.10 : (a) TEM image and (b) EDS mapping of powders mechanically for 15 h and followed by annealing for 1 h at 1000°C.

Figure 4.10 displays transmission electron microscope (TEM) images and element analysis of powders mechanically alloyed for 15 h and then annealed at 1000 ° C for 1 h. Figure 4.10 (b) shows the elemental analysis of the powder particles represented in Figure 4.10 (a) by mapping method. The parts marked by green reveal the W phase and the parts marked by red show the C phase. Figure 4.10 (b) demonstrates that the majority of the powders contain the WC phase.

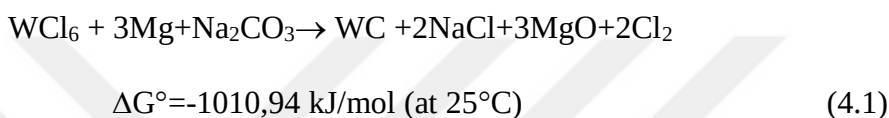
These preliminary investigations of the dissertation reveals that an alternative source of W powders as a reactant should be used to completely synthesize WC powders in a short time in addition to methods of annealing or adding excess amount of C source. It has been observed from these experiments that when W was used as a reactant, long duration of milling, high energy (high temperature) or excess amount of powders (C) are required to produce completely WC powders.

4.2 Mechanochemical Synthesis (MCS) of Tungsten Carbide Powders

This section explains the results of a detailed phase analyses on the milled powders of WCl_6 - Na_2CO_3 -Mg and followed on the leached powders. Firstly stoichiometry of the initial powders (WCl_6 - Na_2CO_3 -Mg) with different milling durations were used to produce tungsten carbide powders. Later different excess amounts of Na_2CO_3 and Mg reactants were utilized to examine the optimum synthesis conditions of tungsten carbide powders. In this way, the optimum synthesis conditions of tungsten carbide powders were examined in regard of MCS duration and weight amounts of Na_2CO_3 and Mg reactants. Phase, microstructural and thermal characterizations of the MCS'd

and leached powders were implemented using X-ray diffractometer (XRD), stereo microscope (SM), scanning electron microscope/energy dispersive spectrometer (SEM/EDS), particle size analyzer (PSA), differential scanning calorimeter (DSC) and transmission electron microscope (TEM).

The predicted reduction reaction for acquiring WC in the presence of solid and gaseous by-products such as NaCl, MgO and Cl₂ is given in Eq.(1). It has a large negative Gibbs free energy change value at 25°C, indicating that the initial materials favorably react with each other driven by a thermodynamically feasible chemical reaction.



The XRD patterns of the as-blended stoichiometric WCl₆-Na₂CO₃-Mg powders and those after MCS for 15,30,45 min and 1,3,5,8 h are shown in Figures 4.11 (a), (b) and (c), respectively. As-blended powders have WCl₆, WO₂Cl₂, Na₂CO₃, Na₂CO₃.H₂O, NaHCO₃ and Mg phases, as compatible with the XRD patterns of raw materials in Figure 3.2 (a)-(c). After MCS for 45 min, a chemical reaction between initial powders took place, and W₂C, WC, W, MgO and NaCl phases emerged as reaction products. The type of constituents does not change as MCS duration prolonged up to 8 h. W₂C phase has the highest intensity than those of WC and W for the powders MCS'd at the time range of 45 min and 8h. The WC, NaCl and MgO reaction products predicted in Eq.(1) conform well with those of synthesized powders. It should be also noted that a gas was discharged from the milling vial at the time of unloading the MCS'd powders. Similarly, Ma and Du (2008) obtained WC, NaCl and MgO phases in the autoclave processed WCl₆-Na₂CO₃-Mg powders. Additionally, the reactions in Eq.(2) and (3) which have larger negative Gibbs free energy changes than that of Eq.(1) are not congruent with the products of the WCl₆-Na₂CO₃-Mg system. MgCl₂ or Na₂O phases did not detected in the reaction products.

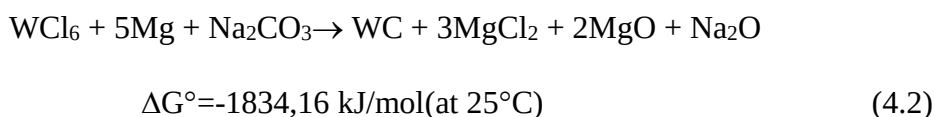


Table 4.2 : The average crystallite sizes and lattice strains of the WC and W₂C phases in the MCS'd powders using stoichiometric WCl₆-Na₂CO₃-Mg powders.

MCS duration (h)	Average crystallite size (nm)		Average lattice strain (%)	
	WC	W ₂ C	WC	W ₂ C
1	25.50	72.70	0.41	0.23
3	17.00	41.40	1.30	0.98
5	15.80	29.10	1.50	1.39
8	6.60	12.90	1.56	2.20

Furthermore, the detection of major W₂C phase as a result of MCS process is not expected since the formation of WC is more favorable than that of W₂C phase. However, there are some similar investigations in which W₂C phase were synthesized in large amounts rather than WC phase (Jiang et al., 2004; Öveçoğlu and Özkal, 2004; Bolokang et al., 2010; Tan and Mu, 1998; Tan, 2009). As formerly reported, W₂C is a metastable hexagonal phase occurred at low carbon amount and low temperature (Bolokang et al., 2010). Since milling was performed without applying an external heat and the temperature increase in the milling vial, which was triggered with the continuous collisions, did not measured, the occurrence of W₂C phase can be only explained with the C content in the present system. Stoichiometric amounts of reactants resulted in an incomplete reaction between W and C. It can be said that there is C deficiency in the system and more C source should be added for the transformation of W₂C to WC phase. Additionally, the formation of WC phase was evaluated in terms of the increase in milling time (Bolokang et al., 2010; Yusoff et al., 2011). Bolokang et al. (2010) reported that longer milling durations provided enough energy to constitute the reaction between C and W₂C in order to form WC phase, and hence W₂C phase disappeared. In other words, WC occurred from transformation of the intermediate W₂C phase which is instable at low temperature (Singla, 2014). According to Yusoff et al. (2011), the temperature inside the vial increased as milling duration increased, and this increased the rate of alloying which created a new phase (WC) formation. Although the transformation of W₂C to WC completed after milling for 60 h in a planetary ball mill rotated at 400 rpm, the dominant phase was still W₂C after MCS for 8 h in a high-energy ball mill rotated at

1200 rpm in the present study (Yusoff et al., 2011) . This means that the temperature in the milling vial was not high enough to enable W_2C transformation. Nevertheless, utilizing unconventional raw materials such as WCl_6 , Na_2CO_3 and Mg in this study enabled the formation of W_2C and WC phases in a short time. For comparing the products of W sources, when the same milling conditions were applied to the elemental W-C powder system in section 4.1 WC incubation starts in their structure after MA for 7 h. Thus, the comparison of the XRD patterns in Figures 4.1 and 4.11 (b) reveals the solid proof of advantage of using WCl_6 - Na_2CO_3 -Mg powder system rather than elemental W-C system.

Figure 4.12 shows the XRD patterns of the stoichiometric WCl_6 - Na_2CO_3 -Mg powders after MCS for 5 h and 7 M HCl leaching. The resultant powder contains WCl_6 , WO_2Cl_2 , W_2C , WC and W phases without any presence of unwanted NaCl and MgO by-products. Surprisingly, WCl_6 and WO_2Cl_2 phases were detected after leaching with 7 M HCl. They were amorphized during extended milling and did not participate into the reduction reaction emerged as products in the leached powders. Furthermore, the intensities of W_2C are still higher than those of WC and W phases after purification.

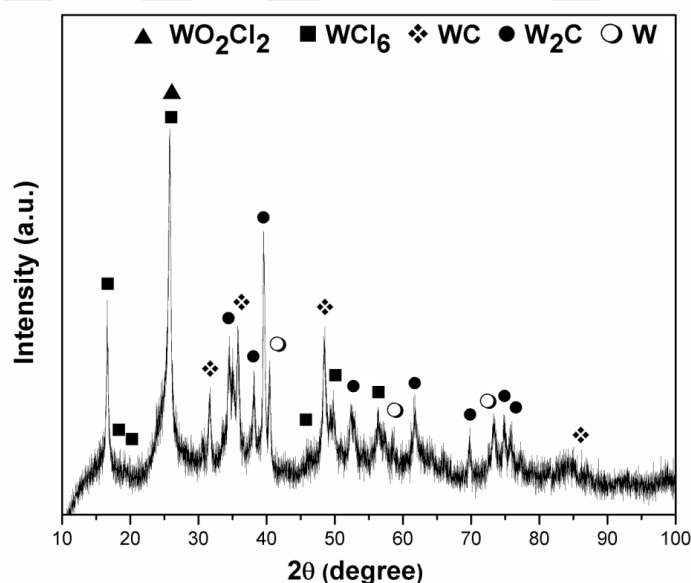


Figure 4.12 : XRD pattern of the stoichiometric WCl_6 - Na_2CO_3 -Mg powders after MCS for 5 h and 7 M HCl leaching.

Figure 4.13 (a) displays the XRD pattern of the 8 h MCS'd WCl_6 - Na_2CO_3 binary powder system in order to show the role of Mg reductant in the reaction. There are high amounts of WCl_6 , WO_2Cl_2 and NaCl phases in addition to WC phase in the

structure of the binary powders. This infers that there should be a reducing agent in the powder constituents to enable the complete reduction of WCl_6 and WO_2Cl_2 phases. The use of Mg is critical for the reduction and carburization reactions. Figures 4.13 (b) and (c) show the XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 50 wt.% excess Mg after MCS for 5 h and 7 M HCl leaching, respectively. The type of present phases after MCS for 5 h did not change with the addition of excess Mg (50 wt.%), as compared with the stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders (Figure 4.11(c)). However, the XRD intensities of W and W_2C phases increased as the intensity of WC phase decreased (Figure 4.13 (b)), in comparison with those detected in the stoichiometric powders (Figure 4.11 (c)). After leaching, NaCl and MgO were completely removed from the powders leaving behind WCl_6 , WO_2Cl_2 , W_2C , WC and W phases (Figure 4.13 (b)), similar to the XRD pattern of the stoichiometric powders in Figure 4.12. Unlikely to Figure 4.12, the W phase has the highest XRD intensity than those of WC and W_2C in Figure 4.13 (b). The excess amount of Mg enabled the conversion of WCl_6 to W phase in higher amounts than that of stoichiometric one, and hence the intensity of WCl_6 seems to be decreased in the XRD pattern in Figure 4.13 (b). There is still lack of carbon in the overall powder for obtaining high amounts of WC and/or W_2C phases.

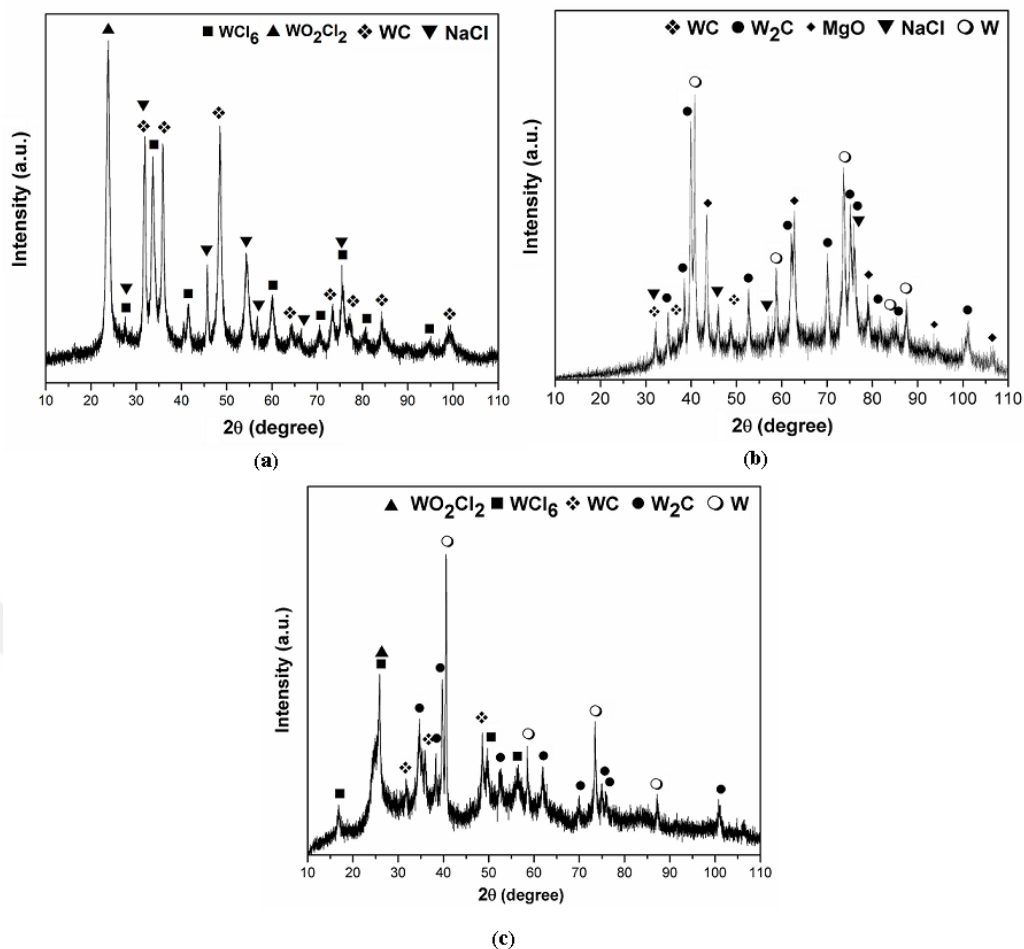


Figure 4.13 : (a) XRD pattern of the $\text{WCl}_6\text{-Na}_2\text{CO}_3$ binary powder system after MCS for 8 h, and XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 50 wt.% excess Mg after (b) MCS for 5 h and (c) 7 M HCl leaching.

