FABRICATION OF TiC-REINFORCED IRON BASED COMPOSITE THROUGH MECHANICAL ACTIVATION AND CARBOTHERMAL REDUCTION OF HEMATITE AND ANATASE

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Fabrication of TiC- Reinforced Iron Based Composite through Mechanical Activation and Carbothermal Reduction of Hematite and Anatase". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title for any other examining body or University.

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Witness by

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LIST OF ABBREVIATIONS

BPR	Ball to powder ratio
BSE	Backscattered electron
CTE	Coefficient of thermal expansion
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
GD	Green density
MA	Mechanical activation
MMC	Metal matrix composite
PM	Powder metallurgy
SD	Sintered density
SEM	Scanning electron microscopy
SHS	Self-propagating high temperature synthesis
TD	Theoretical density
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	Description
n	Order of diffraction
ɚ	Wavelength of X-ray beam
2Ɵ	Angle of diffraction
d	Distance between each of set of atomic plane of the crystal
m	Mass
B	Full width at half maximum
l	Scherrer constant
B_r	Line broadening
k	Arrhenius constant
t	Time
Ɉ	Density
v	Volume
A	Standard enthalpy, $\Delta H°$
B	Negative standard entropy change, $-\Delta S°$
ɸG°	Standard free Gibbs energy
H_v	Vickers hardness
d_1 and d_2	Diagonal length of indentation

LIST OF PUBLICATIONS

1. Hassin, M.S., Z. Hussain, and S. Palaniandy (2011) Formation of TiC-Reinforced Iron Based Composite Through Carbothermal Reduction of Hematite and Anatase. Advanced Materials Research, Vol. 173: p. 670-673.

2. Hassin, M.S., Z. Hussain, and S. Palaniandy (2011) Sintering of Fe-TiC Composite Prepared by Carbothermal Reduction of Hematite and Anatase. Key Engineering Materials, Vol. 471-472: p. 670-673.

3. Hassin, M.S., Z. Hussain, and S. Palaniandy (2010) Formation of TiC-Reinforced Iron Based Composite Through Carbothermal Reduction of Hematite and Anatase. Proceedings of International Conference on X-Rays & Related Techniques in Research & Industry (ICXRI 2010), 2^{th} ï 3^{th} June 2010, Langkawi, Malaysia.

4. Hassin, M.S., Z. Hussain, and S. Palaniandy (2011) Sintering of Fe-TiC Composite Prepared by Carbothermal Reduction of Hematite and Anatase. Proceedings of 8^{th} International Conference on Composite Science and Technology (ICCST8 2011), 22^{th}-24^{th} March 2011, Kuala Lumpur, Malaysia.

Fabrikasi Komposit Besi Diperkuat TiC Melalui Pengaktifan Mekanikal dan Penurunan Karboterma Bijih Besi dan Anatas

ABSTRAK

Dalam kajian ini, pengaruh masa kempaan dan suhu pensinteran dalam pembentukan komposit besi diperkuat TiC oleh penurunan karboterma campuran bijih besi (Fe_2O_3) dan anatase (TiO_2) telah dikaji. Campuran serbuk Fe_2O_3, TiO_2 dan grafit dengan komposisi Fe-30%TiC dilakukan pengaktifan mekanikal dalam kempaan bebola bertenaga tinggi dengan masa kempaan yang berlainan (0 jam-60 jam). Analisis pembelauan sinar-X terhadap serbuk kempaan menunjukkan perlebaran puncak Fe_2O_3 dengan kehilangan puncak TiO_2 dan grafit disebabkan penghalusan serbuk dan serapan grafit. Kempaan yang lebih lama menyebabkan pengurangan saiz hablur Fe_2O_3 kepada julat nanometer dan peningkatan dalam terikan dalaman dan ketumpatan kehelan. Selepas 60 jam kempaan, puncak magnetit (Fe_3O_4) muncul dalam corak XRD akibat penurunan separa oleh Fe_2O_3. Serbuk kempaan telah dipadatkan melalui tekanan sejuk pada 200 MPa dan di sinter dalam atmosfera argon pada pelbagai suhu pensinteran (1100°C-1400°C). Suhu yang tinggi semasa pensinteran mengakibatkan pembentukan fasa besi dan TiC seperti yang disahkan oleh pembelauan sinar-X dan analisis penyerakan tenaga sinar-X. Tanpa kempaan pengaktifan mekanikal, tindak balas pembentukan TiC hanya berlaku pada 1400°C semasa pensinteran yang secara tidak langsung mempamerkan penurunan suhu akibat kempaan mekanikal. Komposit Fe-TiC yang disediakan pada masa kempaan yang lebih lama dan suhu pensinteran yang lebih tinggi (50 jam dan 1400°C) menunjukkan ketumpatan dan kekerasan yang tertinggi. Pembentukan Fe_3O_4 dalam serbuk kempaan selepas 60 jam kempaan mengurangkan ketumpatan dan kekerasan komposit Fe-TiC hasil pembentukan liang dalam komposit.

