DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF MECHANICALLY ALLOYED W-SiC AND W-SiC-Y$_2$O$_3$ COMPOSITES

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MEKANİK ALAŞIMLAMA YÖNTEMİYLE ÜRETİLMİŞ W-SiC VE W-SiC-Y₂O₃ KOMPOZİTLERİİNİN GELİŞTİRİLMESİ VE KARAKTERİZASYONU

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MEKANİK ALAŞIMLAMA YÖNTEMIYLE ÜRETLİŞİ W-SiC VE W-SiC-Y₂O₃ KOMPOZİTLERİNIN GELİŞİTİRİLMESİ VE KARAKTERİZASYONU

ÖZET

Partikül takviyeli kompozitler seramik ve metallerde tek başına bulunmayan eşsiz bir mikroyapı ve özellik kombinasyonuna sahiptirler. Uzay ve otomotiv sektörlerinin yanı sıra birçok farklı uygulamada kullanılan bu malzemeler karakteristik olarak izotropik kimyasal ve mekanik özellikler içerirler. Bunun yanı sıra, göreceli olarak daha ucuz olmaları, kolay şekil alabilme ve işlenebilme gibi özelliklere de sahiptirler.

Son on yılda, yüksek ergime sıcaklığı, yüksek modül, yüksek termal şok direnci, düşük isil genleşme katsayısı, yüksek sıcaklık mukavemeti ve direngenliği gibi özellikleriyle matris malzemeleri olarak kullanılan volfram ve alasımaları yüksek sıcaklık özelliklerinin geliştirilmesi amacıyla çok fazla ilgi çekmektedirler. Volfram ve alasımalarının mekanik özelliklerinin geliştirilmesi için partikül takviye malzemeleri olarak genelde TiC, ZrC, HfC, TiN, Y₂O₃, La₂O₃, Sm₂O₃, ThO₂, ZrO₂ gibi refactor karakterli karbür, nitrür ve oksit fazları kullanılır.

Bu çalışmada, değişen sıcaklıklarda iyi özgül mukavemet ve Young modülü olan, ayrıca iyi bir yoğun direnç ve yüksek erozyon ve korozyon direncini sahip SiC partiküller ile takviye edilmiş volfram matrisli kompozitler, mekanik alaşımlama yöntemi kullanılarak geliştirilmiş ve değişen SiC oranlarının mikroyapı ve mekanik özelliklerine olan etkisi araştırılmıştır. Kompozit tozların ve sinterlenmiş numunelerin faz ve mikroyapı karakterizasyonları TEM ve XRD teknikleri kullanılarak gerçekleştirilmiştir. Ayrıca preslenmiş ve sinterlenmiş numunelerin yoğunluk ve sertlik ölçümleri yapmıştır. Bunun yanı sıra Y₂O₃ takviyesinin W-SiC kompozitlerinin mekanik ve mikroyapı özelliklerine olan etkisi araştırılmıştır. Ayrıca geleneksel sinterleme tekniklerinin yanı sıra sinterleme sırasında tane büyümesini engellemek için iki-basamaklı bir sinterleme rejimi kullanılmış ve farklı sinterleme rejimlerinin kompozit mikroyapı ve mekanik özelliklerine olan etkileri araştırılmıştır.
DEVELOPMENT AND CHARACTERIZATION INVESTIGATIONS OF MECHANICALLY ALLOYED W-SiC AND W-SiC-Y$_2$O$_3$ COMPOSITES

SUMMARY

Particle-reinforced-metal-matrix composite (PRMMC) materials exhibit a unique combination of microstructure and properties which is not found in either ceramics or metals alone. They are used in aerospace, automotive and a lot of other applications due to their characteristic isotropic physical and mechanical properties. Moreover, they have relatively low costs, good formability and machinability as well.

In the last decade, tungsten and its alloys, which are used as matrix materials with their high melting point, high modulus, high resistance of thermal shock, low coefficient of thermal expansion (CTE) and good high temperature strength and stiffness, have received attention with a view of improving elevated temperature mechanical properties. As dispersion strengtheners, refractory carbide, nitride and oxide phases, such as TiC, ZrC, HfC, TiN, Y$_2$O$_3$, La$_2$O$_3$, Sm$_2$O$_3$, ThO$_2$, ZrO$_2$, etc. have been mainly used to improve the mechanical properties of tungsten and its alloys.

In this study, tungsten matrix composites reinforced with SiC particles which have attractive properties, such as good specific strength and Young modulus as a function of temperature, specific stiffness, corrosion and erosion resistance were developed by mechanical alloying and the effect of different SiC amounts on the microstructural and mechanical properties were investigated. Microstructure and phase characterizations of composite powders and sintered samples were carried out via SEM and XRD analyses. In addition, density and hardness measurements of as-consolidated and sintered samples were carried out. Also, the effect of addition of Y$_2$O$_3$ phase to the mechanical properties and the microstructure of W-SiC composites was investigated. Moreover, besides the conventional sintering technique, a two-step sintering regime to inhibit the grain growth was applied to the samples and the effect of these different sintering regimes on microstructural and mechanical properties of the composites was examined.
1. INTRODUCTION

Considering the Stone Age, the Iron Age, the Industrial Revolution, the nuclear age and the electronic revolution, it is undoubtedly clear that the improvement of the materials and the materials technology has always been the key for the important technology breakthroughs throughout the history of mankind. The aerospace era of today is a new revolution which is triggered by the outbreak of the advanced materials called “composites” (Schwartz, 1997a).

Many of our modern technologies require materials with unusual combinations of properties which cannot be met by conventional metal alloys, ceramics, and polymeric materials. Since no single material could fulfill these rising requirements in the last 20 years, an increasing interest in developing new materials has been aroused to serve the need for new materials having unique properties for special applications (Song et al., 2003; Tang et al., 2004). Therefore, in parallel with the development of composite materials, such material combinations which fulfill the requirements of the modern technology have been, and are yet being, extended.

A composite material is a material system which is produced by combining two or more dissimilar materials into a new material which exhibits a significant proportion of the properties of constituent phases, which may be better suited for a particular application than either of the original materials alone (Schwartz, 1984). In general, composites can be defined as materials with embedded high-strength and high-stiffness reinforcements of one material in a surrounding matrix of another material (Schwartz, 1997b)

Composite materials are especially attractive for applications in marine, automotive, aviation and aerospace industries because of their exceptional strength and stiffness-to-density ratios and superior physical properties. As a result, using composite materials in these industries has led to improvements in the technology (Coskun et al., 2004). Furthermore, this great potential raises the need for extensive study of the mechanical properties of these novel materials (Quinta da Fonseca, et. al. 2001).
One simple scheme for the classification of composites is to separate the matrix and reinforcing phase constituents, and divide them into several groups. The first classification is based on the type of the matrix constituent: Polymer-Matrix, Metal-Matrix or Ceramic-Matrix Composites. Composites can also be classified based on the type of reinforcement used: fiber reinforced (continuous or discontinuous) or particulate reinforced (flakes, chopped fibers, shaped particles, and whiskers) (Schwartz, 1984; Coskun et al., 2004). However, the best way to classify the composites is to include both the reinforcement and matrix constituent, such as particle-reinforced-metal-matrix composites (PRMMC).

A metal matrix composite (MMC) combines into a single material a metallic base with a reinforcing constituent, which is usually non-metallic and is commonly a ceramic. It is also possible to use other materials as reinforcements instead of ceramics, for instance refractory metals or intermetallics (Clyne, 2001). There are plenty of well-known reasons to add ceramic particles into a metal, such as to give the metal high hardness and wear resistance (Miserez et al., 2004). Furthermore, MMC’s combine metallic properties such as ductility and toughness with the characteristics of ceramics, namely high strength and modulus (Tjong and Ma, 2000). The mechanical properties of the MMC’s highly depend on the volume fraction and the type of the reinforcement as well as the type of the matrix (Stjernstoft, 2004). On the other hand, while continuous fiber-reinforcement provides the most effective strengthening in a given direction, particle-reinforcement provides cost-effectiveness and especially isotropic properties to the composite. In addition, the latter one can be processed using similar technology used for monolithic materials (Chawla and Shen, 2001.). Furthermore, MMC’S with discontinuous reinforcements are also attractive for their processability into various shapes (Chung, 2001). In overall, there exists a number of variables which determine the characteristics of the composite materials.

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

As interesting and appropriate matrix materials with their high melting point, high modulus, high resistance of thermal shock, low CTE and good high temperature strength and stiffness, in this last decade, tungsten and its alloys have received attention with a view of improving the high temperature mechanical properties. As dispersion strengtheners, refractory carbide, nitride and oxide phases, such as TiC, ZrC, HfC, TiN, Y_2O_3, La_2O_3, Sm_2O_3, ThO_2, ZrO_2, etc. have been mainly used to improve the mechanical properties of tungsten and its alloys (Song et al., 2002; Song et al., 2003; Lee et al., 2004). However, their content in tungsten is usually less than 3 vol. % and to date, unfortunately, research on tungsten matrix composites reinforced with a high content of ceramic phase has been rarely reported. Furthermore, there is no literature which reports on tungsten matrix composites reinforced with SiC which is a hard and strong material with low density.

Keeping the above concepts in mind, the aim of this study has been to develop and characterize nanostructured SiC particle-reinforced tungsten composite powders and their consolidated and sintered counterparts. In addition, the characterization investigations of the sintered end-products and the effect of addition of Y_2O_3 phase to the mechanical properties and microstructure of W-SiC nanocomposites were also carried out.
2. LITERATURE REVIEW

2.1. Particulate Reinforced Metal Matrix Composites (PRMMC’s)

MMC’s have become attractive candidate materials for aerospace, automotive and a lot of other applications due to their physical and mechanical properties. More recently, especially PRMMC’s have received an increasing attention because of their relatively low costs, good formability and machinability as well as characteristic isotropic properties (Ibrahim et al., 1991; Tjong and Ma, 2000; Sun et al., 2003).

Early studies on MMC’s were about the development and investigation of the behavior of continuous fiber reinforced high performance hybrid materials. However, extensive industrial application of these composites has been hindered because of the high production costs of the reinforcement fiber. For this reason, availability of relatively inexpensive reinforcements and the development of various processing methods which result in reproducible microstructures and properties really enhanced the interest on PRMMC’s (Ibrahim et al., 1991). These materials exhibit a unique combination of microstructure and properties which is not found in either ceramics or metals alone. These properties of PRMMC’s mainly depend on the microstructure and properties of the matrix materials, the nature, distribution, size and shape of particles as well as the interfacial behavior between matrix and the reinforcement phase constituents (Liu et al., 1994). An optimum combination of mechanical properties can be achieved when fine and thermally stable ceramic particulates are dispersed uniformly in the metal matrix (Tjong and Ma, 2000). PRMMC’s are most commonly produced either by melt incorporation and casting technique or powder blending and consolidation (Clyne, 2001).

There are two sub-classifications of PRMMC’s. These are large particle and dispersion strengthened composites. The distinction between these two groups is based on reinforcement or strengthening mechanism. The aim of using the term “large” is to point out that particle–matrix interactions cannot be related to the atomic or molecular level; so, preferably, continuum mechanics is used. Generally, the
particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to restrain movement of the matrix phase in the neighborhood of each particle. Basically, matrix transfers some of the applied stress to the particles, which carry a fraction of the load. The degree of reinforcement or improvement of mechanical behavior depends on strong bonding at the matrix–particle interface. For dispersion-strengthened composites, particles are normally much smaller than the former one, having diameters between 0.01 and 0.1 µm (10 and 100 nm). This time, particle–matrix interactions cause strengthening to occur on the atomic or molecular level.

The mechanism of strengthening is similar to that for precipitation hardening. Since matrix carries the major portion of an applied load, small dispersed particles hinder or impede the motion of dislocations. So, plastic deformation is restricted such that yield and tensile strengths, as well as hardness, improve. In addition to that, the volume fraction of the particles in dispersion strengthened composites is very low (%3) comparing to that in large particle strengthened composites (%70-90). (Schwartz, 1984; Demirkesen, 2003).

2.1.1. Large particle composites

Large-particle composites are utilized with all three material types, namely metals, polymers and ceramics. However, the most common large-particle composite is called cermet which is a mixture of ceramics and metals and they offer the engineers an opportunity to combine the properties and take advantage of the unique characteristics of both (Schwartz, 1984). The most common cermet is the cemented carbide, which is composed of extremely hard particles of refractory carbide or oxide ceramic such as tungsten carbide (WC), titanium carbide (TiC), alumina (Al₂O₃) or Magnesium-oxide (MgO) embedded in a matrix of a metal such as cobalt or nickel.

These composites are used widely as cutting tools for hardened steels. The hard carbide particles provide the cutting surface but, are not themselves capable of withstanding the cutting stresses because they are extremely brittle. Toughness is enhanced by their inclusion in the ductile metal matrix, which isolates the carbide particles from one another and prevents particle-to-particle crack propagation. Both matrix and particulate phases are quite refractory, to withstand the high temperatures generated by the cutting action on materials that are extremely hard (Askeland, 1984; Schwartz, 1984).
2.1.2. Dispersion-strengthened composites

Metals and metal alloys may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material. The particle size in dispersion-strengthened composites is very small, with diameters of 10-250 nm (Askeland, 1984). The dispersed phase may be metallic or nonmetallic; oxide materials are often used. Again, the strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with precipitation hardening, namely a pronounced strengthening effect is produced because the particles block the movement of dislocations. However, the strengthening is retained at elevated temperatures and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase. For precipitation-hardened alloys, the increase in strength may disappear upon heat treatment as a consequence of precipitate growth or dissolution of the precipitate phase (Askeland, 1984; Demirkesen, 2003).

For instance, the high-temperature strength of nickel alloys may be enhanced significantly by the addition of about 3 vol% of thoria (ThO$_2$) as finely dispersed particles; this material is known as thoria-dispersed (or TD) nickel. Furthermore, there are tungsten and superalloys which are dispersion-strengthened with addition of about 1-2 vol% of thoria (ThO$_2$). Yttria (Y$_2$O$_3$), alumina (Al$_2$O$_3$) and other oxides perform the same function (Askeland, 1984; Schwartz, 1984; Flinn and Trojan, 1995). For instance, as a dispersion strengthened phase, La$_2$O$_3$ particles exert a significant effect on the microstructure and mechanical properties of materials, such as providing necessary creep resistance or strength at elevated temperatures (Chen et.al., 2000) Additionally, a very thin and adherent alumina coating is caused to form on the surface of extremely small (0.1 to 0.2 µm thick) flakes of aluminum, which are dispersed within an aluminum metal matrix; this material is termed as sintered aluminum powder (SAP) (Askeland, 1984; Schwartz, 1984; Flinn and Trojan, 1995).

