Al-Cr-Fe quasicrystals and their applications as reinforcements in the Ti based metal matrix composites

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**Al-Cr-Fe Quasicrystals and Their Applications as
Reinforcements in the Ti Based Metal Matrix
Composites**

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Nomenclature

CA	Ti based composites reinforced with as-annealed Al-Cr-Fe powders consolidated using high pressure spark plasma sintering
CS	Ti based composites reinforced with sieved Al-Cr-Fe powders consolidated using high pressure spark plasma sintering
D-AlCrFe	decagonal Al-Cr-Fe
DSC	differential scanning calorimetry
EDS	energy-dispersive spectroscopy
HP-SPS	high pressure spark plasma sintering
HR-TEM	high resolution transmission electron microscope
HT-XRD	high temperature X-ray diffraction
I-AlCrFe	Icosahedral Al-Cr-Fe
MMCs	metal matrix composites
OM	optical microscopy
PA	polyamide
SAED	selected area electron diffraction
SEM	scanning electron microscopy
SPS	spark plasma sintering
TACF	Ti/Al-Cr-Fe metal matrix composites consolidated using spark plasma sintering
TEM	transmission electron microscope
TM	transition metal
UHMWPE	ultra-high molecular weight polyethylene
XRD	X-ray diffraction

Abstract

In this study, the microstructural evolution and phase transformations of gas atomized Al-Cr-Fe powders during annealing process, spark plasma sintering (SPS) of Al-Cr-Fe powders and SPS of Ti/Al-Cr-Fe metal matrix composites (MMCs) were investigated.

There are four phases identified in the annealed Al-Cr-Fe powders: icosahedral Al-Cr-Fe, decagonal Al-Cr-Fe, $\text{Al}_9(\text{Cr,Fe})_4$ and $\text{Al}_8(\text{Cr,Fe})_5$, with decagonal Al-Cr-Fe forming in the annealing process. Icosahedral Al-Cr-Fe is face-centered. Decagonal Al-Cr-Fe has a periodicity of about 1.2 nm along its periodic axis and it can be well superimposed by Penrose tilings.

Al-Cr-Fe powders have been successfully sintered using SPS. With the rise of the sintering temperature from 650 °C to 800 °C, the relative density of the pellets increases from 70% to 99% and their microhardness increases from Hv 400 to Hv 810. The dominant densification mechanism of Al-Cr-Fe powders in the SPS process is powder rearrangement and dislocation motion. The SPS process promotes the formation of decagonal Al-Cr-Fe.

Ti/Al-Cr-Fe MMCs with Ti as matrix and Al-Cr-Fe quasicrystals as reinforcements have been successfully prepared using high pressure SPS. Interfacial layer forms between Ti and Al-Cr-Fe during the sintering process. This layer mainly consists of Al_3Ti and AlTi . With the increase of sintering pressure from 50 MPa to 300 MPa, the compositional

changes of Al-Cr-Fe are reduced. The addition of Al-Cr-Fe particles to Ti matrix significantly improves the hardness and reduces the wear rate.

This study shows for the first time that Al-Cr-Fe quasicrystals can be sintered using SPS and SPS process can promote the formation of decagonal Al-Cr-Fe and the increased sintering pressure leads to reduced compositional changes of Al-Cr-Fe reinforcements in the Ti based MMCs prepared using SPS.

Chapter 1   Introduction

1.1   Quasicrystals

In 1984, Israeli physicist Daniel Shechtman discovered a phase with 5-fold symmetries but no translational order using transmission electron microscope (TEM) in a rapidly solidified Al–Mn alloy [1]. He proved that this was a new phase with atoms arranged in a quasi-periodic way in three dimensions, as shown in Figure 1-1. This discovery was revolutionary as symmetries other than 1, 2, 3, 4 and 6 were forbidden in the conventional crystallography. And he was awarded the Noble prize for Chemistry in 2011 for this great discovery, which redefined the crystallography: in solid atoms can be arranged in an ordered but not periodic way. Naturally, materials with this unique atomic arrangement are named quasicrystals. These materials can produce Bragg diffraction like crystals though their atomic arrangement is more complex than crystals which just have one simple repeating unit. After this discovery, more than 100 different types of quasicrystals have been discovered [2], which are found most often in aluminum alloys (Al-Li-Cu, Al-Mn-Si, Al-Ni-Co, Al-Pd-Mn, Al-Cu-Fe, Al-Cu-V, Al-Cr-Fe etc.) and also in other alloys (Cd-Yb, Ti-Zr-Ni, Zn-Mg-Ho, Zn-Mg-Sc, In-Ag-Yb, Pd-U-Si, Ti-Zr-Ni etc.) [3]. As a matter of fact, they are not only created under precisely controlled laboratory conditions but also found in nature: in 2009 Paul Steinhardt discovered a naturally occurring quasicrystal in a rock sample from Russia [4].

Figure 1-1 The diffraction patterns of icosahedral quasicrystal along (a) 5-fold, (b) 3-fold and (c) 2-fold axes. (d) An icosahedron [1].

Because of their special atomic arrangement, quasicrystals have unique bulk and surface properties like low surface energy, low thermal conduction, high hardness, low friction, and good oxidation resistance [5-8]. This set of properties makes them have wide potential applications in catalysis [9], hydrogen storage [10], reinforcement of metal matrix [11] and polymer matrix [12] composites, thermal barrier coatings, non-stick coatings as well as wear resistant coatings [13].

The discovery of quasicrystals opened a fascinating world, which draw a lot of attention from mathematicians, physicists, chemists, materials scientists and crystallographers. The crystallography, preparation, properties and potential applications have been intensively studied. This laid a solid foundation for the understanding the nature of quasicrystals and also utilizing their unique properties in production to benefit human beings.

1.1.1 Crystallography of quasicrystals

Because of their long-range-ordered but not periodic atomic arrangement, quasicrystals cannot be described by the conventional crystallography directly. Mathematicians' discoveries provide tools for the description of quasicrystalline structure. The Fibonacci sequence is a fundamental example of a quasiperiodic structure exhibiting aperiodic long-range order. It illustrates some important properties of quasicrystals. The tiling approach and higher-dimensional approach are adopted to describe the quasicrystalline structure. The tiling or “quasilattice” approach is quite similar to the description of periodic structures but it needs at least two different “unit cells”; while partially overlapping “covering clusters” allow the description of the full quasiperiodic structure using only one type of cluster.

(a) Fibonacci sequence

The Fibonacci sequence is built from two elements ‘L’ (large) and ‘S’ (small), with $L = \tau S$ (τ the golden mean) [14, 15]. The sequence can be generated by a substitution rule $L \rightarrow LS$ and $S \rightarrow L$. The substitution rule is also called inflation operation rule as the number of letters is inflated by each step [15]. The resulting sequence is shown in Figure 1-2. It is ordered but not periodic. The sequence of L and S segments is deterministic. The

frequencies of 'L' and 'S' in each sequence and the ratio of successive Fibonacci number (number of line segments in each generation) is τ in the limit of infinite sequence length [16]. The sequence is self-similar. This implies that inflation or deflation of a Fibonacci sequence yields another Fibonacci sequences with different length segment. The Fourier transform of such arrangements consists of discrete values, which is the defining property for crystals [15]. In an algebraic form the sequence is expressed with a matrix whose eigenvalues are Pisot numbers. This feature guarantees that its Fourier transform is discrete. Material waves with appropriate length would interfere constructively when interacting with a Fibonacci structure.

Figure 1-2 Inflation of Fibonacci sequence [16].

(b) Penrose Tiling

In 1974, British mathematician and physicist, Roger Penrose, found that the 2D plane can be filled non-periodically with two types of rhombi with equal edge length [17]. This filling was named Penrose tiling after him. His findings became even more important after the discovery of quasicrystal in 1984 as it can be used to describe the quasicrystalline structure.

Two types of rhombi, one with an angle of 36° (skinny rhombus) and the other with an angle of 72° (fat rhombus) can fill a 2D plane non-periodically as shown in Figure 1-3. However, a perfect quasiperiodic pattern can be obtained only if the tiles are packed under a specific matching rule. That is, two rhombi can join only if the arrows in their common edge match.

Penrose tiling has self-similarity. That is a Penrose pattern can be transformed to another Penrose pattern by deflating / inflating the skinny and fat rhombi. Figure 1-4 shows the inflating (deflating) scheme, where the smaller fat and skinny rhombi can be combined to form larger fat and skinny rhombi. The fat rhombus is the combination of two fat and one skinny rhombus, while the skinny rhombus is the combination of one fat and one skinny rhombus. The area of the larger fat and skinny rhombi is larger than the respective smaller rhombi by a factor of τ^2 . Starting from a single rhombus, an arbitrarily large section of a Penrose tiling can be produced by continuously applying the inflation (deflation) rule.

Figure 1-3 A rhombic Penrose pattern (right) generated by two rhombi (left) [18].

Figure 1-4 Scaling of the Penrose tiling: (a) the substitution rule for the rhomb Penrose tiling; (b) a Penrose tiling (thin lines) is superposed by its inflated tiling [15].

The Penrose patterns possess many interesting features. Both areas and frequencies of skinny and fat rhombi in the pattern are of a ratio $1 : \tau$. The decoration lines in the two rhombic can form five bundles of parallel lines in the Penrose pattern. The spacing of these lines in any given direction can be described by Fibonacci sequence, as shown in Figure 1-5. This demonstrates the long range order of the Penrose pattern.

Figure 1-5 The decoration lines of Penrose pattern [15].

There are some other 2D quasicrystalline tilings such as the pentagonal Penrose tiling and the octagonal Penrose tiling, which explain the diffraction pattern of other polygonal quasicrystals. The idea of space tiling can be extended into 3D space, where two kinds of rhombohedrons are needed to fill the 3D space aperiodically.

Petra Gummelt proved that a quasiperiodic Penrose tiling can be generated using a single decagon combined with a novel overlapping rule (Figure 1-6 a) [19]. This rule is realized by decorating the interior of the decagons with a subset of shaded tiles, and two decagons may overlap only if shaded areas overlap (Figure 1-6b). This is equivalent to Penrose's

arrow matching rules. In tiling there is no overlapping. But here it becomes a basic construction element.

Figure 1-6 (a) Gummelt's decorated decagon; (b) the resulting quasiperiodic decagonal coverage of the plane [20]

(c) Superspace crystallography

The superspace crystallography was introduced by de Wolff [21], Janner and Janssen [22, 23] to describe incommensurately modulated structure and incommensurate composite crystals. Non-periodic modulated structures are generally viewed as non-periodic long-range-ordered structures. However, they can be viewed as a “perturbation” of a periodic structure. It is proven that an incommensurately modulated structure can be viewed as a periodic structure in superspace having dimensions larger than three. The number of dimensions is equal to $3+n$, where n is the number of independent modulation q -vectors. This approach allows to classify the space groups, and the computation of the structure factor. It can be well demonstrated using one dimensional (1D) quasicrystal, which can be obtained as a section of a decorated 2D square lattice, as shown in Figure 1-7. The square lattice is decomposed in two 1D subspaces: the physical space, also called parallel space, and the perpendicular space. The slope of the parallel space, s , is irrational. The square lattice is decorated by segment lines, lying in the perpendicular direction. The resulting

1D quasiperiodic structure is obtained as a section of the decorated 2D lattice: each time the line crosses the parallel space an atomic position is generated. When the segment line length is equal to the projection of the square, a Fibonacci chain is generated. If the slope of the cut space is rational instead of irrational, this generates a periodic approximant. This is equivalent to approximating s (the slope of the parallel space) by successive rational Fibonacci numbers such as $1/1$, $2/1$, $3/2$ .... In real systems $1/1$ and $2/1$ approximant have been observed. A similar procedure can be performed in reciprocal space. The Fourier transform of the 2D decorated lattice is shown in Figure 1-7. The 1D diffraction pattern is obtained as a projection of the 2D diffraction pattern on the Q_{par} line. As the 2D Fourier transform involves the Fourier transform of the shape function of the segment line, the intensity of the Bragg peaks decays rapidly as their perpendicular component increases. Consequently, the strongest peaks have a small perpendicular component (Figure 1-7). It can be also seen that the 1D diffraction pattern can be indexed using two integer indices. In addition, the number of Bragg peaks is infinite but only a finite number subsists if an intensity threshold is given.

Figure 1-7 Schematic presentation of the superspace approach for 1D quasicrystal: (a) 2D embedding of the Fibonacci chain; (b) reciprocal space [24].

This superspace embedding can be generalized to 3D quasicrystals. In the case of the icosahedral symmetry, a 6D space is required to describe the quasicrystal. This is related to the six 5-fold axes of the icosahedrons. The segment lines are now 3D objects, which

are generally described as polyhedra. The structure is fully described by the position and the detailed shape of these polyhedra.

1.1.2 Energetic stabilization mechanism

Why do atoms array aperiodically in quasicrystals? Two different kinds of mechanism are proposed to explain the aperiodic arrangement of atoms in quasicrystals. One is based on an energetic stabilization and the other one is based on an entropic stabilization. Depending on the specific quasicrystalline phase, one of these two approaches reflects the dominant mechanism of stabilization.

(a) Entropic Stabilization

The energetic stabilization of quasicrystals can be interpreted in terms of a perfect Penrose tiling. The edge-matching rules of the Penrose tiling reflect local rules to attain a minimal binding energy. However, some quasicrystals are stable only at high temperature and convert into crystalline phases at low temperature [25]. Thus, it can be expected that entropy may be responsible for stabilizing the quasicrystalline phases. The entropic stabilization can be described as random tilings. For random tilings, the edge-matching rules of the Penrose tiling are completely discarded and the tiles are allowed to join randomly to fill the space without gaps. This randomness causes topological disorder in the system. The randomization of tilings may not be the only source of entropy. The entropy can be induced by chemical disorder (chemical entropy) as well. If the chemical entropy is dominant, the structure can be topologically ordered even at high temperatures.

(b) Electronic Stabilization

An alternative mechanism to explain the energetic stability of quasicrystals is electronic stabilization. Electronic properties and stoichiometry of many quasicrystals indicate that Hume-Rothery type mechanism of intermetallic compounds may be responsible for the stability of quasicrystals [26-28]. The Hume-Rothery mechanism states that a specific structure of alloy is formed for a fixed effective density of valence electrons in such a way that the Fermi surface matches the Brillouin zone boundary opening a pseudogap [26, 29, 30], which lowers the energy of the system.

In fact, many stable icosahedral quasicrystals are found to have a specific value of electron-per-atom ratio, e/a (2.1 for the Zn-Mg-Al class and 1.75 for the Al-TM class, where TM refers to transition metals) [25, 31], satisfying the condition of gap opening at Fermi level, i.e., $Q=2k_F$ (where Q is the magnitude of reciprocal lattice vector and k_F the radius of the Fermi sphere). In some quasicrystals, a pseudogap at the Fermi level has been found theoretically and experimentally supporting the Hume-Rothery type mechanism for these icosahedral phases.