Fabrication of TiC-Reinforced Iron Based Composite through Mechanical Activation and Carbothermal Reduction of Hematite and Anatase

ABSTRACT

In this research, the influence of milling time and sintering temperature on TiC-reinforced iron composite formation by carbothermal reduction of hematite (Fe_2O_3) and anatase (TiO_2) mixture was investigated. Mixtures of Fe_2O_3, TiO_2 and graphite powders with composition of Fe-30%TiC were mechanically activated in a high energy ball mill at various milling times (0 hour-60 hours). X-ray diffraction (XRD) analysis of as-milled powder showed broadening of Fe_2O_3 peaks with disappearance of TiO_2 and graphite peaks due to powder refinement and diffusion of graphite. Longer milling time resulted in a reduction of crystallite size of Fe_2O_3 down to nanometer range and an increment in both internal strain and dislocation density. After 60 hours milling, magnetite (Fe_3O_4) peaks appeared in the XRD pattern as a result of partial reduction of Fe_2O_3. The as-milled powder was compacted by cold pressing under 200 MPa and sintered in argon atmosphere at various sintering temperature (1100°C-1400°C). High temperature sintering resulted in formation of Fe and TiC phases as confirmed by X-ray diffraction and energy dispersive X-ray analyses. Without mechanically activated milling, the reaction to form TiC only occurred at 1400°C during sintering indicating a reduction of temperature has been promoted by mechanical milling. Fe-TiC composite prepared with longer milling time and higher sintering temperature (50 hours and 1400°C) showed the highest density and hardness which is due to the fineness of the composite powder, together with complete TiC and iron phases formation. Formation of Fe_3O_4 in the as-milled powder after 60 hours milling reduced the density and hardness of Fe-TiC composite as a result of pores formation in the composite.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Iron and iron alloys are common metals in everyday use. Industrial development of iron matrix composites has attracted considerable interest due to the composites' advantages in terms of its usefulness in production of inexpensive wear-resistant parts, the possibility of improving its properties through heat treatment and its suitability to be fabricated using various methods including powder metallurgy, conventional melting, thermal plasma synthesis, self-propagating high temperature synthesis (SHS) and carbothermal reduction (Das et al., 2002; Pagounis et al., 1996; Suryanarayana, 2001). Basically iron metal is produced from iron ore or hematite (Fe_2O_3) according to an opportunity to use relatively cheap and abundant raw materials (Brown, 2002). In term of mechanical properties pure iron is a weak material. Therefore it must be alloyed with another element or incorporated with reinforcement phase to increase the mechanical properties. The reinforcement phase must have excellent mechanical properties to produce outstanding mechanical properties of iron composite.

Typically, an iron matrix is reinforced with hard compounds of ceramic particles such as Al_2O_3, Cr_3C_2 and TiC. With such desirable properties as improved hardness and high chemical stability, TiC is the most suitable compound for reinforcement of a soft iron matrix. Furthermore, iron and TiC wet each other very well (Nuilek et al., 2008). In comparison with tungsten carbide (WC), TiC has 33% higher hardness, lower density and higher thermal stability (Razavi et al., 2008).

Thus, TiC can be used in the manufacture of wear-resistant parts, cutting tools, grinding wheels, high temperature heat exchangers, magnetic record heads, turbine engine seals, and electrode or coating materials (Nuilek et al., 2008). Many researchers try to seek for the best solution to produce Fe-TiC composite with low raw material cost and low fabrication cost without compromising the excellent properties of the composite. One possibility is by carbothermal reduction of hematite and anatase through mechanical activation.

In recent years, carbothermal reduction via mechanical activation (MA) has been used to produce metal matrix composite. Therefore, these methods have been comprehensively studied by many investigators who work on extractive metallurgy, materials synthesis and production of nanocrystalline and amorphous materials. For example, carbothermal reduction of ilmenite ($FeTiO_3$) mineral with carbon under argon or vacuum has resulted in the formation of a fine powder consisting of iron metal and titanium carbide (Brown, 2002). The reductions of iron oxides by graphite have been carried out using mechanical activation (MA) of iron oxides and their mixtures with reductant materials (Tahmasebi et al., 2009). Mechanical activation affects the increasing rate of reduction reaction to form Fe-TiC composite.

Mechanical activation (MA) is a narrow field of mechanochemical application for activation of chemical reaction by mechanical energy. The process has been used in mineral processing to produce finely ground particle, increased surface area and improved chemical reactivity of milled material (Pourghahramani and Forssberg, 2006). The oxide material with mechanical milling has been used to synthesis homogenous and nanostructured material. The fraction of milling energy transfer to powder mixture may affect the properties of powder composition by increasing the crystal defect such as dislocation, structural distortion, atom displacement as well as the formation of amorphous phase (Tahmasebi et al., 2009). Thus, chemical reaction could occur in particle contact area and change the composition of powder mixture. Furthermore, the formation of crystal defect may result in improvement of internal strains and then affect the sinterability. Therefore the sintering temperature may decrease.

Reduction of iron oxide with reductant materials such as graphite has been used to produce iron powder through mechanical activation (Tahmasebi et al., 2009). According to Brown and Owers (2004), synthesis of metal powder using abundant oxide raw materials which is relatively cheap offers good prospect. For example, Brown (2002) reported that ilmenite ($FeTiO_3$) was reduced by adding carbon to produce fine powder of iron-titanium carbide mixture powder under argon or vacuum atmosphere. While, anatase (TiO_2) has been reduced with carbon to produce TiC (Razavi and Rahimipour, 2009; Suryanarayana, 2001). The advantages of producing in situ Fe-TiC composites from oxide raw material include the synthesized reinforcement particles have uncontaminated interfaces and can be further tailored during sintering process to promote adequate bonding between the matrix and the reinforcement. In addition, this route of synthesis of composites may be more economical as the reinforcements are not manufactured and handled separately compared to conventional matrix-reinforcement mixing process. However, the above mentioned research works deal with carbothermal reduction of single metal oxide to produce iron, TiC or TiC reinforced iron composite. Carbothermal reduction of metal oxides mixture not has been reported in published literatures.