Figures 4.14 (a) and (b) show the XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 50 wt.% excess Na_2CO_3 after MCS for 5 h and 7 M HCl leaching, respectively. The excess amount of Na_2CO_3 added into the stoichiometric powders constituted W_2C , WC, W, MgO and NaCl phases (Figure 4.14 (a)), similar to the XRD patterns of the stoichiometric powders (Figure 4.11 (c)) and those 50 wt.% excess Mg added ones (Figure 4.13 (b)). The intensity of W_2C significantly increased and hence the ratio of W to W_2C decreased with the addition of excess carbon source. This means that reduced W got the possibility of reacting with high amount of C to form W_2C phase. As expected, MgO and NaCl dissolved during leaching with 7M HCl solution and W_2C , WC and W phases remained (Figures 4.14 (b)). In the leached powders, the WCl_6 phase, which was previously observed in Figure 4.12 and Figure 4.13 (b), was not detected (Figure 4.14 (b)). It is due to the formation of higher amount of NaCl by means of excess Na_2CO_3 in comparison with the stoichiometric or excess Mg added

powders. Besides, free W is present in the XRD patterns, pointing out that there is still lack of carbon in the system. The conversion of W_2C to WC phase and the disappearance of free W phase can be obtained by the addition of higher Na_2CO_3 amounts.

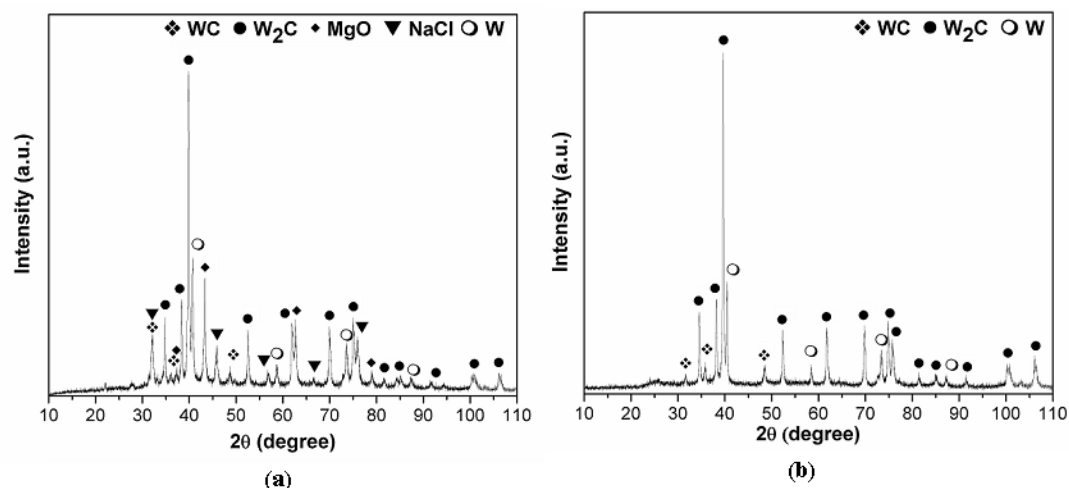


Figure 4.14 : XRD patterns of WCl_6 - Na_2CO_3 -Mg powders with 50 wt.% excess Na_2CO_3 after (a) MCS for 5 h and (b) 7 M HCl leaching.

Figure 4.14 illustrates the XRD patterns of WCl_6 - Na_2CO_3 -Mg powders with 70 wt.% excess Na_2CO_3 after MCS for 1-8 h. For the XRD patterns up to 4 h, NaCl is seen as the dominant phase, probably surpassing peaks of other phases formed during reduction reaction. At 4 h of MCS duration, WC phase incubated with small peaks at 2θ values of $\sim 36^\circ$ and 49° , in addition to the W peak at $\sim 41^\circ$. After MCS for 5 h, the amount of WC phase increased since its intense peaks got a high intensity value. The intensities of detected WC, NaCl and W phases gradually decreased from 5 to 8 h of MCS. Any peak belonging to W_2C phase was not detected, dissimilar with the XRD peaks of stoichiometric powders (Figure 4.11 (c)) and with the XRD peaks of 50 wt.% excess Mg (Figure 4.13 (b)) and Na_2CO_3 (Figure 4.14 (a)) added powders. MgO could not be observed even after MCS for 8 h probably due to its amorphization or its relatively very low intensity dominated by other intense peaks. The higher amount of carbon content resulted in complete WC formation without a sign of W_2C phase. In other words, 70 wt% excess amount of Na_2CO_3 enabled to the conversion of W_2C into WC. Also, the emergence of WC phase from the reaction of W_2C and C was previously reported (Polini et al., 2015; Bolokang et al., 2010; Sakaki et al., 2013; Ebrahimi-Kahrizsangi, 2016). Moreover, the noticeable gradual intensity decrease and broadening in the shape of the peaks arose from severe plastic

deformation during milling, and even at extended milling duration peaks exhibit a tendency to transform to amorphous forms (Lin et al., 2013). This phenomenon in Figure 4.15 was examined taking into account of WC peaks at longer MCS time than 5 h. Table 4.3 lists the average crystallite sizes and lattice strains of the WC phases in the MCS'd (for 5-8 h) powders with 70 wt% excess Na_2CO_3 . The average crystallite size of WC decreased from 29.60 to 19.60 nm whereas the average lattice strain increased from 0.81 to 2.52 %. These are due to the repeated intensive deformation, accumulation of dislocations and high density of defects incorporated into the powders with prolonged milling duration (Bolokang et al., 2010; Hoseinpur, 2013; El-Eskandarany, 2000; 2005).

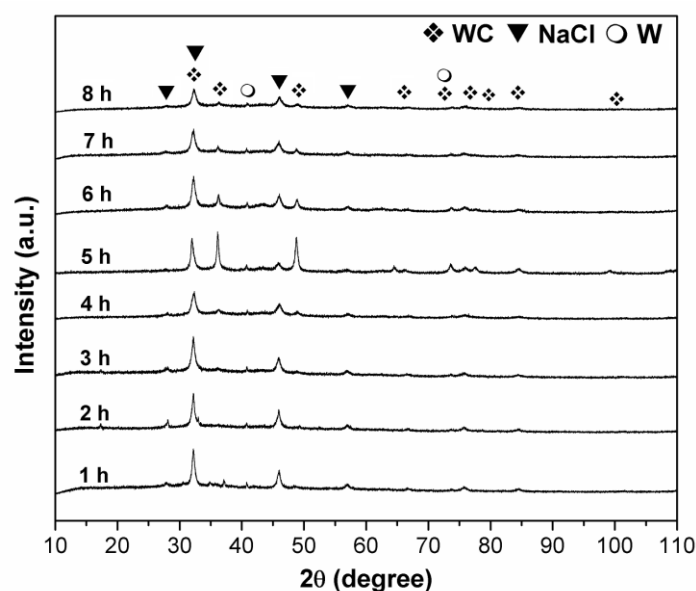


Figure 4.15 : XRD patterns of WCl_6 - Na_2CO_3 -Mg powders with 70 wt.% excess Na_2CO_3 after MCS for 1-8 h.

Table 4.3 : The average crystallite sizes and lattice strains of the WC phases in the MCS'd (for 5-8 h) powders with 70 wt.% excess Na_2CO_3 .

MCS duration (h)	Average crystallite size (nm)	Average lattice strain (%)
5	29.60	0.81
6	28.20	0.83
7	22.30	1.46
8	19.60	2.52

Figure 4.16 (a) and (b) illustrate the XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5 h and leaching with 4 and 7 M HCl, respectively. According to the detection limit of the diffractometer, it can be inferred that unwanted NaCl or MgO by-products were eliminated after leaching with both 4 and 7 M HCl. Powders leached with 4M HCl still contains very small amount of W phase (Figure 4.16 (a)). However, it was not detected in the powders leached with 7M HCl (Figure 4.16 (b)). Thus, the use of 70 wt.% excess Na_2CO_3 over the stoichiometric powders and concentrated (7 M) aqueous HCl solution enabled the synthesis of pure WC powders by leaching out the all W phase.

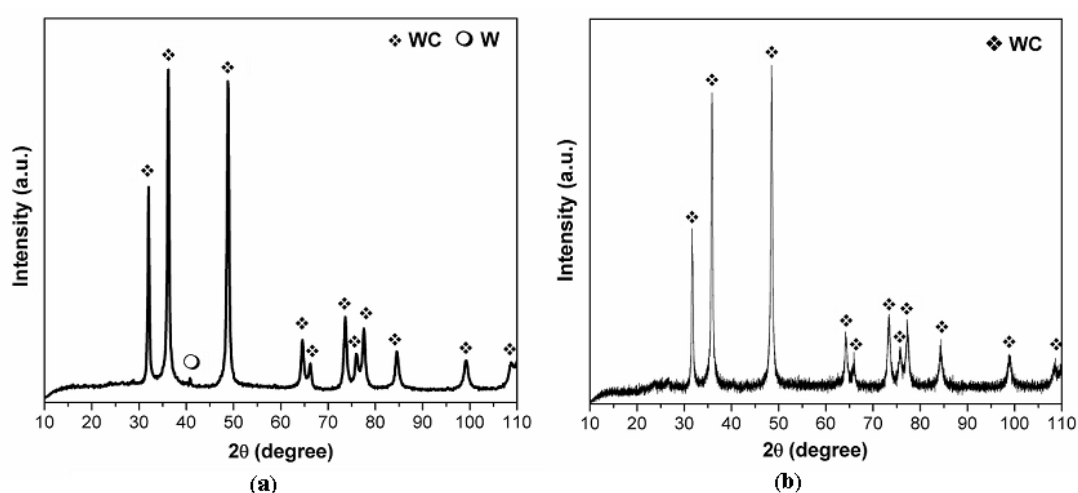


Figure 4.16 : XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5 h and leaching with (a) 4 M and (b) 7 M HCl.

Figure 4.17 (a), (b) and (c) represent DSC curves of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5h, after leaching with 4 and 7 M HCl, respectively. According to Figure 4.17 (a), there is a small endothermic peak and a very broad endothermic peak with onset temperatures of about 350 and 650°C, respectively. These two endothermic peaks correspond to the boiling of WO_2Cl_2 , and melting of Mg and its interaction with the present phases, respectively. Although unreacted WO_2Cl_2 and Mg phases were not detected by the XRD pattern of the 5 h MCS'd powders in Figure 4.15, even their small amounts can be examined with the heat flow difference by DSC analysis. An exothermic peak in the range of 500 and 650°C is observed in the 4 M HCl leached powders in Figure 4.17 (b), probably inferring the oxidation of residual Mg phase and W phase (Ma and Du, 2008). This DSC curve proved the insufficiency of HCl concentration to obtain pure WC powders once more. A similar thermal behavior corresponding to the initiation of

WO₃ about 450°C and the completion of oxidation at 650°C was observed in the autoclave synthesized WC powders (Ma and Du, 2008). Any endotherm or exotherm did not observed in the 7 M HCl leached powders in Figure 4.17 (c). This is a good consistence between the XRD patterns (Figure 4.16 (b)) and DSC curves (Figure 4.17 (c)) of the 7 M HCl leached powders. This points out that the resultant products are pure WC powders. Figures 4.17 (d)-(f) and Figures 4.17 (g)-(i) show the SM images and SEM images of the WCl₆-Na₂CO₃-Mg powders with 70 wt.% excess Na₂CO₃ after MCS for 5h, after leaching with 4 and 7 M HCl, respectively. SM images show the general appearances of the powders after MCS and leaching treatments. As compatible with the DSC curves (Figures 4.17(a) and (b)) of the MCS'd and 4 M HCl leached powders, there are shiny regions throughout the microstructure, indicating the presence of residual metallic Mg or W. Besides, these shiny particles disappeared after 7 M HCl leaching (Figure 4.17 (f)). SEM images of the MCS'd powders composed of particles having sizes smaller than 2.5µm (Figure 4.17 (g)). Besides, the particle size of the 4 M leached powders reduced to lower values than 1 µm (Figure 4.17 (h)). Further reduction in size and unavoidable agglomeration were obviously seen in the 7 M leached powders and Figure 4.17 (i)).