2.2. Strengthening Mechanisms in PRMMC’s

There are a lot of mathematical models which have been formulated for calculating the mechanical properties of PRMMC’s. The simplest model is the rule-of-mixture model which is mainly used for fiber reinforced composites (Ibrahim et al., 1991; Mital, 1996). In this model, the composite is assumed to be fully isotropic. So, the
mechanical properties, such as strength, shear modulus and normal modulus of PRMMC can be estimated from the weighted average of the individual constituents (Ibrahim et al., 1991; Mital, 1996). For instance, for the strength of a PRMMC the equation below can be written;

\[ \sigma_{mmc} = f_r \sigma_r + (1 - f_r) \sigma_m \]  \hspace{1cm} (2.1)

where \( \sigma_{mmc} \) is the yield strength of the composite, \( \sigma_r \) is the yield strength of the reinforcement, \( \sigma_m \) is the yield strength of the matrix and \( f \) is the volume fraction of the reinforcement (Zhang, 2003). However, one must first understand the strengthening mechanisms in PRMMC’s to be able to formulate a reliable mathematical model.

Particulate reinforced composites fall somewhere between the dispersion strengthened and fiber strengthened extremes. A particulate reinforced composite’s place between these extremes is strongly dependent on the size and shape of its reinforcement. In general, as the aspect ratio of the reinforcement increases, the composite tends to exhibit increased amounts of fiber strengthening, but as particle size decreases, the composite will tend to be primarily strengthened by dispersion methods as seen in Table 2.1 (Poquette, 2005).

There are different strengthening mechanisms in PRMMC’s. In the following sections, it will be explained how reinforcement size and geometry affects the strengthening contributions by these mechanisms. Except in the Shear Lag theory, in other theories explaining the strengthening mechanism, the strength of the composite is determined by the stress which is required either to generate or move dislocations in the lattice (Ibrahim et al., 1991). Thus, the more the movement of dislocations is inhibited, the stronger material will be.

2.2.1. Shear lag theory

The shear lag theory assumes that load transfer occurs between a high aspect ratio reinforcement and the matrix by means of shear stresses at the particle-matrix interface. Under an applied load, the load is transferred from the weaker matrix, across the matrix/reinforcement interface, to the typically higher stiffness
reinforcement (Poquette, 2005). In this manner, strengthening takes place by the reinforcement carrying much of the applied load.

Due to the lower aspect ratio of particulate materials, load transfer is not as efficient as in the case of continuous fiber reinforcement, but is still significant in providing strengthening (Poquette, 2005).

**Table 2.1: Metal matrix composite subcategories and the strengthening mechanisms**

<table>
<thead>
<tr>
<th>Type of MMC</th>
<th>Reinforcement Morphology</th>
<th>Primary Strengthening Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Strengthened</td>
<td>Long fibers (aspect ratio &gt;10)</td>
<td>Shear lag theory (Load transfer from matrix to fiber)</td>
</tr>
<tr>
<td>(Continuously Reinforced)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discontinuously Reinforced</td>
<td>Short fibers or whiskers (aspect ratio &lt;10), and/or Large particles (diameter &gt;1µm)</td>
<td>Combination of fiber and dispersion strengthening mechanisms</td>
</tr>
<tr>
<td>Dispersion Strengthened</td>
<td>Small particles (diameter &lt;1µm)</td>
<td>Orowan inhibition of dislocation motion, Boundary strengthening - Matrix/reinforcement - Grain size refinement in the matrix Coefficient of thermal expansion mismatch</td>
</tr>
</tbody>
</table>

Through this mechanism, the particle acts to bear some of the applied load. If the original model is modified considering that the particles are equiaxed, the yield strength of the composite can be found using the equation below:

\[
\sigma_c = \sigma_m + \left( 1 + \frac{1}{2} \cdot f \right)
\]  

(2.2)

where \(\sigma_c\) is the yield strength of the composite, \(\sigma_m\) is the yield strength of the unreinforced composite and \(f\) is the volume fraction of the reinforcement.
2.2.2. Orowan strengthening

According to this theory, in composites containing small (<1µm) particles the materials is strengthened due to the interaction between the particles and dislocations (Mabuchi, 1997; Poquette, 2005). A passing dislocation will bow between small particulate reinforcements and finally pass by leaving behind an “Orowan” loop, as shown in Figure 2.1;

![Figure 2.1: The formation of an Orowan loop](image)

As a result, the strength of the materials is increased when the applied stress to bend the dislocation is increased. This Orowan stress is given below;

\[
\tau = \frac{G \cdot b}{L}
\]

(2.3)

where \( \tau \) is the Orowan stress, \( b \) is the Burgers vector, \( G \) is the shear modulus of the material and \( L \) is the interparticle spacing\( (L = 1.23 \cdot r \cdot \left( \frac{2 \cdot \pi}{3 \cdot f} \right)^{\frac{1}{2}}) \), where \( r \) is the average particle radius and \( f \) is the fraction of reinforcement. According to this equation the strength of the composite is increased with decreasing particle size and increasing volume fraction of reinforcements. This is especially valid for particles in the submicron range. However, for particle sizes greater than 10 µm strengthening mechanism is still predicted but not expected to be as affective as in submicron-range (Mabuchi, 1997; Poquette, 2005).

2.2.3. Boundary strengthening

In this mechanism, again the inhibition of the movement or creation of dislocation causes the increase in the strength of the material. However, this time crystallographic discontinuities or boundaries are the reason for these. When the material is stressed, dislocations tend to pile-up at these incoherent interfaces, so the overall dislocation density and, thus, the strength of the material is increased.
In addition to that, since two grains are differently oriented, a dislocation passing to a neighbor grain has to change its direction as seen in Figure 2.2 and this becomes more difficult as the crystallographic misorientation increases (Callister, 2000). According to this, when the amount of the boundaries is increased, the strength of the material will be increased. This increase in the amount of the boundaries is achieved by grain size refinement. Also the boundaries between two different phases hinder the movement of dislocations. Thus, adding fine particles to a fine grained matrix duplicates the amount of the boundaries (Callister, 2000; Poquette, 2005). Furthermore, grain size refinement improves not only the strength but also the toughness of many alloys (Callister, 2000).

![Image of dislocation motion through a grain boundary](image)

**Figure 2.2:** The motion of a dislocation through a grain boundary (Callister, 2000).

For many materials the yield strength $\sigma_y$ varies with grain size according to Hall-Petch equation;

$$\sigma_y = \sigma_o + k_y d^{\frac{1}{2}}$$  \hspace{1cm} (2.4)

where $\sigma_o$ is the flow stress of undeformed crystal, $k_y$ is a constant and $d$ is the average diameter of the grains (Callister, 2000; Hansen, 2004; Poquette, 2005).

However, not all the explanations of the boundary strengthening mechanism are based on dislocation pileups at grain boundaries. According to a theory of Li, the Hall-Petch behavior can be explained by dislocations which are generated at grain boundary ledges during deformation (Figure 2.3a). On the other hand, Meyers and
Ashworth (Figure 2.3b and Figure 2.3c) also suggested a model in which the strengthening by grain refinement is based on the generation of dislocation at grain boundaries. However, in this model dislocations are generated in the boundary regions where the elastic anisotropy results in stress concentrations, so that a hardened reinforcing second-phase network is formed. So, yielding occurs when the applied stress is high enough to push the dislocations through the hardened layers into the grain interior (Weertman, 2002).

![Figure 2.3: Three models explaining the Hall-Petch behavior (Weertman, 2002).](image)

**2.2.4. Solid solution hardening**

Another mechanism to strengthen metals or composites is alloying with impurity atoms which go either into substitutional or interstitial solid solution. In these mechanism, lattice strain field interactions between dislocations and these impurity atoms cause to inhibit the movement of dislocations (Callister, 2000). A large difference in atomic size between the solvent atom and the solute atom will increase the strengthening effect because larger size difference produces a greater disruption of the lattice, so that the slip of dislocation is made more difficult (Askeland, 1984). For instance a solute atom which is smaller than solvent atoms exerts tensile strains on the lattice, whereas a larger atom exerts compressive strains as seen in Figure 2.4. For this reason, these solute atoms tend to diffuse to and segregate around dislocations, so that the overall strain energy reduced. To achieve this, for example a smaller solute atom is located where its tensile strain and some of dislocation’s compressive strain cancel each other out (Callister, 2000).
2.2.5. **Strain hardening**

Strain hardening is a phenomenon whereby a ductile metal becomes stronger as it is plastically deformed. The dislocation density in the material is increased with deformation, due to dislocation multiplication or the formation of new dislocations (Callister, 2000). Primary dislocations produce loops by interaction with secondary dislocations, which give rise to local dislocation tangles gradually developing into three-dimensional networks of sub-boundaries (Smallman and Bishop, 1999). As a result, the average distance between dislocations decreases. On the average, dislocation-dislocation strain interactions are repulsive. So, the net result is that the motion of a dislocation is hindered by the presence of other dislocations. In this way, the applied stress necessary to deform the material increases with increasing deformation (Callister, 2000).

There are some source mechanisms which explain above dislocation-dislocation interactions that increase the dislocation density in the material. The most important one is the Frank-Read source mechanism (Smallman and Bishop, 1999). In this mechanism, a dislocation line is fixed at the nodes A and B (fixed, since the other dislocations that join the nodes do not lie in slip planes) (Figure 2.5). So, a dislocation loop is formed which expands into the slip plane. This sequence is then repeated and as a result the dislocation density is increased.

**Figure 2.4:** Representation of tensile lattice strain (a) and compressive lattice strain (b) imposed on host atom by impurity atoms (Callister, 2000).

**Figure 2.5:** Forming of a Frank-Read source (Smallman and Bishop, 1999).
Another mechanism is the cross-slip mechanism which depends on the Frank–Read principle but does not require dislocation segment to be anchored by nodes. Thus, if part of a moving screw dislocation undergoes double cross-slip the two pieces of edge dislocation on the cross-slip plane effectively act as anchoring points for a new source. The loop expanding on the slip plane parallel to the original plane may operate as a Frank–Read source and any loops produced may in turn cross slip and become a source. (Figure 2.6) This process therefore not only increases the number of dislocations on the original slip plane but also causes the slip band to widen (Smallman and Bishop, 1999).

![Cross-slip mechanism](image)

**Figure 2.6:** Cross-slip multiplication source (Smallman and Bishop, 1999).

### 2.3. Fabrication of PRMMC

There are various processing techniques used to fabricate PRMMC’s. These fabrication methods can be grouped according to the temperature of the metal matrix during the process. So, there are liquid phase processes, solid state processes and two phase processes. Main liquid phase processes are molten metal mixing process, melt infiltration process and melt oxidation process. On the other hand, major solid state processes are powder metallurgy and high-energy-high-rate process. Finally, two phase processes are Osprey deposition, rheocasting and variable co-deposition of multi-phase materials (VCM) process (Ibrahim et al., 1991).

The selection of one particular process over the others depends on various factors which are types of materials and their properties, final desired properties, size, shape and complexity of the part, subsequent processing and overall cost of the process (Lindroos et al., 2004).

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

2.3.1. Powder metallurgy (PM)

As early mentioned, the PM route is the most commonly used method for the preparation of PRMMC’s (Liu et al., 1994; Huda et al., 1995). Blending of metallic powders with ceramic particles is a versatile technique for PRMMC production (Clyne, 2001). In the basic process, mixed or prealloyed powders are fed into a die, compacted a desired shape and then this pressed powder is sintered in a controlled atmosphere furnace to convert the mechanical bonds to the metallurgical bonds that link the powder particles (Newkirk and Kosher, 2004).

There are numerous advantages which PM process offer. First of all, it is a more economical than many other techniques, since no melting and casting is involved. Secondly, the preparation of PRMMC’s is generally easier using PM blending technique than it is using casting technique (Huda et al., 1995). Furthermore, products with complex shapes can be easily produced without any post-machining process. Also, porous products, such as bearings and filters with better properties can be produced by using the PM technique. In addition to these, full density products having superior properties are produced by PM technique, which are used in critical applications, such as aerospace applications.
2.3.1.1. Starting materials

Starting materials in powder metallurgy processes have a very important role for the success of the process. In addition to the chemistry and the purity of the powders, there are additional issues to concern, such as particle size, size distribution, particle shape as well as the surface texture of the particles (Newkirk and Kosher, 2004). Considering the PRMMC’s, mechanical behavior, chemical stability, thermal mismatch and the cost are another factors which play a significant role in the success of the end-product (Liu et al., 1994).

2.3.1.2. Mixing or blending

After a proper selection of the materials is ensured, the next step is blending or mixing. This step is very important, because it controls the final distribution of reinforcement particles and porosity in green compacts, which strongly affects the mechanical properties of the PM end-products. However, there are some problems, such as segregation and clustering, associated with the today’s modern mixing or blending methods. The reasons of these problems include different flow characteristics between metal powder and reinforcement particles and the tendency of the agglomeration of particles to minimize their surface energy. The segregation behavior of different sized particles is shown in Figure 2.7;

![Figure 2.7: Monte Carlo simulations of shaking of a ternary mixture of particles according to increasing number of cycles.](image)

As seen in Figure 2.7, larger particles rise to top, because they are moved upwards as smaller particles filled the voids beneath the larger particles. Furthermore, the effect of different densities between particles and metal powders of similar size is very important, too. The lighter particles tend to move upwards, while the heavier ones segregate at the bottom. However, these segregation and clustering problems can be
overcome by a technique called “Mechanical Alloying (MA)” (Li et al., 1994). This technique will be discussed in detail in the section 2.3.2.

2.3.1.3. Compaction

The next step after blending or mixing operation, is the consolidation and pressing of the powder mixture to form the green compacts (Liu et al., 1994). This step is the one of the most critical steps in the PM process, because it sets the density of the powder and the uniformity of the density throughout the product. Because final properties strongly depend on density, uniform properties require uniform density (Newkirk and Kosher, 2004). The compaction process has the following major functions:

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

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

![Figure 2.8: Schematic view of a conventional one-directional press.](image)

To control the quality of green compacts better, isostatic pressing techniques were developed, such as cold, warm and hot isostatic pressing (Liu et al., 1994). Characteristics of isostatic pressing techniques have been reported in Metals Handbook vol.7.
2.3.1.4. Sintering

Usually, properly prepared green compacts are sintered. Sintering is a process used which is used to produce density-controlled materials and components from metal and ceramic powders by applying thermal energy (Kang, 2005). In this process, interparticle pores in a granular material are eliminated by atomic diffusion driven by capillary forces (Chen and Wang, 2000). There are different variables which determine sinterability and the sintered microstructure of a powder compact. These variables are given in Table 2.2.