1.2 Problem Statement

Investigations on mechanical activation of in-situ Fe-TiC composite have mostly focused on synthesizing composite powder from direct raw material such as mixture of Fe and TiC or carbothermal reduction of oxide such as ilmenite ($FeTiO_3$). Production of Fe-TiC composite by direct mixing of iron and TiC powder is relatively expensive and difficult to disperse TiC in iron matrix (Nuilek et al., 2006). In literature, there is no information available regarding the effect of processing parameter on characteristics of Fe-TiC composite powder from reduction of mineral hematite (Fe_2O_3) mixed with anatase (TiO_2). However, carbothermal reduction of hematite or anatase but not a mixture of them is available (Ali and Basu, 2010; Berger et al., 1999; Matteazzi and Caër, 1991; Razavi et al., 2008; Setoudeh et al., 2005a; Tahmasebi et al., 2009). Razavi et al. (2008) made a conclusion that milling of TiO_2 and C without subsequent heat treatment could not reduce the mixture to form TiC. In previous study, Karbasi et al. (2009) has shown in their experimental work that reduction of activated hematite with graphite occur in two distinguished stages either in direct reduction and indirect reduction depending on reduction temperature and reduction reaction of hematite.

1.3 Significant of study

Therefore, instead of ilmenite ($FeTiO_3$), the present work aims to reveal the properties of Fe-TiC composite developed using carbothermal reduction of a mixture of two metal oxides, which are hematite (Fe_2O_3) as iron source and anatase (TiO_2) as titanium source. Relationship between processing parameters such as milling time and heat treatment for sintering and carbothermal reduction of hematite (Fe_2O_3) and anatase (TiO_2) has been investigated. The selection of both raw materials instead of ilmenite is no researchers use the combination of the raw materials in synthesizing Fe-TiC composite until measure the mechanical properties of the composite. Besides, the composition of Fe-TiC composite is easily control compared used ilmenite. The effectiveness of carbothermal reduction of hematite and anatase with aid of mechanical milling need to be investigated because increase internal energy of milled powder will influence the reaction of raw material used and consequently it can be expected that the reaction occurred at lower temperature during sintering. Since the previous study on reduction of ilmenite ($FeTiO_3$) with graphite (Bandyopadhyay et al., 2004; Razavi and Rahimipour, 2009) mostly focused on synthesis of Fe-TiC composite by carbothermal reduction, a study on consolidation is required in order to investigate the properties of bulk composite.

The use of mechanical milling not only can reduce activation energy of oxide material but it also can improve homogeneity and diffusion between hematite, anatase and graphite. As a results, mechanical milling may influence the thermodynamic of raw material mixture, shown in Reaction 1.1, because thermodynamic of raw oxide material calculation does not consider the processing used in fabricating Fe-TiC composite. Thus, a study on milling time is required in order to investigate its influence on formation of iron and TiC through carbothermal reduction of hematite and anatase mixture.

$$Fe_2O_3 + TiO_2 + 6C \rightarrow 2Fe + TiC + 5\ CO \qquad \text{(Reaction 1.1)}$$

There are no researchers reported properties of Fe-TiC composite fabricated using carbothermal reduction of hematite and anatase, properties of Fe-TiC composite after sintering need to be studied since two main processes may take place at elevated temperature which are carbothermal reduction and sintering which will strongly affect the final properties of the composite.

1.4 Objectives

The objectives of this research work are:

1. To study the formation of TiC in iron matrix through carbothermal reduction during mechanical activation of Fe_2O_3, TiO_2 and graphite mixture.
2. To study the influence of milling time and sintering temperature on the formation of TiC-reinforced iron based composite.
3. To characterize properties of Fe-TiC composite produced using Fe_2O_3, TiO_2 and graphite mixture.

1.5 Scope of work

The scopes of this research work are:

1. This research is done to investigate possibility formation of Fe-TiC composite using hematite and anatase as raw material with mechanical milling process.
2. Besides, the usage of oxide material can reduce raw material cost and through carbothermal reduction by mechanical milling also can reduce operating cost compare with other processing such as thermal plasma synthesis and self-propagation high temperature synthesis (SHS).
3. The used raw materials (hematite and anatase) are new raw materials used in fabrication of Fe-TiC composite instead of ilmenite and pure iron and TiC powder.

1.6 Expected outcomes

The research is expected to produce new approach of processing Fe-TiC composite using a combination of mechanical activation and carbothermal reduction of oxide raw material that is low cost material. The effect of processing parameters on the properties of Fe-TiC composite could be explained. Furthermore, the research will also open up new possibility for development of new alternative material to replace the conventional materials used nowadays such as steel or cemented carbide.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Manufacturing of metal matrix composite presents interesting properties since they are very promising materials due to their enhanced properties. Nowadays, research about composite emphasizes the tailored assembly of atoms and particles from the atomic of molecular scale to the macroscopic scale. From the previous research, many types of synthesis were done to prove that the metal matrix composite materials can be produced successfully. There are solid state, liquid state and gases synthesis of chemical reactions which are known as common synthesis in producing metal matrix composite (Koch, 2002). For solid state synthesis, the solid raw material, typically powders are brought into close contact by grinding and mixing and followed by subsequently heat treatment this mixture at high temperature to facilitate diffusion of atom or ions in the chemical reactions. The diffusion of atom depends on the temperature of the reaction and grain boundary contacts. The mixing and grinding usually repeated throughout the heat cycle and affect the mixture of materials and by preparing fresh surface for chemical reactions (Koch, 2002).

This chapter will cover the literature review on introduction of metal matrix composite, selected processes, selected parameters and overview of this research regarding to previous research done by other researchers.

