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**Effects of Sintering Process and the Coating
of the Reinforcement on the Microstructure and
Performance of Co-based Superalloy Composites**

by

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fulfillment of the requirements for the degree of

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Abstract

Stellite 712 is an important alloy that has been widely used for high-temperature wear/corrosion resistance. In order to further enhance its wear resistance, Stellite 712 composites were developed with the reinforcement of TiC using powder metallurgy (PM) techniques in this research. Sintering with hot isostatic pressing (HIP) process and HIP'ing powder consolidation process were employed respectively. The reinforcement used was bare TiC or Ni-coated TiC. The emphases of this research were on the effects of the sintering process and the Ni coating for TiC on the microstructure and performance of the developed composites. Calorimetric effects of pure Stellite 712 and mixed composite powders were investigated using the differential scanning calorimetry (DSC) technique, which provided the theoretical basis for designing the sintering and HIP'ing cycles. The microstructures of the specimens were examined using scanning electron microscope (SEM) with energy dispersive X-ray diffraction (EDX). The wear resistance of the materials was evaluated using a pin-on-disc tribometer. It was found that the two PM processes produced identical microstructures but the specimens exhibited different wear resistance. The Ni coating on the TiC particles has improved the fracture toughness of the composites, but lowered the interfacial bonding strength, leading to a reduction of the wear resistance.

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Nomenclature

PM	Powder metallurgy
HIP	Hot isostatic pressing
DSC	Differential scanning calorimetry
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray diffraction
MMCs	Metal matrix composites
FCC	Face-centered-cubic
HCP	Hexagonal-close-packed
UTS	Ultimate tensile strength
SHS	Self-propagating high temperature synthesis
LPS	Liquid-phase sintering
K_{Ic}	The stress intensity factor reaches a critical value
ASTM	American Society for Testing and Materials

Chapter 1

Introduction

1.1 Background and Significance

Wear of materials, one of the most severe causes of material loss in engineering, has been of concern to tribologists for many years. Attempts to reduce wear and develop wear-resistant materials have never ceased. However, there have been few effective methods and materials to combat wear due to the complex mechanisms involved, especially when wear occurs in a corrosive environment and/or at high temperature.

Traditionally, superalloys have been widely used under these application conditions, and they may be identified as belonging to one of three main groups: cobalt base, nickel base, and iron base. They have been employed in various industries such as aircraft, marine, gas turbines, space vehicles, rocket engines, nuclear reactors and so on. In the gas turbine industry, superalloys have been developed for elevated-temperature service, where relatively severe mechanical stressing is encountered, and where high surface stability (oxidation resistance) is frequently required. Many have been developed for utilization for corrosion-resistant applications [1, 2]. Also, other applications where conditions such as corrosion and wear occur simultaneously may not have been adequately considered.

The so-called ultra-high temperature materials, such as intermetallic compounds, refractory metals and alloys, ceramics, and various composite materials have been developed and are expected to surpass the temperature capability of superalloys. Particle-reinforced and fiber-reinforced superalloy composites have been developed in recent years and the mechanical properties, for example, creep resistance, fracture toughness, fatigue strength, impact resistance, of the materials have been extensively studied [3-7]. The main particles present in the particle-reinforced superalloy matrix composites are the carbides, nitrides and/or oxides. Different particles are preferred for different applications [8]. The carbides include WC, SiC, TiC etc. and the oxides are typically Al_2O_3 , SiO_2 and so on [9]. To enhance the surface resistance of superalloys to corrosion, high-temperature oxidation and erosion wear, various coatings have also been developed and used on parts such as gas turbine blades [10-14].

The structure and properties of the interface between a reinforcement and matrix play major roles in the mechanical and physical properties of metal matrix composites (MMCs) [15]. The interface strength depends on the interfacial bonding and fracture toughness. Those composites with weak interfaces generally have relatively low strength and stiffness but high fracture toughness, while a strong interface usually leads to greater strength and stiffness but poorer fracture resistance. These properties are related to the ease of debonding and pulling-out of the reinforcing particles from the matrix during crack propagation [16]. The interface bonding consists of chemical bonding and mechanical bonding. The former occurs when the atoms of matrix and reinforcement are in direct contact and is accomplished by exchange of electrons. The latter arises from mechanical interlocking between the matrix and the reinforcements in the absence of all

chemical sources of bonding [17]. The interface bonding in MMCs is closely related to the nature and surface properties of the reinforcement and matrix, while the fracture toughness is dominated by the thermal stress [18]. Generally speaking, the thermal expansion coefficients of ceramics are lower than those of metals; this difference inevitably results in residual thermal stress at the interface of the ceramic particle and the metal matrix during the fabrication process. In order to enhance the interface bonding and buffer such internal stress, thus reducing cracking at the interface, attempts have been made to modify the reinforcements [16, 19-21]. Modification of the reinforcement surface, such as by coating particles with stable compounds, has been used widely to improve wettability and lower residual thermal stress at the interface [18]. Coatings on reinforcements affect the interfacial bonding of a composite, and are therefore used for improving the composite's properties.

A wide variety of fabrication methods have been employed for MMCs but fortunately they can be classified according to three categories: (i) solid state; (ii) liquid state; and (iii) vapour phase deposition. A fourth classification has also been suggested and is known as *in situ* processing but this may also be considered as a form of liquid phase processing [22]. Powder metallurgy (PM) is one of the solid state processes and is an important method to fabricate the superalloys and their composites to gain the superior mechanical properties required. There are two popular PM methods which are (a) sintering and (b) HIP'ing powder consolidation. The former is simple and easily performed but results in more porosity, while the latter produces higher densification but needs pre-canning of the powder prior to consolidation [23]. In this work a two-stage process involving sintering plus HIPing has been used in an attempt to take advantage of

the best features of both processes. In addition, composites have been prepared by HIP'ing alone, without sintering, so as to provide a base for comparison. Sintering in this work was performed at high temperatures and without applied external pressure and densification or consolidation, involving the closure of porosity, is expected to occur by diffusion controlled processes in the solid state. HIP'ing, or hot isostatic pressing, occurs under the combined action of high temperature and high external pressure and is expected to cause densification through diffusion and plastic flow.

Attempts have been made to develop advanced Co-based superalloy (Stellite 712) composites reinforced with TiC particles for high-temperature wear and corrosion resistant applications. The selection of TiC as the reinforcement was based on its high temperature properties such as the high melting point (3065°C), high hardness (3200 kg/mm²) and low density (4.94 g/cm³) [24]. A coating of Ni on the TiC particles was tried to improve the interface between the alloy matrix and the reinforcement and thus to improve the mechanical properties of the composites. The powder metallurgy composites were fabricated using both sintering plus HIP'ing and HIP'ing techniques, as explained above.

1.2 Objectives

In this research, the emphases were on the effects of the sintering process and the Ni coating for TiC on the microstructure and performance of the developed composites. Ni coating was expected to strengthen the interfacial bonding between the TiC particles and the matrices by changing the nature of the bonding from a mechanical one to a partly

chemical one. Therefore the strengths of the composites should be improved. The following describes the main tasks involved in this research:

1. Fabricating Stellite 712-based composites with bare TiC and Ni-coated TiC particles respectively using the HIP'ing consolidation technique. Different HIP'ing temperatures were used to investigate the effects of the HIP'ing temperature on the microstructure and mechanical properties of the materials.
2. Fabricating TiC/Stellite 712 composites using the sintering technique in conjunction with HIP'ing.
3. Different contents of bare TiC and Ni-coated TiC in the composites were explored in order to obtain the best composition for the developed materials.
4. Examining microstructures of the specimens using scanning electron microscopy (SEM) and x-ray diffraction (XRD).
5. Measuring the densities of the specimens using Archimede's principle and their hardnesses (HRC) using a Wilson Rockwell SERIES 2000 hardness tester.
6. Testing the wear resistance of the specimens using a pin-on-disc tribometer.

7. Analyzing the effects of Ni-coating of the reinforcement on the microstructure and performance of the developed materials.
8. Comparing the microstructures and mechanical properties of the specimens fabricated by the two methods. Optimum sintering and HIP'ing conditions were discussed.

1.3 Organization of the Thesis

This thesis consists of seven chapters.

Chapter 1 is an introduction to the background and significance of this research and the objectives;

Chapter 2 is the literature review on the development, application and properties of Co-based superalloys and their MMCs, as well as information related to this research such as interfacial bonding and PM.

Chapter 3 details the preparation and fabrication of the specimens.

Chapter 4 presents the analysis of the microstructures of the specimens.

Chapter 5 describes the characterization of the mechanical properties of the specimens such as density, hardness and the wear resistance.

Chapter 6 is the discussion of all the results of the experiments.

Chapter 7 provides the conclusions of this research

Chapter 2

Literature Review

2.1 Co-based Superalloys

2.1.1 Cobalt

Cobalt (Co) is a very important metallic element in modern industries. Cobalt was first discovered by Brandt in 1735. The atomic number of cobalt is 27, next to iron (Fe) and Nickel (Ni). Cobalt is a brittle, hard, transition metal with magnetic properties similar to those of iron. Cobalt occurs in the minerals cobaltite, smaltite, and erythrite, and often is associated with the nickel, silver, lead, copper and iron ores from which it is most often obtained as by-product. Cobalt is also present in the meteorites. The melting point of cobalt is 1495°C, its density is about $8.9 \times 10^3 \text{ g/m}^3$ and the Vickers hardness is 1043 MN/m² [25].

Cobalt is available in many forms including foil, pieces, rod, powder, and wire. It can be alloyed with tungsten, nickel, iron and other metals to make Alnico which has useful magnetic properties. Co-based superalloys (Stellite) have good properties for high temperature conditions and other demanding applications. Cobalt can also be used as a trace metal element added to steels and other alloys to improve their

properties. The other very important use of cobalt is as the artificial isotope Co (60) which is a source of gamma rays [26].

2.1.2 Alloys

2.1.2.1 History of development

Historically many commercial Co-based superalloys have been derived from Co-Cr-W and Co-Cr-Mo ternaries which were first investigated by Elwood Hayes at the turn of the last century. He discovered the high strength and stainless nature of binary cobalt-chromium alloys, and later identified tungsten and molybdenum as powerful strengthening agents with this system. When he discovered these alloys, Hayes named them Stellite alloys after latin, Stella, for star because of their star-like luster. Having discovered their high strength at elevated temperature, Hayes also promoted the use of Stellite alloys as cutting tool materials [27].

Following the success of Co-based tool materials during World War I, Co-based alloys were then used from about 1922 in weld overlay form to protect surfaces from wear. These early Co-based “hardfacing” alloys were used on plowshares, oil well drilling bits, dredging cutters, hot trimming dies, and combustion engine valves and valve seats [27].

Later in the 1930s, and early 1940s, Co-based superalloys for corrosion and high-temperature applications were developed in a series of related events involving the Austenal Laboratories and Hayes Stellite Division of Union Carbide. Of the

corrosion resistant alloys, a Co-Cr-Mo alloy with moderately low carbon content was developed to satisfy the need for a suitable investment-cast dental material. This biocompatible material, which has the trade-name Vitallium, is in use today for surgical implants. In the 1940s, this same alloy also underwent investment casting trials for World War II aircraft turbocharger blades, and, with modification to enhance structural stability, was used successfully for many years in this and other elevated-temperature applications. This early high-temperature material, Stellite 21, is still in use today, but predominantly as an alloy for wear resistance [27].

The most recently developed alloys in the Stellite family are those in the 700 series (Stellite 703, 706, 712, and 720). The tungsten in these alloys has been replaced by molybdenum (Mo contents range from 5 to 18%). The 700 series alloys possess excellent corrosion resistance in reducing environments. Molybdenum also partitions to the carbides formed in these alloys to enhance the wear-resistance [27].

2.1.2.2 Typical chemical compositions

Cobalt-based superalloys contain about 50-60% Co, 20-30% Cr, 5-20% W, and 0.1-1% C. The balance of these alloys is made up of nickel, tantalum, iron, niobium, molybdenum, and other elements. Wrought Co-based superalloys contain about 40% Co and increased nickel (20%) for workability, as well as many other element additions [27].

2.1.2.3 Effects of elements alloyed

Carbon (C): The main difference among the individual Stellite wear-resistant alloys is carbon content, which causes changes of the carbide volume fraction. Stellite 3 in which carbon level is 2.4 wt. % has a carbide volume about 30%. The forms of carbides in Stellite 3 are M_7C_3 (chromium-rich primary) and M_6C (tungsten-rich eutectic) types, where M represents the metal components [24]. Stellite 6B contains 1 wt. % carbon in the composition which constitutes approximately 13 wt. % carbides in its microstructure [27]. The microstructures in Stellite B are FCC (face-centered-cubic) cobalt (α -phase) and HCP (hexagonal-close-packed) cobalt (γ -phase) matrix with the $M_{23}C_6$ and M_7C_3 carbides. M_7C_3 is formed at high temperature and transformed into $M_{23}C_6$ at low temperatures. There is some amount of $M_{23}C_6$ precipitated from the cobalt matrix. The main element in these two kinds of carbides is chromium [28].

The size and shape of carbide particles within the Stellite alloys are strongly influenced by cooling rate and subtle chemistry changes. Such differences markedly affect abrasion resistance because there is a distinct relationship among the size of abrading species, the size of the structural hard particles, and the rate of abrasive wear [27].

Tungsten (W): The main function of tungsten in Co-based superalloys is solid solution strengthening of the matrix. The reason is that tungsten has a large atomic size, which can impede dislocation flow when present as solute atoms [27].

Ashwarth *et al.* [29] investigated HS4 containing about 14.4 wt % tungsten. The alloy was made by the HIP'ing process using different temperatures. The phases in the microstructure at 1000°C were the FCC austenitic matrix, $M_{23}C_6$, and Co_2W . When the temperature was 1120°C, the phases were the FCC matrix, $M_{23}C_6$, Co_2W and M_6C . The phases at 1200°C were the FCC matrix, M_6C and $M_{23}C_6$. At the HIP'ing temperature of 1000°C, the hardness of material was higher when the tungsten content was higher.

Chromium (Cr): Chromium has dual functions in Co-based superalloys. It is the predominant carbide former and the most important alloying element in the matrix of the alloys. It provides additional strength for the alloys as a solute and it also resists corrosion and oxidation. The most common carbide in Co-based superalloys is a chromium-rich M_7C_3 type, although chromium-rich $M_{23}C_6$ carbide is abundant in low carbon alloys such as Stellite 21 [27, 28].

Molybdenum (Mo): Molybdenum has the same functions as tungsten in the Co-based superalloys. Its large atomic size can provide additional strength to the matrix. When present in large quantities, it participates in the formation of carbides during alloy solidification and promotes the precipitation of M_6C . Mo also generally improves the corrosion resistance [27]. When 6 wt. % Mo was added to Stellite 6, there were no obvious changes in the microstructure of alloy. The different carbides, such as MC , M_7C_3 , $M_{23}C_6$, M_6C , were all present in the microstructure. A transformation from α -phase with FCC structure to ϵ -phase with HCP structure

occurred when the alloy was water quenched. The amount of the ϵ -phase (martensite phase) was increased in the alloy cooled by liquid nitrogen and the hardness also increased [30].

Silicon (Si): The Tribaloy family of wear-resistant materials contains Lavesphases. Molybdenum and silicon are added to the two Co-based Lavesphase alloys (T-400 and T-800). The contents of molybdenum and silicon are in excess of their solubility limits to induce precipitation of hard and corrosion resistant Laves-phase (CoMoSi or $\text{Co}_3\text{Mo}_2\text{Si}$). Carbon in Lavesphase alloys is as low as possible to ensure that carbide forming elements are free to form the hard Laves phase. The Lavesphase is abundant in Tribaloy family alloys which contain about 35-70 vol. % of this constituent, so it governs all the properties of these materials. The Lavesphase alloys have outstanding abrasion resistance, but the limits are their low ductility and low impact strength [27, 31]. The maximum silicon content in Stellite 6 alloy normally is less than 2 wt. %. An investigation of Stellite 6 alloy containing 5.0 wt. % Si was made by V. Kuzucu *et al.*. The specimens had a dendritic microstructure and contained eutectic carbides such as M_7C_3 , M_{23}C_6 , and M_3C_2 . There were also intermetallic phases such as μ and σ phases and silicon compounds such as CrSi_2 , WSi_2 , and CoSi_2 , which solidified in the interdendritic regions when specimens were quenched into cold water or liquid nitrogen after annealing [32].