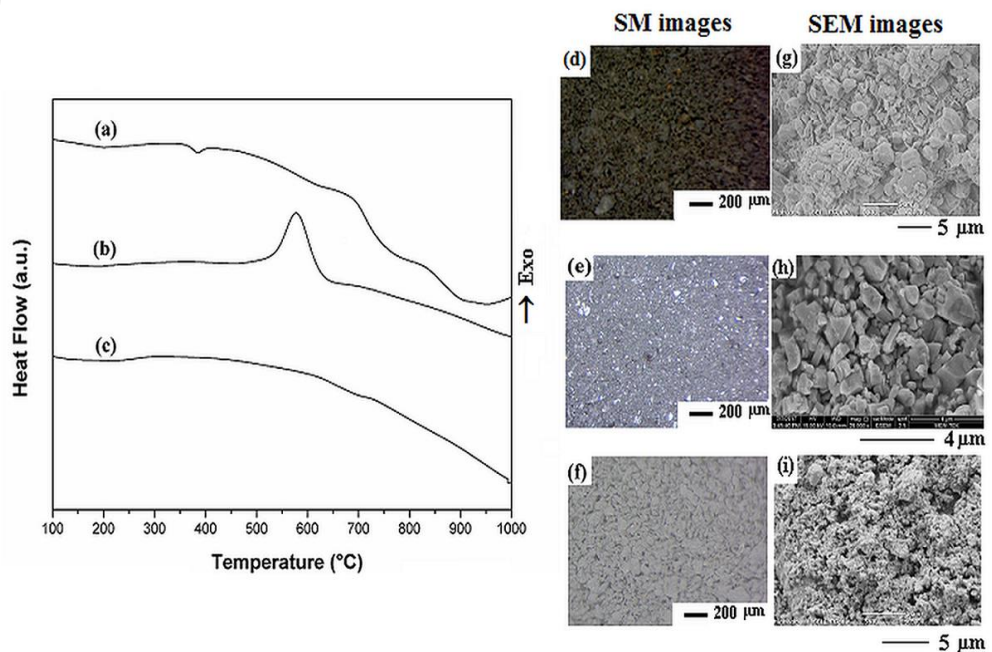


Figure 4.17 : (a-c) DSC curves, (d-f) SM images and (g-i) SEM micrographs of WCl₆-Na₂CO₃-Mg powders with 70 wt% excess Na₂CO₃ after MCS for 5h (a, d, g), after leaching with 4 M HCl solution (b, e, h) and after leaching with 7 M HCl (c, f, i).

Figures 4.18 (a)-(e) represent the SEM micrograph, corresponding elemental W, C and Mg mappings and PSA graph of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5h and leaching with 4 M HCl solution. W and C mappings (Figure 4.18 (b) and (c)) taken from the SEM image in Figure 4.18 (a) coincides well with each other and they are the solid proof of the WC phase as well as XRD pattern in Figure 4.16 (a). Additionally, residual Mg was observed in the 4 M leached powder as compatible with Figures 4.17 (b, e, h). Any signal arose from other elements was not detected in the powders. Besides, the average particle size of the 4 M leached powders was found as 239 nm, with a size distribution between 200 and 900 nm (Figure 4.18 (e)).

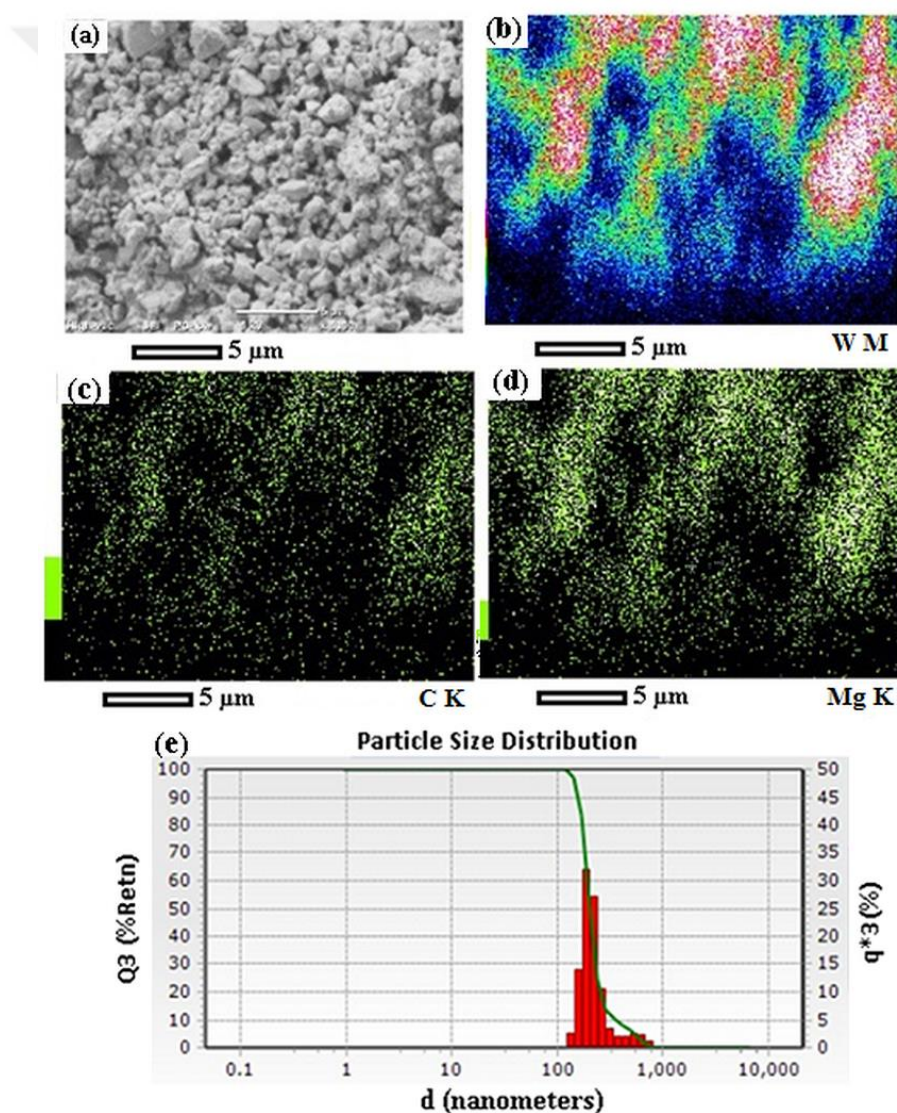


Figure 4.18 : SEM micrograph(a), elemental W (b), C (c) and Mg (d) mappings and PSA graph (e) of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5h and leaching with 4 M HCl.

Figures 4.19 (a)-(d) show the SEM image, W and C mappings and PSA graph of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5 h and leaching with 7 M HCl. As compared to Figure 4.17(a), the sizes of the particles in Figure 4.19 (a) seem to be reduced. Based on Figures 4.19 (b) and (c), the W and C mappings full fill each other, without an indication of any residual phase. It is evident that residual Mg or MgO phases were completely eliminated from the microstructure. Also, particle size distribution curve of the 7 M leached powders lies in between 100 and 500 nm, with an average particle size value of 191 nm. Some former investigations also reported resembling SEM images after WC synthesis (Luković, 2015; El-Eskandarany et al., 2000; Stanciu et al., 2016). It should be also noted that using 7 M concentrated HCl solution enabled reduction in average particle size by means of eliminating residual Mg-based phases.

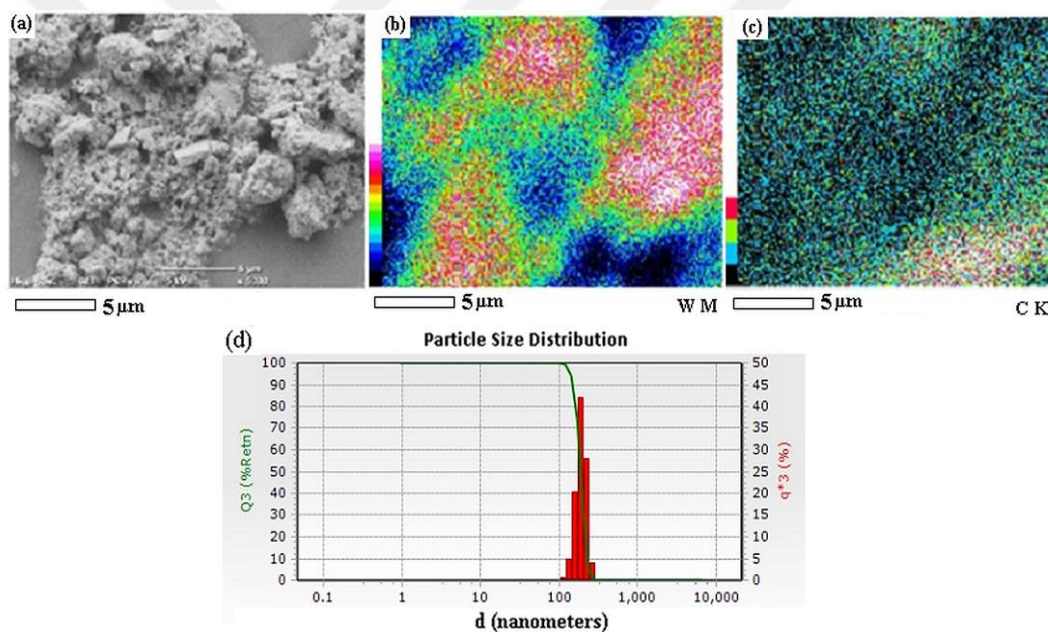


Figure 4.19 : SEM micrograph(a), elemental W (b) and C (c) mappings and PSA graph (d) of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5 h and leaching with 7 M HCl.

Figures 4.20 (a) and (b) show the bright-field (BF) TEM micrographs of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt.% excess Na_2CO_3 after MCS for 5 h and leaching with 7 M HCl solution. TEM micrographs reveal the presence of irregular-shaped (equiaxed or rectangular) particles with sizes lower than 500 nm which was confirmed by the related PSA analysis (Figure 4.19 (d)). Similar agglomerated powder morphologies having particles ranged between 50-200 nm were observed in previous studies (Singh and Pandey, 2013a; 2013b; Kim and Kang, 2014). Fig 4.20

(c) and (d) illustrates the elemental W and C mappings taken from Figure 4.20 (b). Blue regions and green regions indicate W and C elements, respectively. The complete accordance of the W and C mappings strongly proves the formation of WC phase.

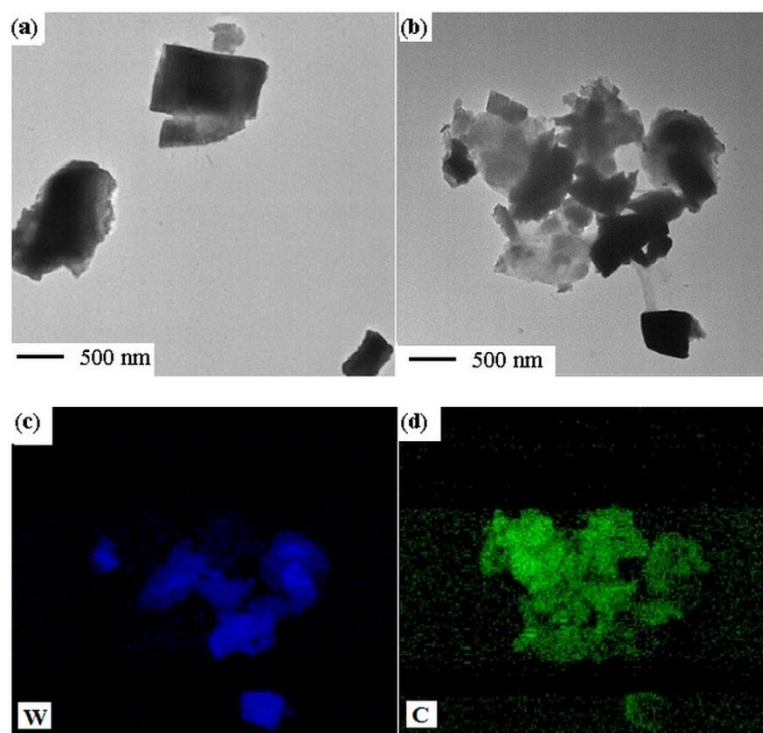


Figure 4.20 : BF TEM micrographs (a, b) and elemental W (c) and C (d) mappings of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 70 wt% excess Na_2CO_3 after MCS for 5 h and leaching with 7 M HCl.