2.2 Introduction of Metal Matrix Composite (MMC)

Metal matrix composite (MMC) is one of composite types which is developed from the idea of combining two basically dissimilar materials with different physical and mechanical properties between matrix and reinforcement to produce superior properties of new material (Das et al., 2002). Besides an advantage of high temperature application, the reinforcement of MMC with ceramic material increases strength, stiffness, wear resistance, high temperature strength, and a decrease in weight (Callister, 2003; Das et al., 2002)

2.2.1 Types of MMC

Metal matrix composite (MMC) is a material which consists of pure metal or alloys reinforced with continuous fibers, whiskers, or particulates (Chawla and Chawla, 2000) which types are shown in Figure 2.1. Based on Chawla and Chawla (2006), the presence of reinforcement in metal matrix composite, for example ceramic reinforcement will change the properties. By adding ceramic reinforcement, it will reduce the coefficient of linear thermal expansion of composite in applications involving electronic packaging. Examples MMC's are the usage of WC/Co composites used in cutting tools or oil drilling inserts and SiC/Al rotor in brakes.

Particulate reinforced composites offer much more outstanding improvement in term of mechanical properties compared with fibers and whiskers reinforcement. The advantages of the particulate reinforced composites are listed as below (Chawla and Chawla, 2006):

I. Simple and low cost of production process.

II. Suitable for most conventional metal processing such as casting and powder metallurgy.

III. Low cost of reinforcement compared to fiber reinforced composite.

IV. Provide isotropic properties compared to fiber reinforced composite.

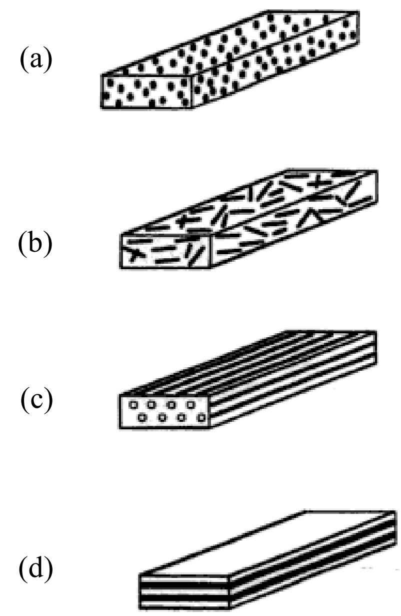

Figure 2.1: Different types of metal matrix composite (a) particles, (b) whiskers/short fiber, (c) continuous fibers and (d) sheet laminate (Chawla and Chawla, 2006)

The particulate reinforcement of Cr_3C_2 embedded in stainless steel composite is attributing to the three dimensional carbide micro networks as a result of diffusion process between stainless steel and Cr_3C_2 reinforcement (Pagounis et al., 1996). As a result, wear resistance of the composite increased. On the other hand, Gómez et al. (2009) reported high hardness of TiCN particles reinforcement in high speed steel composite acting as an interface and creating an appropriate bonding between matrix and the reinforcement. Besides, Fe-Cr-Ni with particulate TiC reinforcement shows improvement of creep resistance of the composite with increasing volume fraction of TiC particulate (Hui et al., 2000).

2.2.2 Fabrication Methods of Metal Matrix Composite (MMC)

Production of MMC normally involves at least two steps including synthesis or consolidation of matrix and reinforcement, and then followed by heat treatment or standard metal forming methods such as forging and extrusion. Methods of fabrication of metal matrix composite may be divided into four types. These are solid phase, in-situ, liquid phase and semi-solid processing. However, only further explanations on first two methods are elucidated here.

2.2.2.1 Solid State Processing

Solid state processing commonly involves bringing the particles or foil into close contact with the reinforcement. Sometimes, solid phase processes yield better mechanical properties. Since there are a lot of problems concerning the distribution of the reinforcement and in obtaining a uniform matrix microstructure, it is necessary to use certain blending routes in order to get a homogenous distribution of reinforcement. Research of Zaberjad and Sajjadi (2007) on Al-Al_2O_3 composite showed segregation effects and formation of intermetallic phase is less compared to in liquid phase process.

Powder metallurgy (PM) method is the most widely used in solid state processing. PM route includes blending, compacting, sintering and/or secondary process as shown in Figure 2.2 (Chawla et al., 2002). For MMCs, blending involves mixing together matrix and reinforcement to produce homogenous distribution.

Compaction involves transformation of bulk powder into desired shape and density preforms.

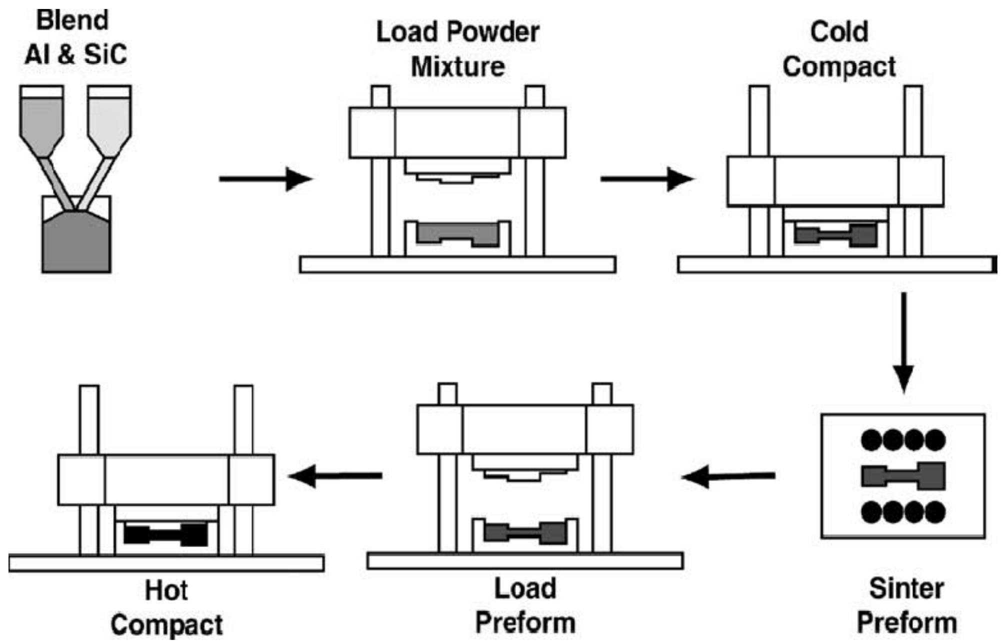

Figure 2.2: Schematic of PM route (Chawla et al., 2002)