1.1.3 Dimensionality of quasicrystals

All quasicrystals known so far are classified into three groups from the dimensionality of view: three-dimension, two-dimension and one-dimension. They have quasiperiodicity in all three dimensions, two dimensions and only one dimension, respectively.

(a) 3D quasicrystals

3D quasicrystals, also called icosahedral phases or icosahedral quasicrystals, exhibit icosahedral diffraction symmetry. Only this phase is quasiperiodic in all three dimensions

[32]. Icosahedral quasicrystals are often classified in terms of the prevalent clusters, which can either be the Mackay or pseudo-Mackay cluster (type A)[33], the Bergman cluster (type B or Frank-Kasper type)[34], and the Tsai (type C) cluster [35].

1) Mackay-cluster based icosahedral phases

All the Mackay-cluster based icosahedral phases discovered so far, have Al as their main constituent, Cu or Pd as their second component and a transition element from group 7 (Mn, Tc, Re) or group 8 (Fe, Ru, Os) as their third constituent [15]. They are also called spd-quasicrystals because of the hybridization between the p states of Al atoms and the d states of the transition metal (TM) atoms [27]. It is a 54-atom cluster with icosahedral symmetry in three successive shells (Figure 1-8): a regular small icosahedron (Al), a large icosahedron (TM) and an icosidodecahedron (Al). An inner icosahedron (II) has twelve vertices. Twelve black atoms are located immediately above them to form a larger icosahedron (TM), which has 30 edges. The 30 mid-edge sites are filled with atoms to form an icosidodecahedron, which has 30 identical vertices. These vertices can be divided into 6 sites MI1 and 24 sites MI2.

Figure 1-8 Mackay icosahedral cluster [36].

2) Bergman-cluster based icosahedral phases

The elements of this type of quasicrystals are those with s and p valence electrons, so this type of quasicrystal is also called sp-quasicrystal [27]. The 3d electrons of Cu are viewed as core electrons as they do not change the Fermi energy much. Their composition is related to an electron concentration of $2.1 \leq e/a \leq 2.4$. This type of icosahedral phases is also named Frank–Kasper-type quasicrystals [15] because their approximants are Frank–Kasper phases. Icosahedral cluster for Frank-Kasper phases consists of 117 atoms. A central atom (1) is enclosed by several shells of atoms, which are placed at the vertices of some polyhedra of increasing size. In successive order these are icosahedron (12), pentagon dodecahedron (20), icosahedron (12), soccer ball (60) and icosahedron (12).

3) Tsai-cluster based icosahedral phases

Tsai-cluster based icosahedral phases were discovered the latest [35]. The most interesting thing for these quasicrystals is that stable phases can exist in the binary systems Cd–Ca and Cd–Yb. This means that chemical order can be more easily determined using X-ray structural analysis. It also means that quasiperiodicity does not necessarily requires chemical disorder and the entropy gain related [15]. These icosahedral clusters consist of four layered atomic shells: a tetrahedron (4), a dodecahedron (20), an icosahedron (12) and an icosidodecahedron (30) from inner to outer [37].

(b) 2D quasicrystals

A 2D quasicrystal is quasiperiodic in two-dimensions and periodic in the third dimension. Shortly after the discovery of the icosahedral quasicrystal, the first 2D quasicrystal, a decagonal quasicrystal which has a point group symmetry $10/mmm$, was discovered [38]. Figure 1-9 shows the schematic of the decagonal phase. The tenfold axis is the axis along

which the diffraction spots are arranged periodically. Perpendicular to this axis is the quasiperiodic plane in which the spots are arranged in a quasiperiodic array with a ten-fold symmetry. 2D quasicrystals with eight and 12-fold symmetries, which are called respectively octagonal and dodecagonal quasicrystals, have also been observed in some alloys.

Figure 1-9 Schematic of decagonal phase [18].

(c) 1D quasicrystals

A 1D quasicrystal is quasiperiodic in only one axis. Perpendicular to this axis is a periodic plane in which atoms are arranged in a periodic array. One class of metastable 1D quasicrystals forms as the intermediate state during the transformation from a decagonal phase to an approximant, such as rapidly solidified $\text{Al}_{80}\text{Ni}_{14}\text{Si}_6$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$ alloys [39]. Such phase transformation can be described by linear phason

strain. Stable 1D quasicrystals have been found in annealed samples with compositions $\text{Al}_{75}\text{Fe}_{10}\text{Pd}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{10}\text{Mn}_5$ [40, 41].

1.1.4 Thermal stability

Quasicrystals can be divided into metastable quasicrystals and stable quasicrystals in terms of their thermal stability. Metastable quasicrystals transform to crystals upon heating and their equilibrium states are generally crystalline compounds, which are called crystalline approximants. These approximants share very similar composition and structural unit with quasicrystals. As metastable quasicrystals are generally prepared by rapid solidification of the corresponding crystalline approximants, they are viewed as energetically nonequilibrium phases or metastable phases with respect to the corresponding crystalline approximants [31, 42]. These quasicrystals are often in micrometers. In contrast, thermodynamically stable quasicrystals can be prepared by slow cooling or casting and they can grow to a considerable size and exhibit the typical features of well-ordered crystalline phases. The first prepared quasicrystals were all metastable until the first stable quasicrystal was discovered in 1987 [43]. Due to their large size, stable quasicrystals make it easier to study the properties of quasicrystals. Some examples of alloys with quasicrystalline structure and the thermal stability of these quasicrystalline phases are listed in Table 1-1.

Table 1-1 Alloys with quasicrystalline structure [2, 44].

Types	Thermal stability	
	Metastable	Stable
Icosahedral	Al-TM (TM=V, Cr, Mn, Ru, Re, ...), Al-(Mn,Cr,Fe)-(Si,Ge), Al-(Cu,Pd)-TM (TM=Cr, Mn, Fe, Mo, Ru, Re, Os), Ga-Pd-Mn, Mg-Al-(Zn, Cu, An, Pd), Al-Mg-(Cu, Ag), Ga-Mg-Zn, Al-Li-(Cu, Au, Zn, Mg), Zn-Mg-RE (RE=Y, Nd, Sm, Dy, Gd, Er, Ho, Tb)	Al ₆₃ Cu ₂₅ TM ₁₂ (TM=Fe, Ru, Os), Al ₇₀ Pd ₂₀ TM ₁₀ (TM=Mn, Re), Al ₇₀ Pd ₂₀ V ₅ Co ₅ , Al ₇₀ Pd ₂₀ Cr ₅ Fe ₅ , Al ₇₀ Pd ₂₀ Mo ₅ Ru ₅ , Al ₇₀ Pd ₂₀ W ₅ Os ₅ , Al ₅₆ Li ₃₃ Cu ₁₁ , Ga ₂₀ Mg ₃₇ Zn ₄₃ , Ti ₄₅ Zr ₃₈ Ni ₁₇ , Zn ₆₀ Mg ₃₀ RE ₁₀ (RE= Y, Dy, Gd, Ho, Tb, Er)
Decagonal	Al-TM (TM=Mn, Cr, Co, Fe, Pd), Al-(Cu, Ni, Pd)-TM, (TM=Fe, Ru, Re, Co, Rh, Ir), Fe ₆₀ Nb ₄₀ , Zn-Mg-RE (RE=Y, Dy, Ho, Lu, Tb, Gd)	Al ₇₀ Ni _x Co _{30-x} (x=10-20) Al ₆₅ Cu ₁₅ Co ₂₀ , Al ₇₅ Pd ₁₅ TM ₁₀ (TM=Fe, Ru, Os) Al ₇₀ Pd ₁₃ Mn ₁₇ , Zn ₆₀ Mg ₃₈ RE ₂ (RE=Y, Dy, Ho, Lu, Tb, Gd)
Octagonal	Cr-Ni-Si, V-Ni-Si	
Dodecagonal	Cr-Ni, Bi-Mn	Ta _{1.6} Te

1.1.5 Properties and potential applications

The thermal conductivity of quasicrystals is much smaller than that of purely metallic compounds [25, 45]. Another important feature of thermal conductivity for quasicrystals is the temperature dependence: at higher temperature, it keeps an increasing trend [46]. This is quite different from classical metals. The temperature-dependent thermal conductivity properties can be applied for thermometry and heat flow detection [46]. More importantly, the quasicrystal coatings on bulk metals as efficient thermal barrier layers for engines can be expected [47].

The electrical conductivity of quasicrystals is generally smaller than that of crystalline metallic alloys. The electrical properties are mainly determined by the electronic structure of materials. In quasicrystals, a gap exists in the density of electron states and it makes the

electron transport difficult [48]. In addition, the electrical conductivity is heavily related to the structural order and stoichiometry [49]. The fewer defects the quasicrystals have, the higher electrical resistivity the quasicrystals possess. And a minor compositional change can lead to a big electrical conductivity difference.

Thermoelectric power properties of quasicrystals also draw a lot of attention [25, 50]. Some quasicrystals have appreciable thermoelectric power of the order of $S=80 \mu\text{V}/\text{K}$ [51]. As they exhibit both low electrical and low thermal conductivity, the corresponding figure of merit reaches 0.1-0.2 [5]. The composition and structural perfection have a big influence on the thermoelectric power [50, 51], which may change from large and positive to weakly negative within a few percent of compositional change. In order to apply quasicrystals to thermopower generators, good stability at high temperatures, high thermopower and also a low lattice thermal conductivity should be achieved by properly choosing their composition and preparation methods.

Quasicrystals also show some special magnetic features. Strictly stoichiometric quasicrystals are diamagnetic with a negative susceptibility [52, 53]. Their frequency dependence $\sigma(\omega)$ of the electrical conductivity is also quite different from that of metals. Possible applications of such properties include energy coatings for solar cells, insulator screens or window glass [46].

Hydrogen storage is also a very significant aspect of properties for some quasicrystals. In the mid 1990's, Ti-Zr-Hf-based quasicrystals were found to store more hydrogen than

competing crystal intermetallic compounds [54]. The tetrahedral interstitial sites in icosahedral quasicrystals favor the absorption of hydrogen atoms [55]. Since Ti, Zr or Hf alloys are favorable of hydrogen absorption, Ti-Zr-Hf based quasicrystals are believed to be the most promising hydrogen storage quasicrystalline materials.

Some other important properties of quasicrystals include high hardness, low wetting, good corrosion resistance, a brittle-ductile transition, and super plasticity above 700 °C (for most quasicrystals) [2, 5, 13]. Some of these properties can be applied in combination to meet the special needs of certain components. Unfortunately, quasicrystals are very brittle at room temperature. This restricts their applications as bulk load-bearing components, even though super plasticity shows up at high temperature.

Unlike amorphous alloys, which benefit from the disordered state in corrosion resistance, quasicrystalline alloys do not show a better or a poorer corrosion resistance in corrosive solutions than their crystalline counterparts [56]. Composition is more important than structure in determining the corrosion resistance of quasicrystals. However, the compositional range of quasicrystals enables them to exhibit good corrosion resistance. Moreover, addition of Cr was found to be a very effective way to reduce the corrosion of quasicrystals [56].

Anti-adhesion and low friction coefficients are two very important features for tribological applications. In terms of adhesion properties, quasicrystal appears as an intermediate between polytetrafluoroethylene, a well-known low wetting material, and the

native oxide of its main constituent [57]. The low friction coefficient of a quasicrystal against a typical indenter like high-Cr hard steel is also interesting: under the same experimental conditions, the coefficient of friction of quasicrystal is about half of that of hard steel, though the mechanical properties (hardness, Young's modulus, etc.) of the two materials are comparable [58, 59].

The combination of non-sticking, high hardness and good corrosion resistance properties make quasicrystals good candidates for coatings on the cookware: the non-sticking property of the coatings makes cooked food not stick to the pan; the good corrosion resistance property makes the food unspoiled by chemical reaction. Also a combination of properties, such as low friction coefficient, high hardness, low thermal conduction as well as good corrosion resistance make quasicrystals good coating materials for cylinder liners and piston as such coatings can reduce surface damage and energy dissipation [46]. These properties together with good biocompatibility enable quasicrystals to be used for surgical applications like bone repair and prostheses [60].

1.1.6 Preparation methods

The preparation methods of quasicrystals generally depend on their thermal stability. Thermodynamic stable quasicrystals can be prepared by conventional equilibrium methods including fusion of the constituents, homogenization of the liquid, solidification [61]. The preparation process is often under vacuum or inert atmosphere, since most alloys, capable of forming quasicrystalline phases, are easily oxidized. In contrast, the metastable quasicrystals are in a non-equilibrium state. Thus, they cannot be synthesized by conventional casting methods. Rapid solidification including melt spinning and gas

atomization, and mechanical alloying are applied to prepare metastable quasicrystals [2, 62].

The powders prepared by rapid solidification techniques can retain the high-temperature microstructure and they can have an extended solid solubility of elements because the melt solidifies so rapidly that there is no time for the microstructural changes to occur. It can yield new non-equilibrium phases, including quasicrystals. Melt spinning and gas atomization are the two most widely used rapid solidification techniques. They can also be utilized to produce quasicrystals [38, 47, 63]. During melt spinning process, the liquid metal, which is ejected from a nozzle, impinges a rotating copper roller, forming very small ribbons. The quenching rate in this process can reach $\sim 10^4\text{-}10^7 \text{ K s}^{-1}$ [64]. Processing parameters have significant influences on the microstructure and properties of the resultant ribbons [65]. Therefore, they need to be carefully chosen to prepare quasicrystals. During gas atomization process, molten metal is broken up into fine droplets, producing fine spherical powders [66]. The quenching rate of gas atomization is higher than that of melt spinning [67]. It's worth mentioning that most available commercial quasicrystal powders are produced by gas atomization due to the spherical shape and good flowing properties of gas atomized powders [2]. Powders produced this way can be used as feeding powders of thermal spray and starting powders for sintering [47, 63].

Mechanical alloying is capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases, starting from blended elemental or prealloyed powders [68]. The

non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys [62, 68]. The elemental powder mixture, grinding media and also the process-controlling agent are added into the grinding vessels. Then the grinding vessels, which are driven by a motor, rotate in a certain way, causing the repeated welding, fracturing, and re-welding of powder particles located between the colliding balls. Generally, the ball milled powders need to be further annealed to obtain quasicrystals.

Besides the methods mentioned above, various methods like electrodeposition, physical vapor deposition, gas evaporation and laser- or electron-beam superficial fusion are also reported to be able to prepare quasicrystals [43, 69-72]. In addition, low-temperature annealing of amorphous alloys or high-temperature heat treatment of crystalline intermetallic can also attain quasicrystals [2].