In literature, nanocrystalline hexagonal WC powders were synthesized from the same raw materials (WCl_6 , Na_2CO_3 and Mg) using the co-reduction process in an autoclave operated at 600°C for 8 h and subsequent purification in HCl and ethanol solutions (Ma and Du, 2008). Ma and Du (2008) obtained pure WC particles with an average size of 20 nm. This value is notably lower than that of achieved in the present study, considering that the autoclave processing requires high temperature, pressure and long reaction time than those of MCS.

Consequently, this study introduced a different way of synthesizing W carbide powders. In the literature, research studies about the synthesis of W carbides via MA, MCS or subsequent annealing processes generally started from common raw materials such as W, WO_3 , activated carbon or graphite. However, this study put forward the possibility of obtaining pure submicron-sized WC and/or W_2C powders using unconventional starting materials such as WCl_6 , Na_2CO_3 and Mg by room-

temperature and economical processes. This study can give motivation for further studies about the preparation of other metal carbides.

4.3 Autoclave Processing Synthesis (MCS) of Tungsten Carbide Powders

This section explains the synthesis of tungsten carbide powders via mechanical activation assisted-autoclave processing synthesis. This section consists of two parts since experiments were performed in two different autoclave systems.

4.3.1 Autoclave processing in a hastelloy autoclave with a vessel.

In this part variable amounts of experiments were performed in a hastelloy autoclave with a vessel by applying Ar gas in order to increase the pressure during chemical reaction. In other words Ar gas amount was varied to obtain different pressure values. The system was heated to the temperature of 500°C which is the maximum temperature of system, and it was kept constant during the autoclave processing. Synthesis of WC powders was attempted from the same raw materials (WCl_6 - Na_2CO_3 -Mg) by the mechanochemical synthesis in previous section. The experiments were carried out at 500 °C by varying pressure values and durations.

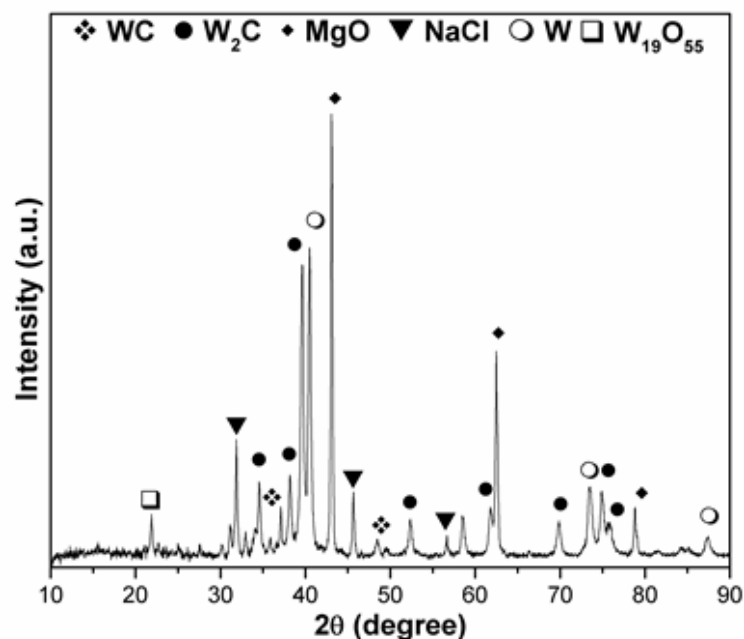


Figure 4.21 : The XRD pattern of the autoclaved powders at 500°C and 9 bar for 6 h.

Figure 4.21 illustrates the XRD patterns of autoclaved powders at 500°C and 9 bar for 6 h. MgO, WC, W₂C, NaCl, W and W₁₉O₅₅ phases were detected after the chemical reactions in the autoclave system. MgO has the highest intensity and W₂C phase has higher intensity than the WC phase. In order to increase, the amount of the WC phase, the temperature value and duration of the experiment were increased.

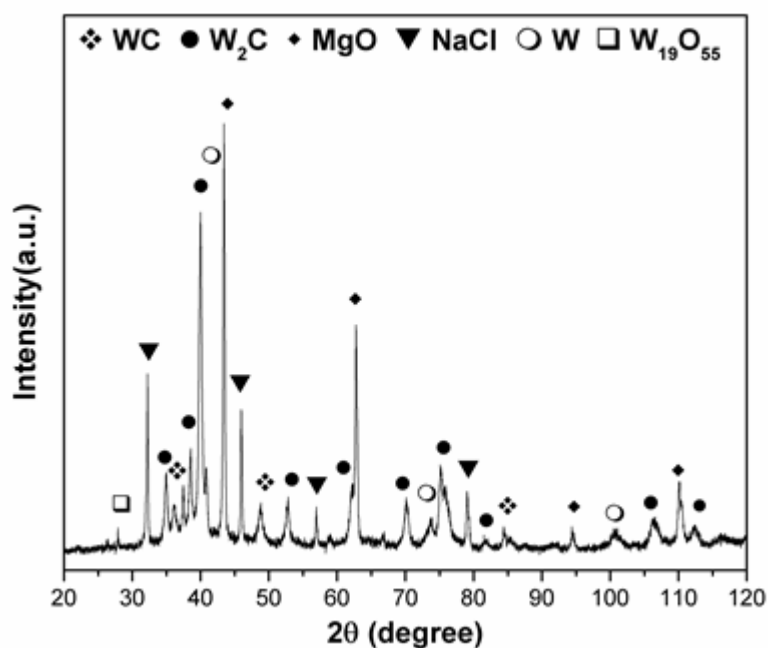


Figure 4.22 : The XRD pattern of the autoclaved powders at 500°C and 15 bar for 8 h.

Figure 4.22 shows the XRD pattern of the autoclaved powders at 500°C and 15 bar for 8 h. All the same phases existed in this graph and the intensity of the W phase decreased.

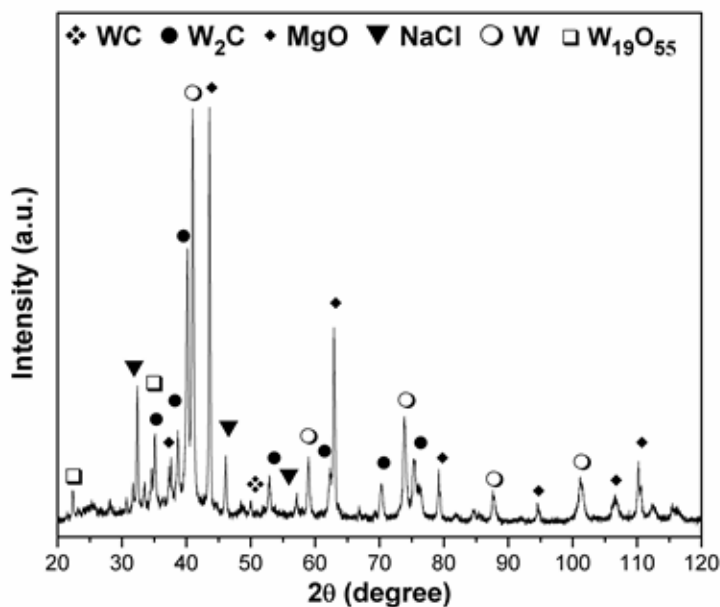


Figure 4.23 : XRD pattern of the autoclaved powders at 500°C and 15 bar for 10 h.

The XRD pattern of the autoclaved powders at 500°C and 15 bar for 10 h is shown in Figure 4.23. When the duration of experiment changed from 8 h to 10 h, the intensity of W phase increased significantly. But when the temperature of the system increased to 50 bar from 15 bar as shown in Figure 4.2, the same phase prevailed with nearly no change in the intensities of phases.

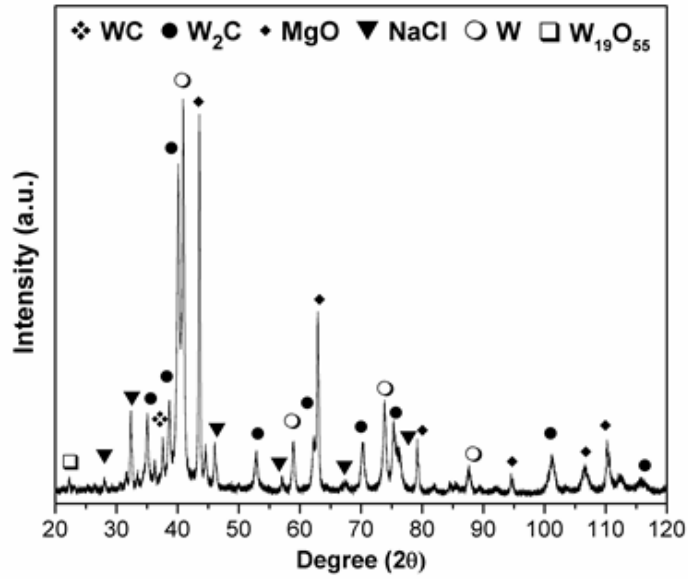


Figure 4.24 : XRD pattern of the autoclaved powders at 500°C and 50 bar for 10 h.

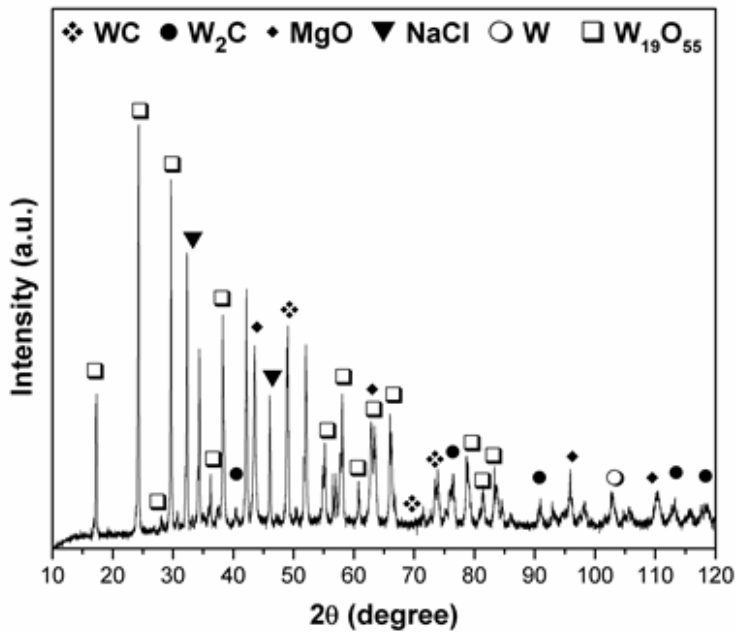


Figure 4.25 : XRD pattern of the autoclaved powders at 500°C and 50 bar for 10 h with with 70 wt% excess Na_2CO_3 .

XRD patterns of the autoclaved powders at 500°C and 50 bar for 10 h with with 70 wt.% excess Na_2CO_3 is illustrated in Figure 4.25. As the amount of oxygen in the structure of Na_2CO_3 increased, the free tungsten in the system reacted with oxygen and $\text{W}_{19}\text{O}_{55}$ phase emerged into existence by decreasing the intensity of the W phase. When the duration of experiment increased to 12 h in Figure 4.26 and 24 h in Figure 4.27, there was not any noticeable change occurred.