Powder metallurgy process is the most widely used method in producing metal matrix composite by using metal powder as raw material. Powder metallurgy process has been used to make semifinished and finished product either from individual, mixed or alloyed metal powders (Angelo and Subramanian, 2008). This method is the most attractive processing route for particulates reinforced iron based composite (Anal et al., 2006). Powder metallurgy process promotes good properties of composite materials in term of compositional flexibility, minimized segregation as well as non compromise quality, cost, precision and productivity of good composite materials (Angelo and Subramanian, 2008).

Based on reviewed article by Das et al. (2002), this method is suitable for the production of TiC reinforced Fe-based composites because it is able to produce composites with wide range of reinforcement volume fraction and size and also homogenous distribution of reinforcement in iron matrix. They also highlight that powder metallurgy process is suitable to produce iron based composite because these materials are difficult to be fabricated by conventional liquid process due to high temperature processing involved. As a result of the efficient process, the composite produced by this method offered high dislocation density, small subgrain size and limited recrystallization resulting in outstanding mechanical properties.

Among powder metallurgy process, hot isostatic pressing is more frequently used to produce iron titanium carbide composite. Compared with casting process, TiC reinforced iron based composite produced by hot isostatic press provide more homogenous TiC in iron matrix (Das et al., 2002). Therefore, the composite has improved fracture properties since full densification of the composite and also reduced machining and trimming cost due to near net shape product. An example of using hot pressing method is shown in preparation of iron based composite done by Pagounis et al. (1996). The authors claimed that the presence of fine particulate TiC in iron matrix formed bonding and contact between the ceramic particles within iron matrix which increase densification of the composite by using hot isostatic pressing.

Another solid state processing is diffusion bonding. This process involves makes a fiber in sandwich mat either similar or dissimilar metals and then heat and pressure is applied (Figure 2.3). The advantages of these techniques are the ability to process a wide variety of matrix metals and fiber orientation and volume fraction can be controlled. However, such method required long processing times, high processing temperature and pressure, giving limitation on producing near net shape composite.

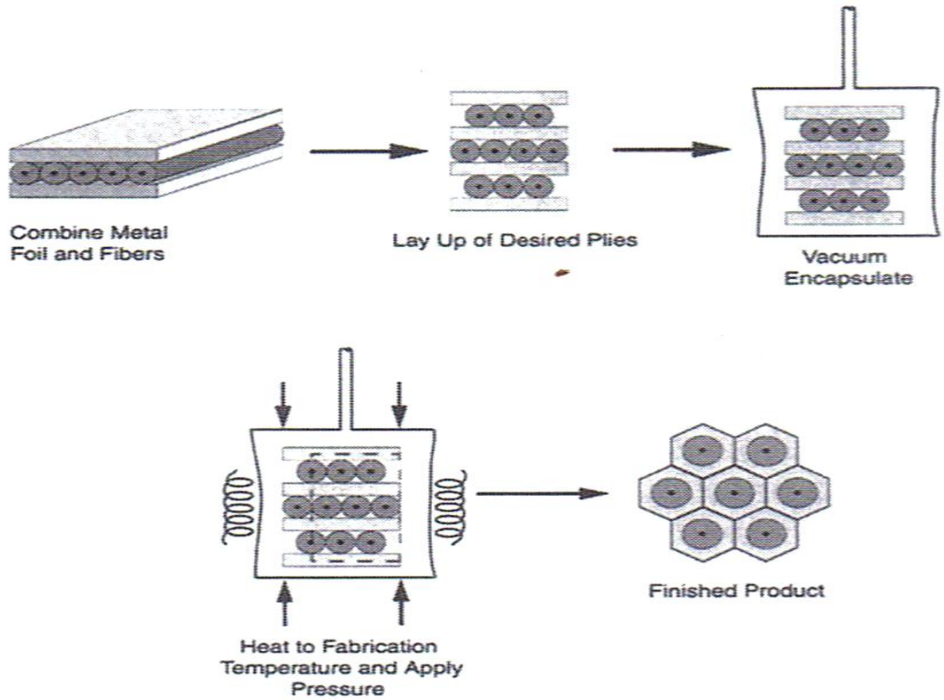

Figure 2.3: Diffusion bonding processing (Chawla and Chawla, 2006)

2.2.2.2 In-situ Process

Usually during blending of metal matrix and ceramic reinforcement powder, which refer to ex-situ route of metal matrix composite fabrication in PM route, agglomeration becomes a major problem as the metal and reinforcement powder are very fine. When high energy impact is subjected to the particles, agglomeration of the reinforcement is avoided. In addition, this technique normally generates problem of contaminated interface in the ex-situ composite and difficulties of producing strong interfacial bonding. This problem can be avoided using new technique of in-situ metal matrix composite processing method. In-situ method involves synthesizing reinforcement in metallic matrix by chemical reaction during mixing and the subsequent processing. According to Tjong (2007) and Tjong and Ma (2000), the formation of both fine in-situ reinforcements and metal matrix during formation of nanocomposite exhibited superior mechanical properties when compared with the conventional processes. The processing route may be subdivided into three classes which are solid-liquid reaction process, vapor-liquid-solid reaction process, and liquid-liquid reaction process.