1.2 Spark plasma sintering

1.2.1 Spark plasma sintering technology

Spark plasma sintering (SPS), also known as field assisted sintering or pulsed electric current sintering, is a low voltage, direct current activated, pressure-assisted sintering technique, which enables sintering to occur in a short time [73]. Figure 1-10 is a schematic of SPS system. It is similar to hot pressing, but how the heat is produced and transmitted to the sintered materials is different.

Figure 1-10 Schematic drawing of an SPS apparatus [74].

It is believed that the spark plasma generated momentarily plays an important role in sintering [75]. In sintering process, ON-OFF DC pulse voltage and current from a special pulse generator generates spark plasma, spark impact pressure, Joule heating and also an electrical field diffusion effect. Additionally, discharge between particles occurring at the initial stage promotes sintering. Such sintering mechanism is illustrated in Figure 1-11. High temperature sputtering phenomenon generated by spark plasma and spark impact pressure eliminates adsorptive gas and impurities existing on the surface of the powders [76]. Thus, a high-quality compact can be obtained.

Figure 1-11 The theoretical principle of SPS heating process [74].

Local high temperature at the connection points make particles form necks through material transport, including evaporation, surface diffusion, grain boundary diffusion and also volume diffusion, as shown in Figure 1-12. Then these necks further expand as the sintering process proceeds. In addition, powders may experience plastic flow to achieve a higher density.

Figure 1-12 Mass transport mechanisms in SPS [77].

Pressure also plays a very important role in the densification process. It can cause the rearrangement of particles in the densification process, as shown in Figure 1-13. This promotes the densification as it can reduce the inter-particle porosity and increase inter-particle connections. The applied stress can also cause plastic deformation when it exceeds the compressive yield stress of the materials. This also promotes the densification of particles.

Figure 1-13 Schematic of particle rearrangement caused by the applied stress [77]
(σ is the stress on the particles).

SPS has some advantages over conventional systems like hot press sintering, hot isostatic pressing and atmospheric furnaces as the former provides an accurate control of sintering energy, a high sintering speed and good reproducibility [76]. The applications of SPS in preparing new materials like functionally graded materials [78], intermetallic compounds [79], fiber reinforced ceramics [80] and metal matrix composites [81], which are difficult to sinter by conventional sintering methods, are now intensively studied.

1.2.2 Metal matrix composites by SPS

Metal matrix composites (MMCs) with reinforcements dispersed in a metallic matrix, exhibit characteristics that are superior to the matrix materials [82]. They often retain some of the characteristics of the metal matrix, such as ductility, formability, while improve certain properties, such as strength and stiffness, by the addition of reinforcements [82, 83].

The reinforcements of MMCs can be ceramic or metallic materials in the form of particulates or short fibers [84]. Generally, the reinforcements are characterized by high stiffness and hardness [84]. Quasicrystals are emerging reinforcements in MMCs thanks to their special physical and mechanical properties, such as high hardness, good wear resistance and low surface energy [85, 86].

Titanium is well known for its high strength-to-weight ratio, low density and high ductility, high corrosion resistance as well as good biological compatibility. However, it has poor wear resistance, which limits its applications. One of the methods to improve properties of titanium is to prepare Ti based MMCs, where the strength and ductility are provided by titanium and the wear resistance and stiffness are enhanced by the reinforcements. Titanium-based MMCs have wide potential applications in aerospace, automobiles, prosthetics and sports equipment. Therefore, it is of great significance to study Ti-based MMCs reinforced with quasicrystals, which can combine their respective advantages.

The sintering of Ti and its alloys by ordinary sintering methods like hot press sintering is difficult because this process requires maintaining a high sintering temperature (1200–1400 °C) in high vacuum ($> 10^{-4}$ Pa) for a long time (24–48 h) as a consequence of stable surface oxide film of Ti powders [87, 88]. However, the SPS process can easily sinter Ti powders for the reasons mentioned above. Masayuki Kon et al. [89] sintered porous Ti and Ti-6Al-4V compacts with both biological and biomechanical compatibilities and high strength by SPS at 600-700 °C. The spark plasma melts only the local surface of the particles in contact to form junctions and eliminates adsorbed substances and impurities like oxide film of the powders [76]. Also, the grain growth in SPS process is much smaller than in other processes like pressureless sintering. In a word, SPS can sinter titanium and its alloy into compacts of high quality at a relatively low temperature.

SPS system can sinter titanium alloys at a low temperature, at which Al-Cr-Fe quasicrystals retain their quasiperiodic atomic arrangement or transform to their approximants. Thus, it is expected that MMCs with titanium as matrix and Al-Cr-Fe quasicrystals (or their approximants) as reinforcements can be prepared by SPS.

1.3 Research contents

Al-based quasicrystals are promising candidates for coatings and reinforcements as the constituent metals of these quasicrystals are non-toxic and less costly [2, 5]. Among them, Al-Cr-Fe quasicrystals are expected to have outstanding corrosion resistance properties due to their high Cr content. So they should be fit for protection coatings and reinforcements in composites. Moreover, Al-Cr-Fe quasicrystal powders are already

commercially produced. However, these quasicrystals are less studied than other Al based quasicrystals like Al-Cu-Fe quasicrystals. Therefore, it is of great significance to study their microstructure, properties and applications.

Titanium and its alloys are widely applied in aerospace, chemical, petrochemical and marine industries as structural materials thanks to their high specific strength and excellent corrosion resistance [90-92]. They can also be used as biomaterials due to their good biocompatibility [93, 94]. However, due to the inherent low hardness and low wear resistance of Ti, there is need to incorporate hard reinforcements to form MMCs to expand the applications of Ti [91, 95]. The commonly seen reinforcements of Ti based MMCs are TiC, TiN and TiB [96-98]. These ceramic reinforcements have difficulty in forming strong bonding with Ti matrix. The weak bonding is unfavorable to the wear resistance of MMCs [99, 100]. Thus, an attempt is made to search unconventional reinforcements for Ti matrix, which can form strong bonding layer between reinforcements and matrix.

Quasicrystals have been reported to be incorporated in composites to improve the wear resistance, hardness and strength etc., due to their unique properties, such as high hardness, high wear resistance, low surface energy and low friction coefficient [2, 5, 101-103]. For example, Kenzari et al. [104] prepared nylon based composites reinforced by icosahedral AlCuFeB particles by selective laser sintering. These composites exhibit improved wear resistance compared to polyamide (PA) and PA + Al, as shown in Figure 1-14. Guo et al. [105] prepared tin-bronze/TiN and tin-bronze/quasicrystal (AlCuFeB) composite coatings

by cold spray. Their experimental results show that the incorporation of AlCuFeB quasicrystals improves the wear resistance, as indicated in Figure 1-15. Ali et al. [106] prepared Al/AlCuFe MMCs by uni-axial hot pressing followed by hot extrusion. Their experiments show that the incorporation of AlCuFe quasicrystals improves the compression strength, as indicated in Figure 1-16. Quasicrystals are metallic compounds, so they are expected to form metallic bonding between reinforcements and matrix when used as reinforcements in MMCs. It's worth mentioning that Ali et al. [107] reported that Al-based MMCs reinforced with AlCuFe quasicrystals are strengthened by interfacial reaction. Quasicrystals reinforcements can improve some properties of MMCs, such as wear resistance and compression strength (mentioned above), and they are expected to form strong bonding layer with Ti matrix. Thus, it is of great importance to study the preparation and properties of Ti based MMCs with quasicrystals as reinforcements.

Figure 1-14 Volume loss of three kinds of samples with PA [102].

Figure 1-15 Wear rates of bronze and its composites coatings [103].
(QC is short for AlCuFeB quasicrystals).

Figure 1-16 Compression true stress–true strain curves for samples with different AlCuFe content [104].

Quasicrystals have low surface energy [108], so it is expected that the incorporation of quasicrystals could reduce the wetting of MMCs, which is good for cutting tools. Furthermore, the density of Al-Cr-Fe quasicrystals (about 4.2 g/cm^3 for Al-Cr-Fe quasicrystals) is lower than commonly seen reinforcements for Ti matrix, such as TiC (around 5.2 g/cm^3 [109]), TiN (5.4 g/cm^3 [110]) and TiB (4.5 g/cm^3 [111]). Therefore, if the same volume ratio of Al-Cr-Fe quasicrystal reinforcements is used, the total weight of MMCs can be reduced, which is very important for automobile, aviation and aerospace industries. The low wetting and density of quasicrystals provide additional advantages if they are used as reinforcements in Ti based MMCs for some applications because of the reduced wetting and density.

Based on the above literature review, this thesis has the following main objectives: the phase transformations of Al-Cr-Fe quasicrystals and their approximants, the microstructure of Al-Cr-Fe quasicrystals, the spark plasma sintering of Al-Cr-Fe powders

and also the spark plasma sintering of Ti based metal matrix composites with Al-Cr-Fe as reinforcements.

Knowing the phase transformations of Al-Cr-Fe powders is very important for their preparation and applications. Therefore, in this thesis the process of the phase transformations of Al-Cr-Fe powders was studied. This laid a foundation for the preparation of Al-Cr-Fe compacts and Ti/Al-Cr-Fe metal matrix composites using spark plasma sintering.

As it is difficult to test some properties, such as corrosion resistance and wear resistance, of Al-Cr-Fe quasicrystals in the form of powders, it is important to consolidate them into bulk materials. In this thesis Al-Cr-Fe powders were consolidated using spark plasma sintering. How the sintering parameters affect the phases and microstructure of the sintered Al-Cr-Fe pellets were studied. The mechanical properties of bulk Al-Cr-Fe pellets were also tested. The mechanism of sintering was also investigated.

Quasicrystals are reported to be added into polymers or metals with a low melting point like Al and Mg to form composites to improve the hardness and wear resistance [112-115]. But they are seldom reported to be added into metals with a higher melting point to form metal matrix composites. If they can be added to metals with a higher melting point, their applications as the reinforcements in MMCs are extended. In this thesis, the sintering of Ti/Al-Cr-Fe MMCs was studied, including how the sintering parameters affect the phases, microstructure and mechanical properties of the obtained composites.

Chapter 2   The characterization of Al-Cr-Fe and Ti powders

2.1 Introduction

Gas atomization is a rapid solidification technique for preparing both pure metal and alloy powders [116, 117]. Metal or alloy is first melted and then exposed to a high velocity gas jet which causes the liquid to break up into small droplets [117]. These droplets subsequently solidify in flight to form powders. The quenching rate attainable by gas atomization is about 10^5 - $10^7 \text{K}\cdot\text{s}^{-1}$ [118, 119]. The powders produced are widely used in chemical, paint and powder metallurgy industries [116]. In powder metallurgy industry, they can be used to prepare advanced metallic structural materials, including particulate reinforced metal matrix composites, superalloys, steels and light alloys [2].

Since Shechtman et al. [1] discovered quasicrystal in 1984, gas atomization has also been used to prepare quasicrystals, due to its high quenching rate. Actually, this technique has already been commercially used to produce quasicrystal powders thanks to its ability to generate powders with spherical shape and good flowing properties [2]. These characteristics make gas atomized quasicrystalline powders suitable materials for thermal spray and powder metallurgy as well as mechanical alloying.

Quasicrystals can be obtained directly by gas atomization or by successive heat treatment [2]. It is of great importance to study the microstructure of the gas atomized powders and

their phase transformations during heat treatment because such information will lay a foundation for the applications of gas atomized quasicrystals in powder metallurgy.

2.2 Experiments

2.2.1 Materials

$\text{Al}_{70}\text{Cr}_{20}\text{Fe}_{10}$ powders (purchased from Saint Gobian, France) were annealed at 800 °C for 1 h in vacuum oven. Both as-received powders and annealed powders were characterized in terms of their phases and microstructure. Commercial pure titanium powders were purchased from Titan, Singapore.

2.2.2 X-ray diffraction (XRD) analysis

The X-ray diffraction analysis was performed on a Rigaku CN-2301 X-ray diffractometer using $\text{CuK}\alpha$ radiation to determine the phases of the as-received powders. The scanning range is from $2\theta=10^\circ$ to 90° with a step size of 0.02° .

2.2.3 High temperature X-ray diffraction (HT-XRD) analysis

HT-XRD tests were performed for the analysis of the phase transformations during the heating process. The measurement was conducted in 2θ range of 10° to 70° at a scan speed of $1^\circ/\text{min}$ and a step size of 0.02° . The experiment was carried out at RT, 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C in vacuum.

2.2.4 Scanning electron microscopy (SEM)

The microstructural characteristics of as-received powders were studied using a JEOL JSM-5600LV scanning electron microscope.

2.2.5 Particle size analysis

The particle size distribution of Al-Cr-Fe and Ti powders was measured using Fritsch Particle Size Analysette 22.

2.2.6 Differential scanning calorimetry (DSC)

The phase transformation behavior of as-received Al-Cr-Fe powders was determined by Netzsch Sta 449c differential scanning calorimetry in a flowing argon atmosphere at a heating rate of 10 K/min from room temperature to the melting point.

2.2.7 Optical microscopy

The cross-section of Al-Cr-Fe particles was observed using optical microscope after etching in a 5% solution of fluorohydric acid for five seconds.

2.2.8 Transmission electron microscope (TEM)

Al-Cr-Fe powders and epoxy were first blended and then cured to form a bulk compact epoxy-powder composite. Then, the composite mixture was sawed, mechanically polished, dimpled and finally ion-milled to get electron-transparent TEM samples. The TEM samples were observed using the JEOL 2010 and JEOL 2100F TEM system.

2.3 Results

2.3.1 Al-Cr-Fe powders

Figure 2-1 shows the morphology of as-received Al-Cr-Fe powders. Most powders are spherical (Figure 2-1a). The surface of particles below 20 μm is very smooth, whereas larger particles present rough surfaces. Some powders agglomerated as indicated by the black circle and there are some satellite particles present on the relatively large powders as indicated by the black arrows in Figure 2-1b. In the gas atomization process, the gas velocity direction close to the wall of the spray chamber is contrary to the main flow direction and small particles are transported to the spray cone again and collide with the droplets [120, 121]. When the droplets solidify, satellites or agglomeration form [121]. The particle size distribution analysis indicates that the distribution of particles is narrow with $D_{10}=9.0\ \mu\text{m}$ and $D_{90}=23.4\ \mu\text{m}$ (Figure 2-2).

Figure 2-1 Morphology of Al-Cr-Fe powders: (a) low magnification; (b) high magnification. (The black circle indicates agglomerated powders; the arrows indicate satellite powders.)

Figure 2-2 Particle size distribution of as-received Al-Cr-Fe.

Figure 2-3 shows the XRD pattern of as-received Al-Cr-Fe powders, demonstrating that there are three phases in the Al-Cr-Fe particles: γ -brass $\text{Al}_8(\text{Cr,Fe})_5$, $\text{Al}_9(\text{Cr,Fe})_4$ and icosahedral Al-Cr-Fe (I-AlCrFe). The largest diffraction peak at about $2\theta=42^\circ$ is the combination of diffraction peaks from these three phases. $\text{Al}_9(\text{Cr,Fe})_4$ and γ -brass $\text{Al}_8(\text{Cr,Fe})_5$ are considered as approximants of both icosahedral and decagonal quasicrystals [122].