Basically, sintering process can be divided into the two types;

1. Solid-state sintering

2. Liquid phase sintering

Solid-state sintering occurs when the powder compact is densified fully in a solid state at the sintering temperature, while liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering as seen in Fig. 2.9 (Kang, 2005).

<table>
<thead>
<tr>
<th>Table 2.2: Variables affecting sinterability and microstructure (Kang, 2005).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variables related to raw materials (material variables)</td>
</tr>
<tr>
<td>Powder;</td>
</tr>
<tr>
<td>Shape, size, size distribution, agglomeration, etc.</td>
</tr>
<tr>
<td>Chemistry;</td>
</tr>
<tr>
<td>Composition, impurity, homogeneity, etc.</td>
</tr>
<tr>
<td>Variables related to sintering conditions (process variables)</td>
</tr>
<tr>
<td>Temperature, time, pressure, atmosphere, heating and cooling rate, etc.</td>
</tr>
</tbody>
</table>

The solid-state sintering is carried out in protective atmospheres within a furnace at a temperature below the melting point of the base metal. The process leads to a decrease in the surface area, an increase in compact strength and mostly shrinkage in the compact. Sintering for longer times at high temperature decreases the number of pores and smoothens the pore shapes. Also, grain growth can be expected (Upadhyaya, 2000).
The process of sintering is mainly the result of atomic motion aroused by the high temperatures. The initial strains, surface area and curvature of the pressed powder compact drive the atomic motions which are responsible for sintering. In Fig. 2.10, different patterns of atomic motion can be seen.

**Figure 2.9:** Illustration of various types of sintering (Kang, 2005).

**Figure 2.10:** Various sintering mechanisms (Upadhyaya, 2000)
Mostly, sintering kinetics are determined by several parameters including pressed density, material, particle size, sintering atmosphere and temperature. The selection of a correct isothermal sintering temperature is important in successful densification. Higher temperatures lead to faster densification, however, the rate of coarsening also increases. This increased coarsening rate can lead to abnormal grain growth with pores trapped inside large grains. As a result, the final density may be limited, although densification proceeds faster (Upadhyaya, 2000). So, sintering process is a complicated process with different variables and one must take all these variables into consideration while designing a sintering process.

2.3.2. Mechanical alloying (MA)

2.3.2.1. History and definition of mechanical alloying (MA)

Materials scientists have continuously tried to improve the properties and performance of materials. Important developments in mechanical, chemical, and physical properties have been achieved through chemistry modifications and conventional thermal, mechanical, and thermo-mechanical processing methods. However, the ever-increasing demands for better materials have led to the design and development of advanced materials. High-technology industries have given an added stimulus to these efforts (Suryanarayana, 2001). As a result, non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials than it is possible by conventional methods (Suryanarayana et al., 2001)

As mentioned above, the structure and constitution of advanced materials can be better controlled by processing them under non-equilibrium (or far-from-equilibrium) conditions and mechanical alloying (MA) is such a processing method that materials can be produced under non-equilibrium conditions (Suryanarayana, 2001). MA can be defined as a powder metallurgy process for producing composite metal powders with a controlled fine microstructure by repeated cold welding, fracturing and rewelding of powder particles in a high–energy ball mill (Öveçoğlu, 1987; Benjamin, 1992; Suryanarayana et al., 2001). It utilizes various types of milling machines in which a blend of different powders is subjected to a highly energetic compressive force (Tang et. al., 2004)
The mechanical alloying (MA) process is usually dated back to the pioneer work of Benjamin at the International Nickel Company’s Paul D. Merica Research Laboratory in the late 1960’s. It started as an industrial necessity to produce oxide-dispersion-strengthened nickel-based superalloys for gas turbine engine components (Öveçoğlu, 1987; Suryanarayana et al., 2001; Delogu et al., 2003). However, the subsequent discovery of metastable phase formation by MA opened the door to important applications in Materials Science (Delogu et al., 2003). In addition to the metastable phases, equilibrium phases of commercially useful and scientifically interesting materials can be synthesized by MA, too (Suryanarayana et al., 2001).

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

2.3.2.2. Processing equipment and process variables

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

Spex shaker mills are most commonly used for laboratory investigations and they mill about 10±20 g of the powder at a time depending on the density of starting constituents (Goff, 2003). The common variety of these mills has one vial, containing the sample and grinding balls, secured in the clamp and shakes the milling container in three-mutually perpendicular directions at about 1200 rpm resulting in powder microstructural refinement with time (Suryanarayana, 2001; Goff, 2003).
Ball-ball and ball-container collisions continually trap and refine the powder constituents with time ultimately leading to an overall homogeneously dispersed microstructure (Goff, 2003). There are different vial materials available for the SPEX mills, which are hardened steel, alumina, tungsten carbide, zirconia, stainless steel, silicon nitride, agate, plastic, and methacrylate (Suryanarayana, 2001). In Figure 2.11, a typical spex mill and tungsten carbide vial set can be seen.

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

Figure 2.11: a) A typical Spex shaker mill b) Tungsten carbide vial set consisting of the vial, lid, gasket, and balls (Suryanarayana, 2001).
Therefore, compared to SPEX mills, planetary ball mills can be considered lower energy mills (Suryanarayana, 2001). In Figure 2.12, a schematic view of ball motion in a planetary ball mill can be seen.

![Figure 2.12: A schematic view of ball motion in a planetary ball mill (Suryanarayana, 2001).](image1)

Another type of mills is the attritor mills. Large quantities of powder (from about 0.5 to 40kg) can be milled at a time in an attritor (Suryanarayana, 2001). It contains a vertical shaft with a series of impellers that rotates in the tank of about 250 rpm (Goff, 2003). As the shaft rotates, the balls drop on the metal powder that is being ground. The impellers energize the ball charge, causing powder size reduction because of impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers. The rate of grinding increases with the speed of rotation. However, at high speeds the centrifugal force acting on the balls exceeds the force of gravity, and the balls are pinned to the wall of the container. At this point the grinding action stops (Suryanarayana, 2001). In Figure 2.13, a schematic view of an attritor mill can be seen.

![Figure 2.13: A schematic view of an attritor mill (Goff, 2003)](image2)
Finally, commercial mills for MA are much larger in size than the mills described above and can grind several hundred kilograms of powders at a time. Mechanical alloying for commercial production is carried out in ball mills of up to about 1250 kg capacity (Suryanarayana, 2001). A picture of commercial-size ball mills can be seen in Figure 2.14.

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

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

**Figure 2.14:** Commercial production-size ball mills used for mechanical alloying (Suryanarayana, 2001).
The material used for the milling container (grinding vessel, vial) is important since the impact of the grinding medium on the inner walls of the container will result in tiny fractions of milling material that fracture off and disperse into the composite powder. These can contaminate the powder or alter the chemistry of the powder. If the material of the grinding vessel is different from that of the powder, then the powder may be contaminated with the grinding vessel material. On the other hand, if the two materials are the same, then the chemistry may be altered (Suryanarayana, 2001; Goff, 2003). Regardless of the type of mechanical alloying process, the most appropriate type of container and milling media for the given system should be chosen. Generally, milling media that is made of a similar material as that of the material to be processed is used to reduce contamination during processing (Goff, 2003). Additionally, the density of the grinding medium should be high enough so that the balls create enough impact force on the powder (Suryanarayana, 2001).

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

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

The time of milling is the most important parameter. In most of the cases, the rate of refinement of the internal structure (particle size, crystallite size, lamellar spacing, etc.) is roughly logarithmic with processing time (Fig. 2.15) and therefore the size of the starting particles is relatively unimportant. In a few minutes to an hour, the lamellar spacing usually becomes small and the crystallite (or grain) size is refined to
nanometer dimensions. Normally, the time is so chosen to achieve a steady state between the fracturing and cold welding of the powder particles. Furthermore, the times required depend on the type of mill used, the intensity of milling, the ball-to-powder ratio, and the temperature of milling. These times have to be decided for each combination of the above parameters and for the particular powder system. However, it should be realized that the level of contamination increases and some undesirable phases form if the powder is milled for times longer than required. Therefore, the powder has to be milled just for the required duration and not any longer (Suryanarayana, 2001).

Figure 2.15: Refinement of particle and grain sizes with milling time. Rate of refinement increases with higher milling energy, ball-to-powder weight ratio, lower temperature, etc. (Suryanarayana, 2001).

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

2.3.2.3. The technique and mechanism of mechanical alloying (MA)

MA is an advanced fabrication process that can produce ultra-fine and homogenous powders (Ryu et al., 2000). Even, nanocrystalline materials (with a grain size of few
nanometers, usually <100 nm) are also produced by MA of powder mixtures. Additionally, it has been recognized that this technique can be used to induce chemical (displacement) reactions in powder mixtures at room temperature or at much lower temperatures than normally required to synthesize pure metals (Suryanarayana et al., 2001).

In any MA process, starting powder constituents are first mixed or blended according to the required stoichiometry for the given composite formulation. Then, they are put in the milling container with the appropriate ball charge and milled until a steady state of homogeneous dispersion is achieved (Goff, 2003). The central event of MA is the ball-powder collisions (Fecht, 2002). Microstructural refinement during the MA process occurs due to the repeated welding, fracturing, and rewelding of the dry powder constituents during their impact between ball-ball and/or ball-container collisions. Whenever two balls collide, typically, around 1000 particles with an aggregate weight of about 0.2 mg are trapped during each collision (Fig. 2.16). The force of the impact plastically deforms the powder particles leading to work hardening and fracture (Suryanarayana, 2001; Fecht, 2002).

![Figure 2.16: Schematic view of a ball-powder-ball collision (Suryanarayana, 2001).](image)

Also, this severe working of powders produces a very fine grain size and substructural strengthening via high dislocation density and fine subgrain size. As a result, MA provides several strengthening mechanisms which are oxide dispersion strengthening, carbide dispersion strengthening, fine grain size strengthening, substructural strengthening and solid solution strengthening (Öveçoğlu, 1987).
In order to understand the physical phenomena that occur during MA processing better, it is useful to divide the typical process into three or four stages (Öveçoğlu, 1987; Goff, 2003).

In the early stages of milling, the particles are soft (if either ductile-ductile or ductile-brittle material combinations used), their tendency to weld together and form large particles is high (Suryanarayana, 2001). A broad range of particle sizes develops, with some as large as three times bigger than the starting particles (Suryanarayana, 2001; Goff, 2003). The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents (Figure 2.17.) (Öveçoğlu, 1987).

![Deformation characteristics of starting powders used in a typical MA process (Suryanarayana, 2001).](image)

**Figure 2.17:** Deformation characteristics of starting powders used in a typical MA process (Suryanarayana, 2001).

As the metallic phases are flattened and overlap during ball collisions, atomically clean surfaces are placed in contact with one another and subsequently cold weld together. At the same time, brittle constituents (intermetallics and dispersoids) are occluded by the ductile constituents thus becoming trapped along cold-weld interfaces (Goff, 2003). Figure 2.18 shows early stage of processing in which particles are layered composites of starting constituents.

In the intermediate stage, the composite powder particles are further refined due to continual welding and fracturing of excessively work-hardened metallic phases and brittle intermetallics and/or dispersoids (Goff, 2003).
Figure 2.18: Early stage of processing in which particles are layered composites of starting constituents (Öveçoğlu, 1987).

At this stage the tendency to fracture predominates the over cold welding (Suryanarayana, 2001). The particles consist of convoluted lamellae. The reduction in particle size, increased microstructural mixing, and elevated temperature of the powder constituents due to the adsorbed kinetic energy of milling balls all help to form areas of solute dissolution throughout the metallic powder matrix (Öveçoğlu, 1987). So, this potentially may lead to areas where new phases develop which is mainly due to an overall decrease in atomic diffusion distances between individual phases and decreased activation energies for diffusion due to the increase in temperature (Öveçoğlu, 1987; Goff, 2003). Consequently, the inter-layer spacing decreases and the number of layers in a particle increase (Suryanarayana, 2001). Figure 2.19 shows the reduced lamellae thickness, solute dissolution, and formation of new phases in the intermediate stage of processing.

Figure 2.19: Intermediate stage of processing showing reduced lamellae thickness, solute dissolution, and formation of new phases (Öveçoğlu, 1987).
In the final stage (Figure 2.20.), steady-state equilibrium is attained when a balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average composite particle size. As a result, smaller particles are able to withstand deformation without fracturing and tend to be welded into larger pieces, with an overall tendency to drive both very fine and very large particles towards an intermediate size (Suryanarayana, 2001).

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

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

![Figure 2.20: The final stage of processing and consolidation (Öveçoğlu, 1987).](image)
It is possible to conduct MA of three different combinations of metals and alloys:

(i) Ductile-ductile,

(ii) Ductile-brittle,

(iii) Brittle-brittle systems.

Therefore, it is convenient to discuss the mechanism of MA also under these categories (Fecht, 2002).

Ductile-ductile combination is thought to be the ideal combination for MA process. It is suggested that it was necessary to have at least 15% of a ductile component for achieving alloying. This was true because alloying occurs due to the repeated action of cold welding and fracturing of powder particles; cold welding cannot occur if the particles are not ductile. In the early stages of MA, the ductile components get flattened to platelet/pancake shapes. A small quantity of the powder, usually one or two particle thickness, also gets welded onto the ball surfaces. This coating of the powder on the grinding medium is advantageous since it prevents excessive wear of the grinding medium and the contamination of the powder is prevented. However, the thickness of the powder layer on the grinding medium must be kept to a minimum to avoid forming a heterogeneous product (Suryanarayana, 2001). In the next stage, these flattened particles get cold welded together and form a composite lamellar structure of the constituent metals (Öveçoğlu, 1987). An increase in particle size is also observed at this stage (Suryanarayana, 2001). For instance, it has been found that during MA of Fe-Cu powder mixture, agglomerates of multilayers are formed leading to microstructures very similar to those obtained by cold-rolling (Fecht, 2002). With increasing MA time, the composite powder particles get work hardened, the hardness and consequently the brittleness increases, and the particles get fragmented resulting in particles with more equiaxed dimensions (Suryanarayana, 2001). With further milling, the elemental lamellae of the welded layer and both the coarse and fine powders become convoluted rather than being linear. Alloying begins to occur at this stage due to the combination of decreased diffusion distances (interlamellar spacing), increased lattice defect density, and any heating that may have occurred during the milling operation (Öveçoğlu, 1987). The hardness and particle size tend to reach a saturation value at this stage, which is called the steady-state processing stage. With further milling, true alloying occurs at the atomic level.
resulting in the formation of solid solutions, intermetallics, or even amorphous phases. The layer spacing becomes so fine or disappears at this stage that it is no longer visible under an optical microscope (Öveçoğlu, 1987; Suryanarayana, 2001).