Nitrogen (N): As an alloying element, nitrogen is quite benign [33]. The bigger grains that enhanced the tensile and fatigue strength of austenitic stainless

steels can be obtained through high nitrogen additions [34]. The nitrogen would behave in a similar manner in Co-based alloys. The effects of nitrogen additions to Stellite 21 have been explored by Kaelsen [35]. The nitrogen was added to Stellite 21 alloys through nitrogen-high pressure melting (N-HPM) and the maximum content of nitrogen reached 1.34 wt. %. The increase of nitrogen not only increased the second phase contents but also increased the favored Cr_2N second phase over the traditional Cr_{23}C_6 . The results for the microstructure led to the elevation of the incipient melting temperature to above 1260°C .

Titanium (Ti), Nickel (Ni) and Boron (B): Titanium is a carbide former (MC) and can also form intermetallic compounds (Co_3Ti), and Ni_3Ti with sufficient nickel. The functions of nickel are to stabilize the FCC matrix and form the Ni_3Ti intermetallic compound. The main purpose of boron added to Co-based alloys is to increase the stress-rupture strength [27].

Aluminum (Al), Tantalum (Ta) and Yttrium (Y): Aluminum provides oxidation resistance and forms the intermetallic compound (CoAl). Tantalum is a solid-solution strengthener, carbide former (M_6C) and forms the intermetallic compound (Co_3M). Yttrium is added mainly to provide oxidation resistance [27].

2.1.2.4 Microstructures

The microstructure of Co-based superalloys is mainly a FCC matrix and carbides of various types. Strengthening in Co-based superalloys is obtained primarily through a combination of solid-solution strengthening and carbide precipitation. On the other hand, unalloyed cobalt transforms from FCC to HCP (hexagonal close-packed) structure at 417°C when cooled very slowly. In this case, small volumes of HCP structure are created by stacking faults. The tendency to form stacking faults is related with the stacking fault energy and is affected by alloying elements. Elements such as chromium, molybdenum, and tungsten can stabilize the HCP structure and can lower the stacking fault energy. However, elements such as nickel, iron, zirconium, and tantalum can increase the stacking fault energy and stabilize the FCC structure [26].

Carbides are the most important “second phase” in Co-based superalloys. When the carbides have a fine dispersion in Co-based superalloys, they can significantly strengthen these materials. Normally there are three main types of carbides in Co-base superalloys [36]:

(i) $M_{23}C_6$ carbide, where “M” is mostly chromium but can be substituted by tungsten and molybdenum;

(ii) MC carbide, where “M” stands for the reactive metals such as tantalum, titanium, zirconium and niobium;

(iii) M_6C carbide, where “M” stands for tungsten or molybdenum; these carbides form when tungsten or molybdenum content exceeds about 5 at. %.

There are two ways that the carbides increase the strength of Co-based superalloys. One way is that they ($M_{23}C_6$) precipitate at the grain boundaries in Co-based superalloys to decrease the grain boundary sliding, thus prolonging rupture life; the other is that some carbide particles precipitate in the stacking faults to impede dislocation movement, thus strengthening the material. However these precipitates can also significantly decrease the ductility of Co-based superalloys [36].

2.1.2.5. Mechanical properties

2.1.2.5.1 Hardness

Hardness is the resistance of a metal to dislocation motion and hence plastic flow, and it is usually measured by indentation. However, the term may also refer to stiffness or temper or to resistance to scratching, abrasion, or cutting. It is the property of a metal, which gives it the ability to resist being permanently deformed (bent, broken, or have its shape changed), when a load is applied [37]. The greater the hardness of the metal, the greater resistance it has to deformation. Hardness measurement can be defined on the macro-, micro- or nano- scale according to the forces applied and the deformation induced. There are three types of testing method

used in the metals industry; they are Brinell hardness, Rockwell hardness, and Vickers hardness [38].

Stellite 6B is mostly used in hot or possibly corrosive environments where lubrication is difficult or impossible, because it has high resistance to atmospheric oxidation at ordinary temperatures with good resistance to oxidation at elevated temperature. It also has excellent resistance to a variety of aqueous corrosive media. The hardness of Stellite B is 39 HRC for 2 mm thick sheet or 38 HRC for 13 mm thick plate. Stellite 6K is the material used for machine knives for cutting rubber, plastics, wood, leather, food products, synthetic fibers, and paper, etc. Its hardness is HRC 46 for 2 mm thick sheet and 45 HRC for 13 mm and 23 mm thick plate [27].

The hardness test (200 g load) on five Stellite alloys fabricated by powder HIP'ing consolidation was conducted by Ashwarth *et al.* [29]. It demonstrated that the highest hardness level was attained for HS4 alloy, which certainly possessed high contents of carbides and solid solution strengthening imparted by high tungsten contents. HS6 alloy possessed the next highest hardness, while HS7, HS21, and HS31 alloys displayed similar hardness levels and a general trend that reflects the carbon contents in these alloys. The alloys HS4, HS6, HS31 exhibited a general decrease in hardness as the HIP'ing temperature increased owing to coarsening of the second phase particles and grain growth. For HS7, the hardness increase was coincident with the formation of the M_7C_3 phase at the expense of $M_{23}C_6$. These carbides have been reported to have hardness of 2100 and 1650 HV respectively.

The hardness of the cast Stellite 6 containing 6 wt. % Mo was 40 HRC. When the specimen was quenched by water after 950°C for two hours, the hardness was 46

HRC. When the specimen was cooled again in liquid nitrogen for five minutes, the hardness became 49 HRC. The increase in hardness by different heat treatments may be due to the martensitic transformation occurring as a result of rapid cooling and super cooling, or due to the distribution of the carbides in the matrix being more homogeneous [30].

The cast Stellite 6 alloy with 5 wt. % silicon had a hardness of 44 HRC. When samples of the same composition were treated by water cooling and liquid nitrogen cooling after annealing, the hardness was increased to 49 HRC and 50 HRC respectively. The hardness increase of the specimens with the heat treatments was due to the redistribution of carbides. In the as-cast condition the carbides were localized in the interdendritic regions of the alloy but when the alloy was annealed some carbon was taken back into solution. When the alloy was subsequently quenched into water or liquid nitrogen carbides were re-precipitated to form a fine and uniform dispersion in both the interdendritic and dendritic regions of the alloy [32].

2.1.2.5.2 Tensile strength

The yield strength of a material marks the point where the material starts to flow plastically. The ultimate tensile strength (UTS) of a material is the maximum ability of the material to bear load in tension [39]. Co-based superalloys have good tensile strength and high resistance to deformation.

Stellite 6B fabricated by vacuum sintering was investigated and compared with the cast equivalent [28]. The yield strength increased from the 680 MPa to 775

MPa for 5 mm diameter bar. The UTS was improved from 670 MPa to 877 MPa. After deformation and solid solution strengthening, the yield strength was increased to 812 MPa and the ultimate tensile strength was increased to 1091 MPa. The elongation was improved from 3% in diameter strain for the cast specimen to 3.5% of the vacuum sintered specimen. The elongation after deformation and solid solution strengthening treatment was 3.6% in diameter.

The typical tensile strength for Stellite 6B is 1010 MPa and yield strength is 635 MPa at room temperature for 1.6 mm thickness sheet and the elongation is 11%. For Stellite 6K, the tensile strength is 1220 MPa and the yield strength is 710 MPa for 1.6 mm thickness sheet at room temperature and the elongation is 4% [27].

The powder metallurgy Stellite alloys exhibit much higher strengths than their cast equivalents, owing to the increase of chemical homogeneity and a more refined carbide distribution, although they typically have lower ductilities, except HS6 which has about 3~4% ductility after HIP'ing at 1200°C compared with 2% for the cast alloy. For HIP'ed Stellite powders, the carbon content plays a very important role contributing to the ductility of the specimens. The highest ductility of specimens was found with the lowest carbon content. HS4 possessed very low ductility (1%) even at the highest HIP'ing temperature owing to its high carbon content. The Young's modulus is also greater than that of their cast equivalent. The enhanced modulus may be a result of the increased homogeneity in the powder metallurgy materials or increased carbon levels in the HIP'ed powders, resulting in an increase in the volume fraction of carbide phases compared with cast equivalents [29].

Porous-surface-layered cobalt-chromium surgical implants were investigated by Kilner *et al.* who fabricated specimens using the sinter-annealing process [40]. Specimens were found to lack ductility after a sintering treatment and after rapid cooling from elevated temperature. This was due to incipient melting of the interdendritic material which was subsequently retained in the grain boundaries as a brittle solid after quenching. Two methods were found to reduce the amount of this brittle solid and obtain better ductility: (i) heat treatments were modified to include a slow cooling step to the temperature below that at which incipient melting first occurred; and (ii) the carbon content of the alloy may be reduced. Reduced-carbon alloys gave the greatest post-sintering ductility, but showed a lower strength in terms of 0.2% yield strength. The work-hardening rate from the elastic limit to a total strain of about 0.01 to 0.02 partially depends on the volume fraction of the second phase.

2.1.2.5.3 Wear resistance

Wear is the damage to a surface as a result of contact with or without relative motion with respect to another substance. Of many failure modes associated with hardware, wear presents a unique challenge to the designer and developer of mechanical systems. The reduction and control of wear tend to be especially frustrating because of the complexity of the wear process and the lack of a unifying theory or model, such as those used for fracture and fatigue. There are two basic reasons for this; (i) wear is a system property and not a material property; and (ii) wear, apart from its own unique phenomena, generally involves the interaction of

other failure modes (e.g., fracture and fatigue) on a microscopic level and the relative contributions of these various mechanisms change with the wear situation [41].

There are generally three categories of wear: (i) abrasive wear; (ii) sliding wear; (iii) erosive wear. Sliding wear occurs when two surfaces slide over each other. It is called dry sliding wear when it occurs in gaseous environment without lubrication, and lubricated sliding wear when lubrication is present. [42].

It is very important to recognize that wear is a very complex process that is affected by the properties of the materials involved and external parameters such as loading conditions, component geometry, surface finish, temperature, corrosive environment, and presence or absence of lubrication. In some cases, adequate performance might be achieved simply by improving tolerances, modifying the shape of the part, reducing the amount of slip *etc.*. The main guidelines for wear design are: use of lubrication, increasing the hardness of both the components in contact, use of the coatings on the surfaces, optimizing the contact, and so on [41].

Co-based superalloys have been used extensively in wear environments mainly due to their high strength and corrosion resistance. Hard Co-based superalloys rely primarily on the carbides formed in the Co matrix and at the grain boundaries to impart wear resistance. The distribution, size and shape of carbides basically depend on processing conditions. For materials such as the Co-based wear-resistant superalloys with a hard phase dispersed throughout a softer matrix, the sliding wear properties are controlled predominantly by the matrix. Indeed, within the cobalt alloy family, resistance to galling is generally independent of hard-particle volume fraction and overall hardness [27].

Erosion-corrosion tests were performed by Malayoglu and Neville under liquid-solid erosion conditions in 3.5% NaCl liquid medium on HIP'ed and cast Stellite 6 [43]. The results showed that HIP'ed Stellite 6 possessed better erosion and erosion-corrosion resistance than those of cast Stellite 6 and two stainless steels (UNS S32760 and UNS S31603) under the same solid loading (200 and 500 mg/l)(liquid impingement) at the same temperature (20 and 50°C). The material removal mechanism was shown to involve preferential removal of the Co-rich matrix, which was less extensive in the HIP'ed material.

2.1.2.5.4 High temperature properties

Since Co-based alloys have good high-temperature properties, they are frequently used in elevated temperature environments such as gas turbine engines. They are also used for cutting tools where high temperatures are generated at the tool tip due to frictional heating. However it is not easy to determine the mechanical properties of the Co-based superalloys at high temperatures due to the difficulty of designing the test equipment that can operate effectively under rigorous high temperature conditions. Hot hardness may be closely related to the abrasive wear resistance for Co-based alloys. The Stellite 6B hot hardness is 226 HB at 540°C to 102 HB at 870°C. The hot hardness of the other kinds of Co-based superalloys also decreases when the temperature increases. Co-based superalloys also possess excellent resistance to various forms of high temperature attack including oxidation, sulfidation, and carburization [27].

2.1.2.6 Applications

Co-based superalloys are used in the aerospace, automotive, mechanical, chemical and petro-chemical industries. A variety of applications for them include (1) metalworking: deep-drawing tools, calibrating tools, bending and flanging tools, cutting and punching tools, cold extrusion moulding tools; (2) plastics processing: injection moulds and gates, ultrasonic welding sonotrodes, palletizing and crushing tools; (3) chemical plants: valve seats and cones, spray diffusers, scrapers, gear-type pumps; (4) pumps and fittings: plunger for high-pressure pumps, components for valves; (5) special applications: grinding spindles, boring bars, guide rails, gauges and measuring tools, crushing tools, sockets and guide arms, guide and straightening rolls.

2.2 Metal Matrix Composites (MMCs)

2.2.1 Development and applications

A composite is a material having two or more distinct constituents or phases which include a matrix and one or more reinforcements. The matrix normally refers to the phase which is continuous and is often, but not always, present in greater quantities in the composite than the reinforcement. The reinforcements refer to the phases that are added to the matrix to enhance the mechanical properties of the matrix [22].

Composite materials were developed as an alternative for obtaining materials with high stiffness (high strength /modulus and low density) by combining two or more material properties with special interest for aerospace and aeronautical industries [44].

The history of modern composites dates back to the 1940s. During this period, glass fiber reinforced materials were used in radomes, rubbers and flaps. However, lack of stiffness and a low compressive strength of these materials prevented their wide application. During the period of 1966 to 1967, there was a sudden surge in research and development activities on composite materials mainly due to the introduction of high stiffness boron, graphite and aramid fibers. Maturity in the application of composites occurred very rapidly due to enormous expenditure on research and development and also to favorable forecasts for the structural improvements of these materials. Weight savings and lower costs of the composites are also advantageous for their wide development and use [45].

2.2.2 Types of composites

There are three types of matrices in composites: ceramics, metals and polymers. Therefore the composites are also classified into three categories. They are ceramic matrix composites (CMCs), metal matrix composites (MMCs) and polymer matrix composites (PMCs) [22].

2.2.3 Metal matrix composites (MMCs)

Metal matrix composites have been among the key research subjects in materials science during the past two decades. The reinforcing constitute is normally a ceramic, although occasionally a refractory metal is preferred [44].

2.2.3.1 Types of reinforcements

In terms of the microstructures, the metal matrix composites (MMCs) can be subdivided into three categories. They are monofilaments (fibers), whisker/staple fibers, and particulate metal matrix composites. Figure 2.1 shows the three classes of MMCs [46].

Interest in fibrous metal matrix composites mushroomed in the 1960s, with efforts directed mainly on aluminum and copper matrix systems reinforced with tungsten and boron fibers. In such composites, the primary role of the matrix is to transmit and distribute the applied load to the fibers. Volume fractions of reinforcements are typical (~40-80%), giving rise to excellent axial performance. Titanium matrix composites underwent a resurgence of interest after the 1970s. The attention was focused on hoop-wound unidirectional systems. Factors such as thermal fatigue, interfacial chemical stability and thermal shock resistance have become of equal importance to conventional mechanical performance [47].

Discontinuous (short fiber) or particulate reinforced metal matrix composites possess other attributes such as comparatively low cost, high machinability and good workability, compared with continuous fiber reinforced composites [48]. It is widely recognized that the properties of MMCs are controlled by size and volume fraction of the reinforcement phase as well as the nature of the matrix-reinforcement interface: an optimum set of mechanical properties tends to be obtained when fine and thermally stable ceramic particulates are dispersed in a metal matrix [49].

The main reinforcements present in the particulate metal matrix composites are the carbides, nitrides and/or oxide particles for different applications [8]. The carbides include WC, SiC, TiC etc. and the oxides are Al_2O_3 , SiO_2 and so on [9].

2.2.3.2 Fabrication methods

A wide variety of fabrication methods have been employed for MMCs but fortunately most of these can be conveniently classified into one of the following categories: solid state, liquid state, and vapour phase deposition. *In-situ* processing has been described as a fourth approach [22], but it will be described here as a special case of liquid phase processing..

Solid state processing is employed for the solid matrix materials in the form of either particles or foil. In these forms there is a large surface area of high-energy solid-gas interfaces. Solid state processing involves bringing the particles or foil into close contact with the reinforcement by the application of a suitable combination of temperature and pressure. For the foil materials, the methods are usually called

“diffusion bonding”. For the particles, they are referred to as powder metallurgy methods [22]. Diffusion bonding is an expensive process and generally used in the limited shapes and formed into the fiber reinforced composites or the “sandwich structure”. The powder metallurgy method is especially suited for the production of discontinuous fiber, whisker or particulate reinforced metals. The components are simply mixed and then pressed, often at an elevated temperature, to achieve consolidation. If pressure is applied at ambient temperature and then removed prior to high temperature exposure then the process is known as sintering and densification occurs by a diffusion controlled process. If high pressure and high temperature are applied simultaneously then the process is known as hot pressing or hot isostatic pressing (HIP) [9]. In this case densification occurs by a combination of diffusion and plastic flow, the latter being controlled by dislocation motion.