Figure 2-3 XRD pattern of as-received Al-Cr-Fe powders.

Figure 2-4 exhibits the HT-XRD patterns of Al-Cr-Fe powders. The peak at around $2\theta=42^\circ$ shifts left as the temperature increases from room temperature to 400 °C due to the lattice expansion in this process (Figure 2-4a). And this broad peak begins to split into two peaks at 400 °C as indicated by the rectangle: the left peak is corresponding to icosahedral phase and the right peak is corresponding to $\text{Al}_8(\text{Cr,Fe})_5$. This is because in the gas atomization process, the cooling rate is so high that the high temperature state of the atomic arrangement in the alloy is retained and the increased temperature enables the atoms to diffuse faster, generating more ordered atomic arrangement. In addition, decagonal phase begins to form at 400 °C, as indicated by the arrow in Figure 2-4b. As temperature further rises from 500 °C to 900 °C, no obvious phase transformation is observed from the HT-XRD patterns.

Figure 2-4 HT-XRD patterns of Al-Cr-Fe powders: (a) RT-900 °C; (b) 300 °C -500 °C. The rectangle in (a) indicates the splitting of peak around $2\theta=42^\circ$; the arrow in (b) indicates the peak corresponding to decagonal Al-Cr-Fe

Figure 2-5 shows the DSC curve of the as-received Al-Cr-Fe powders. A wide exothermic peak ranges from about 500 °C to about 970 °C, showing that exothermic reaction begins to occur at about 500 °C. This is correlated with the recovery of the $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$, formation of decagonal phase and also grain growth of these phases. The

wide exothermic peak ranges from about 500 °C to 970 °C but HT-XRD patterns show that the overlapped peak at about $2\theta=42^\circ$ begins to split starting from 500 °C and no obvious phase transformation occurs above 700 °C. This is probably because of the difference in the thermal process: during HT-XRD test, there were isothermal processes for XRD data acquisition from $2\theta=10^\circ$ to 70° at a rate of $1^\circ/\text{min}$ (at a constant temperature for about 50 min); while during the DSC process the temperature increased at a constant rate of $10^\circ\text{C}/\text{min}$ and the whole process took about 90 min. The isothermal process provides the time for the atomic diffusion. A distinct endothermic peak can be observed from 1070 °C to 1110 °C, showing that the powders melt in this temperature range. This DSC curve reflects that Al-Cr-Fe powders can only be sintered at a temperature lower than 1070 °C.

Figure 2-5 DSC curve of as-received Al-Cr-Fe powders.

Figure 2-6 is a typical cross-sectional view of etched Al-Cr-Fe powders. It shows a multi-phase structure of atomized particles. The bright regions in the image are the quasicrystalline phase and the grey regions are the crystalline phases. It was suggested

that the quasicrystalline phase formed from the undercooled liquid in a dendritic manner and the other phases solidified at the interdendritic region of the quasicrystalline phase at a later stage of the solidification process [123].

Figure 2-6 OM image of cross-section of Al-Cr-Fe powder after etching.

Figure 2-7 shows the bright field TEM image and the selected area electron diffraction (SAED) patterns of the as-received powders. It can be seen that the grains are in sub-micrometers and there are two types of grains: textured grains and featureless grains in the image. The textured grains are confirmed by SAED patterns (Figure 2-7c, d) to be $\text{Al}_8(\text{Cr,Fe})_5$ or $\text{Al}_9(\text{Cr,Fe})_4$ while the featureless grains are confirmed to be icosahedral Al-Cr-Fe (Figure 2-7b). And the textured crystal grains are surrounded by the featureless icosahedral grains. In addition, it can be seen that the textured grains generally have a curved shape. This is probably because these parts are still liquid when the dendritic regions are solidifying and the curved surface can reduce the surface energy of the overcooled liquid metals.

Figure 2-7 Bright field TEM image and SAED patterns of the phases in the as-received powders: (a) bright field TEM image; (b) SAED pattern taken along 3-fold axis of icosahedral phase; (c) SAED pattern taken along $[4 \bar{2} \bar{2} 3]$ zone axis of $\text{Al}_8(\text{Cr,Fe})_5$ and (d) SAED pattern taken along $[1 0 1]$ zone axis of $\text{Al}_9(\text{Cr,Fe})_4$.

Figure 2-8 shows the HR-TEM image taken along $[1 1 1]$ of $\text{Al}_9(\text{Cr,Fe})_4$. It can be seen that there is evident lattice distortion. This is because the high cooling rate in the gas atomization process makes the atoms have no time to diffuse to their equilibrium state, preserving the high temperature microstructure at a low temperature.

Figure 2-8 HR-TEM image taken along $[1\ 1\ 1]$ axis of $\text{Al}_9(\text{Cr,Fe})_4$.

Figure 2-9 shows a typical bright field TEM image and SAED patterns of the annealed Al-Cr-Fe powders. It can be observed that grains are polygonal. This indicates that there are morphological changes in the annealing process, as the grains in the as-received powders have curved surfaces. The high annealing temperature provides the energy needed for the atoms in the gas atomized powders to diffuse to form new phases and reduce the surface energy of the grains. There are four phases identified through the SAED patterns in the annealed powders, as shown in Figure 2-9b-e. The SAED pattern taken along the 2-fold axis of the decagonal phases confirms that the decagonal phase forms in the annealing process.

Figure 2-9 Bright field TEM image and SAED patterns of the phases in the annealed powders: (a) bright field TEM image; (b) SAED pattern taken along 3-fold axis of icosahedral phase; (c) SAED pattern taken along 2-fold axis of decagonal phase; (d) SAED pattern along $[1\ 0\ 1]$ zone axis of $\text{Al}_9(\text{Cr,Fe})_4$ and (e) SAED pattern taken along $[4\ \bar{2}\ \bar{2}\ 3]$ zone axis of $\text{Al}_8(\text{Cr,Fe})_5$.

2.3.2 Ti powders

Figure 2-10 shows the morphology of Ti powders. It can be observed that Ti particles have an angular morphology. Figure 2-11 shows the particle size distribution of Ti

powders. It can be found that the particle size of titanium lies in a relatively broader scope with $D_{10}=8.1\ \mu\text{m}$ and $D_{90}=31.4\ \mu\text{m}$ (Figure 2-11).

Figure 2-10 Morphology of as-received Ti particles.

Figure 2-11 Particle size distribution of Ti.

2.4 Discussion

Figure 2-12 and Figure 2-13 show the Al-Cr-Fe liquidus and solidus surface for the Al-rich region, respectively. It can be seen from the diagram that in a slow cooling process γ_1 and γ_2 phase solidifies first and then D3 (decagonal Al-Cr-Fe) forms.

Figure 2-12 Liquidus surface for the Al-rich region of Al-Cr-Fe [124].

Figure 2-13 Solidus surface for the Al-rich region of Al-Cr-Fe [124].

However, the high cooling rate in gas atomization process makes the solidification proceed in a different way from the slow cooling. The TEM images as well as the cross-sectional view of etched powders show that the quasicrystalline phase forms first in the undercooled Al-Cr-Fe liquid in a dendritic manner while γ_1 and γ_2 form later in the interdendritic region. In addition, there are no appreciable XRD peaks corresponding to D3 phase for the as-received powders. Only after annealing, the XRD peaks corresponding to D3 phase can be obviously observed. It can be inferred that the formation and growth of D3 phase need a relatively long atomic diffusion process: in the slow cooling process and annealing process, there is enough time for atom to diffuse to

form D3 phase while in the gas atomization process, there is not enough time for atoms to diffuse to form D3 phase. Moreover, there is no icosahedral phase in the equilibrium phase diagram. However, both XRD pattern and TEM image indicate that this phase forms in the gas atomization process. HT-XRD results indicate that the icosahedral phase is stable even at 900 °C. There are icosahedral atomic units in the liquid, thus it is much easier for icosahedral phase to form due to the low energy barrier.

2.5 Conclusions

Icosahedral Al-Cr-Fe and two approximants $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ phases are present in the as-received Al-Cr-Fe powders. During the gas atomization process, icosahedral phase forms first in a dendritic manner and then $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ form in the interdendritic regions. These two crystalline phases have curved grain boundaries. The lattice in the crystal phases are distorted due to the high cooling rate in the gas atomization process.

At about 500 °C the distorted lattice begins to recover to equilibrium state and decagonal Al-Cr-Fe forms. There are four phases in the annealed Al-Cr-Fe powders: $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$, icosahedral Al-Cr-Fe and decagonal Al-Cr-Fe. Grains in the annealed powders have polygonal morphology.

Chapter 3   Spark plasma sintering of Al-Cr-Fe quasicrystal powders

3.1   Introduction

Quasicrystals can be prepared by various methods including casting [125], melt spinning [126], gas atomization [63], mechanical alloying [127], physical vapor deposition [128] and gas evaporation [129]. The obtained quasicrystals can be in the form of bulk, powder, coating and ribbon. The quasicrystal powders or ribbons can be sintered into bulk materials by several techniques, such as hot isostatic pressing [130] and spark plasma sintering (SPS) [131]. In SPS process, besides the Joule heat generated by the power supply and the plastic flow of the material under the pressure, the spark plasma plays a very important role in the sintering: spark plasma can activate the particle surface and promote the material transfer, leading to a rapid sintering at a low temperature [132, 133]. Thus, SPS can be a promising technique for sintering quasicrystals.

Hundreds of quasicrystals have been reported [2, 44]. They have been found in aluminum, copper, gallium, magnesium, nickel, tantalum, titanium, zinc and zirconium alloys. Among them, Al-based quasicrystals have been most widely investigated. Al-Cr-Fe quasicrystals are developed as they have good corrosion resistance besides other unique properties of quasicrystals due to their high content of Cr. Moreover, Al-Cr-Fe powders are already commercially available. Therefore, it is worthwhile to study the sintering and properties of Al-Cr-Fe quasicrystals.

In the chapter, the preparation of Al-Cr-Fe bulk alloys using SPS is demonstrated. Specimens were prepared at various temperatures between 650 °C and 800 °C. Phase transformation, microstructure and mechanical properties of the sintered pellets were illustrated.

3.2 Experiments

3.2.1 Sample preparation

The $\text{Al}_{70}\text{Cr}_{20}\text{Fe}_{10}$ powders were purchased from Saint Gobian, France. They were prepared by gas atomization and consolidated by SPS (Sumitomo Coal Mining Company, Ltd., Tokyo, Japan). A graphite mold with an inner diameter of 10 mm was used to surround the powders to be sintered. The sintering was conducted at a constant heating rate of 100 °C/min under a uniaxial pressure of 50 MPa in vacuum (<10 Pa). The powders were heated to various temperatures between 650 °C and 800 °C in order to investigate the effects of the sintering temperature under a constant holding time of 30 minutes and under the same pressure. The resulting pellets with a diameter of 10 mm and a thickness of about 1mm were named ACF-650, ACF-700, ACF-750 and ACF-800, respectively.

3.2.2 Phases analysis and microstructural characterization

The X-ray diffraction (XRD) analysis (using a PANalytical Empyrean X-ray diffractometer, $\text{CuK}\alpha$ radiation) was performed to determine the phases of the sintered pellets. Scanning electron microscopy (SEM, JEOL JSM-5600LV), energy-dispersive spectroscopy (EDS, Oxford), and transmission electron microscopy (TEM, JEOL 2010, JEOL 2100F and also JEOL Cs -corrected 2100F) were employed for the characterization

of the microstructure and the phase analysis of the samples. The TEM sample was prepared by a conventional method. ACF-800 pellet was sawed, mechanically polished, dimpled and finally ion-milled to get electron-transparent TEM samples. The density was measured by the Archimedes principle. Three samples for each sintering temperature were measured to get an average value of density. The porosity was measured through image analysis.

3.2.3 Mechanical properties testing

The microhardness of the pellets was determined using CSM microhardness tester. 16 random points on a sample were chosen for the test. Mechanical properties of sintered composites were also evaluated from the penetration force–displacement curves obtained from nanoindentation tests using Agilent G200 Nanoindenter with a Berkovich diamond indenter. The elastic modulus (E) and hardness (H) in nanoindentation test are directly obtained from the indentation force and the penetration depth measurements of a hard element (indenter) of known properties and shape. The applied forces are in the mN range, and penetration depths from several nanometres to microns are used.

3.3 Results

3.3.1 The influences of sintering temperature

Figure 3-1 presents the backscattered SEM images of the Al-Cr-Fe pellets sintered at different temperatures. It can be observed that as the temperature rises, the porosity reduces: Al-Cr-Fe powders begin to form inter-powder necks in ACF-650 and there are pores of micron size. When temperature reaches 700 °C, the porosity significantly

reduces, but the powder boundaries can still be clearly seen. In ACF-750, the porosity further reduces. As the sintering temperature further rises to 800 °C powder boundaries cannot be clearly seen and only a few small pores were present. The porosity of the samples sintered at different temperatures is shown in Table 3-1. It can be found that with the increase of sintering temperature, the porosity decreases.

Figure 3-1 BSE images of Al-Cr-Fe samples sintered at different temperatures: (a) 650 °C; (b) 700 °C; (c) 750 °C; (d) 800 °C. (Arrows in b,c,d indicate small pores).

Table 3-1 Porosity of the Al-Cr-Fe samples sintered at different temperatures.

Sintering temperature (°C)	650	700	750	800
Porosity (Vol%)	29.3	3.1	2.4	0.8

Figure 3-2 shows the XRD patterns of the Al-Cr-Fe samples sintered at different temperatures. By comparing the patterns of as-received powders and ACF-650, it can be found that for ACF-650 the peaks corresponding to icosahedral phase (indicated by the hollow arrows) decrease and the peaks corresponding to decagonal phase increase. This is probably because the metastable icosahedral phase transformed to decagonal phase in the

SPS process with the segregation of $\text{Al}_9(\text{Cr,Fe})_4$ and $\text{Al}_8(\text{Cr,Fe})_5$. With the increase of the sintering temperature from 650 °C to 700 °C and then to 800 °C, stable icosahedral phase formed, as indicated by the solid arrows. There are four phases identified in ACF-700, ACF-750 and ACF-800: icosahedral phase (I-AlCrFe), decagonal phase (D-AlCrFe), $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$.

Figure 3-2 XRD patterns of Al-Cr-Fe pellets sintered at different temperatures. (Hollow arrows indicate metastable icosahedral Al-Cr-Fe. Solid arrows indicate stable icosahedral Al-Cr-Fe.)