Considering ductile-brittle combinations, in the initial stages of milling, the ductile metal powder particles get again flattened by the ball-powder-ball collisions, while the brittle oxide or intermetallic particles get fragmented. These fragmented brittle particles tend to become occluded by the ductile constituents and trapped in the ductile particles. The brittle constituent is closely spaced along the interlamellar spacings (Figure 2.21a) (Öveçoğlu, 1987). With further milling, the ductile powder particles get work hardened, the lamellae get twisted, and refined (Figure 2.21b). With continued milling, the lamellae get further refined, the interlamellar spacing decreases, and the brittle particles get uniformly dispersed, if they are insoluble, in the ductile matrix (Figure 2.21c) (Öveçoğlu, 1987; Suryanarayana, 2001). For instance, 10 nm sized Ge particles can be embedded in a ductile matrix of Sn or Pb. Similarly, very fine dispersions at the nanometer scale have been found for example, in TiNi-C (Fecht, 2002). On the other hand, if the brittle phase is soluble, alloying occurs between the ductile and brittle components also and chemical homogeneity is achieved (Suryanarayana, 2001).

![Figure 2.21: Schematics of microstructural evolution during milling of a ductile-brittle combination of powders. This is typical of an oxide dispersion strengthened case (Suryanarayana, 2001).](image)

If a brittle-brittle combination is the case, it would appear that it is unlikely that alloying occurs in a system consisting of two or more brittle components. The reason for that is that the absence of a ductile component prevents any welding from occurring, and in its absence, alloying is not expected to occur. However, alloying has been reported to occur in brittle-brittle component systems such as Si-Ge and Mn-Bi or Fe₂O₃-Cr₂O₃ and ZrO₂-Y₂O₃ (Suryanarayana, 2001; Fecht, 2002). Milling
of mixtures of brittle intermetallics also produced amorphous phases. During milling, the brittle components get fragmented and their particle size gets reduced continuously. However, at very small particle sizes the powder particles behave in a ductile fashion, and further reduction in size is not possible; this is termed the limit of comminution. Furthermore, during milling of brittle-brittle component systems, it has been observed that the harder (more brittle) component gets fragmented and gets embedded in the softer (less brittle) component (Suryanarayana, 2001).

Considering all scientific points and the foregoing facts, from the foregoing facts it is clear that research in the area of MA is continuing to develop. There is so much more to learn on the "science" of MA, and it is assured that the future of MA is wide open for novel discoveries.

2.3.2.4. Nanostructured materials

Mechanical alloying (MA) which is a well known process for preparing several amorphous, metal nitrides, metal carbides and alloys, has been considered as a powerful technique for synthesizing numerous nanostructured materials (El-Eskandarany et al., 2000).

Nanostructured materials that are defined as materials with grain sizes less than 100 nm have received much attention as advanced engineering materials with improved physical and mechanical properties (El-Eskandarany et al., 2000). Because of the extremely small size of the grains, a large fraction of the atoms in these materials is located in the grain boundaries and as a result the material exhibits enhanced combinations of physical, mechanical, and magnetic properties (compared to material with a more conventional grain size, i.e., >1 µm) (Fecht, 2002) (Suryanarayana, 2001). Nanostructured materials show increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction (Suryanarayana, 2001).

Recently, MA process has become a popular method to fabricate nanocrystalline materials due to its simplicity and requiring relatively inexpensive equipment (El-Eskandarany et al., 2000) The advantage of using MA for the synthesis of nanocrystalline materials lies in its ability to produce bulk quantities of material in the solid state using simple equipment and at room temperature (Suryanarayana, 2001). In this process, lattice defects are produced by pumping energy into powder
particles of typically 50 µm particle diameter. This internal refining process with a reduction of the average grain size by a factor of $10^1$-$10^4$ results from the creation and self organization of small-angle and high-angle grain boundaries within the powder particles during the mechanical deformation process (Fecht, 2002). Grain sizes with nanometer dimensions have been observed in almost all mechanically alloyed pure metals, intermetallics, and alloys (Suryanarayana, 2001). The elemental processes leading to the formation of nanostructures include three basic stages. Firstly, the deformation is localized in shear bands which contain a high dislocation density (Fecht, 2002). Their typical width is approximately 0.5-1 µm (Suryanarayana, 2001). At a certain level of strain within the high strained regions, these dislocations annihilate and recombine to small-angle grain boundaries separating the individual grains (Fecht, 2002). This results in a decrease of the lattice strain. With the continuing process, deformation occurs in shear bands located in previously unstrained parts of the material. The grain size decreases steadily and the shear bands unite. The small angle boundaries are replaced by higher angle grain boundaries and, consequently, dislocation-free nanostructured grains are formed (Suryanarayana, 2001).

After the MA process, fabricated powders are compacted to obtain a useable bulk composite form. In principle, the compaction of nanopowders is similar to that of the conventional powders. However, some differences in nanoparticles appear from the specifics of small particle sliding and friction. Sliding and rearrangement in nanopowders are severely limited because of the large frictional forces. These forces are a result of mechanical, electrostatic, Van der Waals phenomena that become more important with decreasing particle size. Mechanical friction resistance is high due to the numerous interparticle contact points. Furthermore, irregular boundaries favor agglomerate formation. As a result, particle rearrangement is limited and lower green densities are achieved compared to the conventional powders (Groza, 2002.).

The key to the consolidation of nanopowders is to achieve densification with minimal microstructural coarsening and undesirable microstructural transformations (Suryanarayana, 2001; Groza, 2002.).

Mainly, the sintering mechanism of these powders is the same as the sintering mechanism of conventional powders, which is explained in the section 2.3.1.5. However, the tendency of the grains to grow is very strong due to the very little
diffusion distance and extreme curvature of nanoparticles. The coarsening kinetics may be slowed down by limiting the grain boundary mobility using a solute drag or particle pinning effect. Small particles stabilize a fine grain size at high temperatures. On the other hand, the solute drag effect is based on the decrease of grain boundary mobility and the free energy when solute atoms segregate at grain boundaries. However, the simplest way to control grain coarsening is to take advantage of the pinning effect of open pores and limit the density to ~90%, if it is acceptable for the final product. However, grain growth is accelerated, as soon as the pores are closed (Groza, 2002.). On the other hand, sintering of nanoparticles was found to start at temperatures of 0.2-0.4 T_m when compared to 0.5-0.8 T_m for conventional powders due to the increasing driving forces. Thus, these lower temperatures may minimize or even eliminate the use of grain growth inhibitors or sintering additives (Groza, 2002.). Additionally, a way has recently been found to solve this grain growth problem, which is a two-step sintering process that allows full density while grain growth is arrested during the second stage (Chen and Wang, 2000; Chen, 2000).

The detailed information’s on the processing, properties and the application of nanostructured materials are reported elsewhere (see the reference Nanostructured Materials: Processing, Properties and Potential Application, Ed. Koch, 2002.) So, this topic will not be discussed further.

### 2.4. Materials Selection

From the beginning, the selection of a proper combination of matrix and reinforcement has been the main goal of design and production of PRMMC’s. Since, the great advantage of MMC materials is providing a superior combination of different properties of metallic matrix and hard reinforcement. However, these properties can only be obtained with proper selection of matrix material and reinforcement (Lindroos et al., 2004).

The matrix of the composites has to be mainly designed for two major tasks, which is firstly to bind and support the reinforcing phase and, secondly, to satisfy special properties based on the requirements in service. Binding strength between the matrix, whose main function is to transfer and distribute the load to the reinforcement, and the reinforcement depends on the type of matrix and reinforcement (Huda et al., 1995; Lindroos et al., 2004). The interface formed between the matrix and the
reinforcement is interesting because the characteristics of this region determine load transfer and crack resistance of the composite during deformation. It is now widely known that in order to maximize interfacial bond strength, it is necessary to promote wetting (when a liquid phase process is present), control chemical interactions and minimize oxide formation (Ibrahim et al., 1991). On the other hand, the hardness of the matrix is the key factor in supporting the reinforcing phase. Furthermore, other considerations such as, cost, weight, fabricability and availability of the matrix materials should be made (Lindroos et al., 2004). Generally, Al, Ti, Mg, Ni, Cu, Pb, Fe, Ag, Zn, Sn and Si are used as the matrix materials (Huda et al., 1995). In addition to these, tungsten (W) has lately received some attention as a matrix material (Song et al., 2002; Song et al., 2003).

Reinforcing phase in the composites are mainly used to increase the strength, stiffness, temperature resistance capacity and to lower the density. Generally, ceramics are used as the reinforcement phase, which are typically oxides, carbide and nitrides (Huda et al., 1995). The selection criteria for these ceramic reinforcements include elastic modulus, tensile strength, density, melting temperature, thermal stability, coefficient of thermal expansion, size and shape, compatibility with matrix material and cost (Ibrahim et al., 1991). Common reinforcement elements are SiC, Al₂O₃, SiO₂, TiC, B₄C and Si₃N₄ (Huda et al., 1995).

Considering these reported studies, tungsten has been chosen as the matrix material in this investigation.

2.4.1. Tungsten (W)

The refractory metals are conveniently described as those which, first of all, melt at temperatures well above the melting points of the common alloying bases, iron, cobalt, and nickel. When the refractory metals are considered to be those metals melting at temperatures above 1850°C, twelve metals are in this group: Tungsten (W), Rhenium (Re), Osmium (Os), Tantalum (Ta), Molybdenum (Mo), Iridium (Ir), Niobium (Nb), Ruthenium (Ru), Hafnium (Hf), Rhodium (Rh), Vanadium (V), Chromium (Cr).

Among these, W has superior properties like good high temperature strength, high elastic modulus, good corrosion resistance and low coefficient of thermal expansion (Song et al., 2002). These superior properties make tungsten an attractive material for
many important applications (Song et al., 2003). A list of properties of W is given in Table 2.3.

A large number of tungsten alloys and composites were investigated in the past. However, only some of them achieved technical importance. The aim of alloying tungsten is to improve its chemical, physical and mechanical properties at both ambient conditions and at elevated temperatures. However, alloying of tungsten (W) has been relatively less studied than of some of the other refractory metals. Most of the tungsten used until now in aerospace applications has been in the unalloyed form, which is much easier and less expensive to produce and fabricate. Also, it has been found that, particularly at temperatures above 2200°C, the strengthening effects of many alloying agents decrease disproportionately (Lassner and Schubert, 1999).

Table 2.3: Properties of Tungsten (Lassner and Schubert, 1999).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period</td>
<td>6</td>
</tr>
<tr>
<td>Atomic Number</td>
<td>74</td>
</tr>
<tr>
<td>Atomic Mass</td>
<td>183.85</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.7</td>
</tr>
<tr>
<td>Space Group</td>
<td>Im3m</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>3.16524 Å³</td>
</tr>
<tr>
<td>Density</td>
<td>19.25 g/cm³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>3422 °C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>5663 °C</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.0317 cal/gK</td>
</tr>
<tr>
<td>CTE</td>
<td>4.32-4.68x10⁻⁶ K⁻¹ (25 °C)</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>172.4 MPa</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>390-410 GPa</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>156-177 GPa</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>305-310 GPa</td>
</tr>
<tr>
<td>Poisson’ Ratio</td>
<td>0.28-0.30</td>
</tr>
<tr>
<td>Hardness</td>
<td>350-450 kg/mm²</td>
</tr>
</tbody>
</table>

Tungsten is mainly consumed in three forms:

1. Tungsten carbide
2. Alloying additions
3. Pure tungsten

Tungsten carbide accounts for about 65% of tungsten consumption (Lassner and Schubert, 1999). It is combined with cobalt as a binder to form the so-called cemented carbides, which are used in cutting and wear applications because of their high hardness, good wear resistance, good fracture resistance and high temperature strength (Zhang et al., 2003) Cemented carbides such as WC-Co and WC-Co-TiC are the most widely used material for metalworking. As a consequence, a considerable
amount of research effort has been spent to develop alternative cemented carbide systems in order to improve the microstructure and mechanical properties of these materials (Acchar et al., 2004). Characteristically, most of the carbides used in cermets have high hardness, good electrical and thermal conductivity, and high stability. The brittleness of carbides, however, has prevented their use as single-phase materials in highly stressed structural applications and has led to the development of metal-bonded composites (cemented carbides or cermets) (Anonymous, 2005a).

Metallic tungsten and tungsten alloy mill products account for about 16% of consumption. Tungsten and tungsten alloys dominate the market in applications for which a high-density material (19.3 g/cm$^3$) is required, such as kinetic energy penetrators, counterweights, flywheels, and governors. Other applications include radiation shields and x-ray targets. In wire form, tungsten is used extensively for lighting, electronic devices, and thermocouples (Anonymous, 2005b; Lassner and Schubert, 1999).

The high melting point of tungsten makes it an obvious choice for structural applications exposed to very high temperatures. Tungsten is also used at lower temperatures for applications that can use its high elastic modulus, density, or shielding characteristics to advantage (Anonymous, 2005c).

### 2.4.1.1. Tungsten alloys

Three tungsten alloys are produced commercially: tungsten-titanium, tungsten-tantalum, and tungsten-rhenium (Lassner and Schubert, 1999).

Re is the most important alloying element for tungsten. Re additions increase the ductility at low temperatures and also improve the high temperature strength and plasticity. Moreover, Re additions stabilize the grain structure, increase the recrystallization temperature and improve the weldability. It also improves the corrosion resistance of tungsten (Park, 1993). On the other hand, tantalum-tungsten alloys combine the good corrosion resistance and high elasticity of tantalum with the better high temperature strength of tungsten and tungsten-titanium alloy is used as a sputtering target in the manufacture of microelectronics devices (Lassner and Schubert, 1999).
Another type of tungsten alloys are the tungsten heavy-metal alloys (WHA’s). These are a category of tungsten-base materials that typically contain 90 to 98 wt% W in combination with some mix of nickel, iron, copper, and/or cobalt (Ryu and Hong, 2003.). The bulk of WHA production falls into the 90 to 95% W range. As a consequence, WHA’s gain their basic properties from those of the tungsten phase, which provides both high density and high elastic stiffness. These are the two properties that give rise to most applications for this family of materials (Lassner and Schubert, 1999).