Liquid state processing deals with matrices in a temporary molten condition when they are introduced to the particulate, whisker or discontinuous fiber reinforcements. There are different types of liquid state processing such as melt stirring, compo-casting, infiltration, squeeze casting, directional solidification and so on [22].

Deposition processes typically involve atomizing a melt and introducing the reinforcement particles into the spray of fine metal droplets and then the metal and the reinforcement particles are co-deposited on to a substrate. Many other deposition techniques include chemical or physical vapour deposition, electroplating, sputtering and plasma spraying, but they have not been widely employed [22].

In-situ process involves forming reinforcements by an in-situ reaction. *In-situ* means “at the same site and position” [9, 50]. For example, the *in-situ* TiC reinforced Hadfield steel composites were fabricated by adding titanium filings into the melted ductile iron and low carbon steel at temperature 1450~1600°C. The experiments were conducted in an induction furnace under argon protection. The TiC volume fraction was 2.5%, 5% and 10% [51]. 5%, 10% and 16% TiC reinforced Fe-Cr-Ni composites were also made by adding the desired ratios of titanium and graphite powders into the melted alloy [52]. In another form of in-situ processing, eutectic alloy compositions are melted and then caused to solidify in a directional manner so that growth of two or more phases occurs to form unidirectional and parallel laths or plates.

2.2.3.3 Microstructures of MMCs

The distribution of the added ceramic particles is of great importance to the mechanical properties of composites. Clusters of reinforcing particles, resulting from insufficient mixing or electrostatic phenomena, deteriorate the properties of the materials by serving as sites for micro-porosity and crack initiation. On the other hand, a homogeneous distribution of a reinforcement ensures isotropic properties and uniform distribution of stresses into materials. In the typical microstructures of HIP'ed composites, the reinforcement distribution is inherently uneven because of the relatively coarse matrix powder size. The ceramic reinforcements surround the coarse matrix powder and local agglomeration takes place at the junctions of three or four

matrix particles. On the other hand, the use of fine matrix powder size results in a more uniform reinforcement distribution [53].

For the cast metal matrix composites, there are some factors to consider for obtaining a homogeneous distribution of reinforcement by stirring techniques. The particle density, size, shape and volume fraction will influence the reinforcement settling rate. Surface properties of particles will affect the ease or difficulty of wetting achieved. The rheological behavior of the matrix alloy melt and the reinforcement slurry is influenced by reaction of the particles with the liquid, and with each other. Gas entrapment during particle incorporation or mixing will lead to poor distribution when particles attach to gas bubbles and porosity is increased. In this case, mixing parameters must be selected to produce a uniform particle distribution in the radial and axial directions. During solidification, settling time must be minimized. In general, the reinforcement particles occupy interdendritic regions or between secondary dendrite arm spacing; therefore the finer the spacing or the finer the matrix grain size gains, the better the particle distribution [54].

The *in-situ*-grown composites show clean interfaces, strong interfacial bonding, a uniform spatial distribution of particles and a narrow particle size distribution. The geometry, size and spacing of second phase can be controlled by controlling the cooling rate and temperature gradient. Further structural changes are affected using secondary process such as mechanical working, infiltration and controlled solidification [55].

2.2.3.4 Mechanical properties of MMCs

2.2.3.4.1 Relative density

Relative density is a very important index for composites and it has a great effect on the other mechanical properties of the MMCs. The densification of the MMCs is expressed by the relative density which uses the measured density compared with the theoretical value. The measurement method is based on the use of Archimedes' principle according to MPIF Standard 42 [56].

The densification behavior of the TiC-Ni composites made using self-propagating high-temperature synthesis (SHS) reaction was investigated by Choi *et al.* [57]. The composites were prepared by two routes. The first method involved consolidation during the SHS reaction and the density of the products was relatively low, at about 90% of theoretical density. The second method was consolidation after SHS reaction and densification rates were reduced due to the excess carbon in the combustion products of titanium carbide. The densities of liquid-phase sintered specimens were more than 97% of the theoretical density.

Presson *et al.* studied TiC reinforced iron matrix composites produced by two manufacturing methods. One was self-propagating high temperature synthesis (SHS), the other was liquid-phase sintering (LPS) [58]. LPS was found to be more effective due to easier process control and the process yielding a more homogeneous material. Both LPS and SHS produced a material with a relatively high degree of porosity. The porosity in the LPS experiments could be decreased by varying the process

parameters, such as having a protective atmosphere and increasing the compaction pressure, but this is not possible in the SHS process.

An investigation was made by Mei *et al.* on the effect of size of TiC on the properties for the Ni₃Al-matrix composites [59]. It showed that the densities reduced with the increase of the TiC size. The relative density was decreased from 99% for 5 µm of the TiC particle size to 96.5% for the 35 µm of the particle size. The reason could be that the larger particles of TiC exhibited poor wetting with the liquid matrix.

The NbC and TaC reinforced high-speed steel matrix composites produced using powder metallurgy methods were studied by Gordo *et al.* [60]. When the sintering temperature was 1190°C, the relative density decreased while the carbide content increased. But the relative density was increased to almost 100% at the sintering temperature of 1230°C. The reason was clear that the former temperature was not high enough to produce sufficient liquid phase to promote proper sintering and achievement of the maximum relative density for the base material. The higher content of carbides could cause more porosity in the composites and decrease their densities at the two sintering temperatures.

2.2.3.4.2 Hardness

Hardness is also an important property for MMCs, but it is more complicated for the MMCs, because there are at least two phases present in the microstructures, which usually have quite different hardness values [61].

The Al/TiC composite was investigated by Mitra *et al.* [62]. In that research, the specimens were held at 640°C for varying lengths of time to study the effects of heating on the microstructure and mechanical properties. The average macro-hardness changed from 60 VHN for the as-received specimen to 270 VHN after 500 hours exposure at 640°C when the TiC particle size was 0.7 μm . However when the size of TiC was 4 μm , the macro-hardness was lower than that of Al/TiC specimens and no significant effect due to the heating treatment was observed. The macro-hardness was 35 VHN for the as-received specimen to 45 VHN for the specimen exposed to 350 hours at 640°C. The high-temperature hardness for the TiC particle size of 0.7 μm was also measured. The heat-treated composites again were much harder than the as-received material over the entire temperature range tested. At all temperatures, the micro-hardness increased with the time of the heat treatment at 640°C.

The TiC reinforced ferrous composites produced using solidification processing were investigated by Rai *et al.* [63]. The contents of TiC were 8, 15 and 25 vol. % respectively. The macro-hardness for the composites changed from 500 VHN at 8 vol. % to 550 VHN for 15 and 25 vol. % TiC contents. The micro-hardness for the matrix, Fe₂Ti and TiC particles were obtained as 500, 1520, and 2300 VHN respectively where Fe₂Ti was formed by the reaction of iron and TiC.

For the Al₂O₃ (15 vol. %) reinforced Al MMCs, the composite fabricated with by extrusion attained a higher Vickers hardness (103 HV) than the non-reinforced Al alloy (83 HV). The composites in the “as quenched” and “peak aged” conditions obtained lower Vickers hardness than the Al alloy counterparts [64]. When the Al₂O₃ reinforced particle volume increased in the Ni-based composites produced by HIP,

the Vickers hardness gradually increased from 80 HV for the pure alloy to 180 HV at the 45 vol. % Al_2O_3 content [65].

Research was made by Xu *et al.* on the composite coating of the WC particulate reinforced Ni_3Al produced by a laser powder deposition method [66]. The results showed that the micro-hardness distribution of the composite coating was uniform, and the average value, $\text{HV}_{0.1}475$, was much higher than the mild steel substrate ($\text{HV}_{0.1}174.4$) and the Ni_3Al -Fe coating ($\text{HV}_{0.1}195.6$). It was also higher than the common casting or powder metallurgy Ni_3Al (HV 187-224), Ni_3Al -Cr (HV260-289) and Ni_3Al -Fe alloy (HV 196). This should be mainly attributed to the WC particulate reinforcement.

2.2.3.4.3 Tensile strength

Metal matrix composites can obtain higher tensile strengths by adding high strength reinforcement to the matrix. However the interface between the strong reinforcement and the matrix also plays a very important role if the desired properties are to be attained. This is because the load acting on the matrix has to be transferred to the reinforcement via the interface [22]. Many studies on tensile strengths of the TiC reinforced metal matrix composites have been carried out. The following will describe several studies in this field.

Cast Al matrix composites were fabricated with TiC and TiB_2 reinforcements in 10 vol. %. The composites with the TiC and TiB_2 reinforcement all obtained higher ultimate tensile stress compared with the un-reinforced Al. The UTS for 10 vol. % is

105 ± 6 MPa and almost double that of the pure Al with 66 ± 3 MPa. The UTS for TiB_2 reinforcement also reached 80 ± 5 MPa. However the ductility of the composites was unavoidably decreased to $25 \pm 3\%$ for TiC and $18 \pm 2\%$ for TiB_2 , compared with the pure Al $37 \pm 2\%$ [67].

Al metal matrix composites with TiC reinforcement were fabricated using a flux-casting technique by Karantzalis *et al.* [68]. The ultimate tensile strength showed the same trend as the cast counterparts mentioned above. The TiC reinforcement increased the UTS, compared with the pure Al and the UTS also increased with the increase of the TiC volume in the composites. Similarly the elongation decreased with the increase of the TiC volume content.

The influence of the particle size on the strength was investigated by Pagounis, and Lindroos [53]. The composites reinforced with coarse ceramic particles showed higher tensile strength and this effect was more evident in the low reinforcement volume fraction. It appeared that fine particles tended to agglomerate and this affected the tensile behavior of the composite. In regions of local reinforcement clusters the matrix might have insufficient ductility to redistribute the highly localized stresses; therefore, the composite failed before being able to reach stable plastic flow and normal ultimate strength. In composites with a higher reinforcement volume fraction, the difference in the ultimate tensile strength was not significant because the extent of local agglomeration of the particles may be similar, and another possible reason was the presence of porosity in the composites.

2.2.3.4.4 Wear resistance

Wear-resistant metal matrix composites have been developed by reinforcing the matrix with hard materials such as carbides, borides and nitrides and so on. Wear resistance of the composites depends on the amount, size and distribution of hard particles as well as the hardness and fracture toughness of both constituents and the bond between them [69]. The following examples show the wear resistance properties of metal matrix composites reinforced by different ceramic particles.

TiC-reinforced Al metal matrix composites were developed by Shipway *et al.* using a novel liquid route [70]. The sliding wear behavior for these composites was studied as a function of load and particle volume fraction, compared with a commercially available SiC-reinforced composite. In all cases, TiC particle reinforcement resulted in a reduction in wear rate and an increase in the load under which the transitions from low rate wear to high rate wear occurred. In the low rate regime, the wear coefficients of all the specimens in both the reinforced and unreinforced states were similar. Since the TiC-reinforced composites were the harder (due to the grain refining action of TiC), they exhibited the lower wear rate (lower than that of the SiC-reinforced composite). An increase in load generally resulted in an increase in wear rate of both the composite pin and the counterface. Increasing the volume fraction of particles in a composite reduced its wear rate but generally increased the wear rate of the counterface.

Effects of SiC particle reinforcement on the un-lubricated sliding wear behavior of ZA-27 alloy composites were studied by Sharma *et al.* [71]. The results

showed the phenomena in most engineering metals and materials. An approximately linear relationship existed between hardness and wear resistance, showing that wear resistance increased with hardness, or in other words, wear rate decreased as hardness increased. The hardness increased with an increase in the SiC content in the composites. In contrast the wear rates decreased as the hardness increased. Therefore the composites with SiC particles exhibited superior wear resistance due to the high hardness of SiC, which implied that hardness was directly proportional to wear resistance.

Tu *et al.* tested the friction and wear behavior of Cu-Fe₃Al PM composites on a block-on-ring test machine [72]. The average micro-hardness of the composites increased with the increase of Fe₃Al reinforcement content and the coefficient friction decreased under the same conditions. Meanwhile, the wear rates of the composites decreased. However, the experiments also showed that friction was almost the same when the sliding distances increased for the composite with 18% Fe₃Al, although the wear rate continued to decrease. This meant that the friction could be a reason, but not the only reason, to improve the wear resistance property of the composites.

Sliding wear behavior of TiC-reinforced steel matrix composites at elevated temperature was investigated by Degnan *et al.* [73]. The unreinforced steel was BS970:070M15 steel and the reinforced composite contained 5 wt% TiC using SHS with particle size of 5-10 μm . At room temperature under a load of about 300 N, the wear rate of the reinforced composites was a factor of 1.5-2 times lower than that of the unreinforced steel. At higher loads both materials exhibited significantly higher wear rates, which indicated the operation of a more severe regime of wear. At the

temperature of 250°C, the transition to the more severe regime was observed, which occurred at a substantially higher load for the TiC-reinforced steel than for the unreinforced material. At 500°C, wear at the interface was dominated by oxidation and both materials exhibited mild wear (characterized by extremely low wear rates) over the range of loads considered in the experiments.

Kumar *et al.* investigated the effect of interfacial characteristics between SiC_p and Mg/Al metal matrix on wear, coefficient of friction and microhardness [74]. The types of SiC_p were uncoated, Ni-coated, Cu-coated and dynamically oxidized. The preheat temperatures were 500, 550, 600 and 650°C. The experiments used the interparticle distance as the index of the interfacial properties. The bigger interparticle distance meant the better interfacial strength of the composites. Coatings of Ni or Cu on SiC reinforcements generally lead to good quality interface characteristics in Al matrix composite as both microhardness and wear properties were improved. Oxidized SiC reinforcements behaved in a complex manner in influencing the interfacial characteristics in Al/Mg matrix composites, possibly due to the formation of a reaction product at the interface.

2.2.3.4.5 Fracture toughness

The stress intensity factor is the magnitude of the ideal-crack-tip stress field (a stress-field singularity) for a particular deformation mode in a homogeneous, linear-elastic body. As the stress intensity factor reaches a critical value (K_{Ic}), unstable fracture occurs. The critical value of the stress intensity factor is known as the

fracture toughness of a material. The fracture toughness can be considered as a limiting value of stress intensity just as the yield stress might be considered as the limiting value of applied stress. Fracture toughness varies with specimen thickness until limiting conditions (maximum constraint) are reached. The plane strain fracture toughness, K_{Ic} , is dependent on specimen geometry and metallurgical factors. The evaluation of K_{Ic} can use the following formula [75].

$$K_{Ic} = \frac{3PLYa^{1/2}}{2BW^2}, \quad (2-1)$$

where K_{Ic} is the critical value;

P is failure load;

L is the loading span;

B is the specimen thickness;

W is the specimen width;

Y is a compliance factor;

a is pre-crack length.

ASTM Designation E-399, Standard Method of Test for Plane Strain Fracture Toughness of Metallic Materials, sets forth accepted procedures for determining this value [76]. A high fracture toughness means high resistance to crack extension and fracture. There are few studies on the fracture toughness of the MMCs.

The fatigue crack-growth in shape memory NiTi and NiTi-TiC composites was studied by Vaidyanathan *et al.* [77]. The volume content of TiC in the

composites was 10% and 20% respectively. The overall fatigue crack-growth characteristics were similar between the unreinforced and reinforced materials. However, a slight increase in the threshold for fatigue crack initiation was noted for the composites. The fracture toughness, as indicated by the failure stress intensity factor range, was found to be similar for all the materials.

The crack-growth resistance of the graded SiC particulate reinforced Al composites was higher than that of the homogeneous counterparts, which meant that the former had a higher fracture toughness K_{IC} than the latter [78]. The finer TiC reinforcement particles obtained higher fracture toughness in Ni3Al matrix composites and had a better crack-growth resistance [59].

2.3 Interface

2.3.1 Definition

There is a distinct interface or inter-phase region separating the two distinct materials in all types of composites. Composites rely on the inter-phase region to transfer properties (e.g. stress) from the matrix to the reinforcement and thus the behavior of interfaces critically determines the performance of the composites themselves. It is of great interest and very important to investigate the properties of interfaces and develop stronger interfaces for composites [79].

2.3.1 Wetting

Wetting of the reinforcement by molten metal, an important aspect in MMCs synthesis, is favored by the formation of strong chemical bonds at the interface. The presence of oxide films on the surfaces of molten metal and the absorbed contaminant on the reinforcement surfaces generally lead to non-wetting of reinforcement with molten metal. The wettability of a solid by a liquid is indicated by the contact angle, as shown in Figure 2.2. The contact angle θ between solid, liquid and gas/vapor is related by the Young-Dupre equation [80],

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}, \quad (2-2)$$

where γ_{lv} is the surface tension of the liquid metal,

γ_{sv} is the surface energy of the solid,

γ_{sl} is the solid/liquid interfacial energy.