In order for the reaction to start, minimum energy must be introduced, for example, hot isostatic pressing with thermal energy, after extrusion with thermal treatment or high kinetic energy by mechanical alloying. As a result, uniform distribution of fine particle and thermodynamically stable phase of reinforcement in composite is produced. Another example of in situ composite is the novel TiC and TiB_2 reinforced iron matrix thick films as shown in Equation 2.1:

$$2Ti + C + 2FeB \longrightarrow TiC + TiB_2 + 2Fe \qquad \text{(Equation 2.1)}$$

where TiC and TiB_2 are synthesized (Akhtar, 2008). The reactions are widely used to fabricate Ti-B_4C and Ti-C system as shown in the following reactions:

$$5Ti + B_4C \longrightarrow 4TiB + TiC \qquad \text{(Equation 2.2)}$$

$$Ti + C \longrightarrow TiC \qquad \text{(Equation2.3)}$$

In-situ synthesis offers interesting ways to produce MMC by powder metallurgy. The simplicity of the concept and large variety of possibilities is very attractive. Most in situ composites are particulate or dispersoid reinforced MMCs. The advantages of in situ processing over ex situ processing are:

(a) Thermodynamically stable reinforcing phases

(b) Clean particle-matrix interface with improved wettability

(c) Finer reinforcing particle size

(d) More uniform particle distribution

(e) No difficulties or safety risk in handling fine reinforcing particulate

The in situ production of particulate may also lead to single stage processing technique and can be more cost effective in comparison to conventional processing which generally involve multi-stage processes (Daniel et al., 1997).

2.3 An Introduction to Iron Based Composite

Iron based composite as advanced material has gained attention especially for wear resistant part with lower cost of product (Das et al., 2002; Pagounis et al., 1996). Iron based composite has good possibility to replace conventional cemented tungsten carbide as it has the required properties of abrasion resistance owing to their lower fabrication cost, better fracture properties and heat or corrosion resistance (Pagounis et al., 1996). Iron and its alloys, as engineering materials, are yet to be displaced from the top slot by polymers, ceramics, or other metals in terms of volume of consumption; thus it becomes imperative to further improve their properties.

The outstanding properties of iron based composite give advantages to the type of composite in critical application. Development of iron matrix composite reinforced by hard ceramic particles is to improve wear resistance of base material in order to have the toughness of the matrix and hardness of the ceramic particles in the same material (Upadhyaya, 2000). As mentioned by Berns and Wewers (2001), fracture toughness of hardened steel reinforced by 10-30vol.% of hard particles such as Cr_3C_2, CrB_2 and the eutectic WC/W_2C offer good combination of mechanical properties with wear resistance properties but highly pure hard particles are expensive to produce.

Nowadays researchers try to investigate and develop nanocomposite due to the attraction of outstanding properties as new and novel material. For example, cementite-iron nanocomposite fabricated by hot isostatic pressing method give near full density and it is responsible for significantly enhanced mechanical properties like hardness and wear resistance (Goodwin et al., 1997). The use of TiB_2 as reinforcement in iron based composite is considered as the best reinforcement due to high specific modulus (120 Gpa/Mg m^{-3}) and also stable in liquid iron (Anal et al., 2006). Apart from these, they also state that the reinforcement is also well known for its hardness (3400 Hv), high thermal conductivity (~110Wm^{-1} K^{-1} at 25 ◦C) and a significantly lower coefficient of thermal expansion than steel (~13×10^{-6} K^{-1} for steel and ~7.2×10^{-6} K^{-1} for TiB_2). Indeed, it is a very promising material due to enhanced properties with iron matrix.

Based on the exceptional properties, industries put their attention on the processing and fabrication of iron based composite because of favorable manufacturing costs and performance of the material (Ramesh and Sagar, 1999). As commercialized under trade name such as FERROTiC, TiCALLOY and FERROTITANIT, the primary application of these products, mostly produced by powder metallurgy are for cutting tool, machining and high performance wear resistance part (Terry and Chinyamakobvu, 1992).

2.4 Fabrication Method of Iron Based Composite

There are several synthesis methods of TiC reinforced iron based composite. Based on review paper by Das et al., (2002), various routes that have been used in fabricating and synthesizing Fe-TiC composite are conventional melting and casting, carbothermic reduction, combustion synthesis, and plasma spray synthesis. Each route in producing Fe-TiC composite has advantages and disadvantages based on the application of the composite. Nowadays, researchers try to find the most economical method to produce the composite. This is able to contend with other type of steels already available in the market because the composite has already gained attentions essentially for high engineering application, especially for wear resistance parts. The next subtopic will discuss on various synthesis methods of Fe-TiC composite.

2.4.1 Conventional Melting and Casting route

Conventional melting and casting route basically consist of casting together the liquid matrix material (such as iron and titanium) and solid reinforcement (such as graphite) by conventional melting and casting processes. As reported by Terry and Chinyamakobvu (1991a), to produce Fe-TiC composite, coal as C source was added in molten of Fe-Ti in an induction furnace and complete reaction occurred at 1550°C for 20 minutes. The microstructure of the composite showed a uniform distribution of TiC particles in iron matrix.

Uniform distribution of TiC particles in liquid iron matrix can be achieved depending on various process parameters such as temperature, type of liquid matrix composite, composition, surface properties of dispersoid and ambient atmosphere condition (Terry and Chinyamakobvu, 1992). Good dispersion properties of TiC can be tested by dispersion test, developed by Terry and Chinyamakobvu (1992). The test was developed to provide a qualitative measurement of conditions of dispersion of solid ceramics particles in liquid metals.