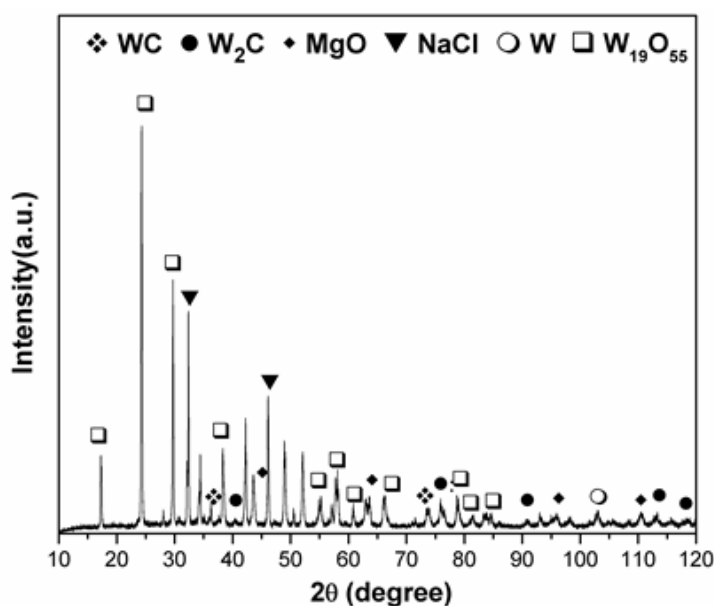


Figure 4.26 : XRD pattern of the autoclaved powders at 500°C and 50 bar for 12 h with 70 wt.% excess Na_2CO_3 .

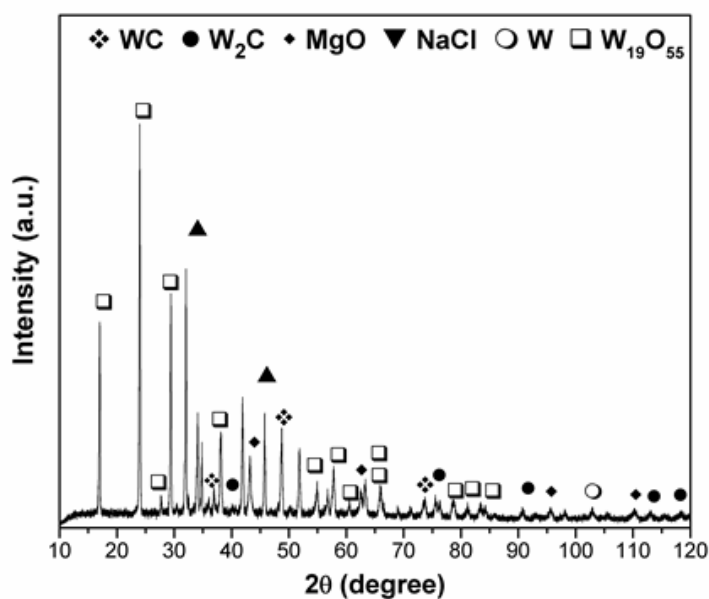


Figure 4.27 : XRD pattern of the autoclaved powders at 500°C and 50 bar for 24 h with 70 wt.% excess Na_2CO_3 .

In summary, in Figures 4.21 through 4.27 the MgO, WC, W_2C , NaCl, W and $\text{W}_{19}\text{O}_{55}$ phases are present after the chemical reactions in the autoclave system. Peak intensities of W and MgO phases are high, but the intensity of the WC phase is very low in the XRD patterns. When the pressure increased, the intensity of the W phase increased surpassing that of the MgO phase (Figure 4.24). If the amount of Na_2CO_3 increased to 70 wt.% excess, the intensity of $\text{W}_{19}\text{O}_{55}$ phase increased shown in Figure 4.26 and 4.27. In these experiments WC phase in the amount of requested

could not be synthesized despite of trying different experimental conditions. Despite of increasing the pressure, the amount of Na_2CO_3 and the duration time, WC phase with the high intensity could not be obtained. In these experiments there was gas leakage which caused decreasing the pressure values and occurrence of $\text{W}_{19}\text{O}_{55}$ phase. In addition temperature is thought to be insufficient for obtaining tungsten carbide powders. Thus, it was decided to set up another experiment that overcomes all these problems and to use hydrothermal reactor heating by furnace for autoclave processing.

4.3.2 Autoclave processing in a hydrothermal reactor

XRD patterns of the as-blended with the stoichiometric WCl_6 - Na_2CO_3 -Mg powders, MAC'd stoichiometric WCl_6 - Na_2CO_3 -Mg powders, MAC'd WCl_6 - Na_2CO_3 -Mg powders with 5 wt% excess graphite powders, MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess graphite powders, MAC'd WCl_6 - Na_2CO_3 -Mg powders with 5wt% excess activated C powders and MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C powders were illustrated respectively in Figure 4.28 (a), (b), (c), (d) and (e). S powders have WCl_6 (ICDD Card No:74-0455), Na_2CO_3 (ICDD Card No: 19-1130), $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ (ICDD Card No:15-0700) and Mg (ICDD Card No:89-5003) phases (Figure 4.28 (a)). $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ phase occurred due to having hygroscopic characteristic of Na_2CO_3 . After the stoichiometric WCl_6 - Na_2CO_3 -Mg powders MAC'd for 2 min only WCl_6 , Mg, Na_2CO_3 , WCl_2 (ICDD Card No:17-0261) and NaCl (ICDD Card No:05-0628) phases were observed that means initial powders have just started to react each other Figure 4.28 (b)). A chemical reaction took place between WCl_6 and Na_2CO_3 powders and NaCl and WCl_2 phases formed. After WCl_6 - Na_2CO_3 -Mg powders MAC'd for 2 min with 5 wt% excess graphite powders, $(\text{NaO})_2\text{C}_6\text{O}_4$ (ICDD Card No:04-0515) and $\text{WO}_2(\text{ClO}_4)_2$ (phases were detected in addition to WCl_6 , WCl_2 , NaCl, Mg and Na_2CO_3 phases (Figure 4.28 (c)). $(\text{NaO})_2\text{C}_6\text{O}_4$ phase occurred due to reaction between excess graphite and Na_2CO_3 . Also $\text{WO}_2(\text{ClO}_4)_2$ phase emerged into existence due to a chemical reaction between WCl_2 and oxygen. After WCl_6 - Na_2CO_3 -Mg powders MAC'd for 2 min with 100 wt% excess graphite powders, WCl_6 phase disappeared in the XRD pattern (Figure 4.28 (d)). Also the intensity of WCl_2 and Mg decreased as compared to the WCl_6 - Na_2CO_3 -Mg powders with 5 wt% excess graphite powders MAC'd (Figure 4.28 (c)). It simply means that WCl_6 powders in the reactor were used up and the amount of

the Mg powders in the reactor was decreased. When $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders MAC'd for 2 min with 5wt% excess activated C powders, the phase of $(\text{NaO})_2\text{C}_6\text{O}_4$ disappeared (Figure 4.28 (e)) as compared to the XRD pattern of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 5 wt% excess graphite powders MAC'd for 2 min (Figure 4.28 (c)). Moreover, the intensity of Na_2CO_3 and Mg decreased and the intensity of NaCl increased (Figure 4.28 (e)) when the type of carbon source changed to active C. When the excess amount of active C increased to 100 wt%, WCl_6 phase disappeared (Figure 4.28 (f)) similar to the XRD pattern of powders with 100 wt% excess graphite (Figure 4.28 (d)). Differently from the XRD pattern of powders MAC'd with 100 wt% excess graphite (Figure 4.28 (d)) the intensity of $\text{WO}_2(\text{ClO}_4)_2$ phase increased and the major peak of the WCl_2 phase has the highest intensity (Figure 4.28 (f)).

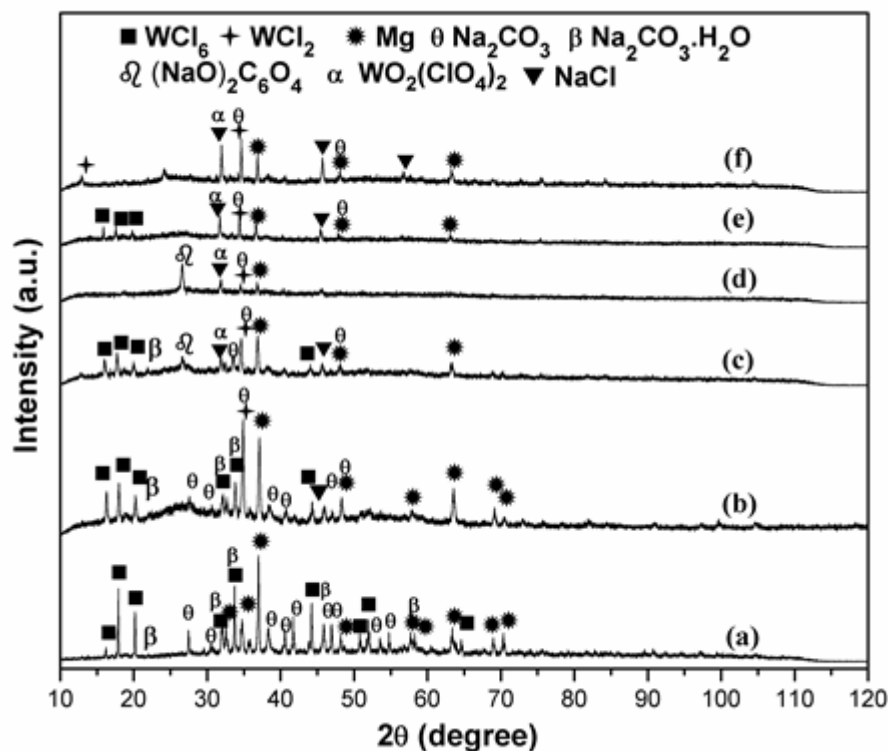


Figure 4.28 : XRD patterns of the (a) as-blended with the stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders, and MAC'd (b) stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders, (c) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 5 wt% excess graphite powders, (d) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess graphite powders, (e) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 5wt% excess activated C powders and (f) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders.

Figure 4.29 shows XRD patterns of the MAC'd stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders after autoclaved for 8 h at 400° C, 500° C and 600° C, respectively. In all temperatures initial powders reacted to each other. At 400° C , 500° C and 600° C

,WC (ICDD Card No:892727), W_2C (ICDD Card No:65-3896), NaCl (ICDD Card No:05-0628), MgO (ICDD Card No:65-0476) and W (ICDD Card No:47-1319) phases appeared as reaction products observed in XRD patterns. The type of phases did not change when the temperature of the reaction differed from 400° C to 600 °C . In Figure 4.29 (b), when the experiment of temperature increased from 400° C to 500° C, the intensity of the W phase decreased that indicates more W powders reacted in the synthesis reaction as the temperature of reaction increased. As the temperature increased to 600° C, the intensity of WC, W_2C and W phases also increased. In comparison with the study of Ma and Du (2008), W_2C and W phases are dissimilar phases. Ma and Du (2008) obtained WC, NaCl and MgO powders with the stoichiometric amounts of WCl_6 -Mg- Na_2CO_3 after autoclaved at 600° C for 8h.

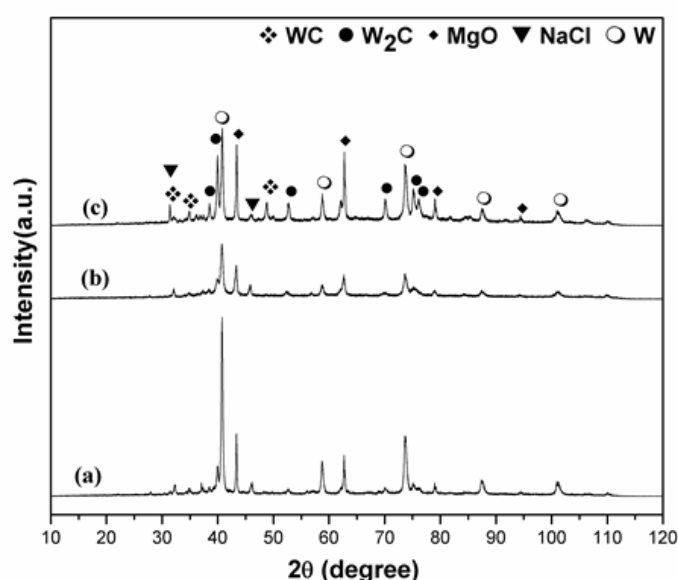


Figure 4.29 : XRD patterns of the MAC'd stoichiometric WCl_6 - Na_2CO_3 -Mg autoclaved powders after autoclaved for 8 h at (a) 400°C, (b) 500°C, (c) 600°C.