Based on the above equation, the contact angle, θ , can be decreased by increasing the surface energy of solid, γ_{sv} , decreasing the solid/liquid interfacial energy, γ_{sl} , or by decreasing the surface tension of liquid, γ_{lv} . The liquid is said to wet the solid when $\theta < 90^\circ$, that is, when $\gamma_{sv} > \gamma_{sl}$ [80].

2.3.3 Interfacial bonding

Once the matrix has wet the reinforcement, it is in intimate contact with the reinforcement and bonding occurs. In general, there are four types of interfacial bonding in composites: mechanical bonding, electrostatic bonding, chemical bonding and reaction or interdiffusion bonding [22].

Mechanical bonding is a mechanical interlocking or keying of two surfaces to lead to a reasonable bond. The mechanical bond is most effective when a force is applied parallel to the interface, in other words, the shear strength may be considerable [22].

Electrostatic bonding occurs between the matrix and the reinforcement when one surface is positively charged and the other negatively charged. This leads to an electrostatic attraction between the components of the composite, which depends on the difference of charges on their surfaces. Electrostatic interactions are short range and are only effective over small distances, of the order of atomic dimensions [22].

Chemical bonding is the bond formed between chemical groups on the reinforcement surfaces. The strength of chemical bonds depends on the number of bonds per unit area and the type of bond [22].

Reaction or interdiffusion bonding is caused by the interdiffusion of the atoms or molecules of the two components in composites. For systems involving metals and ceramics, the interdiffusion of species from the two components can produce an interfacial layer of different compositions and structures from either of the components. The interfacial layer will also have different mechanical properties from

either the matrix or reinforcement and this consequently greatly affects the characteristics of the interfaces. For a given system, more than one bonding mechanisms may be operative at the same time and the bonding mechanisms may change during the various production stages or service. The type of bonding varies from system to system and depends on details such as presence of surface contaminants or added surface active agents (coupling agents) [22].

Particles-matrix bonding in Al-TiC MMCs has been characterized by Kennedy and Wyatt measuring the changes in elastic modulus with increasing plastic strain [81]. Data showed that the rates of damage accumulation in cast composites were the lowest; damage initiation stresses were the highest and hence interfacial bonding was the strongest, compared with the counterparts fabricated by several other methods. This was due to the attainment of intimate contact between Al and TiC, through the use of a flux that dissolves surface oxides, and the nucleation of solid Al on the particle surface. Intimate metal-ceramic contact was not so easily achieved in composites manufactured from metal powders, owing to the presence of oxide films on their surfaces. The shear stress was increased during solid state consolidation process and this increase improved the particles-matrix interface strength due to more effective break-up of the oxide barrier.

Reactions in 10% wt. % TiC/Al metal matrix composites have been investigated by Kennedy *et al.* [82]. The specimens were heated between 600°C and 900°C for 48 hrs and held at 700°C for periods up to 240 hours. A maximum reaction rate was observed at 700°C and at this temperature the reaction products formed were large Al_3Ti precipitates in the bulk of the matrix and Al_4C_3 blocks at the particle-

matrix interfaces. At 900°C, TiC appeared to be stable in Al. The reaction kinetics for TiC followed a parabolic rate indicating a diffusion-controlled process. The rate of TiC dissolution was very much less than that for SiC in pure Al.

Chen and Beraun built a simple model for interfacial phase growth in metal matrix composites [83]. The simple equation is expressed as follows.

$$h = a \ln(bt + c), \quad (2-3)$$

where h is the thickness of a reinforcement-matrix interfacial layer;

$a = \sqrt{D/\alpha}$, D is the diffusion coefficient and α is equilibrium constant;

$b = \frac{\rho_A}{\rho_B} \alpha^2$, ρ_A is the density which is the diffusion controlling

constituent;

This model was used in several composites such as SiC/Ti-6Al-4V and SiC/Ti MMCs and it was able to predict the thickness of the reinforcement-matrix interfacial layer in these composites.

2.3.4 Methods for improving the interface bonding

The techniques used to improve metal-reinforcement wettability include metallic coatings on the reinforcements, addition of reactive elements such as magnesium, calcium or titanium, to the melt, or heat treatment of particles before

addition. The improved wettability of reinforcements benefits the interfacial bonding between the metal matrices and the reinforcements [80].

2.3.4.1 Addition of reactive elements

Leon *et al.* investigated the effects of alloying elements on the wettability of TiC in commercial aluminum alloys (1010, 2024, 6061 and 7075) at 900°C using a sessile drop technique [84]. The contact angles between the TiC and the aluminum were measured. The decreasing order of contact angles was $6061 < 7075 < 2024 < 1010$ in both argon and vacuum atmospheres, which meant that the wettability of the TiC in these alloys increased $1010 > 2024 > 7075 > 6061$. The contact angles would reach equilibrium as the time continued. The drop radii for all these alloys were also measured and found to increase when the contact angle decreased. Furthermore, evaporation of Zn and Mg under vacuum conditions contributed to the rupture of the oxide film covering the aluminum drop and thereby improved wetting and spreading.

2.3.4.2 Coatings

Coating of reinforcement is one of the successful techniques adopted to prevent the interfacial reaction and enhance increase the wetting of the reinforcement. Coatings also prevent the diffusion of liquid metal into the reinforcements. Diffusion types of coatings applied to reinforcements are metallic, ceramic, bilayer or multilayer coatings containing metals and/or ceramics and system specified. Some of

the important coating techniques are chemical vapor deposition (CVD), physical vapor deposition (PVD), thermal spraying, Sol-gel process, electrolytic, electro-less and cementation methods [80].

For cast composites, the first and most important step is the transfer of solid particles into the melt. Particles can be immersed into the melt depending on two conditions which are the contact with the melt (by replacing S-G and G-L interface with S-L interfaces) and the favorable transfer energy. The total changes in energy of the system are:

$$\Delta E_t = \sum_{i=1}^n \Delta E_i, \quad (2-3)$$

where ΔE_i are the contributions of changes in surface, potential, kinetic, buoyancy and thermal energies. Figure 2.3 shows the change in energy for the immersion of particles into the melt. Ni coating on a graphite particle (when $\theta = 60^\circ$) reduced the energy for complete immersion of single-graphite particles by ~ 10 ergs over that for an uncoated particle ($\theta = 157^\circ$) [85].

Leon and Drew investigated the wetting behavior and interfacial phenomena of plain and nickel-coated alumina and silicon carbide with liquid aluminum at 800°C [86]. The coatings applied to ceramic plates improved wettability with aluminum, resulting from the dissolution of the coatings in the liquid drop. The non-wetting condition of the as-received ceramics was overcome and the contact angles decreased from 87.3° for bare SiC to 12.2° for Ni-coated SiC and from 115.2° for bare Al_2O_3 to

11.6° for Ni-coated Al_2O_3 . With the addition of nickel as a coating, there was no dissolution of SiC in the alloy, and interfacial carbides did not appear.

2.4 Powder Metallurgy Technique

2.4.1 Introduction

In the late 1960s, powder metallurgy (PM) was almost synonymous with a low-cost manufacture technique for mass produced precision parts. Within several years, a series of completely new technologies evolved to what has become known as powder metallurgy of superalloys. Inert gas powder atomization, sintering, hot isostatic pressing, isothermal forging, and oxide dispersion strengthening were established as important and often novel steps in superalloys processing. The main driving force for all these new developments has been to meet the demands of increased strength and temperature capability of superalloys to be used as turbine disks, and turbine blades and vanes in aircraft and industrial gas turbines [87].

For Stellite alloys, they are difficult to process owing to the 10~20 vol. % carbides and FCC to HCP transformation. Therefore, a practical limitation to machining techniques existed in their manufacture. These difficulties in processing make Stellite alloys ideal candidates for exploitation by PM processing using near net shaping techniques. The PM route also provides additional metallurgical benefits, namely refined microstructures and improved mechanical properties compared with conventional cast products [29]. Among all the powder metallurgy methods, the

sintering and hot isostatic pressing (HIP) methods are the most important and popular in the modern industries.

2.4.2 Hot isostatic pressing (HIP)

Hot isostatic pressing (HIP) has grown from the concept to the brink of broad commercial application in only several decades. It was conceived as a relatively low volume process for cladding high-cost nuclear fuel elements and has grown into a process that can process several tons of low cost materials, such as the high-speed tool steels, in a single and rapid cycle [88].

Hot isostatic processing is defined as the simultaneous application of high-pressure (usually inert) gas and an elevated temperature in a specially constructed vessel. The isostatic pressure is obtained because of the gas applied. Under these conditions of heat and pressures, the solid body with pores and defects will be consolidated and welded up. The mechanical properties of the products should be improved. HIP'ing can be used for several purposes: upgrading castings by elimination of casting defects such as shrinkage pores; densifying pre-sintered components; consolidating powders and interfacial or diffusion bonding [89].

2.4.3 Technology for HIP

The HIP'ing process relies upon heating a gas (generally inert, although there are exceptions) to a temperature typically in the region $500 \sim 2000^{\circ}\text{C}$ under pressure

of 100 ~ 200 MPa. The heating source is usually molybdenum or graphite elements. An inert gas such as pure argon is used to achieve the pressure in most HIP'ing systems. Fig 2.4 shows a cut-away view of an ASEA HIP. Components processed are placed within the central core and enclosed within the heater-insulation package. The hot isostatic pressing cycle is defined by the procedures for the operation, described as follows [23].

(1) Preparation - Components are placed on the tray and separated by a dusting of ceramic powder or by other proprietary methods.

(2) Loading - Individual trays are assembled into supporting furniture; the completed charge is lowered into the pressure vessel and the vessel is closed.

(3) Purging - The pressure vessel is evacuated and purged with the pressurizing gas.

(4) Equalization - High-purity argon is admitted to the vessel from the storage system until the vessel pressure has risen to the storage pressure.

(5) Compression - Gas is pumped via a compressor from the storage system to the vessel until the required 'start pressure' is reached. Heating may take place while this is occurring and this contributes to the pressurization.

(6) Heating - The required HIP'ing temperature is achieved and sustained for about 1 to 4 hours depending on the nature of the charge.

(7) Cooling -At the end of the sustaining period, the furnace is cooled down.

(8) Charge removal - The charge is removed from the pressure vessel finally.

2.4.4 HIP powder consolidation

The high pressure gas must not be allowed to penetrate into the bulk of the charge through interconnected surface pores, and therefore if surface connected porosity exists the charge must be contained within a pressure-tight container that will transmit the pressure to the charge at high temperature. . This technique can improve the interface bonding and in some case benefits the sealing of surface-connected porosity. The basic requirements for the containers are that they are relatively strong, gas tight, inert and plastic under the applied temperature and pressure conditions. The containers are also required to be compatible with the material to be pressed so as to minimize diffusion reactions and be readily removable. There are three main types of materials for the encapsulation containers: metal, glass and ceramic [23].

The filled, evacuated and sealed cans are put into the furnace for HIP'ing at the designed temperature and pressure for the designed time. Figure 2.5 shows the whole process and the procedures of the HIP powder consolidation. It mainly contains five steps [90]:

- (1) Container is fabricated to fit formed parts;
- (2) Load and vacuum and seal container;
- (3) Hot isostatically press (HIP);
- (4) Strip the container;
- (5) Machine the consolidated part.

The products fabricated with HIP powder consolidation should have higher purity than the cast or pre-sintered components, which are exposed directly to the

processing gas. HIP powder consolidation is often utilized when the cast plus forge route is not viable due to high flow stress, limited ductility and high melting points of the starting ingots [23].

HIP'ing powder consolidation allows both a sintering step and a HIP'ing step to be carried out in one vessel. The temperature for HIP'ing powder consolidation is higher than the conventional HIP'ing treatment. The microstructures that occurred in this process can be described by several states: particle rearrangement, fragmentation and plastic flow, replacement of the interconnected network of open porosity by isolated pores, spheroidization of the isolated pores, closure of the spherical pores [87].

2.4.5 Sinter plus HIP process

The sinter plus HIP processing route contains two sub-processes: sintering the powders for the designed time in vacuum and then using the HIP process to increase the densification. There are two kinds of sintering processes: solid state sintering and liquid state sintering. In solid state sintering, the sintering temperature is normally below, and in many cases significantly below the melting point of the metal, and the welding together the particles occurs by atomic diffusion. In liquid state sintering, the sintering temperature is sufficient to generate a small amount of liquid. In alloys, where melting occurs over a range of temperature, the HIPing temperature is usually just above the solidus of the alloy so that small amounts of liquid will form usually in interdendritic regions. In some cases discrete second phase particles may melt just

above the solidus and these will provide the liquid for super-solidus processing. [91]. There are 4 stages in the sintering process, which are adhesion, diffusion-controlled neck growth, intermediate stage densification, and finalstage densification. The Figure 2.6 illustrates these steps [23].

The first stage is *adhesion* when the particles in are contact with adjacent particles and they become bonded by the interatomic forces. The volume of porosity in this stage is hardly affected although necks are formed between particles. When the particles are covered by oxide films or other contaminants, adhesion will be inhibited.

The second stage is *diffusion-controlled neck growth* when the necks of the particles grow and open porosity decreases by the diffusion. The driving force is reduction of the surface energy.

The third stage is *intermediate stage densification* when necks become quite large, pores spheroidize and all interconnected porosity disappears. No more separate alloy powder particles can be distinguished.

The last stage is *final* densification when grain boundary migration occurs and the isolated spherical pores disappear. It is important to avoid the grain boundary migration for achieving the full density [23].

The major effect of HIP'ing for sintered products is the removal of the internal porosity and increased densification. However, it is difficult to eliminate the surface-connected porosity unless the pre-sintered charge is sealed inside a protective container[23].

2.4.6 Differences of the fabrication between the two PM methods

Table 2.1 lists the advantages and limitations of sinter plus HIP processing versus HIP powder consolidation. The main advantages for sinter plus HIP processing are that canning is not absolutely required and the process is easily carried out. The main limitations are that high porosity may be induced and coarse grains are produced. High porosity will only occur if the sintering stage is carried out under cover of an inert gas, as the gas will remain trapped in the internal pores and will resist subsequent pore-closure during HIP'ing. If sintering is carried out under vacuum, this should not be a problem. For HIP powder consolidation, the advantages are that no pre-HIP sintering is required and higher densification can be obtained. The disadvantages lie in the required coating or canning and the difficulty in handling the pre-forms [23].

2.4.7 Metal matrix composites with HIP'ing treatment

As mentioned before, products after casting or sintering have relatively high porosity and low density. The HIP'ing process can eliminate the interior pores and increase the densification for these products, thus providing higher quality materials.

Xu *et al.* studied two as-cast SiC particulate reinforced composites treated by HIP under different pressures and temperatures [92]. It was found that the ductility of the as-cast composites was increased greatly by the HIP treatment but yield stress was

reduced drastically. The HIP'ing process effectively reduced the pores in the cast composites whose porosity was 0.5% after the HIP'ing, compared with porosities of 1.2-1.95% before HIP'ing. The improvement was attributed to the diffusion bonding of adjacent pore surfaces as the composites were under high isostatic pressure and temperature during one-hour treatment. It was also found that the pressure had little effect on the strength and ductility, whilst increasing the temperature tended to improve the tensile properties.

Effects of HIP on cast A357 aluminum alloy with and without SiC particle reinforcement were investigated by Zulfia *et al.* [93]. Several HIP'ing processes were studied, but not every process reduced the porosity for the reinforced composites. The optimum HIP'ing process enhanced the bend yield strength, bending moment and bend normal strength by around 10~30%. However, the mechanical properties were consistently lower than those of the unreinforced materials, contrary to expectations.

The effects of HIP on the wear and mechanical properties of TiC/TiNi and TiN/TiNi composites were investigated by Ye *et al.* [94]. The HIP treatment removed the porosity and increased the density from $5.22 \times 10^3 \text{ kg/m}^3$ without HIP treatment to $5.94 \times 10^3 \text{ kg/m}^3$. Clearly, a significant densification of the specimens was accomplished by the HIP process. The HIP treatment generally reduced the wear loss of the composites. Particularly at the highest load, the wear loss of the specimens was 40~50% lower than the counterparts without HIP treatment.

Li *et al.* investigated the casting and HIP'ing effects on Al-based MMCs [95]. The porosity decreased from 3% in the as-cast specimen to 1% in the counterpart with HIP'ing treatment. The 0.2% yield strength was also increased by the HIP'ing process.

2.4.8 Metal matrix composites by HIP powder consolidation

The high purity and densification attained by HIP powder consolidation are very attractive in developing new and high quality materials.