However, there are some limitations regarding to casting method due to high processing temperature required to fabricate iron based composite with titanium carbide reinforcement. Besides, this method is only applicable for lower volume faction of TiC reinforcement. The other problem that may occurred during this process is non-uniform distribution of TiC particles in iron matrix related to solubility of TiC (Das et al., 2002).

2.4.2 Carbothermal Reduction via Mechanical Activation Process

Mechanical activation (MA) is a term applied to powder processing in producing nanostructured material which often offer unusual properties compared with materials prepared by other methods (Welham, 1998b). The mechanical activation considerably affected physical and chemical properties of activated powder such as reduction of particle size and heat treatment temperature (Li and Liang, 2008; Welham, 1998b; Welham, 1998c). Application of mechanical activation to facilitate carbothemal reduction of metal oxides has been increasingly studied because this method is able to induce reaction at higher rate or at lower temperature during subsequent heat treatment processing.

Carbothermal reduction of metal oxides is usually carried out at high reduction temperature in suitable condition by considering the equilibrium thermodynamic aspect (Tokumitsu, 1997). Frequently researchers used mechanical activation of the metal oxides in a high energy ball mill followed by a subsequent heat treatment processing or thermal analysis (Chen et al., 1996; Razavi and Rahimipour, 2009; Razavi et al., 2008; Setoudeh et al., 2005a; Tokumitsu, 1997; Welham, 1998a; Welham, 1998c). They concluded that via mechanical activation of metal oxides such as Fe_2O_3, TiO_2, and $FeTiO_3$ with C and Al as reductant material, the carbothermal reduction process with subsequent heat treatment can reduce reaction temperature and increase reduction rate of the metal oxides. As mentioned by Chen et al. (1996), complete reaction of ilmenite ($FeTiO_3$) to rutile and iron can be achieved at 760°C for 30 minutes.

According to Matteazzi and Caër (1991), nanoscale oxide composite has been successfully synthesized by solid state reduction of hematite with reductant agent such as Al, B, Cr and Si added by room temperature ball milling. Carbothermal reduction of ilmenite ($FeTiO_3$) with carbon black via mechanical activation has been successfully conducted due to reduction of formation temperature from range of 1250ºC-1500ºC to 1000ºC-1250ºC (Razavi and Rahimipour, 2009). Besides, Koc and Folmer (1997) showed that when the carbon-coated titania was carbothermal reducted at 1550ºC for 4 hours in flowing argon atmosphere, the obtained titanium carbide powder shows good characteristics such as fine particle size (0.1-0.3 μm), uniform particle shape and loose agglomeration between particles.

2.4.2.1 Mechanism of Carbothermal Reduction Process

Nowadays, carbothermal reduction process becomes important in a study of solid state reduction of iron oxides with its increased industrial application for the production of iron (L'vov, 2000). General reaction of the carbothermal reduction process for oxide materials is displacement reaction as shown in Equation 2.4:

$$MO + R = M + RO \quad \text{(Equation 2.4)}$$

where a metal oxide (MO) is reduced by a more reactive metal (reductant, R) to the pure metal (M) (Suryanarayana, 2004). From the general reaction, Berger et al., (1999) has proposed 3 stages for the carbothermal reduction reaction of TiO_2 according to Equation 2.5 based on Figure 2.4:

$$TiO_2 + C = TiC + 2CO \quad \text{(Equation 2.5)}$$

I. Reaction between carbon and oxygen occurs during carbothermal reduction of TiO_2 by C and CO gases. The reduction reaction takes place on the surface of TiO_2 due to formation of substoichiometric titanium oxide with lower degree of oxygen ($TinO_{2n+1}$) for instance Ti_3O_5 and Ti_2O_3 which resulted from the regeneration of CO gases by conversion of CO_2 to CO on the solid carbon.

II. The oxide particles are the precursors for oxycarbide to form. Formation of TiC_xO_y from Ti_3O_5 and Ti_2O_3 as a replacement of oxygen with carbon. CO and CO_2 is generated which simultaneously acts as a reducing agent.

III. Based on thermodynamic calculations, it is shown that CO has been removed in the formation of TiC.

The carbothermal reduction of metal oxide such as TiO_2 is completed when CO has been totally removed for the preparation of nearly pure TiC based on reaction mechanism of continuous transformation of CO and CO_2 simultaneously as described in Equation 2.6 (Berger et al., 1999; Berger et al., 1993; Razavi et al., 2008):

$$2CO = C + CO_2 \qquad \text{(Equation 2.6)}$$

CO_2 produced then react with C by Boudouard reaction (Equation 2.6) to generate CO.