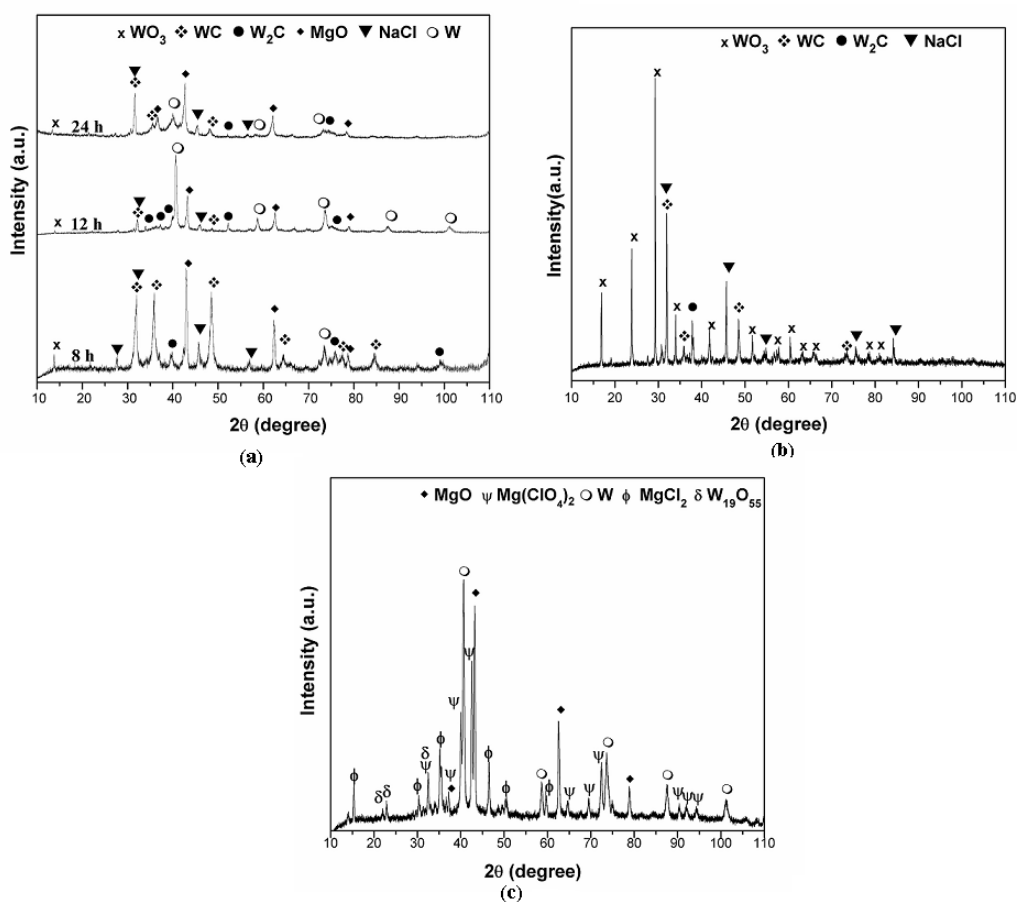


Figure 4.30 : XRD patterns of the MAC'd (a) stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders after autoclaved at 700°C for 8, 12 and 24 h, (b) binary $\text{WCl}_6\text{-Na}_2\text{CO}_3$ powders after autoclaved at 700°C for 8 h and (c) binary $\text{WCl}_6\text{-Mg}$ powders after autoclaved at 700°C for 8h.

Figure 4.30 (a) illustrates XRD patterns of the MAC'd stoichiometric $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders after autoclaved at 700°C for 8, 12 and 24 h. When the hydrothermal reactor was heated to 700°C for 8h, the resultant powder contains WC, W_2C , NaCl, W and MgO. When the powders autoclaved for 12 h the major peak of the W phase has the highest intensity. Also the intensity of MgO phase decreased significantly. The intensity of W decreased and the intensity of WC and NaCl phases increased for the duration of 24 h. As compared to the XRD pattern of powders autoclaved for 8h, W phase still present at the XRD patterns of powders autoclaved for the duration of 24 h. Also the duration of 8h has the highest intensity of WC phase. Figure 4.30 (b) illustrates the XRD pattern of binary $\text{WCl}_6\text{-Na}_2\text{CO}_3$ powders after autoclaved at 700°C for 8 h. The aim of this experiment is to observe the effect of Mg reductant in the reaction. High amount of WO_3 phase is observed in addition to WC, W_2C , NaCl, MgO phases and W phase is not detected in the XRD pattern. Since all amount of W

powders in the system reacted with the oxygen as a result of formation of WO_3 . It shows that there should be reducing agent in the initial powders to prevent emerging WO_3 . Because the reducing agent acquires the free oxygen in the system and in this way prevents the reaction between tungsten and oxygen. The XRD pattern of binary WCl_6 -Mg powders after autoclaved at 700°C for 8h is shown in Figure 4.30 (c). This experiment was carried out to observe the effect of Na_2CO_3 as a carbon source. MgCl_2 (ICDD Card No:45-0167), $\text{Mg}(\text{ClO}_4)_2$, MgO and $\text{W}_{19}\text{O}_{55}$ (ICDD Card No:45-0167) phases were observed differently from other phases. NaCl phase did not emerge into existence due to absence of Na_2CO_3 . Cl elements reacted with Mg instead of Na and MgCl_2 phase occurred similar to the product from the reaction given in the study of Ma and Du (2008).

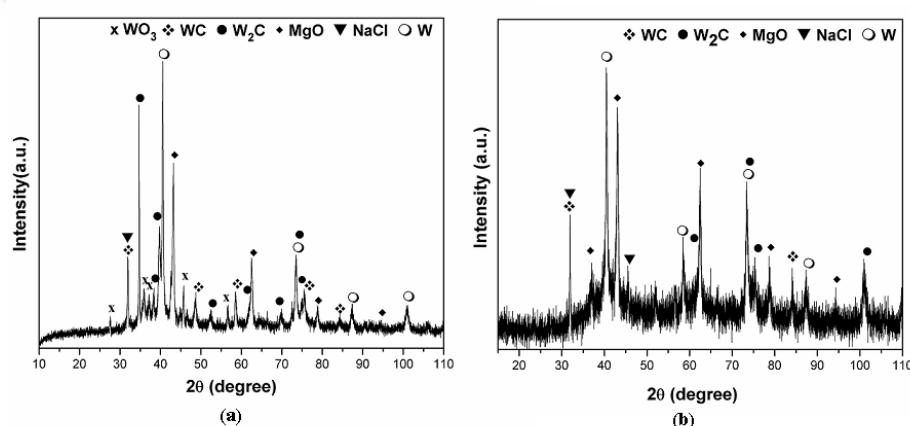


Figure 4.31 : XRD patterns of the MAC'd (a) WCl_6 - Na_2CO_3 -Mg powders with 100 wt % excess Na_2CO_3 and (b) with 100 wt % excess Mg powders after autoclaved at 700°C for 8h.

The Figure 4.31 (a) displays the XRD pattern of the MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess Na_2CO_3 after autoclaved at 700°C for 8h. There is a little amount of WO_3 phase in addition to other phases (WC , W_2C , MgO , W) in comparison with the XRD pattern of the MAC'd stoichiometric WCl_6 - Na_2CO_3 -Mg powders after autoclaved at 700°C for 8h (Figure 4.30 (a)). Also the XRD intensities of W_2C phase increased as compared to those observed in XRD pattern of stoichiometric WCl_6 - Na_2CO_3 -Mg powders after autoclaved at 700°C for 8h (Figure 4.30 (a)). When the excess amount of Mg increased to 100 wt%, the product powders comprise of WC , W_2C , NaCl , MgO and W phases (Figure 4.31 (b)) absence of WO_3 phase differently from the XRD pattern of binary WCl_6 - Na_2CO_3 powders and WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess Na_2CO_3 powders after autoclaved at

700°C for 8 h. Because the excess amount of Mg picked up all free oxygen in the system and avoid to form WO₃ phase.

Figure 4.32 (a) represents the XRD pattern of WCl₆-Na₂CO₃-Mg powders with 5 wt% excess graphite powders after autoclaved at 700°C for 8h. In comparison with XRD pattern of stoichiometric WCl₆-Na₂CO₃-Mg after autoclaved at 700°C for 8h (Figure 4.30 (a)), the same phases (WC, W₂C, MgO, NaCl and W) were detected and the intensity of WO₃ phase increased. When the excess amount of graphite increased to 10 wt %, all W₂C phase was converted to WC phase and free W phase was almost disappeared (Figure 4.32 (b)) by the high amount of carbon source (Bolokong et al., 2010; Yusoff et al., 2011; Singla et al., 2014). Also, high intensity of WO₃ phase was detected dissimilar to the XRD pattern of stoichiometric WCl₆-Na₂CO₃-Mg autoclaved powders (Figure 4.30 (a)) and WCl₆-Na₂CO₃-Mg powders with 5 wt% excess graphite (Figure 4.32 (a)) powders after autoclaved at 700°C for 8h. Due to the stability of graphite some amount of tungsten could not react with carbon, but reacted with oxygen and the WO₃ phase emerged into existence (Figure 4.32 (b)). However, by increasing the amount of excess graphite to 100 wt%, a noticeable gradual intensity of decrease in WC phase and increase in W₂C phase occurred (Figure 4.32 (c)). When excess activated carbon was added as carbon source in the amount of 5 wt% in Figure 4.32 (d), the amount of free W seems to be decreased gradually as compared to the XRD pattern of stoichiometric WCl₆-Na₂CO₃-Mg powders after autoclaved at 700°C for 8h (Figure 4.30 (a)) and the phase of WO₃ was not detected as compared to the XRD pattern of WCl₆-Na₂CO₃-Mg powders with 10 wt% excess graphite (Figure 4.32 (b)) and WCl₆-Na₂CO₃-Mg powders with 100 wt% excess graphite powders after autoclaved at 700°C for 8h (Figure 4.32 (c)). When the amount of excess activated carbon was increased to 10 wt% (Figure 4.32 (e)), there is not noticeable difference in type and intensity of phases between the XRD patterns of WCl₆-Na₂CO₃-Mg powders with 5 wt% excess activated C after autoclaved at 700°C for 8h (Figure 4.32 (d)). But, as increased the activated carbon to 100 wt % (Figure 4.32 (f)), the intensity of MgO and W₂C phases decreased in comparison with the XRD pattern of WCl₆-Na₂CO₃-Mg powders with 10 wt% excess activated C powders after autoclaved at 700°C for 8h (Figure 4.32 (e)). Most importantly, observed free W phase and WO₃ phases were completely disappeared as compared to the XRD pattern of WCl₆-Na₂CO₃-Mg powders with 5, 10 and 100 wt% excess graphite powders after autoclaved at 700°C for 8h (Figure 4.32 (a), (b) and (c)).

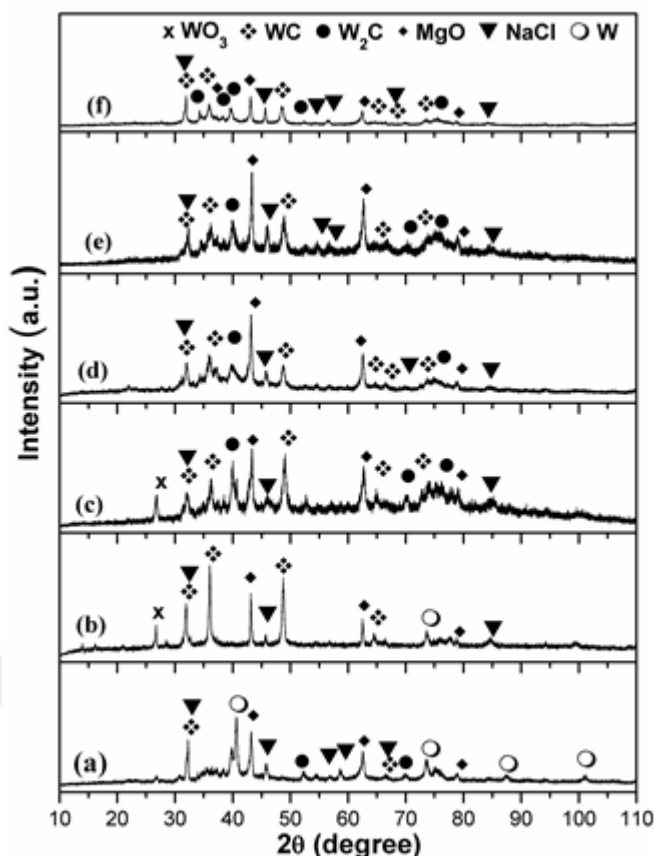


Figure 4.32 : XRD patterns of the MAC'd and (a) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 5 wt% excess graphite (b) with 10 wt% excess graphite, (c) with 100 wt% excess graphite, (d) with 5wt% excess activated C, (e) with 10 wt% excess activated C and (f) with 100 wt% excess activated C powders after autoclaved at 700°C for 8h.