Currently WHA’s are used in various applications. These applications include:

1. Damping weights for computer disk drive heads,
2. Balancing weights for ailerons in commercial aircraft, helicopter rotors, and for guided missiles,
3. Kinetic energy penetrators for defeating heavy armor,
4. Fragmentation warheads,
5. Radiation shielding, radio isotope containers for cancer therapy devices,
6. Weight distribution adjustment in sailboats and race cars (Lassner and Schubert, 1999; Ryu and Hong, 2003; Anonymous, 2005b).

The choice of alloy composition is driven by several considerations. The primary factor is the density required by the given application. Further considerations include corrosion resistance, magnetic character, mechanical properties, and post-sinter heat treatment options (Lassner and Schubert, 1999). The mechanical properties of WHA’s are known to improve through refinement of their microstructures (Ryu et al., 2000). Refinement of WHA’s is achieved by alloying with Re and Mo, solid state sintering and mechanical alloying (Ryu and Hong, 2003.).

The first WHA developed was a W-Ni-Cu alloy. Alloys of this ternary system are still occasionally used today, primarily for applications in which ferromagnetic character and electrical properties must be minimized. W-Ni-Cu alloys otherwise offer inferior corrosion resistance and lower mechanical properties than the present industry standard W-Ni-Fe alloys (Lassner and Schubert, 1999).

The majority of current uses for WHA’s are best satisfied with the W-Ni-Fe system. Alloys such as 93W-4.9Ni-2.1Fe and 95W-4Ni-1Fe represent common compositions.
The addition of cobalt to a W-Ni-Fe alloy is a common approach for slight enhancement of both strength and ductility. The presence of cobalt within the alloy provides solid-solution strengthening of the binder and slightly enhanced tungsten-matrix interfacial strength. Cobalt additions of 5 to 15% of the nominal binder weight fraction are most common (Lassner and Schubert, 1999).

For extremely demanding applications, even higher mechanical properties are obtainable from the W-Ni-Co system with nickel-to-cobalt ratios ranging from 2 to 9. Such alloys require resolution/quench, however, due to extensive intermetallic (Co$_3$W and others) formation on cool down from sintering (Anonymous, 2005d; Lassner and Schubert, 1999).

A number of special WHA’s are known as well. An example is the W-Mo-Ni-Fe quaternary alloy, which utilizes molybdenum to restrict tungsten dissolution and spheroid growth, resulting in higher strengths (but reduced ductility) in the as-sintered product (Lassner and Schubert, 1999).

2.4.1.2. Tungsten-based composites

In addition to these alloys, there exists also two groups of tungsten based composites. These are tungsten dispersion-strengthened and precipitation hardened composites. First, non-sag tungsten (tungsten doped with potassium) which is used as filaments in lamps is one kind of dispersion-strengthened composites, which have excellent creep resistance. The term non-sag refers to the resistance of the material against deformation (sagging) under its own weight at incandescent temperatures (Lassner and Schubert, 1999).

Second, there are oxide-dispersion-strengthened tungsten composites. The addition of small amounts of finely dispersed oxides increases the mechanical properties of tungsten. The most common one is the W-ThO$_2$ alloy which contains a dispersed second phase of 1 to 2% thorium. The thorium dispersion enhances thermionic electron emission, which in turn improves the starting characteristics of gas tungsten arc welding electrodes. It also increases the efficiency of electron discharge tubes and imparts creep strength to wire at temperatures above one-half the absolute melting point of tungsten (Mabuchi et al, 1997; Lassner and Schubert, 1999; Chen et. al, 2000). However, it is desirable to replace ThO$_2$ with non-radioactive activators.
because of the radioactive pollution of thorium during fabrication, service or handling.

In the last decade, considerable efforts have been directed to develop new materials, especially to explore new activators. It has been found that tungsten electrodes activated with rare-earth metal oxides (such as La$_2$O$_3$, Y$_2$O$_3$, CeO$_2$, etc.) exhibit superior arc characteristics compared to pure W and W-ThO$_2$ electrodes (Chen et al., 2000). Particularly, W- La$_2$O$_3$ composites exhibit good mechanical properties and have no radioactive potential (Mabuchi et al., 1997). Furthermore, there are studies about strengthening the WHA’s by adding Y$_2$O$_3$. As a result, the strength of WHA’s are improved with decreasing particle size which is proportional to the Y$_2$O$_3$ content (Ryu and Hong, 2003.).

Noting the effect of Y$_2$O$_3$ on the microstructure of WHA’s (Some properties of Y$_2$O$_3$ is shown in table 2.4 and table 2.5), it is decided to use Y$_2$O$_3$ in this study for refining the microstructure of new developed W-based PRMMC.

Finally, there are carbide-dispersion-strengthened tungsten composites. Hafnium carbide (HfC) is the strongest strengthener for tungsten at elevated temperatures. The outstanding strength of HfC is attributed to its high thermodynamic stability and its comparatively low solubility and diffusivity in tungsten at high temperatures. Furthermore, W-Re alloys strengthened with HfC are the strongest man-made metallic materials at temperatures above 2000 K (Park, 1993; Lassner and Schubert, 1999).

**Table 2.4:** Some properties of Y$_2$O$_3$ (Anonymous, 2002b; Anonymous, 2004).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>Ia3</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>10.6073 Å</td>
</tr>
<tr>
<td>Melting Temp.</td>
<td>2410 °C</td>
</tr>
<tr>
<td>Max. Working Temp.</td>
<td>2000 °C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>0.3 W/mK</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>7.9 $10^{-6}$ K$^{-1}$ (20-1020 °C)</td>
</tr>
<tr>
<td>Density</td>
<td>5.03 g/cm$^3$</td>
</tr>
<tr>
<td>Elastic Modulus</td>
<td>171.5 GPa @ 23 °C</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>135.7 GPa @ 23 °C</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>66.5 GPa @ 23 °C</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.298 @ 23 °C</td>
</tr>
</tbody>
</table>
Table 2.5: Hardness and fracture toughness of Y$_2$O$_3$ according to varying temperature and grain size (Anonymous, 2002a).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Grain Size (µm)</th>
<th>Hardness (GPa)</th>
<th>Fracture Toughness (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.2</td>
<td>9.1</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>1.2</td>
<td>8.0</td>
<td>2.1</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
<td>7.5</td>
<td>1.8</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>6.9</td>
<td>1.3</td>
</tr>
<tr>
<td>20</td>
<td>210</td>
<td>7.3</td>
<td>1.6</td>
</tr>
<tr>
<td>500</td>
<td>0.21</td>
<td>5.5</td>
<td>1.6</td>
</tr>
<tr>
<td>500</td>
<td>1.2</td>
<td>5.1</td>
<td>1.5</td>
</tr>
<tr>
<td>500</td>
<td>15</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>500</td>
<td>160</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>210</td>
<td>4.2</td>
<td>1.0</td>
</tr>
<tr>
<td>1000</td>
<td>0.21</td>
<td>4.8</td>
<td>1.5</td>
</tr>
<tr>
<td>1000</td>
<td>1.2</td>
<td>4.0</td>
<td>1.8</td>
</tr>
<tr>
<td>1000</td>
<td>15</td>
<td>2.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

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

However, there is no such a study in which SiC is used as dispersoid in a tungsten matrix. SiC possess similar mechanical properties (shown in Table 2.6, Table 2.7 and Table 2.8) but different thermodynamic characteristics than other carbides which are used as dispersoids in tungsten matrix. So, the encouraging factor to begin this study was the idea of doing something which has been never done or tried before.

Table 2.6: Comparison of Young’s modulus of some carbides (Shackelford, 2001).

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Young’s Modulus (GPa)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Carbide (B$_4$C)</td>
<td>290-450</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Silicon Carbide (SiC)</td>
<td>303</td>
<td>Room temp.</td>
</tr>
<tr>
<td>(pressureless sintered)</td>
<td>440</td>
<td>Room temp.</td>
</tr>
<tr>
<td>(hot pressed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tantalum Monocarbide (TaC)</td>
<td>285-629</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Titanium Monocarbide (TiC)</td>
<td>439</td>
<td>Room temp.</td>
</tr>
<tr>
<td></td>
<td>310-379</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Tungsten Monocarbide (WC)</td>
<td>669-714</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Zirconium Monocarbide (ZrC)</td>
<td>195-480</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Hafnium Monocarbide (HfC)</td>
<td>424</td>
<td>Room temp.</td>
</tr>
</tbody>
</table>
Table 2.7: Comparison of tensile strength of some carbides (Shackelford, 2001).

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Tensile Strength (MPa)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Carbide ($B_4C$)</td>
<td>155</td>
<td>980 °C</td>
</tr>
<tr>
<td>Silicon Carbide (SiC)</td>
<td>34-138</td>
<td>25 °C</td>
</tr>
<tr>
<td>(hot pressed)</td>
<td>200</td>
<td>20 °C</td>
</tr>
<tr>
<td>(hot pressed)</td>
<td>40-150</td>
<td>1400 °C</td>
</tr>
<tr>
<td>Tantalum Monocarbide (TaC)</td>
<td>14-290</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Titanium Monocarbide (TiC)</td>
<td>119</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Tungsten Monocarbide (WC)</td>
<td>345</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Zirconium Monocarbide (ZrC)</td>
<td>110</td>
<td>Room temp.</td>
</tr>
<tr>
<td></td>
<td>81-99</td>
<td>980 °C</td>
</tr>
<tr>
<td></td>
<td>89-109</td>
<td>1250 °C</td>
</tr>
</tbody>
</table>

Table 2.8: Comparison of hardness of some carbides (Shackelford, 2001).

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

Among the various non-oxide ceramics that have found commercial applications, SiC is the best one. The attractive properties, such as good specific strength and Young modulus as a function of temperature, the specific stiffness, corrosion and erosion resistance have made SiC an attractive alternative to the hard metal compositions (Rafaniello and Srinivasan, 1997). Furthermore, it is an important ceramic used in structural applications, such as automotive engines, cutting tools, heat exchange and mechanical seals (Marchi, 2001). The characteristics and the properties of SiC are summarized in table 2.9.

Table 2.9: Summary of characteristics and properties of SiC (Pierson, H.O., 1996)

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiC (very narrow range) see figure 2.22.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>40.097 g/mol</td>
</tr>
</tbody>
</table>
| Density | αSiC 3.211 g/cm³  
βSiC 3.214 g/cm³ |
| Lattice Parameter | 3C-SiC a= 4.3596 Å  
6H-SiC a= 3.0813 Å c= 15.1198 Å |
| Space Group | 3C-SiC $F\bar{4}3m$  
6H-SiC $P6_3mc$ |
| Melting Point | 2545 °C @ 1atm(βSiC)  
2830 °C @ 35 atm(βSiC) |
| Specific Heat | αSiC 27.69 J/molK  
βSiC 28.63 J/molK |
| Heat of Formation(ΔH) | αSiC -25.73 ± 0.63 kJ/molK @ 298.15K  
βSiC -28.03 ± 2 kJ/molK @ 298.15K |
| Thermal Conductivity | αSiC 41 W/m °C  
βSiC 25.5 W/m °C |
| Thermal Expansion | αSiC 5.12 x10⁻⁶/°C  
βSiC 3.8 x10⁻⁶/°C |
| Vickers Hardness | 30-35 GPa |
| Modulus of Elasticity | 300-475 GPa |
| Shear Modulus | 192 GPa (βSiC) |
| Bulk Modulus | 96.6 GPa (βSiC) |
| Flexural Strength | 350-600 MPa |
| Poisson’s Ratio | 0.183-0.192 |
| Oxidation Resistance | Excellent due to the formation of a layer of SiO₂ |
| Chemical Resistance | Essentially inert at room temperature |

SiC has a close-packed crystal structure depending on the stacking order which can exist in either cubic or hexagonal orientations (Rafaniello, 1997). Silicon carbide exists in a large number of different polytypes. Basically, all polytypes have a
hexagonal frame with a C atom in center of mass of a triangle of Si atoms (Figure 2.22) (Syväjärvi, 1999).

**Figure 2.22:** Si-C phase diagram (Pierson, H.O., 1996).

The structural unit of the tetrahedron (Fig.2.23.) consists of primarily covalent Si-C bonds (88% covalent and 12% ionic) (Marchi, 2001). The crystal structures of SiC are cubic, hexagonal and rhombohedral and often the Ramsdell notation is used for describing the polytypes. This notation system indicates the number of layers in the unit cell and a letter representing the crystal symmetry of the polytype (C for cubic, H for hexagonal and R for rhombohedral) (Rafaniello, 1997). Generally, the 3C-SiC polytype is referred to as β-SiC and the hexagonal polytypes as α-SiC. The 3C-SiC polytype has a zinc-blende structure, and is the only polytype which is cubic. Furthermore, the 2H polytype represents the wurtzite structure of the SiC polytypes (Syväjärvi, 1999).

**Figure 2.23:** The tetrahedral structure of the C and Si atoms in SiC and the double layer stacking sequence of the 6H, 3C, and 4H-SiC polytypes (Syväjärvi, 1999).
There are various applications where SiC is used. Because of its thermal mechanical and chemical properties it can be used in extremely harsh environments (Raffray et al., 2001). Firstly, it is used in powder form as deoxidizer in steel production and other metallurgical processes, as powder, bonded and coated abrasives and as filler materials in refractory cements. Additionally, it is used in bulk form as refractory products, as electric heating elements and resistors, as igniters for gas appliances, as ceramic burners, as mechanical seal faces, as radiation sensors, as low-weight high-strength mirrors, as high power and high temperature semiconductor devices, as radiation resistant semiconductors and as light-weight armors (Pierson, 1996; Rafaniello and Srinivasan, 1997). Furthermore, it is used as coatings for fusion reactor applications, for nuclear waste containers, for oxidation resistance of carbon-carbon composites and for blue light emitting diodes (LED) (Pierson, 1996).

2.4.3. W-SiC system

In literature, there exists no study regarding mechanical alloying of a W-SiC powder mixture. In fact, SiC has never been used as a particulate reinforcement material in tungsten matrix composites fabricated by powder metallurgy techniques. However, there are other investigations which used W and SiC together. In this context, before beginning this study, it is necessary to take a look to these studies to understand the behavior of the W-SiC system.