Jarvenpaa studied the wear resistance of steel matrix composites fabricated with hot isostatic pressing [96]. The reinforcements were TiC and WC+Co. The metallographic observations confirmed that the HIP'ed composites were extremely dense and the TiC and WC+Co particles were homogeneously distributed in and strongly bonded to the steel matrix. The interface between the WC-Co particles and the steel was about 5 μm thick. The Vickers hardness measurements showed that the hardness mainly depended on the matrix steel's carbon content and heat treatment, especially the tempering temperature. This is obvious because small carbide particles cannot carry heavy loads. The volume loss of the wear disc was lower when the pin material was TiC reinforced steel composites (TiC particle size of 43 μm) than when the pin material was WC-Co reinforced steel composites (WC-Co particles size of 250 μm). The abrasion resistance of those low-carbon steel matrix composites was higher, even though their hardness was lower.

The Ni₃Al-matrix composites strengthened by TiC particles were developed by Keskinen *et al.* using SM (self-propagating high temperature synthesis and melting process) [97]. There are two types of TiC particles used: the commercial one and the synthesized one. For the commercial TiC, the weight percentages in the composites were 35%, 20%, 10% and 0% respectively. The particle sizes of TiC were 35 μm , 25 μm , 15 μm and 5 μm respectively. It was demonstrated that the high-temperature

bending strengths decreased with the increase of the TiC weight percentage. The high temperature toughness increased when the TiC content increased, but they all decreased when the particles size of TiC increased. The relative densities of the composites also decreased when the TiC particles became larger. Comparing the synthesized TiC and the commercial TiC at the same percentage, the former produced better strengthening effects in composites than the latter.

Sargent *et al.* employed hot isostatic pressing (HIP) to manufacture aluminum alloy 6061 reinforced with 30 wt. % particulate silicon carbide (SiC) [98]. Evaluation of the HIP'ed material was achieved by comparing the structure and properties between the alloy 6061 and a corresponding composite material produced by the more conventional route of extrusion. The results showed that the 30% SiC reinforced composite produced by HIP powder consolidation had increased the strength by 25% compared with the corresponding one using blending and extrusion, but this was accompanied by a decrease in strain at failure. The HIP'ing consolidation also removed the porosity and increased the densification and finally led to better mechanical properties than the conventional routes.

Perez conducted a study of the influence of powder particle size on tensile properties of Ni_3Al processed by rapid solidification and HIP'ing [99]. The highest values of yield stress, tensile strength and elongation were obtained for the smaller particle size compact. Differences of their mechanical properties were more significant at the lower temperature range (room temperature to 400°C). The HIP temperature of 1100°C in this research was proved to be adequate. A higher

temperature of 1200 °C gave rise to grain growth and a slight decrease of the mechanical properties.

Chapter 3

Specimen Fabrication

3.1 Powder Compositions and Properties

3.1.1 Powder compositions

Stellite 712, TiC powder and Ni-coated TiC powder were provided by Deloro Stellite Inc. The chemical composition of Stellite 712 is given in Table 3.1. The particle size of Stellite 712 powder was about 44 μm . The bare titanium carbide (TiC) and the Ni-coated carbide (Ni-TiC) had the sizes of 10 and 5 microns respectively.

The composites were created by adding bare TiC particles or Ni-coated TiC particles to Stellite 712 powder. The content of TiC in the composites varied from 20% to 50% in weight.

The pure Stellite 712 was also considered in each group of specimens for comparison.

3.1.2 Microstructure of pure powders

The SEM image of as-received pure Stellite 712 powder is illustrated in Figure 3.1. The geometry of the powder is generally spherical with a large number of fine satellite particles associated with them. From the image, the sizes of the particles are as large as about 30 μm and as small as 2-3 μm . The average size is about 10 μm , which is the size marked in the specification by Deloro Stellite Inc. The BEI images of the as-received pure Stellite 712 powders are shown in Figure 3.2. There was not any carbide observed in the microstructures of Stellite powders.

The microstructure of the bare as-received TiC particles is illustrated in Figure 3.3. The shapes of particles are much more angular and much finer than the Stellite 712 powder. The size of the bare TiC appears to be about 1-10 micron from the image.

The image of the as-received Ni-coated TiC is shown in Figure 3.4. Most of Ni-coated TiC particles are agglomerate together. The shape of the particles generally is spherical. The size is almost uniform and appears to be about 2-3 μm from the images.

3.1.3 Microstructures of Composites

Figure 3.5 shows the microstructure of 80% Stellite 712 mixed with 20% bare TiC particles. The microstructure of the composite powder with 80% Stellite 712 and 20% Ni-coated TiC powders is shown in Figure 3.6. The Ni-coated TiC particles were also distributed around the big Stellite 712 particles. The Ni-coated TiC particles were

easily agglomerated together and more uniform than the bare TiC reinforced composite mixture.

3.2 Preparation of “Green Body” Specimens

3.2.1 HIP powder consolidation

A mass of 600 or 800 g of the composite powders was put into a plastic bottle according to the composition, then was mixed for 24 hours on an electric blending machine. In order to ensure the successful HIP'ing consolidation, the powder had to be sealed in cans. The canning material used for the specimens was stainless steel pipe (SSL316). The melting point of SSL316 is 1370°C, which was much higher than the HIP'ing temperatures for the specimens. One end of a stainless steel tube is crimped and sealed by tungsten arc welding, and then the powders were loaded into the can by a paper-made funnel. The can was generally 2 inch in diameter and 15 inch in length. The powder was pressed for a few minutes using a steel bar to obtain a compact “green body”.

Figure 3.7 illustrates the vacuum system for the specimen cans. A glass wool plug was put at the end of the can after the powder was loaded in order to prevent the powder from being drawn into the vacuum system. The vacuum system consists of a roughing pump and a three-stage diffusion pump, as shown in section in Figure 3.6. The pre-filled cans were evacuated to less than 5×10^{-5} mbar at room temperature and then evacuated until a vacuum of less than 5×10^{-5} mbar stabilized. Finally the cans were kept

evacuating for about twenty-four hours and the vacuum as low as 2×10^{-7} mbar could be achieved.

The powder-containing cans with vacuum atmosphere were hydraulically crimped and isolated from the vacuum system in the next step, while maintaining the crimping pressure. The filling tube was then tungsten arc welded between the crimping tool and glass wool, and finally the crimping pressure was released.

3.2.2 Sintering plus HIP'ing

The Figure 3.8 illustrates the schematic representation of the sintering plus HIP'ing process. The powders were mixed for at least 45 mins, with 3.5% binder mixture (50-50 PVA/menthocol) added to the mixture. The mixture was then poured into a beaker with 7% hot water and mixed on a hot plate until a uniform paste of medium consistency was obtained. The time of mixing varied with the quantity of powder made. The paste was then poured in an alumina mould and left to dry for at least one week in room air. The mould had a ring shape, with an inside diameter of 40 mm, a wall thickness of 2 mm and a height of 8 mm.

3.3 Differential Scanning Calorimerty (DSC) Analysis

The sintering and HIP'ing temperatures in the specimen fabrication processes were determined in terms of the solidus/liquidus properties of the pure Stellite 712 powder and their composite powder which could be investigated using the DSC

technique. The DSC 404C was provided by NETZSCH DSC. DSC is a technique which has sample and reference pans in a variety of static or dynamic atmospheres under vacuum down to 10^{-4} bar. The range of the temperature of DSC 404C is from -120 to 1650°C. The data are collected and analyzed by special software to obtain the solidus/liquidus temperatures and the thermal calorimetry properties of the sample.

3.3.1 DSC procedures

The mass of each sample for the DSC was about 50 mg. An aluminum crucible containing the sample was put on a layer of aluminum powder at the bottom to protect the pan from sticking with the molten sample. The sample was also covered with another layer of aluminum powder to avoid the mass loss of the sample, for example, the gas volatilizing from the sample. The mass of the aluminum powder in the reference crucible was about 30 g, which was the same mass as in the sample crucible. The gas atmosphere in the furnace was argon. The vacuum in the furnace was about 1.9 mbar.

The DSC heating and cooling cycle for all the sample powders was a single-loop, as illustrated in Figure 3.9. The time of heating from room temperature to 100°C was about 5 minutes and this temperature was kept for 10 minutes. Then the furnace was heated up to 1500°C at a rate of 20°C/min. The maximum temperature, 1500°C, was kept for 5 minutes. This temperature was determined based on the melting point of Co (1495°C). The furnace was then cooled down to 500°C with the rate of 20°C/min. Finally the furnace was cooled down to room temperature using the furnace natural cooling rate.

3.3.2 DSC results

The DSC heating/cooling curves of pure Stellite 712 are illustrated in Figure 3.10. There are mainly two liquid phase transformations in the heating process and three solid phase transformations in the cooling process. The starting temperature and ending temperatures of the first liquid phase transformation are 1102.1°C and 1249.1°C respectively. The peak temperature of the first phase is 1135.9°C. The starting and ending temperatures of the solid phase transformations are 1225.3°C and 1070.4°C respectively, which are lower than the corresponding liquidus temperatures. The first peak may be caused by dissolution of one of the carbides.

Figure 3.11 illustrates DSC results of the 20% TiC/Stellite 712 composite powder. Similar to pure Stellite 712 powder, there are also two liquid phase transformations and three solid phase transformations. It is evident that the bare TiC addition in the Stellite 712 did not change the phase transformations of the Stellite 712 matrix. This is because TiC didn't melt at the temperatures (below the melting point of TiC, 3065°C). The starting temperature and the ending temperatures for the first liquid phase transformation is 1076.4°C and 1221.4°C respectively. The peak temperature of the first phase is 1109.6°C. The starting and ending temperatures of the solid phase transformations in composite powder are 1190.5°C and 1040.7°C respectively, which are about 20~30°C lower than those of the pure Stellite 712.

The DSC results of the 20% Ni-coated TiC/Stellite 712 composite powder are illustrated in Figure 3.12. There are the same two solid and three liquid phase transformations with pure Stellite 712 powder and the 20%TiC/Stellite 712 composite

powder. For the Ni-coated TiC reinforced composite powder, the solidus/liquidus temperatures are almost the same as those of the pure Stellite 712 powder. The starting temperature and ending temperatures of the first liquid phase transformation are 1110.0°C and 1254.6°C respectively. The peak temperature of the first phase is 1133.6°C. The starting and ending temperatures of the solid phase transformations are 1131.2°C and 1067.6°C respectively.

3.4 Determination of Sintering and HIP'ing Temperatures

3.4.1 HIP powder consolidation

The HIP powder consolidation process was conducted in a unit of an Autoclave Engineers Press. The maximum operating temperature and pressure of the unit are 2000°C and 207 MPa respectively. The specimen chamber is 240 mm by 120 mm. The operating procedure was first to load the vacuum encapsulated powder in the press and purge with high purity argon for three times to ensure that air was removed. The specimen chamber was then pressurized with argon to about 55 MPa before heating commenced. The remaining pressure required was generated by the heating cycle, which took about one and half hours to heat from room temperature to the HIP temperature. The specimens in the furnace were cooled using the natural furnace cooling rate (about 750°C/hr). Figure 3.13 shows a typical temperature and pressure profile for HIP'ing [100].

The HIP powder consolidation process was performed at 1080°C under the pressure of 100 MPa, and at 1120°C or 1160°C under the pressure of 200 MPa, respectively, in order to investigate the optimum HIP'ing conditions. In terms of the DSC results, the two HIP'ing temperatures were 1120°C and 1160°C under and above 1135.9°C which was the first liquid phase transformation peak temperature of pure Stellite 712. The HIP'ing time for all the groups was four hours.

3.4.2 Sintering plus HIP'ing

The sintering cycles for pure Stellite 712 and the 20%TiC/Stellite 712 composites are shown in Figure 3.14 and Figure 3.15. For pure Stellite 712, the furnace was heated up to 537°C, allowing about 10 minutes to stabilize the furnace. The debinding temperature was 815°C, which was kept for 20 minutes. In the first two hours, the pressure in the furnace was maintained at 200mT using argon gas, and the furnace then was evacuated. The pre-sintering temperature was 1096°C for 30 minutes and the sintering temperature was 1152°C for 25 minutes. Finally the furnace was naturally cooled to room temperature. The sintering process for the 20%TiC/Stellite 712 composites was the same as pure Stellite 712, except that the pre-sintering temperature was 1150°C and the sintering temperature was 1224°C for 30 minutes. The selections of the sintering temperatures were based on the ending temperature of the liquid phase transformation, which would be higher than the temperature used in the HIP powder consolidation process due to the lack of pressure.

Half of the sintered specimens then experienced a HIP'ing process, in an effort to minimize the porosity. The HIP'ing was performed at 1065°C for 4 hrs under the pressure of 137.9 MPa. The HIP'ing temperature was selected to be 85%~90% of the corresponding sintering temperature used in the sintering process.

Chapter 4

Microstructural Analysis

4.1 Microstructural Examination

The fabricated specimens were cut into small pieces with ceramic blades for microstructural analysis.

Metallographic examination of the microstructures, phases and compositions of the specimens was conducted using the Hitachi S-570 SEM with an EDX. X-ray diffraction (XRD) was also employed to investigate the phases present in the microstructures. The specimens were mounted and ground with grit paper from 180 to 600 and polished with abrasive cloth plus 1 μm alumina powders.

The microstructures of the specimens prepared under different HIP'ing conditions and with different TiC contents were examined. Most of the specimens HIP'ed at 1080°C were observed to be still in a powder state, which meant the powder particles were not well bonded at the low temperature. Therefore most of these specimens were not considered in the following discussion.

4.2 Microstructural Results

4.2.1 Specimens by HIP powder consolidation

4.2.1.1 Microstructures of pure Stellite 712

Figure 4.1 shows the SEM backscatter images of the pure Stellite 712 specimens HIP'ed at 1120°C and 1160°C respectively. There are apparently three phases present in the microstructures, characterized by white areas, black areas and grey-black areas respectively. The EDX spectrum and composition of the white areas are presented in Figure 4.2. This phase is M_7C_3 which is molybdenum and chromium rich carbide. The EDX spectrum and composition of the black areas are shown in Figure 4.3. This phase is $M_{23}C_6$ which is the chromium rich carbide. The EDX spectrum and the composition of the grey-black area are shown in Figure 4.4. This phase is the cobalt solid solution.

Comparing the microstructures in Figure 4.1 (a) and (b), it is found that the phases present in the specimens HIP'ed at 1120°C and at 1160°C are the same. This can also be confirmed in Figure 4.5 for the carbide of M_7C_3 , Figure 4.6 for the carbide of $M_{23}C_6$ and Figure 4.7 for the cobalt solid solution.

Although the higher temperature did not change the nature of the phases in the microstructure, differences can be seen in the carbide particle sizes and the amounts of the carbides. The size of black $M_{23}C_6$ at 1120°C was about 1.5 μm on average with the biggest particle being about 4 μm and the smallest one being only 0.5 μm . In contrast, the size of black $M_{23}C_6$ at 1160°C was about 2.2 μm on average with the biggest particle

being 6 μm and the smallest particle being 0.5 μm . The results for the black M_{23}C_7 showed that at the higher temperature the particles increased in size by about 50%.

Similarly, the size of white M_7C_3 at 1120°C was about 0.7 μm on average with the biggest particle being about 1.5 μm and the smallest particle being 0.3 μm . On the other hand, the size of white M_7C_3 at 1160°C was about 1.5 μm with the biggest particle being 2.25 μm and the smallest one being about 0.5 μm . For the white M_7C_3 carbide at 1160°C, the particle size increased almost 50% compared to that of the counterpart at 1120°C.

The differences in carbide particle size caused by the HIP'ing temperature are probably caused by coarsening or Ostwald ripening, a process whereby smaller particles are thermodynamically unstable compared with the larger particles, and hence the smaller particles dissolve to increase the solute and carbon contents of the matrix while the larger particles grow by consuming these elements. .

There were no obvious pores found in the microstructures and almost the full density was obtained for all the specimens. This will be confirmed by the density measurements discussed later.

4.2.1.2 Stellite 712 Composites reinforced with bare TiC

Figure 4.8 shows the microstructures of the Stellite 712 composite with 20% bare TiC reinforcement HIP'ed at 1120 °C. The Stellite 712 matrix particles were observed to be about three times bigger than the TiC reinforcement particles.

Figure 4.8 (a) shows the bare TiC particles surrounding the Stellite 712 particles homogeneously. In Stellite 712 matrix particles, there were also three different areas in the microstructure, which were in white, black and grey-black respectively. The EDX spectra corresponding to the areas are shown in Figure 4.9. It is apparent that the white area is the chromium and molybdenum rich carbide, M_7C_3 . The black area is the chromium rich carbide, $M_{23}C_6$ and the grey-black area is the cobalt solid solution.

Comparing the microstructures and compositions of Stellite 712 matrix in the composites with those of pure Stellite 712 alloy, the presence of TiC did not change the phases present in the matrix.