3.3.2 Sintering mechanism

In order to investigate the densification mechanism of sintering Al-Cr-Fe, the densification process of Al-Cr-Fe powders was monitored. The instantaneous height variation of the powder bed, ΔL , was continuously measured and recorded during the sintering process. Then correction was done to subtract the dimensional changes of the

SPS system by a “blind test”. The instantaneous height of the powder bed can be obtained by the following quotation, $L=L_f+ \Delta L_t-\Delta L$, where L_f is the final height of the sintered compact and ΔL_t the total height variation recorded at the end of the test. Finally, the instantaneous sample height L and its instantaneous relative density, D , are linked by the following relationship

$$D = \frac{L_f}{L} D_f \quad (3-1)$$

where D_f is the final relative density of the samples.

The major driving sources of densification-contributing mass transfer in the sintering process can be classified into: (i) externally applied load, (ii) sintering stress (i.e. surface tension), (iii) steady-state electromigration (i.e. electric field contribution to diffusion), and (iv) presence of momentarily generated spark plasma between particles [134]. The existence of plasma in the SPS sintering process is quite a controversy. Hulbert et al. [135] gave an experimental demonstration of the absence of spark discharge and plasma during the SPS process using *in situ* atomic spectrometry, direct visual observations and ultrafast *in situ* voltage measurements. However, Zhang et al. [136] demonstrated the existence of the plasma at the initial stage of the SPS process through experiments. As certain conditions are needed to excite the discharge between the sintered particles and such discharge stops once connections between the sintered particles are built by plasma sputtering [136], it is reasonable to conclude that the plasma at the initial stage of sintering does not play a dominant role in the densification of relatively large powders. And it is also reasonable to conclude that the contribution of the electromigration to the densification would be negligible if the materials have low electrical conductivity.

Moreover, the sintering stress, which mainly depends on the level of grain–pore and grain–grain interface areas, is not significant if the applied pressure is high enough [137].

Based on these hypotheses, the main driving force for the densification of quasicrystal powders during SPS process would be related to the external pressure. Previous works [138-142] have illustrated that the dominant mechanism of densification for pressure sintering of ceramics or metallic materials is creep. Assuming that the major driving force for densification in pressure-assisted sintering is the macroscopic pressure, it is proposed that the pressure-assisted kinetic equation for densification can be written as [142]:

$$\frac{1}{\mu_{eff}} \frac{1}{D} \frac{dD}{dt} = K \frac{e^{-\frac{Q_d}{RT}}}{T} \left(\frac{b}{G}\right)^p \left(\frac{\sigma_{eff}}{\mu_{eff}}\right)^n \quad (3-2)$$

where t is time, μ_{eff} the instantaneous shear modulus of the compact, K a constant, R the gas constant, T the absolute temperature, Q_d the apparent activation energy of the mechanism controlling densification, b the Burgers vector (close to the lattice parameter), G the grain size, σ_{eff} the instantaneous effective stress acting on the compact, n the apparent stress exponent and p the apparent grain size exponent.

It is also proposed that μ_{eff} and σ_{eff} can be written as [140, 141, 143]:

$$\mu_{eff} = \frac{E_{th}}{2(1+\nu_{eff})} \frac{D-D_0}{1-D_0} \quad (3-3)$$

$$\sigma_{eff} = \frac{1-D_0}{D^2(D-D_0)} \sigma_{mac} \quad (3-4)$$

where E_{th} is the Young's modulus of the theoretically dense Al-Cr-Fe, ν_{eff} the effective Poisson's ratio, D_0 the starting green density of the powder compact and σ_{mac} the macroscopic compaction pressure.

The densification curves obtained are shown in Figure 3-3. As there was an applied uniaxial pressure of about 10 MPa during the heating process (to ensure the current flowing of the system), the samples exhibited different relative density values at the beginning of holding process. However, all the curves exhibit similar sintering behavior: accelerated densification at the beginning and stagnant densification after a certain period of time.

Figure 3-3 Densification curve of Al-Cr-Fe at different temperatures.

In addition to the key parameters n , p and Q_d in Equation (3-2), μ_{eff} remains unknown. This parameter depends on relative density and temperature. To determine values of μ_{eff} , the compression tests for the SPSed samples were performed in the SPS system at 700 °C,

750 °C and 800 °C with the displacement recorded and corrected with the displacement of the SPS system. It is worth mentioning that a value of 0.25 is chosen for σ_{eff} regardless of temperature.

To determine the key parameters n , p and Q_d in Equation (3-2), the average grain size is assumed to be constant (this is confirmed by the BSE images of the sintered compacts). Then the SPS kinetic Equation (3-2) turns to

$$\frac{1}{\mu_{eff}} \frac{1}{D} \frac{dD}{dt} = K_0 \frac{e^{-\frac{Q_d}{RT}}}{T} \left(\frac{\sigma_{eff}}{\mu_{eff}} \right)^n \quad (3-5)$$

where $K_0 = K \left(\frac{b}{G} \right)^p$ is a constant. To have access to n , Relation (5) can be transformed as follows, assuming only one constant value of Q_d .

$$\ln \left(\frac{1}{\mu_{eff}} \frac{1}{D} \frac{dD}{dt} \right) = n \ln \left(\frac{\sigma_{eff}}{\mu_{eff}} \right) + K_1 \quad (3-6)$$

Where K_1 is a constant for a fixed holding temperature. Then, the slope of the straight line obtained when drawing $\ln \left(\frac{1}{\mu_{eff}} \frac{1}{D} \frac{dD}{dt} \right) = f \left(\ln \left(\frac{\sigma_{eff}}{\mu_{eff}} \right) \right)$ should provide the n value.

Such a representation is shown in Figure 3-4. In order to make the plot easy to read, the curve for 750 °C is not shown. It is obvious that for both temperatures n changes during the sintering process. At the beginning, n is around 1. Then it increases to about 5. And finally, it increases to more than 10. This indicates that the dominant densification mechanism changes in the sintering process.

Figure 3-4 Plot reflecting the calculation of stress exponent.
(The stress exponent values are the slopes of the different straight lines.)

Under the same condition regarding the grain size as the one introduced above for the calculus of n and with the n values calculated, Relation (2) can be transformed as follows to be able to evaluate Q_d , assuming also a unique value for n and p for a given value of the activation energy.

$$\ln \left[\frac{T}{\mu_{eff}} \left(\frac{\mu_{eff}}{\sigma_{eff}} \right)^n \frac{1}{D} \frac{dD}{dt} \right] = -\frac{Q_d}{RT} + K_2 \quad (3-7)$$

where K_2 is a constant. So, the slope of the straight line obtained when drawing

$$\ln \left[\frac{T}{\mu_{eff}} \left(\frac{\mu_{eff}}{\sigma_{eff}} \right)^n \frac{1}{D} \frac{dD}{dt} \right] = f \left(\frac{1}{T} \right) \text{ corresponds to the value of } -\frac{Q_d}{R}.$$

Figure 3-5 shows the methodology used to calculate Q_d when the stress exponent value is 1 for an applied stress of 50 MPa. The variation of $\frac{1}{D} \frac{dD}{dt}$ as a function of D has been drawn. Then fixed value of 0.004 was chosen (corresponding to $n=1$ in Figure 3-4), then the corresponding relative density and the corresponding values of μ_{eff} and σ_{eff} can be

accessible. Here only $n=1$ is chosen for the calculation of Q_d . For $n=1$, in the temperature range of 700 °C to 800 °C, the apparent activation energy is calculated to be about 72 kJ/mol, as shown in Figure 3-6.

Figure 3-5 Methodology used for the calculation of apparent activation energy.

Figure 3-6 Apparent activation energy for densification when $n \approx 1$.

It is reported that the sintering mechanism controlled by dislocation gliding exhibits a high stress component value ($n \geq 3$), while a low value is relevant to an inter-granular gliding [134]. The stress component and the apparent activation energy calculated in the range of 700 °C to 800 °C suggest that the densification mechanism changes from the grain boundary sliding (particles rearrangement) at the beginning to dislocation motion later.

3.3.3 Microstructure of ACF-800

Figure 3-7 is a bright-field TEM image of ACF-800. Typically, most grains have a polygonal morphology. An inter-particle bonding layer with a thickness of around 50 nm can be observed, as indicated by the arrows. The crystallographic information of the four phases in the sample is given in Table 3-2. It can be seen from the table that both quasicrystals have close composition and Al content in the quasicrystals is higher than that in the two approximants, $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$.

Figure 3-7 Bright field TEM image of ACF-800.
(Arrows indicate the inter-particle layer.)

Table 3-2 Crystallographic information about the phases in the sintered pellets.

Designation	Lattice parameters	Space group	Compostion
			measured by EDS
$\text{Al}_9(\text{Cr,Fe})_4$	$a=9.12\text{\AA}$	Cubic $\bar{I}43m$	$\text{Al}_{69.2}\text{Cr}_{22.2}\text{Fe}_{8.6}$
$\text{Al}_8(\text{Cr,Fe})_5$	$a=7.811\text{\AA}$ $\alpha=109.13^\circ$	Rhombohedral $R3m$	$\text{Al}_{62.5}\text{Cr}_{28.2}\text{Fe}_{9.3}$
I-AlCrFe		Icosahedral	$\text{Al}_{80.6}\text{Cr}_{10.4}\text{Fe}_{10.0}$
D-AlCrFe		Decagonal	$\text{Al}_{72.4}\text{Cr}_{15.8}\text{Fe}_{11.8}$

Figure 3-8 presents the bright field TEM image, selected area electron diffraction (SAED) patterns taken along the 3-fold, 5-fold and 2-fold axes as well as the high resolution TEM (HR-TEM) image taken along the 5-fold axis of I-AlCrFe. The bright field image shows that it is in micrometer scale (Figure 3-8a). The SAED patterns with 3-fold, 5-fold and also 2-fold symmetries (Figure 3-8b, c, e) confirm that this phase is icosahedral. Icosahedral quasicrystals show quasi-periodicity in all three dimensions. Theoretically, they have three translational symmetries in high dimensions: primitive (P-type), body centered (B-type), and face centered (F-type) [144]. The primitive and face-centered icosahedral quasicrystals have been discovered. These two types of quasicrystals can be distinguished by their 2-fold patterns. The SAED pattern taken along the 2-fold axis of I-AlCrFe (Figure 3-8e) shows this icosahedral phase is F-type. Figure 3-8d shows that the arrangement of diffraction points is inflated by τ . This is also a character of F-type icosahedral phase. HR-TEM image (Figure 3-8f) taken along the 5-fold axis reflects the atomic arrangement with the 5-fold symmetry. It can be seen that spots form five sets of

virtually parallel lines with a mutual orientation of 72° , which is the angle between lines connecting the center and vertices of a pentagon. However, the quantitative interpretation of HR-TEM images of icosahedral phase depends strongly on specimen thickness [145, 146], because dynamical diffraction effects can generate extra spots, leading to new diffraction patterns of reduced scale but similar symmetry.

Figure 3-9 shows the bright field TEM image, SAED patterns along the 10-fold and 2-fold axes as well as the HR-TEM image taken along these two axes of D-AlCrFe. This phase is quasi-periodic in two dimensions and periodic in the third dimension. Along the 10-fold axis, the cores of the atomic clusters are imaged as rings with a diameter of approximately 1.5 nm, while the full clusters have a diameter of about 2.10 nm, as shown in Figure 3-9c. It can be found that the HR-TEM image taken along the 10-fold axis (Figure 3-9d) can be well superimposed with Penrose tiles. Figure 3-9e, f show that the periodicity along the 10-fold symmetry axis is about 1.2nm, which is in a good agreement with the reported value $\sim 1.2\text{nm}$ [147].

Figure 3-10 shows the bright field TEM image, the SAED patterns taken along $[1\ 1\ 2]$ and $[0\ 0\ 1]$ as well as HR-TEM image taken along $[0\ 0\ 1]$ of $\text{Al}_8(\text{Cr,Fe})_5$. The bright field image shows that the particle is in micrometer scale. $\text{Al}_8(\text{Cr,Fe})_5$ is isostructural to rhombohedral Al_8Cr_5 with $a=7.811\ \text{\AA}$, $\alpha=109.13^\circ$ and considered as an approximant of both icosahedral and decagonal phases [148]. Its unit cell consists of 26 atoms: an inner tetrahedron of four atoms is surrounded by an outer tetrahedron, then an octahedron of six atoms, followed finally by a cubo-octahedron of 12 atoms [149].

Figure 3-8 (a) Bright field TEM image, diffraction patterns taken along (b) 3-fold, (c) 5-fold, (e) 2-fold axis and (f) HR-TEM image taken along 5-fold axis of icosahedral Al-Cr-Fe; (d) Magnification of $\frac{1}{4}$ part of (c).

Figure 3-9 (a) Bright field TEM image of decagonal Al-Cr-Fe; (b) diffraction patterns taken along its 10-fold axis; (c) HR-TEM image taken along its 10-fold axis; (d) magnification of (c); (e) diffraction pattern taken along 2-fold axis and (f) HR-TEM image taken along 2-fold axis of decagonal Al-Cr-Fe.

Figure 3-10 (a) Bright field TEM image of $\text{Al}_8(\text{Cr,Fe})_5$, diffraction patterns taken along zone axis (b) $[0\ 1\ \bar{1}\ 2]$, (c) $[0\ 0\ 0\ 1]$ and (d) HR-TEM image taken along $[0\ 0\ 0\ 1]$ axis.

Bright field TEM image, SAED patterns along $[1\ 1\ 1]$ and $[1\ 0\ 0]$ as well as HR-TEM image taken along $[1\ 0\ 0]$ of γ -brass $\text{Al}_9(\text{Cr,Fe})_4$ are shown in Figure 3-11. This phase is isostructural to the binary Al_9Cr_4 compound and also considered as an approximant of both icosahedral and decagonal phases. The atomic structure of the γ -brass with the space group $I4\bar{3}m$ can be described by locating the 26-atom cluster at the center and corner of the bcc lattice. The cluster consists of four atoms in the inner tetrahedral sites, four atoms in the outer tetrahedral sites, six atoms in the octahedral sites, and 12 atoms in the cubooctahedral sites [149, 150].

Figure 3-11 (a) Bright field TEM image, diffraction patterns taken along (b) $[1\ 1\ 1]$, (c) $[1\ 0\ 0]$ and (d) HR-TEM image taken along $[1\ 0\ 0]$ of $\text{Al}_9(\text{Cr,Fe})_4$.