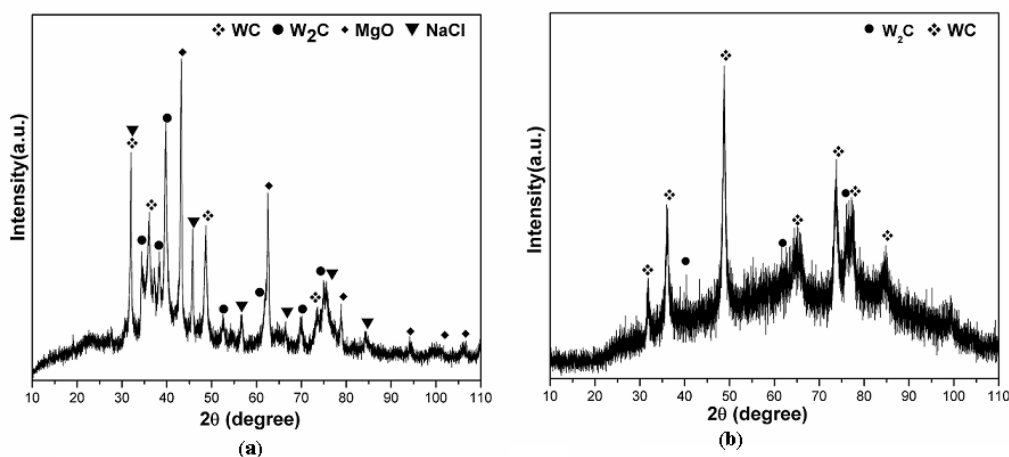


Figure 4.33 : XRD patterns of the MAC'd (a) $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h, and (b) those subsequently leached with 7M HCl.

XRD patterns of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 10 wt% excess activated C at 700°C for 8 h after MAC'd for 2 min with and those subsequently leached with 7 M HCl is illustrated in Figure 4.33 (a) and (b) respectively. After the autoclave

processing at 700°C for 8h, WC, W₂C, NaCl and MgO phases were observed (Figure 4.33 (a)). After the purification process with 7M HCl resultant powders contains WC and a little amount of W₂C phases with absence of NaCl and MgO. It can be explained that unwanted MgO, NaCl and also a big amount of W₂C were eliminated after leaching with 7M HCl ((Figure 4.33 (b)). In this way the use of 100 wt% excess activated carbon over the stoichiometric powders by autoclave processing after mechanically activation and using 7M aqueous HCl solution for purification method achieved the production of WC and a small amount of W₂C powders.

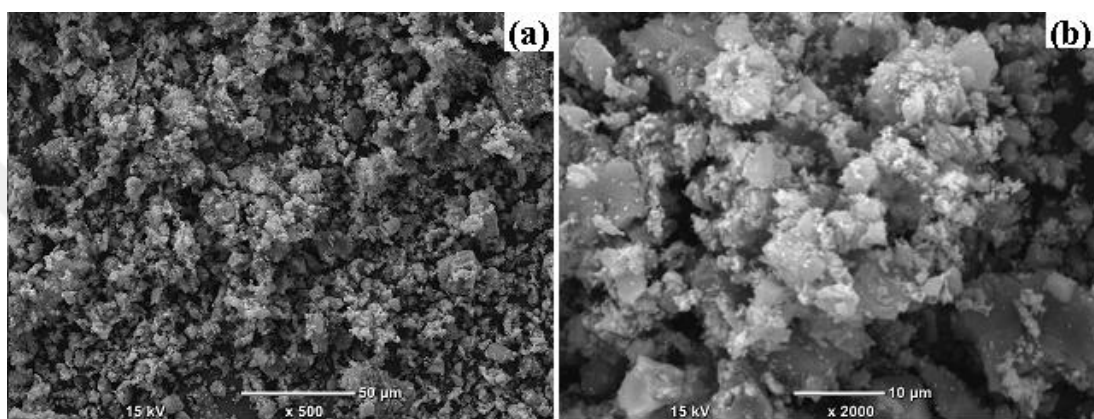


Figure 4.34 : SEM micrographs of the MAC'd WCl₆-Na₂CO₃-Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl at magnifications (a) 500X and (b) 2000X.

Figure 4.34 displays SEM micrographs of the MAC'd WCl₆-Na₂CO₃-Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl at different magnifications. There are both small and large flake-shaped particles. The magnitudes of particles are distributed from 100 nm to 10 µm.

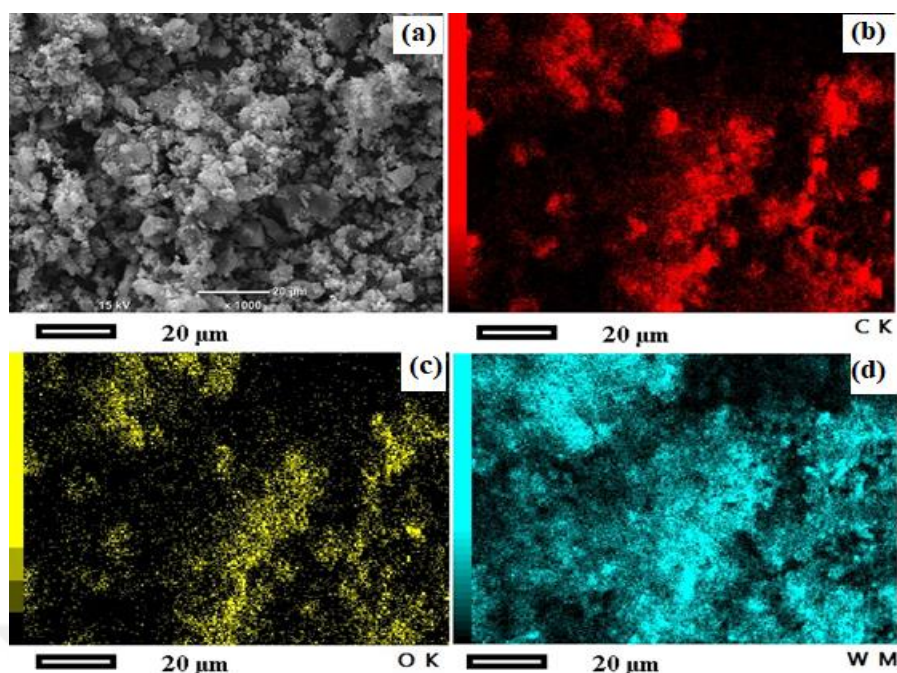
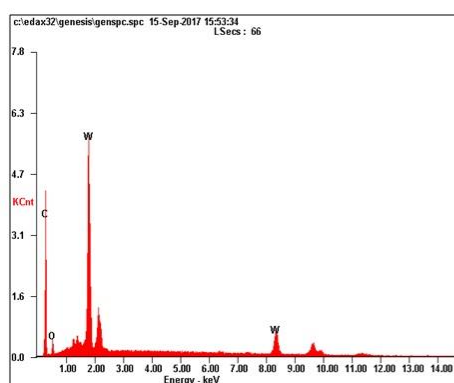


Figure 4.35 : SEM micrograph (a), elemental C (b), O (c) and W (d) mappings of the the MAC'd $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl.

Figures 4.35 (a)-(d) represent the SEM micrograph, corresponding elemental C, O and W mappings of the MAC'd $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl. W and C mappings (Figure 4.35 (b) and (d)) taken from the SEM image in Figure 4.35 (a) coincides well with each other and they prove existing of the WC phase as well as XRD pattern in Figure 4.33 (b). Additionally, O was observed in the resultant powder which is attributed to conditions of laboratory and SEM equipment.



Elements	Wt. %	At. %
C	41.87	86.25
O	4.20	6.49
W	53.93	7.26

Figure 4.36 : EDS results taken from the SEM image of the MAC'd $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl.

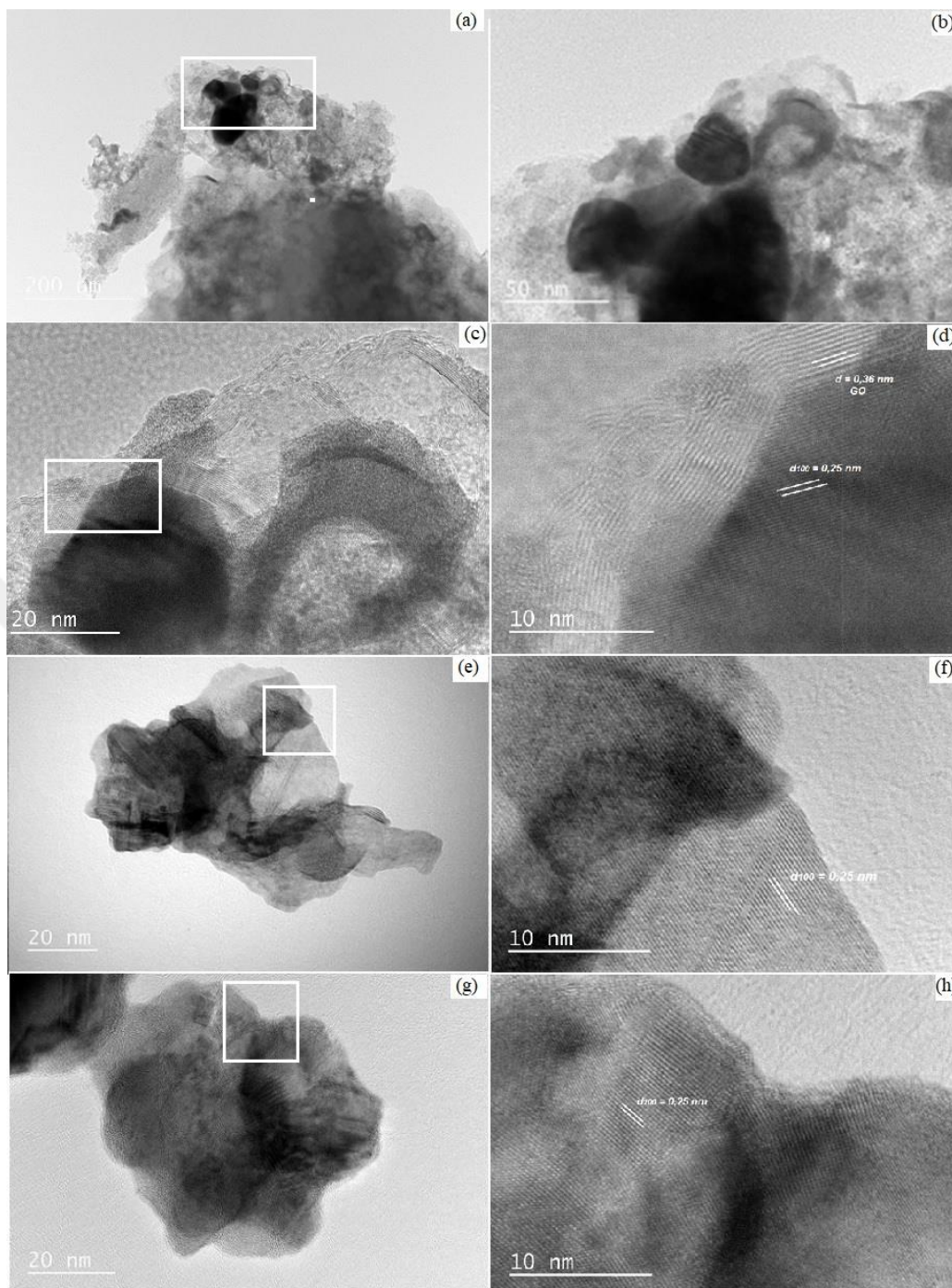


Figure 4.37 : (a) TEM image of the MAC'd $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl, (b) higher magnification of the image from the region indicated in (a), (c) HR-TEM image of powder particle, (d) higher magnification of the image from the region indicated in (b) showing an interplanar spacing of 0.34 and 0.25 nm between graphite sheets, (e) HR-TEM image of another particle, (f) higher magnification of the image from the region indicated in (e) showing an interplanar spacing of 0.25 nm between graphite sheets, (g) HR-TEM image of another particle, (h) higher magnification of the image from the region indicated in (g) showing an interplanar spacing of 0.25 nm between graphite sheets.

EDS results are illustrated in Figure 4.36 taken from the SEM image of WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C at 700°C for 8 h after mechanically activated for 2 min and subsequently leached with 7 M HCl. These results are compatible with the mappings of the resultant powders in Figure 4.35 (b)-(d).