Figure 4.8 (b) shows the microstructure of the TiC particle agglomeration area. The TiC particles formed the matrix phase in these regions in between the Stellite 712 particles, but the matrix also contained small discrete particles of a white phase whose EDX spectrum is shown in the Figure 4.9 (d). The elements involved in this phase included titanium and almost all the elements found in the Stellite 712 matrix. According to the DSC results in Figure 3.8, most of the first phase in Stellite 712 matrix was melted because the HIP'ing temperature of 1120°C was in the liquidus temperature range of 1076°C~1123°C. The first phase that melted in the Stellite 712 matrix diffused into the TiC particle areas and contributed to binding of the un-melted TiC particles. The TiC particles might have undergone a chemical reaction with the matrix due to the high titanium content. The microstructure also showed that the HIP'ing time was long enough for elements from the matrix to diffuse into the TiC agglomeration area. The TiC particles almost kept their original shapes in the composite during the HIP'ing process.

Figure 4.10 shows the microstructure of the composite reinforced by the bare TiC HIP'ed at 1160°C. In Figure 4.10 (a), it is observed that the TiC particles were distributed around the Stellite 712 particles somewhat homogeneously. There were also the same three different areas in the matrix particles as in pure Stellite 712. The EDX spectra corresponding to the areas are shown in Figure 4.11. From the compositions shown in the EDX spectra, it is known that there were no compositional changes in the phases at the higher HIP'ing temperature. They are still the white M_7C_3 , the black $M_{23}C_6$ and the cobalt solid solution.

The microstructure of the TiC agglomeration area is shown in Figure 4.10 (b). The TiC reinforcements again contained the white or grey-white phase, and the EDX spectrum is given in Figure 4.11 (d). This area contained all the elements that existed in the Stellite 712 matrix, which must have diffused from the matrix particles.

Comparing with Figure 4.10 (a), it is found that there was no M_7C_3 precipitate in the Stellite 712 matrix particles close to the TiC agglomeration areas. Perhaps the M_7C_3 carbides in these matrix particles were the first phase to melt and diffuse into the TiC reinforcements, thus contributing to binding. An alternative explanation is that the dissolution of M_7C_3 leads to regions in the Stellite 712 matrix that are enriched in Mo and C, and that these elements depress the melting point of the matrix in local regions to cause melting. These local regions may be the so-called "first phase to melt" suggested by the DSC results. This explanation seems more plausible in view of the known high melting points of carbides such as M_7C_3 . The net effect would be the same as described earlier. That is, the disappearance of M_7C_3 , local melting of the Stellite 712, and the

enrichment of the matrix in elements that would then tend to diffuse into the TiC reinforcement areas where they might recombine to form additional phases.

4.2.1.3 Stellite 712 composites reinforced with Ni-coated TiC

Figure 4.12 shows the microstructure of the Stellite 712 composite with 20% Ni-coated TiC reinforcement HIP'ed at 1120°C. In Figure 4.12 (a), it is observed that Ni-coated TiC particles surround the Stellite 712 particles homogeneously. The matrix particles contained three phases and no changes were observed compared with pure Stellite 712 and the bare TiC reinforced composites. The EDX spectra for the three areas are presented in Figure 4.13. From the compositions shown in the spectra, it appears that the three areas were the white M_7C_3 , the black $M_{23}C_6$, and cobalt solution in grey-black.

The microstructure of Ni-coated TiC agglomeration is shown in Figure 4.12 (b). The Ni-coated TiC reinforcements were bound by the white phase. The EDX spectrum of this area is presented in Figure 4.13 (d), which contained all the elements found in the Stellite 712 particles, such as Ni, Ti and so on. Again this phase should be the first phase melted and diffused into the Ni-coated TiC areas being a binder.

The microstructures of the composite HIP'ed at 1160°C are illustrated in Figure 4.14. There were no new phases precipitated in the Stellite 712 matrix compared with the composite HIP'ed at 1120°C. The only difference was the size of the white M_7C_3 and the black $M_{23}C_6$, which similarly occurred in pure Stellite 712 alloy HIP'ed at the higher temperature. In the Ni-coated TiC agglomeration area, it seems that more elements from the Stellite 712 matrix diffused into this area at the higher HIP'ing temperature.

4.2.1.4 Other composites

The microstructures of the composites reinforced with 30% TiC or Ni-coated TiC HIP'ed at 1160°C are illustrated in Figure 4.15. The white M_7C_3 , black $M_{23}C_6$ and the cobalt solid solution were precipitated in the matrix particles and no changes were observed compared with the corresponding composites reinforced by 20% TiC or Ni-coated TiC reinforcements. Regardless of whether the reinforcements were bare TiC or Ni-coated TiC, the reinforcing particles were partially bound by the white phase from Stellite 712 matrix. For the bare TiC reinforced composites, the TiC particle shapes were large, irregular and angular. Large particles with quadrilateral shapes could be found. The sizes of the bare TiC reinforcements were changed from 0.5 μm to 8 μm . In contrast, the Ni-coated TiC particles had a uniform spherical shape and their sizes were about 1 μm . The presence of the nickel coatings appears to have impeded the growth of the TiC reinforcements

Figure 4.16 illustrates the microstructures of the Stellite 712 composites reinforced by 50% TiC or Ni-coated TiC HIP'ed at 1160°C. Compared with the composites reinforced by the lower contents of the TiC or Ni-coated TiC particles, the difference was that almost no white M_7C_3 was precipitated from the Stellite 712 matrix particles, regardless of whether the TiC particles were coated or uncoated by nickel. The possible reason is that the M_7C_3 carbides were first melted or taken into solution and their constituent elements then diffused into the TiC reinforcement area becoming a binder. . In this case there were insufficient elements from M_7C_3 to allow this phase to reform in

the presence of the more abundant TiC. However, occasionally, there was still a trace of M_7C_3 found in the large Stellite 712 particles, as shown in Figure 4.16 (b).

4.2.1.5 Elements mapping

Element mapping by SEM is a tool to investigate the distributions of elements in the microstructure. Figure 4.17 shows some main element distributions in the composites with 20% bare TiC particles. It confirms that the grey-black area in Figure 4.17 (a) is the Co solution in the matrix, the black area is the Cr-rich phase and the white area is the Mo-rich phase. The matrix phase as a binder for the bare TiC particles mainly consists of Co and Mo. Most of the Cr is present in the solid solution. Ti did not diffuse into the matrix particles.

The element distributions of the composite with 20% Ni-coated TiC particles are illustrated in Figure 4.18. They are almost the same as the counterpart reinforced with bare TiC. For the nickel distribution in the bare TiC reinforced composite, the nickel seems only to be present in the cobalt solution and did not form the carbides in the matrix. However Ni seems present everywhere in the composite reinforced by the Ni-coated TiC. This may be caused by the higher nickel content in the composite coming from the nickel coating on the surface of the TiC reinforcement.

4.2.2 Specimens by sintering plus HIP'ing

The X-ray patterns and the SEM images of pure Stellite 712 and Stellite 712 composite reinforced by 20% bare TiC are presented in Figure 4.19 and Figure 4.20 respectively. The FCC Co-rich solid solution and two types of chromium carbides are found: FCC Cr_{23}C_6 and Cr_7C_3 in both HCP and orthorhombic forms. In addition, a large amount of HCP Co-rich solid solution is observed. Another noteworthy characteristic of this microstructure is the presence of Mo, seen in the EDX spectrums in Figure 4.21. Mo acted as a strengthening element together with Cr in the Co-rich solid solution. The three main phases presented in the microstructure were easily identified by the EDX analysis. The gray area consists of Co-rich solid solution, as seen in Figure 4.21 (a). The light area was found to contain the higher Cr concentration, and therefore is probably a Cr_{23}C_6 region (Figure 4.21 (b)). The black area represented the other carbide phase, which was Cr_7C_3 in this case (Figure 4.21(c)). This area was also Mo-rich. The HIP'ed specimen presented an identical microstructure to the sintered specimen.

The Stellite 712 composite presented a microstructure similar to the Stellite 712 alloy, except for the presence of large amounts of bare TiC which also surrounded the alloy matrix forming a skeleton pattern. The carbides presented in both the sintered and HIP'ed microstructures were Cr_{23}C_6 and Cr_7C_3 , as seen in Figure 4.21 (b). The other phases were FCC Co-rich solid solution with Mo and Cr strengthening elements (Figure 4.22 (a)) and large amounts of bare TiC (Figure 4.22 (b)). Figure 4.22 (c) and Figure 4.22 (d) are the SEM EDX spectrums of the Cr_{23}C_6 rich and Cr_7C_3 rich regions respectively.

Chapter 5

Characterization of Mechanical Properties

5.1 Density

5.1.1 Density measurement

The immersion density was measured according to Archimides principle. In this technique, the final density of materials was determined by measuring the difference in weight of a specimen when measured in air and in distilled water at room temperature.

The density can be calculated in terms of the formula below.

$$\rho_k = \frac{W_a \cdot \rho_{fl}}{W_a - (W_{fl} - W_{string})} , \quad (5-1)$$

where ρ_k = specific density of the specimen;

W_a = weight of specimen in air;

ρ_{fl} = density of liquid (water in this research)

W_{fl} = weight of specimen in liquid (water in this research)

W_{fl} = weight of string which holds the specimen in liquid.

The density of water was determined by measuring the temperature of the water because the temperature of each measurement was different, so that the errors from the density measurement of the water could be avoided.

In general, the relative density of a composite is determined by the ratio of the measured density to the theoretical density of the composite material as it is calculated in terms of the rule of mixtures. The relative density of a composite is an index of the porosity for the composite. Higher relative density of a composite means better consolidation and probably higher mechanical properties. The theoretical density can be obtained by calculating the percentages of the matrix and reinforcements in a composite. For example, the theoretical density of the Stellite 712 composite with TiC content of c_{TiC} is calculated by following formula:

$$\rho_t = \frac{1}{\frac{1 - c_{TiC}}{\rho_{Stellite712}} + \frac{c_{TiC}}{\rho_{TiC}}} , \quad (5-2)$$

where ρ_t is the theoretical density of Stellite 712 composite;

$\rho_{stellite712}$ is the density of Stellite 712 matrix;

ρ_{TiC} is the density of TiC;

c_{TiC} is the TiC content in the composite.

The densities of Stellite 712 and TiC were taken as: $\rho_{stellite712} = 8.25 \text{ g/m}^3$ and $\rho_{TiC} = 4.94 \text{ g/m}^3$. Therefore the theoretical density of 20% TiC/Stellite 712 was calculated to be 7.27 g/m^3 according to equation (5-2).

5.1.2 Results of the densities

Table 5.1 presents the measured densities of pure Stellite 712, the 20% and 30% TiC and Ni-coated TiC reinforced composites using Archimede's principle. Their relative densities were calculated and presented in Figure 5.1. The minimum relative density is greater than 94%. It is noticed that the relatively densities for the Ni-coated TiC reinforced composites are more than 100%. One of reasons for the error might be the calculation error of the theoretical density, because the Ni coating on the TiC particular was not taken into account.

Although there were some errors in the measurements and calculations, the data proved that the porosity of the composites with the TiC reinforcements was very low following the HIP'ing consolidation process. From this point, it is evident that the HIP'ing process is capable of fabricating the specimens with high quality, for example, achieving full density.

5.2 Hardness

5.2.1 Hardness measurement

The hardness of the specimens was measured on the Wilson Rockwell SERIES 2000 with a diamond indenter (HRC). The specimens for hardness testing were ground by grit papers and polished with 1 μ m alumina powder. The indentation surfaces of the specimens were examined using the Hitachi S-570 SEM in order to investigate the micro-cracks induced by the indenter.

5.2.2 Results of the hardness

In the hardness test, each specimen was measured 10 times and the average of the hardness was obtained.

Figure 5.2 presents the hardness of pure Stellite 712 at different temperatures. There is no obvious change of the hardness with the temperature. Although the carbide grains are bigger at higher temperature, they seemed to have little or no influence on the hardness.

Figure 5.3 presents the hardness of bare TiC reinforced composites with different contents of TiC from 20% to 50%, and HIP'ed at 1120°C and 1160°C respectively. The hardness of pure Stellite 712 is also presented for comparison. The hardness of the composites HIP'ed at 1160°C was always higher than that of the counterparts HIP'ed at 1120°C. Under the two temperatures, the 30% bare TiC reinforced composites possessed

the highest hardness. When the content of bare TiC reinforcement reached 50% in the composite, the hardness decreased to below the hardness of non-reinforced Stellite 712.

Figure 5.4 presents the hardness of Ni-coated TiC reinforced composites with different contents of Ni-coated TiC from 20% to 50%, HIP'ed at 1120°C and 1160°C respectively. At 1120°C, the hardness of the composites gradually decreased with the increased content of the TiC. In contrast, the hardness of the composites HIP'ed at 1160°C gradually increased with the increased content of the TiC. With the same Ni-coated TiC content, the composite HIP'ed at 1160°C obtained higher hardness than that HIP'ed at 1120°C. In particular, the composite reinforced with 50% Ni-coated TiC HIP'ed at 1160°C possessed the highest hardness among all the specimens, having reached a hardness of HRC 63.

5.3 Wear Resistance

5.3.1 Wear test

The sliding wear test was conducted on a pin-on-disc tribometer provided by TEER Coatings Limited. Figure 5.5 shows a simple frame for the pin-on-disk test. The ball made of 94% WC and 6% Co, with the hardness of HV 1534, was wearing the specimen surface resulting in a wear track or pit. The wear load was 10 N and the rotational speed was 319 rpm.

The wear loss was evaluated by calculating the volume of the wear pit after the specimen surface was worn for 10^4 s (~2.8 hrs). The diameters of the ball and the worn track are 5 mm and 6 mm respectively.

The friction coefficient for each test was recorded automatically. It was used for the analysis of the wear mechanism of the materials. The worn surfaces and the wear debris were also studied with the Hitachi S-570 SEM with an EDX.

5.3.2 Wear loss

The wear loss was obtained by calculating the volume of the material removed from the surface along the wear track. To calculate the volume of the wear track, the cross-sectional area of the wear track must be evaluated first, and then the volume of the wear track (or pit) was calculated by taking the average of the cross-sectional areas multiplied by the periphery of the circular wear track, which was the wear loss of the material. It is expressed in the formula below:

$$\text{Volume loss (mm}^3\text{)} = 2\pi RS, \quad (5-3)$$

where R is the wear track radius (mm);

S is the average of the cross-sectional area along the wear track.

The cross sections at three locations along each wear track were simulated using a surface profiler, and then the average of the cross-sectional areas was calculated. The

depth of the wear track (vertical scale) shown in the cross-section profiles was measured in the current unit of kA (kilo ampere from the profilometer signal), which could be transferred to the dimensional unit, μm , in terms of the relation of $1 \text{ kA} = 0.1 \mu\text{m}$. The width of the wear track (horizontal scale) was graduated in μm . The average volume losses of all the specimens were calculated according to each individual cross-section profile of the wear track.

5.3.3 Results of the wear loss

5.3.3.1 Wear loss of pure Steillite 712

The cross-sectional profiles of wear tracks for pure Steillite 712 are presented in Figure 5.6. The maximum depths of the three wear tracks of the specimens HIP'ed at the three temperatures are $61 \mu\text{m}$, $41 \mu\text{m}$ and $13 \mu\text{m}$ respectively. Their average wear losses are calculated based on the cross sectional profiles and presented in Figure 5.7. It is shown that the wear loss decreased as the HIP'ing temperature increased. This indicates that the higher HIP'ing temperature benefited the diffusion, improved inter-particle bonding, improved the microstructure, and thus enhanced the wear resistance of the material.

5.3.3.2 Composites with bare TiC reinforcement

Figure 5.8 and Figure 5.9 illustrate the cross-sectional profiles of the wear tracks of bare TiC reinforced composites HIP'ed at 1120°C and 1160°C respectively. In terms of the cross-sectional profiles of the wear tracks, the wear losses were calculated and presented in Figure 5.10. The wear losses of pure Stellite 712 are also presented in the figure for comparison.

It is shown that the composites reinforced with the bare TiC obtained higher wear resistance than pure Stellite 712 regardless of the content of TiC. The volume loss was $9.8 \times 10^{-4} \text{ mm}^3$ for the composite reinforced by 20% TiC and $7.2 \times 10^{-2} \text{ mm}^3$ for pure Stellite 712 HIP'ed at 1160°C, with the difference being two orders of magnitude.

In addition, the wear losses of the specimens HIP'ed at 1160°C were lower than those of the corresponding counterparts HIP'ed at 1120°C. This, again, confirmed that the higher HIP'ing temperature improved the wear resistance of the materials.

For the two HIP'ing temperatures of 1120°C and 1160°C, the least volume loss was obtained for the composites with 30% TiC. For the specimen HIP'ed at 1160°C, the volume loss was $9.8 \times 10^{-4} \text{ mm}^3$, which was less by about one order in magnitude compared with the composites reinforced with 20% and 50% TiC.