3.3.4 Mechanical properties

Figure 3-12 shows the microhardness and relative density of the Al-Cr-Fe pellets sintered at different temperatures. It can be found that with the increase of the sintering temperature, both microhardness and relative density are improved. A higher sintering temperature leads to a higher deformation rate of particles and a higher atomic diffusion rate in the sintering process, improving the relative density. By comparing XRD patterns of the samples sintered at 700 °C, 750 °C and 800 °C (Figure 3-2), it can be found that there is no extinct difference. It means no further phase transformation occurs when the sintering temperature increases from 700 °C to 750 °C and then to 800 °C. Thus, it is reasonable to conclude that for these three samples the increase of microhardness can be

attributed to the decrease of porosity. However, phase transformations occur when the sintering temperature increases from 650 °C to 700 °C, with icosahedral Al-Cr-Fe forming in ACF-700. It is reported that the microhardness of icosahedral Al-Cr-Fe is around Hv 800 [151] and the microhardness of Al_8Cr_5 and Al_9Cr_4 is also around Hv 800 [152], so the formation of icosahedral Al-Cr-Fe does not change the microhardness much. Therefore, it is concluded that the increase in the microhardness can be mainly attributed to the decrease in the porosity. The microhardness of ACF-800 is about Hv 810, which is equivalent to the reported values of other Al-based quasicrystals [2]. The relationship between microhardness and porosity is shown in Figure 3-13. The experimental data are fitted using a straight line. The straight line is governed by the following equation:

$$\text{Microhardness (Hv)} = 824.3 - 15.5 * \text{porosity (Vol\%)} \quad (3-8)$$

Figure 3-12 Microhardness and relative density of Al-Cr-Fe samples sintered at different temperatures.

Figure 3-13 Relationship plot for porosity and microhardness of Al-Cr-Fe pellets.

Figure 3-14 shows the representative load–penetration depth curves obtained from nanoindentation tests in different positions of ACF-800. It can be seen that the curves are in a good agreement. This means that the values of elastic modulus (the slope of the unload curves) and hardness (penetration depth) in different regions are very close. Modulus and microhardness of ACF-800 are around 199.7 GPa and 13.3 GPa, respectively. The value obtained using nanoindentation is larger than that from micro-indentation. The possible cause for the discrepancy in the microhardness and nanoindentation measurement is the significant elastic recovery [153]. Furthermore, the nanoindentation method calculates the projected contact area at full load, as compared to the actual contact area at full unload as is the case with the optical measurement in the microhardness tests [153, 154].

Figure 3-14 Nanoindentation curves made in different regions of ACF-800.

3.4 Discussion

When the sintering temperature increases from 650 °C to 700 °C, the relative density of sintered Al-Cr-Fe pellets significantly improves. Then with the increase of sintering temperature, the relative density slightly improves. SEM images further confirm this: the porosity of the Al-Cr-Fe samples decreases significantly as the sintering temperature rises from 650 °C to 700 °C and the boundaries of powder particles cannot be clearly visible for ACF-800. The pressure applied to the powders through the two punches in the sintering process causes the rearrangement and deformation of the powders. Higher temperature makes the deformation of the powders easier. More importantly, when the sintering temperature reaches 700 °C or above, Al-Cr-Fe powders exhibit softening [155]. Therefore, the applied pressure can cause rearrangement and deformation of the sintered

powders, reducing the porosity. In addition, higher temperature can also accelerate the diffusion of atoms, promoting sintering of Al-Cr-Fe powders.

By comparing the HT-XRD patterns of powders and the XRD patterns of the sintered pellets, it can be found that the phases present in both kinds of samples are the same: they are $\text{Al}_8(\text{Cr,Fe})_5$, $\text{Al}_9(\text{Cr,Fe})_4$, icosahedral Al-Cr-Fe and decagonal Al-Cr-Fe. However, the contents of decagonal Al-Cr-Fe and icosahedral Al-Cr-Fe are higher in sintered pellets than in powders, as indicated by the dotted line for decagonal Al-Cr-Fe and dashed line for icosahedral Al-Cr-Fe in Figure 3-15. This means that SPS promotes the formation of decagonal and icosahedral Al-Cr-Fe. Laure Ramond et al. [156] also reported that the quasicrystal content in the SPS sintered pellets is higher than in the hot-pressing sintered pellets. This is probably because the electrical field in the SPS process promotes the formation of the quasicrystals: the activation energy for the formation of new phases decreases in an electrical field, and the diffusion rate increases significantly in the electrical field [157, 158]. In a word, the quasicrystalline phases are easier to form and grow during SPS process than during annealing process.

Figure 3-15 XRD patterns for Al-Cr-Fe pellets and HT-XRD patterns for Al-Cr-Fe powders. (The dotted line indicates decagonal Al-Cr-Fe and the dashed line indicates icosahedral Al-Cr-Fe).

3.5 Conclusions

Al-Cr-Fe powders have been successfully sintered using SPS. With the increase of sintering temperature from 650 °C to 800 °C, the relative density of the sintered pellets increases from 70% to 99% while the microhardness increases from Hv 400 to Hv 810. In the temperature range of 700 °C to 800 °C the sintering pressure plays a very important role in the densification process and the densification mechanism changes from powders rearrangement at the beginning to dislocation motion later.

Two quasicrystalline phases, icosahedral Al-Cr-Fe and decagonal Al-Cr-Fe, and two approximants, $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ were observed in the pellets sintered at 700 °C

and above. The grains in the pellets are polygonal and in micrometers. The SPS process promotes the formation of decagonal Al-Cr-Fe and icosahedral Al-Cr-Fe.

Icosahedral Al-Cr-Fe is face-centered with its diffraction points inflated by τ and its diffraction points forming pentagons. Decagonal Al-Cr-Fe has a periodicity of 1.2 nm along its periodic axis and it can be well superimposed by Penrose tilings. The HR-TEM images along the 10 fold axis of decagonal Al-Cr-Fe exhibit core circles of 1.5 nm and full circles of 2.1 nm. Approximants $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ are isostructural to binary Al_8Cr_5 and Al_9Cr_4 , respectively.

Chapter 4   Ti based metal matrix composites reinforced with Al-Cr-Fe quasicrystal approximants

4.1 Introduction

Titanium and its alloys are widely applied in aerospace, chemical, petrochemical and marine industries as structural materials thanks to their high specific strength and excellent corrosion resistance [91, 92, 159]. They can also be used as biomaterials due to their good biocompatibility [93, 94]. However, the poor wear resistance of these materials can limit their applications as tribological components [91, 95]. Generally, there are two ways to improve the wear resistance of materials: either to generate a wear resistant coating on the surface or to add reinforcements into base matrix to form composites.

Quasicrystals, first discovered in Al-Mn alloy by Shechtman and Chan [1] in 1984, have rotational symmetries but no translational symmetries [160], which means that they are quasi-periodic. This special atomic arrangement enables quasicrystals to exhibit a unique combination of properties such as low thermal conductivity, low friction coefficient, good oxidation and corrosion resistance [2, 5, 102, 103], which make quasicrystals good candidates for coatings and reinforcements in the composites. Quasicrystals often form in a very narrow compositional range, around which crystalline materials have a very similar local atomic arrangement. These crystal materials are called approximants and they have similar properties to quasicrystals due to their structural similarity [161-163]. Thus, quasicrystals and their approximants can be added into titanium matrix as reinforcement phase. Quasicrystalline Al-Cr-Fe has superior corrosion resistance than other commonly

used Al-based quasicrystals due to their high Cr content. Therefore, it is expected that Al-Cr-Fe can be added into titanium to form metal matrix composites which can improve wear resistance and also maintain good corrosion resistance.

4.2 Experiments

4.2.1 Sample preparation

Ti and Al-Cr-Fe blended powders were sintered in SPS-1050 system (Sumitomo Coal Mining, Japan). The sintering temperature was increased to 750 °C at a rate of 100 °C/min and a uniaxial pressure of 40 MPa was applied. Four different holding times were used: 5, 10, 15 and 20 min and the compacts obtained were labelled as TACF-5, TACF-10, TACF-15 and TACF-20, respectively. These samples had a diameter of 10 mm and a thickness of about 1mm.

4.2.2 Phase analysis and microstructural characterization

The microstructure and composition of the sintered compacts were studied using a JEOL JSM-5600LV scanning electron microscope (SEM) and an Oxford energy dispersive spectroscopy (EDX). Phase analysis was carried out using a Philips MPD 1880 X-ray diffractometer (XRD) system with Cu-K α radiation at 40 kV and 30mA. The reported composition values of the selected regions are averages of five measurements. The data from the XRD and EDX analysis were combined to identify the phases. The density was measured by the Archimedes principle. Three samples for each sintering temperature were measured to get an average value.

4.2.3 Mechanical properties testing

The microhardness of Ti/Al-Cr-Fe composites was measured using CSM microhardness tester. 16 random points on a sample were chosen for the test. Microhardness and elastic modulus of sintered composites were also evaluated from the penetration force–displacement curves obtained from nanoindentation tests using Agilent G200 Nanoindenter with a Berkovich diamond indenter. Hardness and elastic modulus were obtained in interface, Ti matrix and also reinforcements.

The tribological properties of the samples were investigated using a micro-tribometer (CSM) by sliding against a Cr6 steel ball of 6 mm in diameter in a circular path of 2 mm in diameter for about 25000 laps at a sliding speed of 2 cm/s under a normal load of 1 N. The test system is schematically shown in Figure 4-1. The cross sectional profile of the wear track at four places at intervals of 90 ° was measured using a contact stylus profilometer with an accuracy of measurement of 0.01 µm in the vertical axis and of 0.1 µm in the horizontal axis. The wear volume of disk specimen, V_{disc} , is calculated by

$$V_{disc} = 2\pi \times r \times S \quad (4-1)$$

where r is the radius of wear track in mm; S is the cross sectional area on the track circle in mm². Four measurements were made for each sample. The wear rate value is the average of the four measurements.

Figure 4-1 Schematic of the ball-on-disk wear test system.

4.3 Results

4.3.1 Phases and microstructure

Figure 4-2 shows the relationship between the relative density of the sintered pellets and the holding time. It can be seen that with an increase in the holding time, the density of the composites rises. This is because as the holding time increases, the porosity decreases, improving the density of the pellets.

Figure 4-2 Effects of the holding time on the relative density.

Figure 4-3 shows the representative SEM backscattered electron images of the Ti/Al-Cr-Fe composites sintered with different holding time. The related XRD spectra are shown in Figure 4-4. It can be seen from Figure 4-3 that the spherical Al-Cr-Fe particles are dispersed within the Ti matrix and a 5-10 μm thick grey colored ring is present around each Al-Cr-Fe particle as indicated by black solid arrows in Figure 4-3a. Based on EDX and XRD analysis as well as phase diagram [164-166], the rings are determined to be Ti_3Al . In Figure 4-3a, some dark regions can also be found at the interface between Ti_3Al rings and Al-Cr-Fe particles, as indicated by the black hollow arrows. These regions were identified as TiAl by quantitative EDX analysis and also phase diagram analysis [164-166]. Some pores were also observed in the sintered composites, as indicated by the black circles in Figure 4-3a. In Figure 4-3b, inside the grey colored Ti_3Al rings around Al-Cr-Fe particles, dark-grey-dark colored regions can be observed around some relatively large Al-Cr-Fe particles, as indicated by the white arrows, indicating further phase transformations after the formation of Ti_3Al rings. TACF-15 has similar microstructure to

TACF-10, as shown in Figure 4-3b and Figure 4-3c. But more dark-grey-dark colored regions around Al-Cr-Fe particles can be found in TACF-20. Moreover, it can also be seen from Figure 4-4 that the peak corresponding to Al-Cr-Fe for the mixed powders shifts right for the sintered samples, indicating phase transformation of Al-Cr-Fe particles during the sintering process.

Figure 4-3 SEM backscattered electron images of Ti/Al-Cr-Fe samples sintered at 750 °C with different holding time: (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min. (In (a) circles indicate pores; solid arrows indicate interfacial layer; hollow arrows indicate TiAl regions. In (b) arrows indicate dark-grey-dark interfacial layer.)

Figure 4-4 XRD patterns of mixed raw powders and the samples sintered at 750 °C with different holding time

Figure 4-5 shows the high magnification SEM backscattered electron images of the local microstructure near an Al-Cr-Fe particle in TACF-10. The composition and phases of the different regions in this sample are shown in Table 4-1. Particle size was found to affect the content of atoms: Ti content is lower in large Al-Cr-Fe particles than in small ones, while Al content is higher. This is due to higher diffusion rate of Ti into small particles that have a higher specific surface area. Particle size also affects the phases at the Ti/Al-Cr-Fe interface. There are dark-grey-dark regions (⑤④③ in Figure 4-5b) present around large Al-Cr-Fe particles, which are identified as TiAl, Cr₂Ti and L1₂ (with a composition of Al-25.8at.%Ti-6.1at.%Cr-8.4at.%Fe) by EDX analysis and phase diagram analysis [164-166] while only TiAl regions were found around small Al-Cr-Fe particles.

Figure 4-5 SEM backscattered electron images of TACF-10 with a high magnification: (a) around a small Al-Cr-Fe particle, (b) around a large Al-Cr-Fe particle

Table 4-1 Composition and phases of TACF-10.

Region	Composition (at. %)			Phases
	Al	Ti	Cr	
In Figure 4-5a				
①	30.7	19.5	40.9	$\text{Cr}_2\text{Ti}+\text{Al}_8(\text{Cr,Fe})_5+\text{AlCr}_2$ $+\text{Al}_9(\text{Cr,Fe})_5$
②	26.8	21.2	44.2	$\text{Cr}_2\text{Ti}+\text{Al}_8(\text{Cr,Fe})_5+\text{AlCr}_2$ $+\text{Al}_9(\text{Cr,Fe})_5$
③	28.6	61.5	7.4	Ti_3Al
In Figure 4-5b				
①	41.4	12.5	34.5	$\text{Cr}_2\text{Ti}+\text{Al}_8(\text{Cr,Fe})_5+\text{Al}_9(\text{Cr,Fe})_5$
②	39.5	16	29.9	$\text{Cr}_2\text{Ti}+\text{Al}_8(\text{Cr,Fe})_5+\text{Al}_9(\text{Cr,Fe})_5$
③	59.7	25.8	6.1	L1_2
④	40	34.5	11.4	$\text{Ti}(\text{Al,Cr})_2$
⑤	50.0	46.7	2.4	TiAl
⑥	27.7	70.4	1.8	Ti_3Al

Balance: Fe

During the initial stage of sintering, plasma in the small gaps between particles can bring about evaporation and melting of the surfaces of these powders [133, 167, 168]. Therefore, a local region with very high rate of material transfer is formed around the particles, generating Ti_3Al rings. Small Al-Cr-Fe particles have a higher degree of defects as they cool faster during the gas atomization process, leading to a higher rate of diffusion of metals into and out of them during sintering process. Meanwhile, small particles can be heated more quickly, meaning that their thermal diffusion rate is also higher [169, 170]. Therefore, due to higher diffusion of Ti in and Al out, small Al-Cr-Fe particles have a lower Al content and a higher Ti content compared with large ones after the initial stage of sintering. Next, the sintering process is dominated by solid diffusion of atoms through Ti_3Al rings. As the holding time increases, new phases may form due to the local compositional change and the activation of atoms. Large Al-Cr-Fe particles have a higher Al content, so Al-rich phases like L_{12} can form on their boundary when the holding time increases to 10 min.