Gao et al. (2001), analyzed the mechanical properties and microstructure of laminated SiC-W composites. They developed a laminated SiC-W composite using the hot pressing method at 25MPa and 1800°C for 2h under argon atmosphere, in which W powder was first smeared to a SiC ceramic slice and then the samples prepared by this method were laminated and hot pressed. It was found that a chemical reaction between W and SiC occurred during the preparation process and as a result of this reaction, both W$_5$Si$_3$ and WC were synthesized.

However, in another study by Son et al. (2004), joints of W and SiC were produced again by a hot-pressing method but this time both W and SiC powders were used and layers of those were hot pressed at 20 MPa and 1700-1900°C for 10-120 min. Following sintering, the interfacial reactions were characterized. In Table 2.10, the summary of phase identification results of this study is presented.
Table 2.10: The summary of phase identification results (a) at 60 min of process time; (b) at 1780 °C of process temperature (Son et al., 2004).

They found that at temperatures of 1780 °C and above W<sub>5</sub>Si<sub>3</sub> and W<sub>2</sub>C phases were stable (Fig.2.24).

![Diagram of phase relations in the W-Si-C system](image)

**Figure 2.24**: Schematic view of the diffusion path at the W–SiC interface during the elevated temperature reaction (Son et al., 2004).

On the other hand, in another study, Kang, (2004) investigated the microstructure of high volume SiC reinforced tungsten composites by plasma spray method. In this study, W and SiC powders were ball-milled with a weight ratio of 50:50 and the prepared powder was plasma sprayed onto a graphite substrate. However, in this case, expected reactions did not take place because the plasma spray process uses very high temperatures (5000 - 12000 °C). Also, there is not enough resident time for the formation of W<sub>5</sub>Si<sub>3</sub> and WSi<sub>2</sub>, due to the rapid solidification of liquid/semi-liquid droplets in the range of 10<sup>5</sup>-7 K/s. Furthermore, tungsten carbides (W<sub>2</sub>C and WC) could not form due to the absence of dissociated carbon in the deposit from the reaction between carbon and oxygen. Tungsten was oxidized to tungsten oxides (WO<sub>2</sub> and WO<sub>3</sub>) and silicon to SiO<sub>2</sub> after SiC decomposition.

In addition to these investigations, Seng and Barnes (2000), calculated tungsten silicide and carbide formation using Gibbs free energy. Furthermore, a comprehensive study about phase relations and interface reactions in the ternary system W–Si–C was done by Goesmann and Schmid-Fetzer.
According to Seng and Barnes (2000), a system with both a carbide and a silicide would always be the most stable configuration when depositing W on SiC, and that, as temperature increases, the stable phases change. The silicide stable with both SiC and a carbide changed from WSi$_2$ to W$_5$Si$_3$, and the carbide itself changed from WC to W$_2$C. The thermodynamic data and analysis of the ternary phase diagrams shown in Figures 2.25, 2.26 and 2.27 indicated this result.

\begin{table}
\centering
\begin{tabular}{lcccc}
\hline
Reaction & $\Delta G$ at 300 K (kJ mol$^{-1}$) & $\Delta G$ at 2200 K (kJ mol$^{-1}$) \\
\hline
8WSi$_2$ + 7WC + 7SiC + 3W$_5$Si$_3$ & 71.25 & -145.251 \\
3WSi$_2$ + 2WC + 7SiC + 3W$_5$Si$_3$ & 254.97 & -91.802 \\
1WSi$_2$ + 3WC + 2SiC + 3W$_5$Si$_3$ & 26.140 & 29.190 \\
1WSi$_2$ + 5WC + 3SiC + 2SiC & 75.672 & -22.770 \\
1WSi$_2$ + 1WC + WC + 2SiC & 197.618 & 20.076 \\
\hline
\end{tabular}
\end{table}

\begin{table}
\centering
\begin{tabular}{lcccc}
\hline
\multirow{2}{*}{a)} & Reaction & $\Delta H$ (kJ mol$^{-1}$) & $-T\Delta S$ (kJ mol$^{-1}$) & $\Delta G$ (kJ mol$^{-1}$) \\
\hline
\multirow{6}{*}{[31,12]} & WC & 200 & -40.164 & 1.800 & -38.361 \\
& WC & 2200 & -38.469 & 5.539 & -32.870 \\
& W$_5$Si$_3$ & 200 & -135.202 & -8.254 & -143.456 \\
& W$_5$Si$_3$ & 2200 & -276.934 & 138.366 & -130.566 \\
& W$_5$Si$_3$ & 300 & -93.002 & 1.835 & -91.117 \\
& W$_5$Si$_3$ & 2200 & -104.000 & 140.211 & -45.966 \\
& W$_2$C & 2200 & -16.228 & -66.518 & -50.190 \\
& SiC & 200 & -72.223 & 2.286 & -70.835 \\
& SiC & 2200 & -122.178 & 82.205 & -40.973 \\
\hline
\end{tabular}
\end{table}

**Figure 2.25:** a) Possible reactions, b) Gibbs energy of formation of binary compounds in the W-Si-C system at 300 and 2200 K, c) Ellingham plot of important reactions in the W-Si-C system, d) Ellingham plot of critical reactions that change the stable phases as a function of temperature. Reaction 5 shows that above 970 K, SiC no longer reacts with W$_5$Si$_3$. Reaction 6 shows that above 2140 K, SiC now reacts with W$_2$C to form WC, e) Ellingham plot of reactions between SiC and WSi$_2$. Note that over 300–2200 K for both reactions, $\Delta G>0$, indicating there will be no reaction between WSi$_2$ and SiC (Seng and Barnes, 2000).
Figure 2.26: a) 300<T<970 K. The dashed line indicates a stability above 460 K. WSi₂ and WC form upon deposition of W on SiC. b) 970<T<2140 K. WC is still expected to form, but the silicide stable with both SiC and the carbide has changed to W₅Si₃. c) 2140<T<2200 K. The stable carbide has changed to W₂C (Seng and Barnes, 2000).

In addition, these results were generally consistent with the study done by Goesmann and Schmid-Fetzer (1995). They also found that W₅Si₃ and W₂C at elevated temperatures and WSi₂ and WC at low temperatures were the stable phases.

Figure 2.27: a) Isothermal section of the W-Si-C phase diagram at 1800 °C. It is valid down to ≈ 1500 °C, b) Isothermal section at 1300 °C. It is valid up to ≈ 1400 °C. Compared to 1800 °C the homogeneity range of W₂C is reduced, c) Isothermal section at <1250 °C. The tie line W₂C-W₅Si₃ vanishes and the new three-phase field W+W₅Si₃+WC develops. Below 700 °C the tie line WSi₂-WC becomes stable (Goesmann and Schmid-Fetzer, 1995).

Considering all these data, it can be predicted that some amount of tungsten silicides and carbides would form in the present study during processing. Under these circumstances, the properties of these silicides and carbides become significant.

As a class of materials, transition metal silicides have recently been the focus of considerable attention for potential applications as structural high temperature materials to be used at T>1000 °C (Shon et al., 2001a). They are attractive because of their stability in oxidizing environments (Shon et al., 2001b; Fujiwara et al., 2005). WSi₂ has a high melting temperature (2433 K), good strength at high temperatures, good creep resistance, and a high oxidation resistance which comes about from the
formation of a dense vitreous and adherent \( \text{SiO}_2 \) surface layer at high temperatures (Shon et al., 2001a). It has an elasticity modulus of 430 GPa and microhardness \( (100g) \) of 1200 kg/mm\(^2\) (Lassner and Schubert, 1999). Furthermore, it is a stable solid up to 2400 K, which makes it an excellent engineering material (Callanan et al., 1997).

In addition to that, \( \text{W}_5\text{Si}_3 \) was considered as a potential candidate high-temperature structural material, because it has a high melting point, low density, strong covalent-dominated atomic bonds and wide alloying field. From tribological point of view, it is also expected to have a low friction coefficient because of its strong covalent-dominated atomic bonds an outstanding abrasive and adhesive wear resistance due to its inherent high hardness. Additionally, tungsten, which has the highest melting point and strength and strongest atomic bonds among all the metallic elements, is expected to be an ideal reinforcing phase for improving the toughness and strength to the abrasive and adhesive wear resistant for these silicides (Cai and Wang, 2004).

On the other hand, tungsten carbide is a major industrial material with a yearly world production of \( \approx20000 \) tons. Its largest use is in cemented carbides for cutting tools. It is also used in oil-field and mining drilling tools, in drawing and extrusion dies, in balls for ball mills and in rolls, nozzles and sealing rings (Lassner and Schubert, 1999).

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**Figure 2.28:** a) Si-W phase diagram, b) W-C phase diagram
Table 2.11: Some properties of tungsten carbides (Pierson, 1996; Lassner and Schubert, 1999).

<table>
<thead>
<tr>
<th>Phases</th>
<th>$W_2C$</th>
<th>WC see the figure 2.29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure and Lattice Parameters</td>
<td>$W_2C$ hexagonal, $a=0.30008$ nm, $c=0.47357$ nm</td>
<td>WC hexagonal, $a=0.2907$ nm, $c=0.2837$ nm</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>$W_2C$ 379.71 g/mol</td>
<td>WC 195.86 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>$W_2C$ 17.2 g/cm$^3$</td>
<td>WC 15.8 g/cm$^3$</td>
</tr>
<tr>
<td>Melting Point</td>
<td>$W_2C$ 2730$^\circ$C</td>
<td>WC 2870$^\circ$C</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>39.8 J/molK (WC)</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>63 W/m$^\circ$C (WC)</td>
<td></td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>$W_2C$ 1.2 x $10^{-6}$/K(a-axis)</td>
<td>WC 5.2 x $10^{-6}$/K(a-axis)</td>
</tr>
<tr>
<td>Vickers Hardness</td>
<td>$W_2C$ 19 GPa</td>
<td>WC 22 GPa</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>$W_2C$ 420 GPa</td>
<td>WC 670-720 GPa</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>262-298 GPa (WC)</td>
<td></td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.18(WC)</td>
<td></td>
</tr>
<tr>
<td>Oxidation Resistance</td>
<td>Oxidation in air starts at 500-600$^\circ$C</td>
<td></td>
</tr>
</tbody>
</table>
3. EXPERIMENTAL PROCEDURE

The experimental part of this study was designed in order to provide useful information about sintering, microstructural and mechanical properties of W-SiC and W-SiC-Y$_2$O$_3$ composites prepared by mechanical alloying technique.

The first group of experiments deals with the effect of SiC addition on the microstructural and mechanical properties of W depending on the amount of SiC, the duration of mechanical alloying and the sintering regime. On the other hand, the second group of experiments deals with the effect of Y$_2$O$_3$ addition on the microstructural and mechanical properties of W-SiC composites depending on the same variables mentioned above but this time the amount of Y$_2$O$_3$ changes while the amount of SiC does not.

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

3.1. Preparation of Green Compacts

3.1.1. Mechanical alloying

In this study W, SiC, and Y$_2$O$_3$ powders having average particle sizes of 14 µm, 15 µm, and 1 µm were used, respectively. Furthermore, graphite powder with an average particle size of 21 µm was used as a process control agent (PCA) to minimize cold welding between powder particles and thereby to inhibit the agglomeration. In the first group of experiments powder mixtures of W-%10SiC(vol.) and W-%20SiC(vol.) and in the second group of experiments powder mixtures of W-%20SiC-%3Y$_2$O$_3$(vol.) and W-%20SiC-%15Y$_2$O$_3$(vol.) were mechanically alloyed in a tungsten carbide (WC) vial using a 8000D™ Spex mill with a speed of 1200 rpm (Fig. 3.2a). WC balls with a diameter of ¼ inches were used as milling media. The balls-to-powder weight ratio was 10:1. The degree of contamination of the milled powder with WC was determined by weighing the media before and after milling. Mechanical alloying of the first powder mixture was carried
out in ethyl alcohol. However, other three powder mixtures were mechanically alloyed without using ethyl alcohol because the first one was too much contaminated by milling media. All the powder mixtures were mechanically alloyed for 3, 6, 12 and 24 hours.

Figure 3.1: The Flow Chart of the Experimental Procedure

High-purity argon was chosen as the milling atmosphere to prevent oxidation and contamination of the powder in order to prevent the formation of oxides and nitrides in the powder when exposed to air. This is required, especially if the powders are reactive in nature. Thus, the loading and unloading of the powders into the vial was carried out inside a “Pluslabs™” atmosphere-controlled glove box (Fig 3.2b).
3.1.2. Compaction

The mechanically alloyed powders were compacted by cold pressing in a tool-steel die at a pressure of 400 MPa into cylinder shaped green compacts with a diameter of \( \approx 12\text{mm} \) for 1 minute by using a 10 tons “APEX™ 3010/4” one-action hydraulic press shown in Fig 3.3. Liquid paraffin was applied to the walls of the die to take the samples out of the die easily.

**Figure 3.3:** The picture of APEX™ 3010/4 one-action hydraulic press.

3.1.3. Sintering

Sintering was performed in two different furnaces. The First one is a reductive high temperature 1800 M Vac Graphite Linn™ furnace and the second one is actually a high temperature 1700 Anter™ dilatometer. Both equipment works under gas sintering conditions using vacuum and \( \text{H}_2 \), \( \text{Ar} \) and \( \text{N}_2 \) gases as sintering media. Beside its function for measuring the thermal expansion behavior of materials, 1700 Anter™ dilatometer was also used as a reductive high temperature furnace in this
study because the samples were small enough to be sintered in this dilatometer. However, the first objective to use 1700 Anter™ dilatometer was to understand the sintering behavior of the samples. The samples were first sintered in the 1700 Anter™ dilatometer. According to their sintering behavior, other samples were sintered in the reductive high temperature 1800 M Vac Graphite Linn™ furnace. So, there were two different sintering regimes for all powder mixtures. The sintering regimes for both of the furnaces are shown in Fig. 3.4.