Figure 4.37 (a)-(h) shows TEM image of the MAC'd S100C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl at different magnifications. These images show that resultant nanoparticles have graphitic shells with different thicknesses. Figure 4.37 (a) displays a particle which is relatively larger. Figure 4.37 (b) represents higher magnification of the image from the region indicated in (a). HR-TEM (high resolution TEM) image of powder particle is taken in the same region indicated (b) in Figure 4.37 (c). Figure 4.367 (d) illustrates higher magnification of the image from the region indicated in (c) showing an interplanar spacing of 0.34 and 0,25 nm between graphite sheets (d). It shows 14 layers of graphitic shells. The interplanar spacing of 0.34 nm between graphite sheets indicates graphene oxide particle. Also, the interplanar spacing of 0.25 nm between graphite sheets illustrates that the particle is hexagonal WC in the [100] zone axis orientation. Figure 4.37 (e) and (g) show an image of a particle with a diameter of approximately 100 nm. TEM images from the region indicated respectively in (e) and (g) with thicker graphitic shells are illustrated in both Figure 4.37 (f) and (h). In these images the interplanar spacing of 0.25 nm between graphite shells are seen illustrating that the particle is hexagonal WC in the [100] zone axis orientation as well as in the Figure 4.37 (d).

Transmission electron microscope (TEM) image and element analysis of the MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl are illsutrated in Figure 4.38. Figure 4.38 (b) shows the elemental analysis of the powder particles represented in Figure 4.38 (a) by mapping method. The parts marked by blue represent the W phase and the parts marked by red illustrate the C phase. Figure 4.38 (b) indicates that the majority of the powders contain the WC phase.

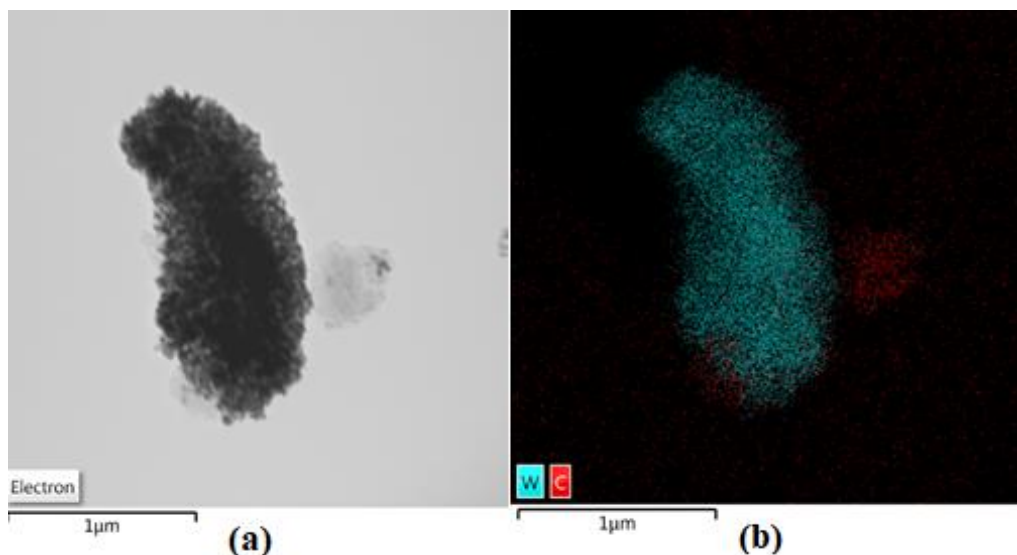


Figure 4.38 : BF TEM micrographs (a) and (b) elemental W and C mappings of the MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl.

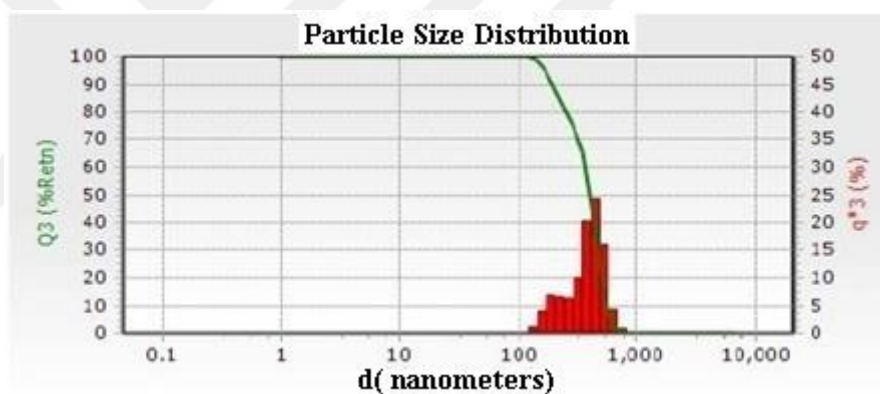


Figure 4.39 : PSA graph of powders of the MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl.

PSA graph of powders of the MAC'd WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl, is represented in Figure 4.39. The average particle size of these powders are measured as 384 nm with a size distribution between 200 and 900 nm.

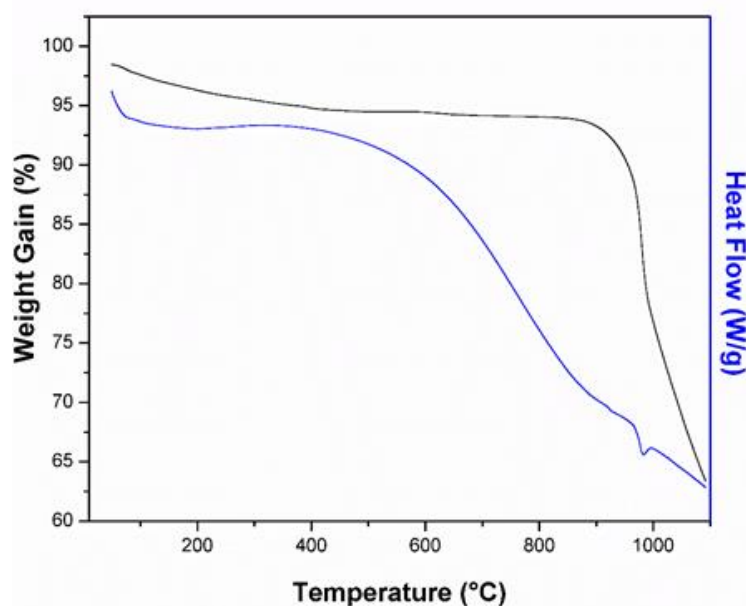


Figure 4.40 : DSC and TGA analyses of powders of the MAC'd $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders with 100 wt% excess activated C powders after autoclaved at 700°C for 8 h and subsequently leached with 7 M HCl.

Temperature-weight gain and temperature- heat flow curves obtained after DSC / TGA analysis of powders of $\text{WCl}_6\text{-Na}_2\text{CO}_3\text{-Mg}$ powders autoclaved with 100 wt % excess activated C at 700°C for 8 h after MA'C for 2 min and subsequently leached with 7 M HCl, are given in Figure 4.40. During the heating process up to 1100°C , heat flow decreased after 600°C , weight gain decreased after 900°C . The WC phase obtained by autoclave processing synthesis with 100 wt % excess activated C at 700°C for 8 h after mechanically activated for 2 min, is not stable up to 1100°C . Also a small endothermic peak is observed in the range of temperature between 950°C and 1000°C which is coincide with weight gain curve. WC could be decomposed into W_2C or W phase. A part amount of powder has W phase could be transformed to lower oxide as a result of oxidation of W. The carbon content of WC can be converted to volatile CO_x gas according to Boudouard reaction. After heating to this powder up to 1100°C , the weight gain of the powder decreases only at a temperature close to 1000°C . This clearly shows that there is no free C phase in the resultant WC powder. In addition, it can be said that the WC powders decomposes at approximately 1000°C .

5. CONCLUSIONS AND RECOMMENDATIONS

This dissertation focused on the synthesis of tungsten carbide powders to find the most efficient method with the most economical way and to investigate all the characteristics of final product. In this study two methods, mechanical alloying/mechanochemical synthesis and autoclave processing, were utilized to produce tungsten carbide powders. Results are expressed in four sections involving conclusions of mechanical alloying using elemental tungsten (W) and carbon (C) powders, mechanochemical synthesis starting from WCl_6 , Na_2CO_3 and Mg powders, autoclave processing in a halloy autoclave system using WCl_6 - Na_2CO_3 -Mg powders and autoclave processing using hydrothermal reactor using WCl_6 - Na_2CO_3 -Mg powders.

The first study investigated production of WC and W_2C powders from elemental W and C powder blends and following annealing treatment to obtain WC powders. Based on the results reported in this study, the following conclusions can be summarized:

- After 7 hours, WC powders were started to be obtained by mechanical alloying method using stoichiometric ratio of elemental W and C powders.
- After the annealing of elemental W and C powders in stoichiometric ratio alloyed for 15 h at 1000°C for 1 h, only WC phase was found in XRD analysis.
- Mechanical alloying of elemental W and C powders in stoichiometric ratio for 15 hours yielded powders with an average particle size of 75 nm. After annealing of these powders at 1000°C for 1 h, the average particle size increased to 305 nm.

- The average density of powders annealed by mechanical alloying method for 15 h and then annealed at 1000 °C for 1 h was measured as 15.1 g / cm³.
- When the thermal analysis of mechanical alloyed for 15 h powders before and after annealing was examined; while the weight of the powders decreased at 700 °C before annealing, the weight of the powders decreased at a temperature close to 1000 °C is observed after annealing.
- Graphitic shells surrounded by WC powders are observed by the imaging of HR-TEM.

The second study investigated the synthesis of WC and W₂C powders from WCl₆, Na₂CO₃ and Mg containing mixtures via mechanochemical reactions and HCl leaching treatment. Based on the results reported in this study, the following conclusions can be summarized:

- Mechanochemical synthesis of stoichiometric WCl₆-Na₂CO₃-Mg powders for 5 h yielded W₂C, WC, W, MgO and NaCl phases. After 7 M HCl leaching, WO₂Cl₂ and WCl₆ phases emerged with major W₂C, WC and W.
- Milling of stoichiometric powder mixtures from 1 to 8 h resulted in a decrease in the average crystallite sizes and increase in the average lattice strains of the W₂C and WC particles.
- In the case of using 50 wt% excess Mg over stoichiometric powders, major W, W₂C, WC, WO₂Cl₂ and WCl₆ phases occurred after mechanochemical synthesis for 5 h and 7 M HCl leaching.
- When 50 wt% excess Na₂CO₃ amount was used, major W₂C, WC and W phases were obtained after mechanochemical synthesis for 5 h and 7 M HCl leaching.

- As Na_2CO_3 content was increased to 70 wt% excess over stoichiometric mixture, XRD patterns showed only the presence of WC phase after mechanochemical synthesis for 5 h and 7 M HCl leaching.
- DSC analysis showed any endothermic or exothermic peaks in the leached powders containing 70 wt% excess Na_2CO_3 , revealing that synthesized WC powders were free of impurities and stable until 1000 °C.
- Pure WC powders were achieved with an average particle size of 191 nm after mechanochemical synthesis (for 5 h) and leaching (7 M HCl) of 70 wt% excess Na_2CO_3 containing powders.

The third study is the synthesis of WC and W_2C powders from WCl_6 , Na_2CO_3 and Mg via autoclave processing in a hastelloy autoclave with a vessel. The experiments were implemented at 500°C at different pressures and for different durations.

- The synthesis of pure WC powders could not be achieved via autoclave processing in a hastelloy autoclave with a vessel.
- The high intensity of WC phase, low intensity of W_2C phase were obtained via autoclaved processing in hydrothermal reactor at 700 °C for 8 h for WCl_6 - Na_2CO_3 -Mg powders with 100 wt% excess activated C and after leaching with 7M HCl.
- The average particle size of autoclaved powders with 100 wt% excess activated C and after leaching with 7M HCl. are measured as 384 nm with a size distribution between 200 and 900 nm.
- The weight of the powders decreased at a temperature close to 1000 °C is observed after annealing and an endothermic peak is observed at the same temperature.

- Graphitic shells are observed enclosed WC powders in the characterization of HR-TEM.



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- **Aytekin, N.Ö.**, Ağaoğulları, D., Öveçoğlu, M.L. 2019. Mechanochemical synthesis of tungsten carbide powders induced by magnesiothermic reduction of WCl_6 and Na_2CO_3 raw materials, Materials Research Express, 6, 096517.
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