4.3.2 Microhardness

Figure 4-6 shows the microhardness of Ti/Al-Cr-Fe composites with different holding time. The incorporation of Al-Cr-Fe particles significantly increases the hardness. This can be attributed to the strong strengthening effect of Al-Cr-Fe particles which can restrain the deformation of the softer Ti. The solution strengthening effect due to the diffusion of Al atoms into Ti matrix is also a factor for the improved hardness. TACF-10 has the highest microhardness of all the samples tested. This is probably due to decreased porosity compared to TACF-5, and the increased presence of hard phases, $(\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$) compared to TACF-15 and TACF-20.

Figure 4-6 Microhardness of Ti/Al-Cr-Fe MMCs with different holding time.

Figure 4-7 shows the load–penetration depth curves obtained from nanoindentation tests in different positions of the sintered Ti/Al-Cr-Fe MMCs. The Ti matrix curves show smaller load at the same displacement and higher displacement under the same load, evidencing its soft nature. The Al-Cr-Fe particles show high slope curves and high load, due to their high elastic modulus and hardness. In between this range are the curves for the interfacial layer. Figure 4-8 shows the microhardness and elastic modulus of different regions in Ti/Al-Cr-Fe MMCs. Al-Cr-Fe reinforcements have highest microhardness and elastic modulus. The microhardness and elastic modulus of the interfacial layer are close to those of the reinforcements while Ti matrix has the lowest microhardness and elastic modulus.

Figure 4-7 Nanoindentation curves made in different regions of Ti/Al-Cr-Fe MMCs.

Figure 4-8 Microhardness and elastic modulus in different regions of Ti/Al-Cr-Fe MMCs.

4.3.3 Wear properties

Figure 4-9 shows the wear rate of Ti/Al-Cr-Fe composites sintered with different holding time. With an increase of holding time in the sintering process, the wear rate first reduces and then increases, with TACF-10 exhibiting the lowest wear rate. Such variation of wear rate with holding time can be attributed to the phase transformations and microstructural changes in the sintering process. When the holding time increases from 5 min to 10 min, the porosity in the sample reduces, leading to higher microhardness and a lower wear rate. However, when the sintering further increases to 15 min and 20 min, more diffusion of Al and Ti in the sintering process reduces the content of hard and wear resistant $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$, thus reducing the wear resistance of the samples.

Figure 4-9 Wear rate of Ti/Al-Cr-Fe composites sintered with different holding time.

Figure 4-10 shows SEM micrographs of the worn surfaces of the Ti/Al-Cr-Fe MMCs. Both SEM backscattered electron images and secondary electron images of TACF-10 are shown. Deep grooves in the wear direction can be found on the worn surface of pure Ti (Figure 4-10a), compared to the smaller and less numerous wear tracks on the surface of TACF-10 (Figure 4-10b). This is due to the increased hardness of the composites which reduces the region of plastic deformation near the worn surface. It can also be seen that there are some small wear debris on the worn surface of TACF-10 as indicated by the white arrow in Figure 4-10b. Figure 4-10c shows that these fine hard particles can adhere to Ti/Al-Cr-Fe MMCs, forming a compact protective layer on the worn tracks (indicated by the black arrows), further increasing the wear resistance. Some of wear debris particles are retained within the tracks where they are comminuted by repeated plastic deformation and fracture while moving freely between the sliding surfaces. However, once they have been reduced to a sufficiently small size, they are agglomerated at certain locations, particularly in grooves, due to adhesion forces between solid surfaces arising from surface energy, and develop compact layers which eventually become load-bearing [171]. This reduces material loss since newly formed debris particles are recycled into the layers while, as the particles are heavily deformed and oxidized, the layers are hard and give protection against wear damage. In addition, hard Al-Cr-Fe particles can reduce the width and depth of the wear track by stopping the movement of wear debris with the sliding ball, as indicated by the solid arrow in Figure 4-10d.

Figure 4-10 SEM images of the worn surfaces of Ti/Al-Cr-Fe MMCs: (a) secondary electron image of pure Ti; (b) secondary electron image of TACF-10; (c) backscattered electron images image of TACF-10 and (d) wear track through an Al-Cr-Fe particle. (The arrows in (c) indicate the protective layer formed; the arrow in (d) indicates an Al-Cr-Fe particle in the wear track)

Figure 4-11 shows the morphology of the wear debris and worn surface of the sliding 100Cr6 ball. The wear debris from these tests was mainly in the form of agglomerates of fine particles, of $<1-2\ \mu\text{m}$ in dimension. The wear debris appears to be agglomerated because of high surface energy of the fine particles. Wear particles undergo the following processes [172]: they are heavily deformed and fragmented to very small particles by repeated plastic deformations and fracture, then these particles are oxidized, coagulated together or agglomerated because of adhesion forces. Agglomerated particles are formed progressively by the agglomeration of small particles. Some of the wear particles are removed from wear tracks to form loose particles while some of the wear particles re-attached to either of the contacting surfaces. The worn surface of the

sliding ball is very smooth. No evident grooves can be found on the worn surface. This is because the sliding ball has high hardness and good wear resistance.

Figure 4-11 (a) Wear debris of TACF-10 and (b) worn surface of the sliding ball.

Figure 4-12 shows the EDX analysis of the worn surface of TACF-10, wear debris and worn surface of the sliding 100Cr6 ball. It can be found that the oxidization of the worn surfaces and wear debris occurs during the sliding tests. Ti is easy to be oxidized and the wear makes the oxidation easier because of the heat generated in the sliding process. Oxidation can have a beneficial effect in reducing wear during sliding of metals and alloys, particularly by preventing metal–metal contact.

Figure 4-12 EDX analysis of (a) worn surface of TACF-10, (b) wear debris and (c) worn surface of the sliding ball.

4.3.4 The influences of Al-Cr-Fe content

Figure 4-13 shows the microhardness of Ti/Al-Cr-Fe MMCs with different content of Al-Cr-Fe reinforcements. The microhardness of MMCs increases with an increase of Al-Cr-Fe content. The hard Al-Cr-Fe particles in Ti matrix can restrain its deformation, thus improving the microhardness. As the Al-Cr-Fe content increases, the deformation of Ti matrix are increasingly restrained, leading to a larger microhardness. Moreover, more Al-Cr-Fe particles mean that more interfacial rings, which are also beneficial in improving microhardness.

Figure 4-13 Microhardness of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content.

Figure 4-14 shows the friction coefficient of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content. It can be seen that the incorporation of Al-Cr-Fe particles makes the friction coefficient more stable. This is probably because the wear mechanism changes from two

body abrasive wear for pure Ti to three body abrasive wear for Ti/Al-Cr-Fe MMCs. Wear debris released into the interface between two rubbing surfaces reduce the friction by lessening direct contact between them when they are freely rolling or sliding under a lateral force. The change of wear mechanism from two body abrasive wear for pure Ti to three body wear for Ti/Al-Cr-Fe MMCs means there are more wear debris particles rolling between the rubbing surfaces.

Figure 4-14 Friction coefficient of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content.

Figure 4-15 shows friction coefficients of Ti/Al-Cr-Fe MMCs as a function of the number of laps. The friction coefficients of the Ti/Al-Cr-Fe MMCs samples rapidly increase with an increase of laps at the beginning as a result of the increased initial wear of rubbing surfaces. Then these coefficients decrease before reaching a stable condition at about 5000 laps. In addition, the composite samples exhibit more stable trends of friction coefficient versus laps than the pure Ti sample due to their more stable wear during the wear tests.

Figure 4-15 Friction coefficients of Ti/Al-Cr-Fe MMCs depending on the number of laps.

Figure 4-16 demonstrates how the Al-Cr-Fe content affects the wear rate of the Ti/Al-Cr-Fe MMCs. With the increasing Al-Cr-Fe content, the wear rate of composites first experiences a sharp decrease to 10 wt.% Al-Cr-Fe and then a slight decrease to 20 wt.% Al-Cr-Fe, followed by a slight increase to 30 wt.% Al-Cr-Fe. Ti/Al-Cr-Fe composites exhibit lower wear rate than its matrix, indicating the incorporation of Al-Cr-Fe reinforcement improves the wear resistance. The first sharp decrease in the wear rate is mainly because the wear mechanism changes from two body abrasive wear for pure Ti sample to three body abrasive wear for Ti/Al-Cr-Fe MMCs with 10 wt.% Al-Cr-Fe reinforcements. The improved wear resistance of the composites with the increasing Al-Cr-Fe content to 20 wt.% can be attributed to the improvement in the hardness. However,

when the Al-Cr-Fe content reaches 30 wt.%, the wear rate increases. This is probably because excessive Al-Cr-Fe content reduces the capability of Ti matrix to “hold” them.

Figure 4-16 Wear volume of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content.

4.4 Discussion

Metal matrix composites can be prepared by different methods, such as spark plasma sintering, conventional melting and casting, carbothermic reduction, self-propagating high temperature synthesis and volume combustion synthesis[75, 173]. Different materials require different preparation methods as each method has its own advantages and disadvantages. Given the low melting point (compared with Ti) and high diffusion of Al-Cr-Fe as well as the oxidation layer on the Ti surfaces, spark plasma sintering is a suitable way of preparing the metal matrix composites with Ti as matrix and quasicrystals (or their approximants) as reinforcement due to its low sintering temperature and short sintering

time. Sintering Ti by conventional methods such as hot pressing needs a high temperature (1200–1400 °C) and a long time (24–48h) as well as high vacuum ($>10^{-4}$ Pa) [87, 88]. Under such extreme conditions, Al-Cr-Fe powders will melt (Al-Cr-Fe powders has a melting point of about 1170 °C) and there will be significant diffusion between Ti and Al-Cr-Fe. This changes the composition of Al-Cr-Fe significantly and reduces the probability of preserving quasicrystals or their approximants. Moreover, the liquid Al-Cr-Fe will form a thin brittle film on the surface of Ti powders, reducing the toughness. SPS system can sinter Ti at a lower temperature (750 °C in our experiment, more than 300 °C lower than the melting point of Al-Cr-Fe) and in a shorter time, thus making it possible to retain Al-Cr-Fe quasicrystals (or their approximants) and also their spherical shape.

4.5 Conclusions

Metal matrix composites with Ti as matrix and Al-Cr-Fe quasicrystal approximants as reinforcements were successfully prepared using spark plasma sintering. A Ti_3Al ring forms around each Al-Cr-Fe particle during sintering. As the holding time increases, TiAl regions also form at the Al-Cr-Fe boundary.

The size of Al-Cr-Fe particles influences the phases at the Ti/Al-Cr-Fe interface, with smaller particles experiencing higher diffusion rate of Ti and Al. L1_2 region forms at the boundary of some large Al-Cr-Fe particles. The particle size also affects the composition of Al-Cr-Fe reinforcements. The Al content in relatively small Al-Cr-Fe particles is lower while the Ti content is higher, due to the higher diffusion rate in these particles.

The addition of Al-Cr-Fe particles into Ti matrix significantly improved the microhardness and wear resistance. TACF-10 exhibits the largest value of microhardness (Hv 460) and the lowest wear rate of all the samples tested. Both improvement of microhardness and modification of wear mechanism are the factors in the improvement in the wear resistance of the composites. A hard layer forms on the worn surfaces of Ti/Al-Cr-Fe composites during the wear tests, reducing the wear rate of materials. In addition, the hard Al-Cr-Fe particles impede the movement of wear debris with the sliding ball, reducing the wear rate.

The content of Al-Cr-Fe powders affects the microhardness and wear resistance of the Ti/Al-Cr-Fe MMCs. With the increase of the Al-Cr-Fe content in the composites, the microhardness increases while the wear rate first decreases and then increases, with MMCs containing 20 wt.% of Al-Cr-Fe exhibiting the lowest wear rate.

Chapter 5   High pressure spark plasma sintering of Ti based metal matrix composites reinforced with Al-Cr-Fe quasicrystals

5.1   Introduction

Titanium and its alloys are well known for their wide applications. They can be used in aerospace, chemical, petrochemical and marine industries as structural materials due to their high specific strength and excellent corrosion resistance [90, 91, 174]. However, the poor wear resistance of these materials can limit their applications [91, 95]. The addition of hard particles into Ti matrix to form metal matrix composites (MMCs) is one of the solutions to improve the wear resistance.

Quasicrystals have drawn a lot of attention from researchers due to their unique atomic arrangement (exhibiting forbidden symmetries in the convention crystallography) since their discovery in 1984 [1]. The unique atomic arrangement enables quasicrystals exhibit a combination of attractive properties such as low thermal conductivity, low electrical conductivity, good wear resistance, high hardness, low friction coefficient, good oxidation and corrosion resistance [2, 5, 45]. These properties make quasicrystals good candidates for various applications, including reinforcements in the MMCs [5, 175]. Gas atomized Al-Cr-Fe quasicrystal powders are already commercially available. It is expected that they can be used as reinforcements in the Ti based MMCs to improve the wear resistance.

Ti/Al-Cr-Fe MMCs can be prepared by sintering Ti and Al-Cr-Fe blended powders [176]. In the densification process, the interfacial diffusion and reactions have big influences on the properties of the obtained MMCs because they lead to the compositional change and possibly phase transformations of the reinforcements as well as the formation of an interfacial layer between the matrix and reinforcements. In order to retain quasicrystals in the Al-Cr-Fe reinforcements, the interfacial diffusion should be controlled as quasicrystals only exist in a small composition range [52, 177]. Therefore, the sintering temperature should be low and also the holding time should be short to avoid excessive interfacial diffusion. However, the oxidation layer on the surface of Ti powders means that the sintering by ordinary methods requires a high sintering temperature and a long sintering time [87, 88]. Thus, appropriate sintering methods should be chosen to prepare Ti/Al-Cr-Fe MMCs.

High pressure spark plasma sintering (HP-SPS) is expected to be able to prepare Ti/Al-Cr-Fe MMCs in a short time at a relatively low temperature due to its unique sintering mechanism. The uniaxial pressure can generate deformation of powders and break the oxidation layer on the surface of Ti powders, promoting densification and sintering. During the initial stage, plasma is generated in the small gaps between particles and a momentary high-temperature field is generated locally by pulse energy, spark impact pressure and electrical resistance heating, eliminating the oxide on the surface of some metal particles and activating the atoms there. The momentary melting and/or vaporization at inter-particle contacts create inter-particles necks. After these inter-

particle necks form, the high density electric current passing through them will result in Joule heating, further promoting bonding of particles.

In this chapter, the preparation of Ti/Al-Cr-Fe MMCs using high pressure spark sintering is reported. How the sintering pressure affects the interfacial microstructure and the phases of the reinforcements is demonstrated. The effects of Al-Cr-Fe reinforcements on the wear resistance and microhardness are also discussed.