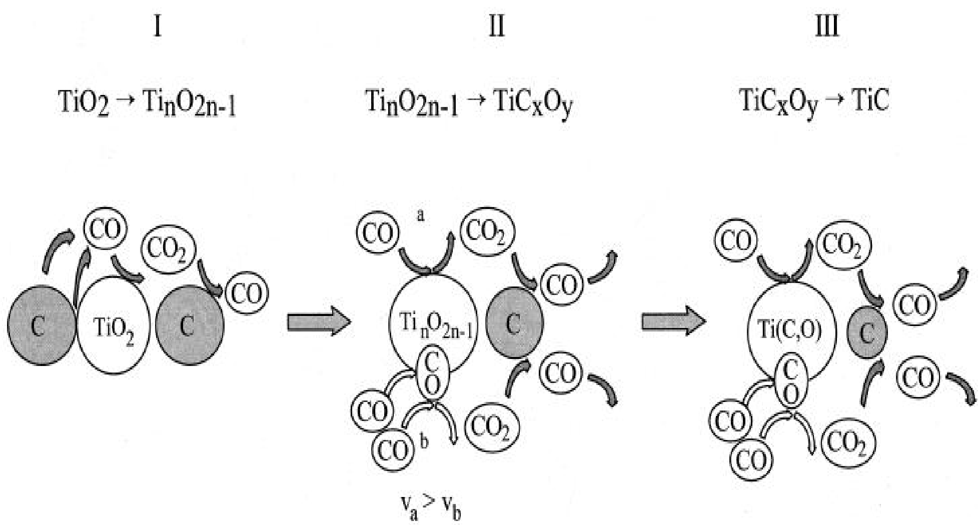

Figure 2.4: Schematic of reaction mechanism of carbothermal reduction of TiO_2 (Berger et al., 1999)

A temperature of an equilibrium formation of carbothermal reduction process can be calculated theoretically based on thermodynamic law. As reported by Razavi and Rahimipour (2009), the equilibrium formation of carbothermal reduction of $FeTiO_3$ in formation of Fe–TiC composite can be calculated and plotted in the Ellingham-Richardson diagram as shown in Figure 2.5. Based on the diagram, the reaction is endothermic and equilibrium reduction temperature of $FeTiO_3$ to TiC is around 1454ºC. However, by aids of mechanical activation, the reduction temperature is reduced to 1000ºC -1250ºC.

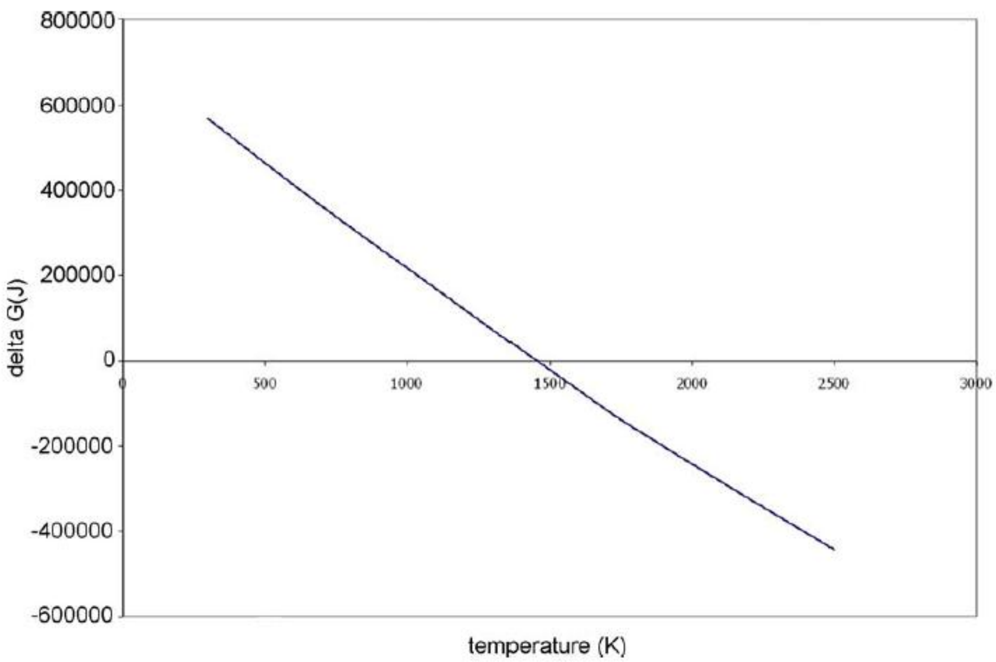

Figure 2.5: The Ellingham–Richardson diagram for the formation reaction of TiC from C and $FeTiO_3$ (Razavi and Rahimipour, 2009)

However, mechanical activation of oxide materials in carbothermal reduction process gives advantages due to chemical reaction and at the same time affects the reduction temperature. According to a number of previous researches, it is proven that mechanical activation by high energy ball mill might affect the activated powder. For example, carbothermal reduction of ilmenite ($FeTiO_3$) with the aids of high energy ball mill and continued with heat treatment or thermal analysis shows a reduction of formation temperature and increase in reduction rate of Fe and TiC (Chen et al., 1996; Nuilek et al., 2008; Razavi and Rahimipour, 2009).

In contrast, without mechanical activation of oxide metals, it shows ineffective carbothermal reduction compared with mechanical activation process. Setoudeh et al. (2005) concluded that un-milled powders of anatase or rutile showed poor reduction reaction during heating at 1400ºC compared with milled powders which showed a complete conversion to TiC. Besides, kinetics of carbothermal reduction of oxide metals such as TiO_2 is affected by reaction temperature, molar ratio of TiO_2/C and TiO_2 grain size (Dewan et al., 2009; Koc and Folmer, 1997).

Continuous study that was conducted by Dewan et al. (2010) has shown carbothermal reduction of ilmenite was faster in hydrogen and occurred at lower temperature compared in argon and helium which reduced at 1000ºC in formation of titanium oxycarbide. Carbothermal reduction of titanium oxycarbide in argon and helium started to form at 1200ºC. They also observed fine grain of metallic iron were uniformly distributed between titanium oxycarbide while course globules were formed during carbothermal reduction in argon and helium.

2.5 Mechanical Activation: High Energy Ball Milling

Mechanical activation (MA) is a generic term of using high energy ball milling such as planetary ball mill, vibatory mill and attritor ball mill in processing of powder materials such as metal oxide powder. However, the way of differentiate between mechanochemical compared to mechanical activated process is chemical