![Figure 3.4: a) Sintering regime in the 1700 Anter™ dilatometer, b) Sintering regime in the 1800 M Vac Graphite Linn™ furnace.](image)

3.2. Characterization of Powder Mixtures and Sintered Samples

3.2.1. Microstructural and phase characterization

The microstructural and phase characterization investigations were carried out by optical microscope, scanning electron microscope (SEM) and X-ray diffraction (XRD) analyses. Before the sintered samples were characterized, they were mounted in bakelite using the Struers™ Labopress-1 machine (Fig.3.5a). After that, samples were polished on the Struers™ Tegrapol-15 automatic polishing machine Fig 3.5b).
XRD analyses were carried out on a Rigaku™ X Ray Diffractometer shown in Fig 3.6 at a generator voltage of 40kV and current of 30 mA. CoK\textsubscript{α} radiation was used to irradiate the samples.

In order to reveal grain boundaries, polished surfaces were etched by using hydrogen-peroxide (H\textsubscript{2}O\textsubscript{2}) for 5 minutes before the microscopic analyses. Optical microscope analyses were carried out on a Nikon™ Eclipse L150 optical microscope. On the other hand SEM analyses were carried out on two different analytical electron microscopes shown in Fig 3.7. The first one is a Jeol™-JSM-T330 scanning electron microscope and the second one is a Jeol™-JSM-7000F field emission scanning electron microscope. The latter one was used for higher magnifications (30000x).
3.2.2. Density measurements

Densities of green compacts were determined by measuring volumetric dimensions. On the other hand density measurements of the sintered samples were carried out by simply using the relationship between volume and mass. In this method the density is determined by using liquid displacement (Archimedean density). First, the sample is weighed in air and then in a liquid. After that, the mass in air is divided by the difference of these results and then multiplied with the density of the liquid. In this study, ethyl alcohol is used as the liquid because of the oxidation risk of the samples.

Figure 3.7: a) Picture of Jeol™-JSM-T330 scanning electron microscope, b) picture of Jeol™-JSM-7000F field emission scanning electron microscope.

Figure 3.8: Precisa™ XB220A weighing machine where density measurements were carried out.
3.2.3. **Hardness measurements**

Hardness measurements were carried out on a Shimadzu™ micro hardness tester with a Vickers indenter under a load of 100g for 15 seconds. Results of hardness tests were averaged out of 25 successive indentations.

![Figure 3.9: Shimadzu™ micro hardness tester.](image)

**Figure 3.9:** Shimadzu™ micro hardness tester.
4. RESULTS AND DISCUSSION

4.1. Characterization of Powders

4.1.1. Phase analyses and microstructure characterizations

Because there is plenty of samples generated in this investigation, code numbers are given to all of the samples, such as 3-10-1680 or 3-3Y-1680. The first term of the code indicates the duration of mechanical alloying, the second term indicates the amount (vol.) of SiC in the composite and the last term (1680) indicates the sintering temperature of the sample. Finally, the term 3Y indicates the amount (vol.) of Y2O3 in the W-SiC composite. All samples containing Y2O3 contains 20% SiC. In Figure 4.1 XRD diffraction patterns of initial powders are shown.
XRD diffraction patterns of mechanically alloyed powders are shown in Figure 4.2. With increasing MA, peaks are broadened and peak heights are decreased, which are due to refining of grain size and increasing of internal strain resulted from mechanical alloying.
Figure 4.2: XRD patterns of mechanically alloyed a) %10 SiC b) %20 SiC c) %3 Y$_2$O$_3$ d) %15 Y$_2$O$_3$ containing powders.
SEM images (Figure 4.3) of 10 vol.% SiC containing as-blended and MA’d for 3h, 6h, 24h powders show that the particle sizes of powders are decreasing with increasing mechanical alloying.

![SEM images of 10 vol.% SiC containing as-blended and MA’d powders.](image)

**Figure 4.3**: SEM images of 10 vol.% SiC containing a) as-blended and b) 3h, c) 6h, d) 24h mechanically alloyed powders.

In Figure 4.3a, round and nearly equiaxed particles are W particles, sharp-edged particles at the left-top of the image are SiC particles and flake like particle at the right-bottom of the image is the graphite particle. It can be clearly seen that in the initial stages of milling the ductile metal (here W) powder particles get flattened by the ball-powder-ball collisions, while the brittle SiC particles get fragmented as expected (Fig 4.3b). With continuing milling, these flattened structures get fragmented (Fig 4.3c) and finally composite powder particles are formed with compositions similar to starting powder blend composition (Fig 4.3d). In figure 4.4, results of particle size analyses are shown. Initial W powders have an average diameter of 14 µm according to SEM analyses. However, the result in Figure 4.4a is 28 µm because of the agglomeration of powders. Same problem also exists for Y₂O₃.
Particle size results show that it has an average diameter of 6.5 µm. Actually, it is 1 µm.

High amount of refining of particles occurred up to 6 hours and after that the grains began to refine according to the XRD results.

**Figure 4.4:** Particle size analyze of a) initial powders – from a) to d): W, SiC and graphite and Y₂O₃, b) 3h MA powder, c) 6h MA powder, d) 24h MA 10 vol.% SiC containing powder.
4.1.2. Characterization of as-consolidated and sintered samples

4.1.2.1. Determination of the sintering regime

Several factors influence the sintering regimes, including time, temperature, particle size, atmosphere, compacted density, particle size distribution etc. Normally, temperatures up to 2400 °C are needed to sinter tungsten powders with an average diameter of 4 µm to high densities in 1-2 hours. Additionally, 110h at 1775 °C, 50h at 1800 °C and 40h at 1825 °C are required to attain 92% density for the same powder. However, this temperature of sintering and time of sintering can be decreased by decreasing the particle size of powders (Cheney, 1984). In Figs. 4.5a-b, this relation between particle size, sintering temperature and sintering time can be seen.

![Figure 4.5](image)

**Figure 4.5:** Relative density vs. the logarithm of a) sintering time for several tungsten powder sizes, b) sintering time for 4 µm tungsten powder.
Taking these facts into account, the sintering regime is mainly determined by several additional experiments using a dilatometer. The curves obtained from the dilatometer experiments are shown in Fig 4.6.

**Figure 4.6:** Sintering curves of a) 24-10-1650, b) 24-10-1680, c) 6-10-1680 samples.

H₂ flow was regulated in accordance with the sintering regime seen in Fig 4.6. In every experiment, different flow rates and flow durations were applied. As a result, a similar sintering behavior was observed. Furthermore, it was observed that the initial reductive effect of H₂ began approximately at the same temperatures, even though its flow had earlier started. Moreover, this initial effect slowed down again at
approximately same temperatures, even the H₂ flow was continuing. Depending on this information gas flow regime was determined.

To determine whole sintering regimes, some literature researches were done and in addition to the conventional sintering regime at 1680 °C, a second sintering regime was chosen to inhibit the grain growth (see the figure 3.4). Sintering at 1680 °C was chosen as conventional sintering which is to heat the powder compact at a certain rate, holding it at the highest temperature until the maximum density is reached. However, second sintering regime is different which uses two steps in the heating schedule. The sample is first heated to a higher temperature to achieve an intermediate density, then cooled down and held at a lower temperature until it is fully dense. By means of 2nd sintering regime, the grain growth is inhibited. The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. However, the important task here is to obtain a sufficiently high starting density during the first step (Chen and Wang, 2000; Chen, 2000).

4.1.2.2. Density measurements

The results of the density measurements of both green compacts and sintered samples are given in Table 4.1. The theoretical densities are 17.3 g/cm³ and 15.7 g/cm³ for the %10 and %20 SiC containing samples, respectively. According to these results, it is clear that the density is increased with increasing sintering temperatures as a result of thermal activation and increased atom diffusivity, which is the key factor for sintering, is increased with increasing temperature. Furthermore, the densities of the sintered samples containing vol. %10 SiC were increasing with increasing mechanical alloying times (Fig 4.5a). This is because of the mechanically activated sintering which is enhanced by the stored energy with severe cold working and homogeneous distribution of matrix phase by MA. In addition, the reason of increasing green densities may be the small amount of Co phase which is the result of contamination by MA. In addition, densities of 24h MA’d 20 vol.% SiC containing samples were increasing sintering temperature. However, the densities of samples containing 20 vol.% SiC slightly changed and densities of samples containing Y₂O₃ decreased with increasing MA and the green densities were lower than those containing 10 vol.% SiC (Fig 4.6). The reason for that was that the
increased amount of SiC and Y\textsubscript{2}O\textsubscript{3} phases which are very brittle makes the compressibility of the powder difficult. Moreover, the surface tensions of the powders were increased with decreasing particle size, due to the increasing surface area and this also makes the compressibility of the powder difficult. Therefore, these samples all have similar low green densities and as a result similar sintered densities.

**Table 4.1: Density Measurements**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Green</th>
<th>%61.5</th>
<th>Sintered</th>
<th>%69.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>24-10-1650</td>
<td>10.64 g/cm(^3)</td>
<td></td>
<td>13.27 g/cm(^3)</td>
<td></td>
</tr>
<tr>
<td>3-10-1680</td>
<td>9.59 g/cm(^3)</td>
<td>%55.4</td>
<td>14.27 g/cm(^3)</td>
<td>%58.5</td>
</tr>
<tr>
<td>6-10-1680</td>
<td>9.28 g/cm(^3)</td>
<td>%57.1</td>
<td>13.53 g/cm(^3)</td>
<td>%69.0</td>
</tr>
<tr>
<td>24-10-1680</td>
<td>10.69 g/cm(^3)</td>
<td>%61.8</td>
<td>13.96 g/cm(^3)</td>
<td>%62.2</td>
</tr>
<tr>
<td>3-10-1770</td>
<td>9.63 g/cm(^3)</td>
<td>%55.7</td>
<td>15.89 g/cm(^3)</td>
<td>%63.3</td>
</tr>
<tr>
<td>6-10-1770</td>
<td>9.83 g/cm(^3)</td>
<td>%56.8</td>
<td>16.25 g/cm(^3)</td>
<td>%65.9</td>
</tr>
<tr>
<td>24-10-1770</td>
<td>10.63 g/cm(^3)</td>
<td>%61.4</td>
<td>16.71 g/cm(^3)</td>
<td>%66.6</td>
</tr>
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<td>3-20-1770</td>
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<td>%50.0</td>
<td>14.98 g/cm(^3)</td>
<td>%59.8</td>
</tr>
<tr>
<td>6-20-1770</td>
<td>8.62 g/cm(^3)</td>
<td>%54.0</td>
<td>15.03 g/cm(^3)</td>
<td>%59.8</td>
</tr>
<tr>
<td>12-20-1770</td>
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<td>%52.2</td>
<td>14.91 g/cm(^3)</td>
<td>%59.2</td>
</tr>
<tr>
<td>24-20-1770</td>
<td>7.96 g/cm(^3)</td>
<td>%51.1</td>
<td>14.94 g/cm(^3)</td>
<td>%59.2</td>
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<td>%59.5</td>
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<td>%58.02</td>
<td>14.23 g/cm(^3)</td>
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<td>%55.33</td>
<td>14.34 g/cm(^3)</td>
<td>%60.4</td>
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<td>15.01 g/cm(^3)</td>
<td>%69.8</td>
</tr>
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<td>%59.2</td>
<td>12.7 g/cm(^3)</td>
<td>%68.9</td>
</tr>
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<td>%58.14</td>
<td>13.19 g/cm(^3)</td>
<td>%69.2</td>
</tr>
<tr>
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<td>8.26 g/cm(^3)</td>
<td>%57.7</td>
<td>12.62 g/cm(^3)</td>
<td>%69.5</td>
</tr>
<tr>
<td>15Y-24-1770</td>
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<td>%56.7</td>
<td>13.91 g/cm(^3)</td>
<td>%69.7</td>
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<td>14.05 g/cm(^3)</td>
<td>%66.2</td>
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<tr>
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<td>%57.4</td>
<td>13.41 g/cm(^3)</td>
<td>%69.3</td>
</tr>
<tr>
<td>20-24-1680</td>
<td>8.05 g/cm(^3)</td>
<td>%51.3</td>
<td>14.63 g/cm(^3)</td>
<td>%62.3</td>
</tr>
</tbody>
</table>
Figure 4.7: a) Relative density of samples with %10 SiC vs. sintering temperature, b) Relative density of 24h MA’d samples with %20 SiC vs. sintering temperature.

Figure 4.8: Relative density vs. amount of MA
4.1.2.3. Phase analyses and microstructure characterizations

XRD diffraction patterns of 10-1680, 10-1770, 20-1770, 3Y-1770, 15Y-1770, 3Y-24-1680, 15Y-24-1680 and 20-24-1680 samples are shown in Figures 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.15 and 4.16.

**Figure 4.9:** XRD patterns of 10-1680 samples due to the mechanical alloying time.

As clearly seen in Figs. 4.9-4.11, at 1680 °C W₂C phase is identified in all of the samples. In addition, there are also some tungsten silicide phases identified, but sometimes it is difficult to determine which tungsten silicide phase is more stable because 2-theta values for these silicides are too close to each other. However, W₅Si₃ phase seems more likely to be stable in the 3-10-1680 samples. Additionally, there is also SiC phase which is stable. With increasing mechanical alloying, the intensities of W, SiC and W₅Si₃ diffraction patterns decrease and WC and WSi₂ peaks appear.

On the basis of this, it can be deduced that a chemical reaction between W and SiC, and between W and W₅Si₃ occurs. Pertinent to this observation, it is appropriate here to list possible reactions, which Seng and Barnes (2000) mentioned about.

\[
\text{SiC} + \frac{3}{2}\text{W} \rightarrow \frac{1}{2}\text{WSi}_2 + \text{WC}
\]

\[
7\text{SiC} + 3\text{W}_5\text{Si}_3 \rightarrow 8\text{WSi}_2 + 7\text{WC}
\]

On the other hand, in the sample MA’d for the intensity of the W₂C diffraction patterns increases while those of WSi₂ decreases. This may be a result of the WC contamination (approximately 1 wt.% for 3h MA’d, 2-3 wt% for 6h MA’d and 4 wt.% for 24h MA’d samples) during the mechanical alloying process, which was
determined according to the weight loss of the balls and vial. This excess amount of 
WC could have been reacted with W to form W₂C.

**Figure 4.10:** XRD patterns of 10-1770 samples due to the mechanical alloying time.

Considering the 10-1770 samples, a little amount of tungsten silicides and W₂C is 
present beside W. Again it is difficult to determine which tungsten silicide phase is 
more stable, however, comparing with 6 and 24h MA samples, W₅Si₃ phase seems 
more likely to be stable. With increasing mechanical alloying, intensity of the W₂C, 
SiC and W₅Si₃ diffraction patterns get stronger. However, with continuing 
mechanical alloying intensity of those drastically decreases, which is believed to be 
due to the refinement of the microstructure depending on the sintering regime.