5.3.3.3 Composites with Ni-coated TiC reinforcement

Figure 5.11 and Figure 5.12 illustrate the cross-sectional profiles of the wear tracks of Ni-coated TiC reinforced composites HIP'ed at 1120°C and 1160°C respectively.

The maximum depths of the three wear tracks of the specimens with the different TiC contents HIP'ed at 1120°C are 38 μm , 25 μm and 34 μm respectively. The depths of the three wear tracks of the specimens HIP'ed at 1160°C are 17 μm , 12 μm and 27 μm respectively. In terms of the cross-sectional profiles of the wear tracks, the wear losses of the specimens are calculated and presented in Figure 5.13.

It is shown that the wear losses of the composites with 20% Ni-coated TiC were higher than those of pure Stellite 712 at the two HIP'ing temperatures. For 1120°C, the wear losses of the two composites with 30% and 50% Ni-coated TiC were lower than that of pure Stellite 712. For 1160°C, the wear losses of the composites with 30% and 50% Ni-coated TiC were all higher than that of pure Stellite 712.

In addition, the wear losses of the specimens HIP'ed at 1160°C were lower than those of the counterparts HIP'ed at 1120°C.

For the two HIP'ing temperatures of 1120°C and 1160°C, the least volume loss was obtained for the composites with 30% TiC.

5.3.3.4 Composites by sintering plus HIP'ing process

The cross-sectional profiles of the wear tracks for Stellite 712 and its composites by sintering plus HIP'ing are shown in Figure 5.14.

Firstly, comparing the cross-sectional profile of the sintered Stellite 712 (Figure 5.14(a)) with that of the sintered TiC/Stellite 712 (Figure 5.14(b)), it is found that the wear depth of Stellite 712 is above two times more than that of TiC/Stellite 712. However,

the differences between the corresponding HIP'ed specimens (Figure 5.14(c) and Figure 5.14(d)) are greatly decreased.

Secondly, comparing the sintered Stellite 712 with the HIPed one, it is found that both the wear width and depth of the HIPed specimen are markedly less than those of the sintered one. Similar results were obtained for the TiC/Stellite 712 samples, but the reduction of the wear width and depth due to the HIP'ing process is less than that of the pure Stellite 712 specimen.

The wear volume losses for all the specimens using sintering plus HIP'ing were calculated based on the cross-sectional profiles and shown in Figure 5.15.

It is clear to see that the wear resistance of the composite with the 20% TiC significantly increase compared with the pure alloys. The volume loss for the composite is about $1.6 \times 10^{-2} \text{ mm}^3$ and about four times less than the pure counterpart. Regardless, the pure alloy or the composite reinforced with TiC, they obtained a very low wear volume losses after the HIP process. For the pure alloy, the volume loss is $3.4 \times 10^{-4} \text{ mm}^3$ and almost two orders of the magnitude lower than the counterpart sintered without HIP'ing process. The same result was also observed for the composite reinforced by 20% bare TiC.

5.3.4 Friction coefficients

5.3.4.1 Pure Stellite 712

Figure 5.16 illustrates the variations of the friction coefficients with time for pure Stellite 712 HIP'ed at different temperatures. For 1120°C, the friction coefficients were at first stable, but changed to become highly variable at the final stage. In contrast, the friction coefficients for 1160°C were unstable at the beginning but became stable during the final stage. The average friction coefficients for all the specimens were obtained by calculating the values for the last 5000 s. For HIP'ed pure Stellite 712, they are 0.65 at 1120°C and 0.93 at 1160°C.

5.1.4.2 Composites with bare TiC reinforcement

Figure 5.17 shows the variations of the friction coefficients with time for the composites reinforced with different contents of the bare TiC at 1120°C. The friction coefficients were all very stable and very close. The average friction coefficients are 0.54, 0.44, and 0.41 for the 20%, 30% and 50% TiC reinforced composites respectively.

Figure 5.18 shows the variations of the friction coefficients with time for composites HIP'ed at 1160°C. The friction coefficients were all very stable for the composites with 20% and 30% TiC, but they were fluctuating for the composite with 50% TiC. The average friction coefficients are 0.52, 0.56, and 0.39 for the 20%, 30% and

50% TiC reinforced composites respectively, which are similar to those of the corresponding counterparts HIP'ed at 1120°C except the specimen reinforced with 30% TiC.

Figure 5.19 illustrates the relationships between the friction coefficients and bare TiC content in the composites. It seems that the friction coefficients generally decreased with the increase in the TiC content except for the composite with 30% TiC HIP'ed at 1160°C. This abnormality might be an error in the measurement. For all the composites, their friction coefficients are lower than that of the pure Stellite 712 HIP'ed at the two temperatures and also the friction coefficients for all the composite specimens are very close.

5.1.4.3 Composites with Ni-coated TiC reinforcement

Figure 5.20 illustrates the variations of the friction coefficients with time of the composites reinforced with Ni-coated TiC HIP'ed at 1120°C. The average friction coefficients are 0.56, 0.61, and 0.69 for the 20%, 30% and 50% Ni-coated TiC reinforced composites respectively.

Figure 5.21 illustrates the variations of the friction coefficients with time of the composites reinforced with Ni-coated TiC HIP'ed at 1160°C. The friction coefficients were all stable for all specimens. The average friction coefficients are 0.57, 0.61, and 0.71 for the 20%, 30% and 50% Ni-coated TiC reinforced composites respectively.

Figure 5.22 presents the friction coefficients versus the content of Ni-coated TiC in the composites. The friction coefficients are almost the same for the specimens HIP'ed at

the two temperatures, but they slightly increased with the TiC content. Again, compared with the friction coefficients of pure Stellite 712, the friction coefficients for the composites are lower.

5.3.5 Worn surface analysis

The worn surfaces of each specimen were examined using SEM in order to understand the wear mechanism. Figure 5.23 shows the wear debris of the composites reinforced with 20% bare TiC and Ni-coated TiC. It was observed that there was a large volume of debris on the specimen surface of the Ni-coated reinforced composite. The black TiC particles were observed in the debris, which indicated that the interfacial bonding in the composite was weak, so that the TiC particles were easily pulled out from the surface. To some extent, this phenomenon may be even worse because the spalled TiC particles may become a third body to wear the surface.

In contrast, only small debris chips were found on the surface of the bare TiC reinforced composite. No TiC particles were found in the debris, which implied that the bare TiC particles had better bonding with the Stellite 712 matrix.

The EDX spectrums for the wear debris from the two surfaces are presented in Figure 5.24. The high Ti content (about 13.55%) in the debris from the Ni-coated TiC reinforced specimen indicated that the entire TiC particles were pulled out from the surface. In contrast, the low Ti content (about 6.44%) in the debris from the bare TiC reinforced specimen implied that only rubbing/wearing chips were removed from the surface. The Ti content in the debris is close to that in the composite.

Figure 5.25 shows the SEM images of the worn tracks. The worn track was very smooth and only some shallow scratching grooves were observed in the surface of the composite with 20% bare TiC. There were no any cavities or pits caused by the spallation of the TiC particles. In contrast, there were a lot of cavities and deep grooves observed on the worn track of the composite reinforced with 20% Ni-coated TiC. The cavities were caused by the spallation of the TiC particles during the wear.

Chapter 6

Discussion on the Results

The primary objectives of this research were to explore the optimum fabrication process for TiC reinforced Stellite 712 composites using the powder metallurgy techniques and investigate the effects of Ni coating of the reinforcement on the microstructures and performance of the Stellite 712 composites. Therefore the discussion made in this chapter will emphasize these goals.

6.1 Stellite 712 Matrix

The microstructure analyses have demonstrated that the sintering plus HIP'ing process and the HIP'ing powder consolidation process produced the same phases and microstructures for the composites. Although these two processes are different in operation, the principles are similar, which all involved increasing movement of the atoms due to the high temperature, changing particle contact surfaces, as well as changing physical and mechanical properties [101]. Since the maximum temperatures applied in the two processes were similar in the present experiments, the recrystallization, which was the process by which structural changes took place through the growth of

some crystals by means of atom migration from one crystal to another, would occur in the same way in the two processes. Atomic mobility would depend primarily on the temperature and to a lesser extent on pressure. The only difference between the two fabrication processes was the pressing process, which might influence the surface contacts in the diffusion and mergence of grain boundaries.

The difference for the white phase M_7C_3 in the composites was that it was the molybdenum-rich carbide in the specimens produced by HIP consolidation process and chromium-rich carbide by the sintering according to the EDX spectrums. The grain sizes of the carbides were also different in the specimen fabricated by the two processes. The sintering process produced the larger grains with higher volume fraction of carbides in the specimen. The carbides in the specimen HIP'ed at 1120°C were the smallest. The carbides in pure Stellite 712 are the main secondary phases and the most important in terms of obtaining the higher mechanical property differences of the alloy, for example, wear resistance. Therefore the differences in the grain size and volume fraction of the carbides in the specimens resulted in the huge changes in their wear resistance.

Figure 6.1 illustrates the wear volume losses of pure Stellite 712 specimens fabricated by the two PM processes. It is apparent that the specimens prepared by the sintering plus HIP'ing process have higher wear resistance or lower wear loss compared with those produced by the HIP powder consolidation process. The specimens HIP'ed at the higher temperature had higher wear resistance than those HIP'ed at the lower temperature. The possible reason for these results is that sintering plus HIP'ing involves longer time at high temperature and hence longer time for pore closure and inter-particle bonding to occur than is available in the HIP only process. . In that it reduced the porosity

and enhanced the interfacial bonding between the powder particles the sinter plus HIP process was able to produce structurally superior materials, thus increasing the wear resistance of the materials.

6.2 Stellite 712 Composites

6.2.1 Microstructures

The microstructures of the Stellite 712 based-composites fabricated by the two PM processes were almost the same. As analyzed in the previous chapters, the matrix particles had two carbides precipitated from the cobalt solution, which were the white M_7C_3 and the black $M_{23}C_6$. However, the increase of the TiC content in the composites would prevent the precipitation of the M_7C_3 . The precise mechanism for this interaction has not been elucidated but it may involve the diffusion of Ti inward into the Stellite particles or the outward diffusion of Mo and carbon from the Stellite matrix into the TiC reinforcement. Further work needs to be done to resolve these issues. However, part of the matrix was melted thus allowing elements to diffuse into the TiC reinforcement, where they might promote the binding together of the TiC particles. In the sintered specimens, there were bigger carbide grains and larger carbide volume.

6.2.2 Relationship between hardness and wear resistance

Hardness is an important factor to predict the wear resistance of a material. For most materials, in general, the materials with higher hardness have higher wear resistance [60]. Figure 6.2 illustrates the relationship between the hardness and the wear loss of the bare TiC reinforced composites prepared by the HIP'ing powder consolidation process. The wear losses of the specimens decreased with the increase of the hardness, which is consistent with the common rule. However, for the Ni-coated TiC/Stellite 712 as presented in the last chapter, the wear resistance was much lower than that of the bare TiC/Stellite 712, and even lower than that of pure Stellite 712. The reason, as indicated before, was that the entire TiC particles were pulled out from the specimen surface during the wear, leading to large wear loss. Therefore, the common relationship between hardness and the wear resistance is not applicable to these composites. That is, hardness was not a key factor determining the wear loss. It appears that nickel coating of the reinforcing particles serves little or no purpose in achieving high wear resistance, and in fact it appears to be deleterious.

6.2.3 Effects of TiC, Ni-coating and temperature on wear resistance

Figure 6.3 summarizes the volume losses of the Stellite 712 composites using HIP powder consolidation. Firstly, the content of TiC in the composite influenced the wear resistance of the material, as shown in Figure 6.3. The wear resistance increased with the TiC content, but when the content reached a certain percentage (about 30 wt. %), the

wear resistance started to decrease. This was due to the interfacial bonding. With the increase of the TiC content, the amount of the matrix available as the binder was reduced in a relative sense, which weakened the interfacial bonding.

Secondly, comparing the wear resistance of the composites reinforced with bare TiC and Ni-coated TiC, it is obvious that the bare TiC reinforced composites have much higher wear resistance than the Ni-coated TiC reinforced ones. This was also attributed to the interfacial bonding strength between the TiC particles and the matrix. As the wear debris analysis demonstrated in the previous chapter the debris from the Ni-coated TiC reinforced composite contained big TiC particles, which meant the interfacial bonding in the composites was weak. This resulted in the spallation of the TiC particle from the matrix, leading to low wear resistance.

Finally, the higher HIP'ing temperature provided the specimen with the higher wear resistance. Similar to the discussion on pure Stellite 712, the carbides were larger in size and present in larger amounts when materials were processed at the higher temperature. Also at high temperature, the atoms in the matrix particles were more active and better able to diffuse into the TiC area, where they contributed to the binding of the reinforcements. This would enhance the interfacial bonding between the matrix and the TiC particles thus leading to increase wear resistance.

6.2.4 Effects of PM methods on wear resistance

A significant difference in the wear performance of the specimens fabricated with the two processes was observed; that is, the sintered plus HIP'ed specimens exhibited

higher wear resistance than the HIP'ed specimens. There are two possible mechanisms for this: one is related to the residual thermal stress, the other is the sintering temperature. In the sintering plus HIP'ing process the sintering stage and the HIP'ing stage were separated, the residual thermal stresses induced at the interface during the cooling from the sintering temperature would be removed in the HIP'ing process, which would reduce cracking, thus increasing the bonding. On the other hand, there was a pre-sintering stage at 1100°C in the sintering plus HIP'ing process, which helped the diffusion and mergence of grain boundaries as discussed for the pure Stellite 712, thus increasing the strength of the materials. Therefore, compared with the sintering plus HIP'ing process, the diffusion of elements at the particle surfaces might be less effective in the HIP'ing powder consolidation process, which weakened the interfacial bonding and thus decreased the strength of the materials. It is suggested that increasing temperature of the HIP'ing powder consolidation process would help the diffusion at the particle interfaces and thereby enhance the interfacial bonding strength, leading to the increase in wear resistance. In addition, post heat treatment of the specimens might be helpful in removing any residual thermal stress induced in the HIP powder consolidation process.

6.2.5 Interfacial bonding

Regarding the Stellite 712 composites with Ni-coated TiC, the wear test has demonstrated that they have much lower wear resistance than the composites with bare TiC. This is also related to the interfacial bonding. As is well known, the interface strength of a composite governs the overall mechanical properties of the material [101].

Since the thermal expansion coefficient of TiC is lower than that of Stellite 712, without the Ni coating the interface between the matrix and the reinforcement is brittle due to the high residual thermal stress from the sintering process. The purpose of employing Ni coating on the TiC surface was to buffer such internal stress, and thus improve the boundary conditions. Figure 6.4, 6.5, and 6.6 show the indentation surfaces of the bare TiC composite specimen and the Ni-coated TiC composite specimen, it is clear that the interface fracture toughness has been improved by the Ni coating. This is evident by the fact that a high concentration of cracks is present along the indent of the bare TiC composite specimen but they are only occasionally observed in the Ni-coated TiC composite specimen. In the meanwhile, the increase of the bare TiC content in the composites also increased the cracking, which indicated a decrease of the fracture toughness. For example, the cracks were long and deep in the specimen with 50% bare TiC/Stellite 712.

However, the increase in the fracture toughness causes the decrease in the strength of the interfacial bonding [16, 102]. This has been confirmed by the wear test. The volume loss of the Ni-coated TiC reinforced composite was much higher than that of the bare TiC reinforced composite. The larger volume loss of the Ni-coated TiC composites resulted from the spallation of TiC from the matrix. This has been evidenced by examining the worn surfaces of the specimens, as presented in the previous chapter. The worn surfaces of the bare TiC composite and the Ni-coated TiC composite are quite different. There is obviously an amount of debris, which has the same shape as the TiC particles, observed on the worn surface of the Ni-coated TiC composite specimen with pits left induced in the surface layer by the spallation of the TiC particles, while there are

only few wear chips observed on that of the bare TiC composite specimen. From the EDX spectrums of the wear debris from the two surfaces, it is seen that the Ti content in the debris from the Ni-coated TiC composite specimen is much higher than that from the bare TiC composite specimen, which implies that the debris from the Ni-coated TiC composite may be entirely composed of TiC particles while those from the bare TiC composite consist only of the chips pulled from the surface. On the other hand, the W content in the debris of the bare TiC reinforced specimen was only from the pinball and was two times higher than that in the debris of the Ni-coated TiC reinforced specimen. That is, the pinball was worn more severely in the bare TiC/Stellite 712 wear test. For the Ni-coated TiC composite specimen, the elements came from the matrix alloy, which was stuck on the particle surfaces when the interfaces were broken. In contrast, for the bare TiC composite specimen, the elements in the debris came from the matrix alloy which was rubbed off from the surface as chips. Some amount of Ni was detected in the debris of the Ni-coated TiC composite, which indicated that the Ni-coating was not spalled off the TiC surface during wear.