**Figure 4.11:** XRD patterns of 20-1770 samples due to the mechanical alloying time.
Considering 20-1770 samples, in the sample MA’d for 3h, all the phases except WC are present, but in 6-20-1770 sample the intensities of the present phases diffraction patterns decreases.

On the other hand, in the 12h mechanically alloyed 20-1770 samples these intensities are again increased and in the 24-20-1770 sample all the peaks except those of SiC and W are disappeared and seem like the diffraction patterns of initial powders (see Figure 4.2a). This is believed to be due to the recrystallization triggered by severe plastic deformation due to the mechanical alloying. New grains might have pumped the excess Si and C in silicides and carbides out. As a result, new strain free grains of W and SiC might have been formed.

**Figure 4.12:** XRD patterns of 3Y-1770 samples due to the mechanical alloying time.
Considering both the 3Y-1770 and 15Y-1770 samples, same phases, namely W, W₂C and W₅Si₃ were identified in all the samples. The amount of W₂C was decreased with increasing amount of MA in both 3 vol.% and 15 vol.% Y₂O₃ containing samples. Y₂O₃ phase could not be identified. In 3Y-1770 samples, the intensities of W₅Si₃ phase were decreasing until the 12h MA’d sample and then increased again in 24h MA’d sample. On the other, in 15Y-samples, XRD patterns of 3h MA’d and 6h MA’d samples were similar except the W₂C amount, however, the intensities of W₅Si₃ phase decreased with further MA.

**Figure 4.13:** XRD patterns of 15Y-1770 samples due to the mechanical alloying time.
Both the 3 vol.% $Y_2O_3$ and 15 vol.% $Y_2O_3$ containing 24h MA’d and at 1680 °C sintered samples have similar XRD patterns. Moreover, patterns were also similar to the XRD pattern of 3 vol.% $Y_2O_3$ containing 24h MA’d and at 1770 °C sintered sample. Again W, W$_2$C and W$_5$Si$_3$ phases were identified. Only difference was that the intensities of W$_2$C and W$_5$Si$_3$ phases decreased in 15 vol.% $Y_2O_3$ containing sample.
In 20 vol.% SiC containing 24h MA’d and at 1680 °C only W and W₅Si₃ phases were identified. All the SiC and W might have reacted to W₅Si₃ where the free carbon in the structure might escape as some CₓHᵧ or COₓ gas. Weight loss of this sample (5%) was more than other samples, which supported this idea.

The optical microscope and SEM images of 10-1680 and 10-1770 samples are shown in Figures 4.17 and 4.18, respectively. It can be clearly seen that the grain sizes of both 10-1680 and 10-1770 samples are decreasing with increasing mechanical alloying. However, the grain size of 3-10-1770 is much larger than that of the 3-10-1680 while the grain size of that of 24-10-1770 is much smaller than that of 24-10-1680. The reason for that is believed to be the sintering regime. In order to achieve the grain growth inhibition in this sintering regime it is required to reach a sufficiently high starting density during the first step and this may be the reason why 3-20-1770 sample has huge grains while 24-20-1770 sample has minute grains. So, the sintering regime to inhibit the grain growth may have an opposite effect on 3-20-1770.

The optical micrographs given in Fig. 4.17 and SEM images in Fig. 4.18 comprise areas with varying contrasts. Dull white areas (bright yellow in OM) consist of W...
and the darker, mottled white areas (dark yellow in OM) consist of W+\textit{W}_2\text{C}. In addition, grey areas (green or brown in OM) consist of the silicide phases and spherical shaped dark grey areas consist of SiC. Spherical shaped black areas are mainly pores.

**Figure 4.17:** a),b),c) Optical microscope (OM) images of 3,6,24h MA 10-1680 samples, respectively. d),e),f) Optical microscope images of 3,6,24h MA 10-1770 samples, respectively.

There is a 2-3 wt.% weight loss of sintered samples. So, H$_2$ or O$_2$ might have reacted with free carbon present in the structure or carbon formed during chemical reactions
and escaped as \( C_xH_y \) or \( CO_x \) gas which is believed to be the reason of pore formation. For more reliable results transmission electron microscope (TEM) analyses should be done.

**Figure 4.18:** a),b),c) SEM images of 3,6,24h MA 10-1680 samples, respectively. d),e),f) SEM images of 3,6,24h MA 10-1770 samples, respectively.

It can be seen that there are cracks in both of 3h mechanically alloyed samples. Especially, in 3-10-1770 sample there are large cracks. 6h mechanically alloyed samples have similar microstructures, however 6-10-1680 sample has finer grains but more cracks. On the other hand, both the 24h mechanically alloyed samples have a
lot of pores. The difference is that the distribution of the pores of 24-10-1680 sample is non-uniform while the distribution of the pores of 24-10-1770 sample is quite uniform. Furthermore, 24-10-1770 sample has very fine and homogenous microstructure compared to others. 24-10-1680 sample has a less homogenous microstructure and it also includes cracks at some regions. The effect of the sintering regime to the microstructures is noteworthy. The objective of the sintering regime at 1770 °C was grain growth inhibition. However, this is achieved only for the 24h mechanically alloyed sample. The reason for that is believed to be due to the 3h and 6h MA samples which did not have a sufficient starting density during the first step of the sintering regime.

The optical microscope and SEM images of the 20-1770 samples are shown in figures 4.19 and 4.20, respectively. In optical microscope images shown in Fig 4.19 Vickers hardness indentation marks can be seen.

Figure 4.19: a),b),c),d) Optical microscope (OM) images of 3h, 6h, 12h, 24h MA 20-1770 samples.

SEM images are consistent with XRD diffraction patterns. It can be clearly seen that 3h and 12h MA samples have similar microstructures. Both of them have a lot of pores, mostly smaller than 0,5 µm. The only differences are that the 3-20-1770 sample contains some cracks and some pores in 12-20-1770 are bigger.
The microstructure of 6-20-1770 sample seems similar, only the grain sizes are bigger than those of 3h and 12h, and there are three different phases visible while there are four in 3h and 12h samples. It is consistent with XRD results where the silicide peaks are barely visible. On the other hand, the microstructure of 24-20-1770 is slightly different than others. It includes a lot big cracks and only two phases are visible which is also consistent with XRD results. Moreover, it can be stated that microstructure of 3h MA samples was refined with increasing amount of SiC. The homogeneity of the distribution of the second phase was also improved with increasing amount of SiC. Furthermore, the amount and sizes of the pores were increased in all samples with 20 vol.% SiC. The optical microscope and SEM images of the 3Y-1770 samples are shown in figures 4.21 and 4.22, and the optical microscope and SEM images of the 15Y-1770 samples are shown in figures 4.23 and 4.24, respectively.
Figure 4.21: a),b),c),d) Optical microscope (OM) images of 3h, 6h, 12h, 24h MA 3Y-1770 samples.

Figure 4.22: a),b),c),d) SEM images of 3h, 6h, 12h, 24h MA 3Y-1770 samples.
Figure 4.23: a), b), c), d) Optical microscope (OM) images of 3h, 6h, 12h, 24h MA 15Y-1770 samples.

Figure 4.24: a), b), c), d) SEM images of 3h, 6h, 12h, 24h MA 15Y-1770 samples.
Considering the 3Y-1770 samples, 3h MA’d sample has larger grains than others. 6h MA’d and 12h MA’d samples have similar microstructures, however, 12h MA’d sample has larger grains than 6h MA’d sample. Furthermore, 12h MA’d sample has also some cracks. In these micrographs white areas are W, darker, mottled areas are W + W₂C and grey or dark white areas are W₅Si₃ phases. Spherical black areas are mainly pores and spherical shaped dark grey areas are generally again W₅Si₃ phases. Finally, 24h MA’d sample has an inhomogeneous microstructure but no cracks. Y₂O₃ phase is not visible in these samples. These results are consistent with XRD results.

Figure 4.25: Optical microscope (OM) images of a) 20-24-1680, b) 3Y-24-1680, c) 15Y-24-1680 and SEM images of d) 20-24-1680, e) 3Y-24-1680, f) 15Y-24-1680 samples.
Considering the 15Y-1770 samples in Figs. 4.23 and 4.24, 3h MA’d sample has a fine but inhomogeneous microstructure. 6h MA’d, 12h MA’d and 24h MA’d samples have generally similar microstructures. However; 12h MA’d sample has a finer microstructure than 6h MA’d and 24h MA’d samples. Moreover, 6h MA’d sample has a finer microstructure than the 24h MA’d one. Differently, black or grey spherical shaped areas in these images consist of W₅Si₃ phase and black or grey non-spherical shaped areas consist of Y₂O₃ phase. Generally, these results are consistent with XRD results.

20-24-1680 sample has only two phases which are W and W₅Si₃ phases. 3Y-24-1680 and 15Y-24-1680 samples have similar microstructures with the same composition samples sintered at 1770 °C (3Y-24-1770, 15Y-24-1770) shown in Figs. 4.23-4.25. Also, these results are consistent with XRD result.

### 4.1.2.4. Mechanical properties

Because the samples were too small only the hardness tests were carried out. The figure 4.26 and table 4.2 show the hardness results of the samples.

![Figure 4.26: Hardness results of the samples as a graph](image-url)
Table 4.2: Hardness results of the samples with standard deviations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HV(kg/mm²)</th>
<th>S.Dev</th>
<th>HV(GPa)</th>
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<tbody>
<tr>
<td>10-3-1680</td>
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<td>4,96</td>
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<td>6,85</td>
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<td>740,64</td>
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<td>5,67</td>
</tr>
<tr>
<td>10-12-1770</td>
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<td>35,90073</td>
<td>6,75</td>
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<td>474,4</td>
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25 indentations were done on each sample to obtain the average values and standard deviations. Hardness values are mainly consistent with SEM and XRD results. Generally, the hardness is increasing with increasing mechanical alloying times, also with decreasing grain size, for samples containing %10 SiC. Also the amount W₂C phase is believed to be a variable for the hardness values. Generally, with increasing amount W₂C the hardness increases. On the other hand, 24-10-1680 has very high standard deviation values and the reason for that is that the pore and crack distributions are non-uniform, so different hardness values obtained from a region with pores and cracks and from a region without any pores and cracks increase the value of standard deviation.

Furthermore, 3-10-1770 has a very low hardness value compared to all other samples. The reason for that is that grain sizes are very large. Also, there are large cracks in this sample. 6-10-1770 and 24-10-1770 samples have higher hardness values depending on decreasing grain size. Because of uniformly distributed pores and cracks the standard deviations for these samples are very low. Sintering regime is believed to be effective on grain sizes and distribution of pores and cracks.
On the other hand, all the hardness values of samples containing %20 SiC except 24h MA sample are higher than other samples. This is the direct effect of increasing amount of SiC. However, the reason for the decrease of hardness at 6h MA sample is the larger grain sizes. Furthermore, higher standard deviation values are caused again by non-uniform microstructures. Finally, there is a drastically decrease of the hardness value in 24h mechanically alloyed sample. The reason of that is believed to be the recrystallization of grains. SEM images and XRD result also support the idea of recrystallization. Also, the difference of sizes of Vickers hardness marks can be seen in figure 4.19. Furthermore, the increase of hardness is mainly proportional to the increase in density for all of the samples when other variables are fixed (same sintering regime and same amount of SiC) for samples that do not contain Y$_2$O$_3$ phase. There are two exceptions, namely 6-20-1770 and 24-20-1770. Both of them have higher densities but lower hardness values than 3-20-1770 and 12-20-1770. The reason for that is that they have larger grains and lower amount of W$_2$C phase. Samples containing Y$_2$O$_3$ are harder than the samples which do not contain Y$_2$O$_3$. The hardness of 3Y-1770 samples is increasing with increasing amount of MA except 12h MA’d sample which has larger grains than both 6h MA’d and 24h MA’d samples. On the other hand, the hardness of 15Y-1770 samples is decreasing with increasing amount of MA except 12h MA’d sample which has a finer microstructure than both 6h MA’d and 24h MA’d samples. The reason for very high standard deviation values in 3Y-24-1770 and 15Y-3-1770 samples is the inhomogeneous microstructure they have. Finally, the hardness of the last three samples, which are MA’d for 24h and all sintered at 1680 °C (20-24-1680, 3Y-24-1680 and 15Y-24-1680) is increasing with increasing amount of Y$_2$O$_3$. 
5. CONCLUSIONS

1. The particle sizes of the powders were extremely decreased and the internal strains were increased with increasing amount of mechanical alloying.

2. The densities were increased with increasing sintering temperatures because the diffusivity of the atoms, which is the key factor for sintering, was increased with the increasing temperature.

3. Generally, the densities were increased when the amount of MA was increased.

4. The green densities of the samples containing %10 SiC were increased with increasing amount of MA.

5. The green densities of the samples containing %20 SiC were slightly changed or decreased with increasing amount of MA.

6. Generally, W₂C and W₅Si₃ (or WSi₂) phases were identified in the samples.

7. The amount of W₂C is believed to affect the hardness of the composite. Generally, hardness was increased with increasing amount of W₂C.

8. Hardness depended on grain sizes of sintered composites. It was increasing with decreasing grain size.

9. Grain sizes were mainly decreased with increasing amount of MA.

10. Homogeneity of the mechanical properties mainly depended on the distribution of the pores and cracks.

11. Hardness was increased with increasing amount of SiC.

12. Similarly, samples with Y₂O₃ phase had higher hardness values than samples without Y₂O₃ phase.

13. Samples with Y₂O₃ phase had lower amount of pores comparing with those without Y₂O₃ phase.

14. Grain growth inhibition was achieved only in a few of samples.
15. Finally, this study has a very high technological significance in terms of the progress of Turkish civil and military industry, which is to produce high hardness materials which are potential candidates for kinetic energy penetrators at 300-400 °C lower sintering temperatures than today’s conventional methods, which means; “This study enables a high amount of energy-saving.”
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Selim Coşkun was born on May 20, 1980 and raised in Istanbul. After he had completed his high school education in Istanbul Erkek Lisesi in 1999, where he learned German, in 1999, he was enrolled in the department Metallurgical and Materials Engineering at Istanbul Technical University. He graduated from this department with B.Sc. degree ranking 1st both in his graduation class and in all three departments of the Chemical-Metallurgical Engineering faculty in 2004. After that, he started his graduate education in Material Science and Engineering Department of Istanbul Technical University. Since then, he has been studying for his M.Sc. degree at Institute of Science and Technology in ITU.