The results and observations from the wear test indicate that the interfacial bonding in the Ni-coated TiC composites is much weaker than that in the bare TiC composites. This issue relates to wetting, interface reaction and material transition on the interface. TiC, with a non-stoichiometric rock salt structure, is energetically stable, but it forms mutual solid solutions with alloys, while Ni forms intermetallic compounds and carbides on the metal side [18]. The bonding by formation of mutual solid solutions is usually stronger than that by formation of intermetallic compounds and carbides on only one side.

6.2.6 Relationship between friction coefficient and wear resistance

From the results presented in the previous chapter, the friction coefficients of the composites reinforced with the bare or Ni-coated TiC were lower than that of pure Stellite 712, and the friction coefficients of the composites varied with the content of TiC, but the variation range was small, from 0.35 to 0.55 for bare TiC reinforced composites and from 0.55 to 0.7 for Ni-coated TiC reinforced composites. In general, wear is related to friction in a complex manner. In this research, the Ni-coated TiC reinforced composites have much lower wear resistance than the bare TiC reinforced ones, but the friction coefficients for the two types of composites were close, although the Ni-coated TiC reinforced composites had slightly higher values than the bare TiC reinforced ones. This demonstrated that the friction coefficients for the materials in the present wear test were not the main factors influencing on the wear losses.

Chapter 7

Conclusions

Based on the results and discussions, the following conclusions can be drawn:

1. TiC-reinforced Stellite 712 composites have been developed using the PM techniques; highly consolidated specimens (relative density > 94%) have been achieved.
2. The two PM methods produced the same phases in the microstructures of the specimens. The main phases in the Stellite 712 matrix are the cobalt-rich solid solution and two carbides: the white M_7C_3 (molybdenum-rich carbide) and the black $M_{23}C_6$ (chromium-rich carbide) as observed in the SEM backscatter images.
3. The specimens fabricated by the sinter + HIP'ing process have larger carbide particle sizes although the sintering temperatures of the two PM methods were the same. The higher temperature promoted the growth of the particles.
4. The hardness of Stellite 712 has been increased by TiC reinforcement, but the hardness of the composites was decreased when the TiC content in the

composite reached a certain level (50 wt. %) due to the brittle interfaces. This brittleness was caused by a reduction of the relative amount of binder phase available.

5. The wear resistance of Stellite 712 has been enhanced significantly by the reinforcement of bare TiC with an optimum content of 30 wt. %. The optimum temperature of the HIP'ing powder solidification process for the composites was 1160°C, which provided the specimens with the highest hardness and wear resistance.
6. The specimens fabricated by the sintering + HIP'ing process exhibited much higher wear resistance compared with that achieved by the HIP'ing powder solidification process.
7. The Ni coating on the TiC particles improved the fracture toughness of the composites. However, it lowered the interface bonding strength and thus resulted in the spallation of the TiC particles from the surfaces during the wear, leading to high wear loss.
8. Although a large difference in wear resistance between bare TiC/Stellite 712 and Ni-coated TiC/Stellite 712 was observed, the friction coefficients for the two composites were close, which indicated that friction coefficient was not the major factor influencing the wear loss of the materials.

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Table 2.1 Advantages and limitations of sinter plus HIP processing
versus HIP powder consolidation

Sinter + HIP	HIP powder consolidation
Advantages	
No canning required	No pre-HIP'ing sinter
Sintered parts easily handled	Lower additive concentrations
Higher packing density in the Autoclave	Minimal grain growth at full density
	Prevent loss of volatile species
Limitations	
Require sintering to state of closed porosity	Require coating or canning
Additions of sintering aids can degrade properties	Lower packing density in Autoclave
May develop coarse grains during sintering reducing product strength	Pre-forms may be difficult to handle
Surfaced-connected defects will not heal during HIP'ing	
Potential volatilization of constituent or decomposition effects	

Table 3.1 The composition of Stellite 712 (wt. %)

C	Si	Fe	Cr	Ni	Mo	Co
1.8	1	2.5	29	2.5	9	Balance

Table 5.1 Measured densities and relative densities of
pure Stellite 712 and its composites

Materials	HIP'ed 1080°C	HIP'ed 1120°C	HIP'ed 1160°C	Theoretical density
Pure Stellite 712 (g/m ³)	7.94	8.08	7.96	8.25
Composites with 20% bare TiC reinforcement (g/m ³)	6.98	7.13	7.18	7.27
Composites with 20% Ni-coated TiC reinforcement (g/m ³)	-	7.13	6.99	7.27
Composites with 20% bare TiC reinforcement (g/m ³)	-	6.471	6.48	6.87
Composites with 20% Ni-coated TiC reinforcement (g/m ³)	-	6.97	6.90	6.87

Figure 2.1 Classes of metal matrix composites (MMCs)

Figure 2.2 Schematic illustration of the contact angle in (a) non-wetting systems, and (b) wetting systems

Figure 2.3 Overall energy changes for immersion of 250-micron graphite particle in alimunum alloys with contact angles $\theta = 157^\circ$ and $\theta = 60^\circ$ (due to the use of metal coating on graphite)

Figure 2.4 A cut-away view of an ASEA HIP

Figure 2.5 Schematic representation of HIP'ing process for HIP powder consolidation

Figure 2.6 Schematic representations of stages of sintering

Figure 3.1 SEM image of pure Stellite 712 powder

Figure 3.2 BEI image of pure Stellite 712 powder

Figure 3.3 SEM image of pure bare TiC powder

Figure 3.4 SEM image of Ni-coated TiC powder

Figure 3.5 SEM image of 20% bare TiC/Stellite 712 powder mixture

Figure 3.6 SEM image of 20% Ni-coated TiC/Stellite 712 powder mixture

Figure 3.7 Vacuum system for canning powders:

(A) roughing pump, (B) vacuum pump, (C) sample tubes

Figure 3.8 Schematic representation of sintering plus HIP'ing process

Figure 3.9 DSC heating/cooling cycle

Figure 3.10 DSC results of pure Stellite 712 powder

Figure 3.11 DSC results of 20% bare TiC/Stellite 712 powder

Figure 3.12 DSC results of 20% Ni-coated TiC/Stellite 712 powder

Figure 3.13 Typical profiles of temperature and pressure for the HIP'ing process

Figure 3.14 Sintering cycle for pure Stellite 712 powder

Figure 3.15 Sintering cycle for 20% bare TiC/Stellite 712 powder

(a)

(b)

Figure 4.1 Backscatter images of Stellite 712 by HIP powder consolidation:
(a) at 1120°C, (b) at 1160°C

(a)

	Element wt%	atom %	app. conc%	ZAF factor	3 sigma
Cr	2.47	26.96	25.88	0.726	0.6335
Fe	0.70	0.86	0.80	0.656	0.1073
Co	35.55	41.30	41.05	0.663	0.8359
Mo	43.27	30.88	32.27	0.428	1.5138
Total	99.99				

(b)

Figure 4.2 EDX spectra for the white area of Stellite 712 HIP'ed at 1120°C:
(a) EDX spectrum, (b) composition

	Element wt%	atom %	app. conc%	ZAF factor	3 sigma
Cr	68.14	72.20	77.08	0.842	1.0498
Fe	0.86	0.85	0.64	0.551	0.1269
Co	25.41	23.75	19.40	0.568	0.7469
Mo	5.57	3.20	2.89	0.386	0.5593
Total	99.98				

(b)

Figure 4.3 EDX spectra of the black area of Stellite 712 HIP'ed at 1120°C:
 (a) EDX spectrum, (b) composition

	Element wt%	atom %	app. conc%	ZAF factor	3 sigma
Si	2.04	4.08	0.52	0.179	0.4217
Cr	32.45	35.03	39.95	0.864	0.7704
Fe	1.83	1.84	1.72	0.658	0.1828
Co	59.31	56.50	55.70	0.659	0.1414
Mo	4.35	2.55	2.11	0.340	0.5675
Total	99.99				

(b)

Figure 4.4 EDX spectra of the grey-black area of Stellite 712 HIP'ed at 1120°C:
(a) EDX spectrum, (b) composition

Figure 4.5 EDX spectra for the white area of Stellite 712 HIP'ed at 1160°C

Figure 4.6 EDX spectra of the black area of Stellite 712 HIP'ed at 1160°C

Figure 4.7 EDX spectra of the grey-black area of Stellite 712 HIP'ed at 1160°C

Figure 4.8 Backscatter images of 20% bare TiC/Stellite 712 HIP'ed at 1120°C:
 (a) Stellite 712 agglomeration area, (b) bare TiC agglomeration area

(a)

(b)

(c)

(d)

Figure 4.9 EDX spectra for 20% bare TiC/Stellite 712 HIP'ed at 1120°C:
 (a) white area, (b) black area, (c) grey-black area, (d) TiC-rich region

(a)

(b)

Figure 4.10 Backscatter images of 20% bare TiC/Stellite 712 HIP'ed at 1160°C:
 (a) Stellite 712 agglomeration area, (b) bare TiC agglomeration area

(a)

(b)

(c)

Figure 4.11 EDX spectra of 20% bare TiC/Stellite 712 HIP'ed at 1160°C:
(a) white area, (b) black area, (c) grey-black area, (d) TiC-rich region.

Figure 4.12 Backscatter images of 20% Ni-coated TiC/Stellite 712 HIP'ed at 1120°C:
 (a) Stellite 712 agglomeration area, (b) Ni-TiC agglomeration area

(a)

(b)

(c)

(d)

Figure 4.13 EDX spectra of 20% Ni-coated TiC/Stellite 712 HIP'ed at 1120°C:
(a) white area, (b) black area, (c) grey-black area, (d) Ni-TiC region

(a)

(b)

Figure 4.14 Backscatter images of 20% Ni-coated TiC/Stellite 712 HIP'ed at 1160°C:
(a) Stellite 712 agglomeration area, (b) Ni-TiC agglomeration area

(a)

(b)

Figure 4.15 Backscatter images of 30% TiC/Stellite 712 HIP'ed at 1160°C:
(a) with bare TiC, (b) with Ni-coated TiC

(a)

(b)

Figure 4.16 Backscatter images of 50% TiC/Stellite 712 HIP'ed at 1160 °C:
(a) with bare TiC, (b) with Ni-coated TiC

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.17 Element mapping in the composite reinforced with 20% bare TiC:

(a) microstructure, (b) Co, (c) Cr, (d) Mo, (e) Ni, (f) Ti

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.18 Element mapping in the composite reinforced with 20% Ni-coated TiC:

(a) microstructure, (b) Co, (c) Cr, (d) Mo, (e) Ni, (f) Ti

(a)

(b)

Figure 4.19 X-ray diffraction patterns:
 (a) sintered and HIP'ed Stellite 712, (b) sintered and HIP'ed TiC/Stellite 712

Figure 4.20 SEM backscatter electron images of the microstructures:
 (a) Sintered Stellite 712, (b) HIP'ed Stellite 712,
 (c) sintered TiC/Stellite 712, (d) HIP'ed TiC/Stellite 712

(a)

(b)

(c)

Figure 4.21 EDX spectra of Stellite 712:
 (a) Co-rich solid solution, (b) Cr-rich Cr_{23}C_6 , (c) Cr-rich Cr_7C_3

(a)

(b)

(c)

(d)

Figure 4.22 EDX spectra of TiC/Stellite 712:
 (a) Co-rich solid solution, (b) TiC -rich region,
 (c) Cr-rich Cr_{23}C_6 , (d) Cr-rich Cr_7C_3

Figure 5.1 Relative densities of pure Stellite 712 and the composites

Figure 5.2 Hardness of pure Stellite 712 specimens by HIP powder consolidation

Figure 5.3 Hardness of bare TiC/Stellite 712 composite specimens
by HIP powder consolidation

Figure 5.4 Hardness of Ni-coated TiC/Stellite 712 composite specimens
by HIP powder consolidation

Figure 5.5 Schematic drawing of sliding wear on a pin-on-disc test tribometer

(a)

Figure 5.6 Cross-sectional profiles of the wear tracks of pure Stellite 712 specimens by HIP powder consolidation: (a) at 1080°C, (b) at 1120°C, (c) at 1160°C

Figure 5.7 Wear losses of pure Stellite 712 specimens by HIP powder consolidation

(a)

(b)

(c)

Figure 5.8 Cross-sectional profiles of wear tracks of the Stellite 712 composite specimens HIP'ed at 1120°C: (a) with 20% bare TiC, (b) with 30% bare TiC, (c) with 50% bare TiC

(a)

(b)

Figure 5.9 Cross-sectional profiles of the wear tracks of the Stellite 712 composite specimens HIP'ed at 1160°C: (a) with 20% bare TiC, (b) with 30% bare TiC, (c) with 50% bare TiC

Figure 5.10 Wear losses of bare TiC/Stellite 712 composite specimens by HIP powder consolidation

(a)

(b)

Figure 5.11 Cross-sectional profiles of the wear tracks of the Stellite 712 composite specimens HIP'ed at 1120°C: (a) with 20% Ni-coated TiC, (b) with 30% Ni-coated TiC, (c) 50% Ni-coated TiC

Figure 5.12 Cross-sectional profiles of the wear tracks of the Stellite 712 composite specimens HIP'ed at 1160°C: (a) with 20% Ni-coated TiC, (b) with 30% Ni-coated TiC, (c) with 50% Ni-coated TiC

Figure 5.13 Volume losses of Ni-coated TiC/Stellite 712 composite specimens by HIP powder consolidation.

Figure 5.14 Cross-sectional profiles of the wear tracks: (a) sintered Stellite 712, (b) sintered TiC/Stellite 712, (c) HIP'ed Stellite 712, (d) HIP'ed TiC/Stellite 712

Figure 5.15 Volume losses of pure Stellite 712 and its composites by Sintering+HIPing process

Figure 5.16 Friction coefficient with time for pure Stellite 712 by HIP powder consolidation: (a) HIP'ed at 1120°C, (b) HIP'ed at 1160°C

(b)

(c)

Figure 5.17 Friction coefficient with time for the Stellite 712 composite specimens HIP'ed at 1120°C: (a) with 20% bare TiC, (b) with 30% bare TiC, (c) with 50% bare TiC

(c)

Figure 5.18 Friction coefficient with time for the Stellite 712 composite specimens HIP'ed at 1160°C: (a) with 20% bare TiC, (b) with 30% bare TiC, (c) with 50% bare TiC

Figure 5.19 Friction coefficients for the TiC/Stellite 712 composites with different bare TiC contents by HIP powder consolidation.

(a)

(b)

(c)

Figure 5.20 Friction coefficients with time for the Stellite 712 composite specimens HIP'ed at 1120°C: (a) with 20% Ni-coated TiC, (b) with 30% Ni-coated TiC, (c) with 50% Ni-coated TiC

(a)

(b)

(c)

Figure 5.21 Friction coefficients with time for the Stellite 712 composite specimens HIP'ed at 1160°C: (a) with 20% Ni-coated TiC, (b) with 30% Ni-coated TiC, (c) with 50% Ni-coated TiC

Figure 5.22 Friction coefficients for the Ni-coated TiC/Stellite 712 composites with different TiC contents by HIP powder consolidation

(a)

(b)

Figure 5.23 Worn surfaces of the specimens by HIP powder consolidation:
(a) with 20% bare TiC/Stellite 712, (b) with 20% Ni-coated TiC/Stellite 712

Figure 5.24 EDX spectra of the worn debris for the composite specimens HIP'ed at 1160°C: (a) with 20% bare TiC 712, (b) with 20% Ni-coated TiC

(a)

(b)

Figure 5.25 Worn tracks of the composite specimens for the composite specimens HIP'ed at 1160°C: (a) with 20% bare TiC 712, (b) with 20% Ni-coated TiC

Figure 6.1 Volume losses of pure Stellite 712 by the two PM methods

Figure 6.2 Relationship between the hardness and the wear loss of the bare TiC reinforced composites by HIP powder consolidation

Figure 6.3 Volume Losses of the Stellite 712 Composite specimens by HIP powder consolidation

(a)

(b)

Figure 6.4 SEM images of the fractured surfaces of the specimens by HIP powder consolidation: (a) with 20% bare TiC/Stellite 712, (b) with 20% Ni-coated TiC/Stellite 712

(a)

(b)

Figure 6.5 the SEM images of the fractured surfaces of the specimens by HIP powder consolidation: (a) with 30% bare TiC/Stellite 712, (b) with 30% Ni-coated TiC/Stellite 712

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(a)

(b)

Figure 6.6 the SEM images of the fractured surfaces of the specimens by HIP powder consolidation: (a) with 50% bare TiC/Stellite 712, (b) with 50% Ni-coated TiC/Stellite 712