5.2 Experiments

5.2.1 Sample preparation

Cristome A5 Al-Cr-Fe powders prepared by gas atomization with a nominal composition of $\text{Al}_{70}\text{Cr}_{20}\text{Fe}_{10}$ were purchased (Saint Gobain, France). These powders were first annealed at 800 °C for 30 min using SPS-1050 system (Sumitomo Coal Mining, Japan). The as-received powders were packed into the graphite die and two punches with the same diameter as the die were used to cover the die. Therefore, no uniaxial pressure was applied on the Al-Cr-Fe powders. The heating rate and cooling rate were both 100 °C/min.

Commercial pure titanium powders were purchased from Titan, Singapore. Two kinds of Al-Cr-Fe annealed powders (20 wt.%) were blend with Ti powders and sintered using the same SPS system: one is as-annealed Al-Cr-Fe powders; the other is sieved Al-Cr-Fe powders (bigger than 20 μm). The resulting pellets are named CA and CS, respectively. The temperature in the sintering process is demonstrated in Figure 5-1. As ordinary graphite dies can only stand a pressure of about 140 MPa [178, 179], in order to increase

the sintering pressure, a modified die setup was employed as schematically illustrated in Figure 5-2. The device is composed of an outer and an inner graphite die, and the powders are pressed by the two WC punches between two WC disks. Apart from the protective WC disks and punches, remaining devices were made entirely of graphite. It allows one to apply a pressure up to 300 MPa on a sample 10 mm in diameter and about 2 mm thick. For CA, six values of sintering pressure, 50, 100, 150, 200, 250 and 300MPa, were chosen to investigate the influences of sintering pressure. Pure Ti powders were also sintered using the same parameters for the comparison of properties. The obtained samples had a diameter of 10 mm and a thickness of about 1mm.

Figure 5-1 Temperature vs time in the HP-SPS process.

Figure 5-2 Schematic of the HP-SPS die setup.

5.2.2 Phase analysis and microstructural characterization

The phase analysis and microstructural characterization were done by the same methods as demonstrated in Chapter 4.

5.2.3 Mechanical properties testing

The microhardness and wear resistance properties of HP-SPSed samples were tested by the same methods as demonstrated in Chapter 4.

5.3 Results

5.3.1 SPS annealing of Al-Cr-Fe powders

Figure 5-3 shows the XRD pattern comparison of as-received and annealed Al-Cr-Fe powders. It can be seen that the peak at $2\theta=43.6^\circ$ corresponding to decagonal Al-Cr-Fe (D-AlCrFe) becomes very evident after SPS annealing, demonstrating that D-AlCrFe

formed in the SPS annealing process. Actually, it is reported in chapter 3 that SPS can promote the formation of decagonal Al-Cr-Fe. There are four phases in the powders: $\text{Al}_8(\text{Cr,Fe})_5$, $\text{Al}_9(\text{Cr,Fe})_4$, icosahedral Al-Cr-Fe (I-AlCrFe) and decagonal Al-Cr-Fe (D-AlCrFe).

Figure 5-3 XRD patterns of the as-received and SPS-annealed Al-Cr-Fe powders.

5.3.2 Phases and microstructure

Figure 5-4 is the backscattered electron SEM image of CA. As Al-Cr-Fe powders are spherical, it can be easily determined that the round particles in the image are Al-Cr-Fe. There is a dark grey ring around each Al-Cr-Fe particle. These rings form as a result of the interfacial diffusion and reaction between Ti and Al-Cr-Fe. From the contrast of the image, it can be found that the size of Al-Cr-Fe powders affects the resulting phases: there is no obvious contrast difference in relatively large particles, indicated by the white circles; but two colors are present for relatively small particles, as indicated by the black

circles. This is probably because smaller powders have a larger specific surface area, which means higher diffusion rate in SPS process. In addition, smaller powders can be heated more quickly, meaning that the thermal diffusion rate is also higher. In the outer layer of small Al-Cr-Fe particles, the contents of Cr and Ti (with larger atomic number Z than Al) are higher due to the higher diffusion rate of Al there, making this region appear brighter in the BSE images. As large Al-Cr-Fe powders have a composition close to the original one, the chance of preserving quasicrystals in the MMCs is higher.

Figure 5-4 SEM backscattered electron image of CA.
(White circles indicate relatively large Al-Cr-Fe particles while black circles indicate relatively small Al-Cr-Fe particles.)

Figure 5-5 demonstrates how the sintering pressure affects the composition of Al-Cr-Fe particles in the MMCs pellets. As particle size influences the composition of Al-Cr-Fe reinforcements in the MMCs, an Al-Cr-Fe particle with a diameter of $20 \pm 0.5 \mu\text{m}$ in each pellet was chosen for EDX analysis and comparison. The central parts with a diameter of

about 10 μm of these particles are compared in terms of Al, Cr and Fe content. It can be found that with the increase of sintering pressure, the content of Al increases significantly at the beginning, but it increases very slowly when the sintering pressure reaches 200 MPa. With the increase of pressure, the composition of Al-Cr-Fe powders gets close to the original one. Thus, in order to retain quasicrystals, the sintering pressure should reach 200 MPa or above to reduce the compositional change.

Based on the influences of particle size and the sintering pressure on the compositional change of Al-Cr-Fe reinforcements, Al-Cr-Fe bigger than 20 μm were chosen to be blended with Ti powders and sintered under 250MPa.

Figure 5-5 Compositional changes in the central part of Al-Cr-Fe with increasing sintering pressure.

The interfacial rings around Al-Cr-Fe particles are about one μm thick. The EDX line scan profile (Figure 5-6) shows that the interfacial rings are transitional regions of Ti and

Al, where the content of these two elements change sharply. Moreover, it can also be found that the content of Al is higher than that of Ti. This is because the diffusion rate of Al is higher than that of Ti [180-182], so there are more Al atoms than Ti atoms in the rings. Based on EDX analysis, these rings may consist of two phases, Al_3Ti and AlTi . This is further confirmed by TEM results.

Figure 5-6 EDX line scan profile of the CS interfacial layer.

Figure 5-7 shows the bright field TEM images and also the selected area electron diffraction (SAED) patterns of the interfacial region. It can be seen that the interfacial layer bonds to the Al-Cr-Fe particle very well without pores. Figure 5-7c is the SAED pattern of Al_3Ti taken along $[0\ 0\ 1]$. Al_3Ti is tetragonal with $a=b=0.385\text{nm}$ and $c=0.86\text{nm}$ (space group $I4/mmm$) [183]. It has a low density, high hardness, and good oxidation resistance [184, 185]. Figure 5-7d shows the SAED pattern of TiAl taken along $[0\ 0\ 1]$. AlTi is also tetragonal with $a=b=0.400\text{ nm}$ and $c=0.407\text{ nm}$ (space group $P4/mmm$) [186].

Like Al_3Ti , it also has a low density, high hardness, and good oxidation resistance [184, 187].

Figure 5-7 Bright field TEM images of the CS interfacial regions and corresponding SAED patterns: (a) bright field TEM image of the interfacial layer near Al-Cr-Fe; (b) bright field TEM image of the interfacial layer near Ti; (c) SAED pattern taken along $[0\ 0\ 1]$ of AlTi and (d) SAED pattern taken along $[0\ 0\ 1]$ of Al_3Ti .

As the composition of Al-Cr-Fe particles in the MMCs is very close to their original one, the quasicrystals are retained in the MMCs. Figure 5-8 shows a bright field TEM image and the corresponding SAED patterns of the quasicrystalline phases in the Al-Cr-Fe reinforcements. The 10 (5)-fold symmetry of the diffraction pattern confirms that

quasicrystals are retained in the MMCs. Figure 5-9 shows bright field TEM images and the corresponding SAED patterns of the two crystalline phases in the Al-Cr-Fe reinforcements. Their specific crystallographic information is provided in chapter 3.

Figure 5-8 A bright field TEM image of Al-Cr-Fe and corresponding SAED patterns: (a) bright field TEM image of Al-Cr-Fe; (b) SAED pattern taken along 5 fold axis of icosahedral Al-Cr-Fe; (c) SAED pattern taken along 10 fold axis of decagonal Al-Cr-Fe

Figure 5-9 (a) Bright field TEM image of $\text{Al}_8(\text{Cr,Fe})_5$; (b) SAED pattern taken along $[0\ 0\ 1]$ axis of $\text{Al}_8(\text{Cr,Fe})_5$; (c) bright field TEM image of $\text{Al}_9(\text{Cr,Fe})_4$ and (d) SAED pattern taken along $[1\ 1\ 0]$ of $\text{Al}_9(\text{Cr,Fe})_4$

Figure 5-10 shows the bright field TEM image of Ti matrix. It can be seen that the dislocation density varies in different regions. In regions ① and ② the dislocation density is very high. While in region ③ it reduces and in regions ④ and ⑤ it becomes quite low. This is due to the difference in stress and deformation of Ti particles caused by uniaxial pressure. Some regions deform more, so the dislocation density there is higher. In addition, the relatively low temperature and short holding time prevent the recovery and recrystallization of Ti particles. Thus the dislocations are retained in the pellets.

Figure 5-10 Bright field TEM image of Ti matrix.
 (① and ② are regions with very high density dislocations; ③ is a region with high density dislocations; ④ and ⑤ are regions with low density dislocations)

5.3.3 Microhardness

Figure 5-11 presents the variation of microhardness of CS with Al-Cr-Fe content. It is found that the addition of Al-Cr-Fe particles into Ti matrix significantly increases the hardness. This can be attributed to the strong strengthening effect of Al-Cr-Fe particles which can restrain the deformation of the softer Ti [105]. In addition, the high sintering pressure generates dislocations in the Ti matrix, increasing the microhardness as well. It can also be found that with the increase of Al-Cr-Fe content, the microhardness improves. This is because more hard Al-Cr-Fe particles restrain the deformation of Ti matrix more.

Figure 5-11 Variation of the microhardness of CS with different Al-Cr-Fe content.

Figure 5-12 shows the load–penetration depth curves obtained from nanoindentation tests in different positions of the sintered Ti/Al-Cr-Fe MMCs. The curves for Ti matrix show small load and low slopes evidencing the soft nature of matrix. The curves for Al-Cr-Fe particles show high slope and high load, due to their high elastic modulus and hardness. In between this range are the curves for the interfacial layer. Figure 5-13 shows the microhardness and elastic modulus of different regions in Ti/Al-Cr-Fe MMCs. Al-Cr-Fe reinforcements have highest microhardness and elastic modulus. The microhardness and elastic modulus of the interfacial layer are close to those of the reinforcements. And Ti matrix has the lowest microhardness and elastic modulus.

Figure 5-12 Nanoindentation curves made in different regions of Ti/Al-Cr-Fe MMCs.

Figure 5-13 Microhardness and elastic modulus in different regions of Ti/Al-Cr-Fe MMCs.

5.3.4 Wear resistance properties

Figure 5-14 shows the friction coefficients of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content. It can be seen that the incorporation of Al-Cr-Fe particles reduces the friction coefficients and makes them more stable. This is probably because the wear mechanism changes from two body abrasive wear for pure Ti to three body abrasive wear for Ti/Al-Cr-Fe MMCs.

Figure 5-14 Friction coefficient of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content.

Figure 5-15 shows friction coefficients of Ti/Al-Cr-Fe MMCs as a function of the number of laps. In order to facilitate reading, only pure Ti and CS with 5 wt.%, 20 wt.% and 30 wt.% are shown in the figure. The friction coefficients of the Ti/Al-Cr-Fe MMCs samples rapidly increase with an increase of laps at the beginning as a result of the increased initial wear of rubbing surfaces. Then these coefficients decrease before reaching a stable

condition at about 5000 laps. In addition, the composite samples exhibit more stable trends of friction coefficient versus laps than the pure Ti sample due to their more stable wear during the wear tests. Similar phenomenon is observed for SPSeD Ti/Al-Cr-Fe MMCs in Chapter 4.

Figure 5-15 Dependence of Friction coefficients on the number of laps.

Figure 5-16 illustrates the effect of Al-Cr-Fe content on the wear rate of CS. The incorporation of Al-Cr-Fe particles makes the wear rate first decrease sharply and then increases slightly, with CS-20 exhibiting the lowest wear rate, which is about 1/3 of that of pure Ti. Similar phenomena were also reported in iron based composites [188] and in aluminum based composites [189]. The first sharp decrease in the wear rate is mainly because the wear mechanism changes from two body abrasive wear for pure Ti sample to three body abrasive wear for Ti/Al-Cr-Fe MMCs with 5 wt.% Al-Cr-Fe reinforcements. The improvement in the hardness of Ti/Al-Cr-Fe MMCs with an increasing Al-Cr-Fe content is one of the factors for the improved wear resistance because higher hardness

means smaller deformation and removal rate when the ball is sliding on the samples. The wear resistance of the composites starts to decrease after Al-Cr-Fe content reaches 20 wt.%. This is probably because the wear resistance of the composites mainly depends on the ability of the matrix to “hold” a high amount of reinforcements [188]. Ti matrix cannot support an extra high amount of Al-Cr-Fe reinforcements, leading to a reduction in the wear resistance when the content of Al-Cr-Fe reaches 25 wt.% or above.

Figure 5-16 Wear volume of Ti/Al-Cr-Fe MMCs with different Al-Cr-Fe content.

Figure 5-17 shows the worn surfaces of pure Ti and CS-20. The worn surfaces of the two samples are quite different. Characteristic grooves in the wear direction can be observed on the worn surface of pure Ti (Figure 5-17a), showing that the main wear mechanism for pure Ti is plowing. Moreover, evident micro-cutting is observed in Figure 5-17c. This is because Ti is so soft that the sliding ball can penetrate into it to cause excessive material removal. However, there are few grooves found on the worn surface of CS-20 (Figure

5-17b). The high hardness of CS-20 prevents the occurrence of large plastic deformation and micro-cutting when CS-20 is under the same wear condition as the pure Ti. In addition, very fine particles can be observed on its worn surface (Figure 5-17d). These fine particles were generated due to repeated deformation and fracture of wear debris. Then they were oxidized, coagulated together or agglomerated because of adhesion forces. Some of the particles are removed from wear tracks while some of the wear particles re-attached to worn surfaces, forming a hard surface layer on the worn tracks and increasing the wear resistance.

Figure 5-17 Worn surfaces of pure Ti and Ti/Al-Cr-Fe MMCs: (a) pure Ti, low magnification; (b) CS-20, low magnification; (c) pure Ti, high magnification and (d) CS-20, high magnification.

Figure 5-18 shows the morphology of the wear debris and worn surface of the sliding 100Cr6 ball. The wear debris from these tests were mainly in the form of agglomerates of fine particles, of $<1\text{--}2\text{ }\mu\text{m}$ in dimension. The wear debris appears to be agglomerated because of high surface energy of the fine particles. The formation process of wear debris is demonstrated in Chapter 4. The worn surface of the sliding ball is very smooth. No evident grooves can be found on the worn surface. This is because the sliding ball has high hardness and good wear resistance.

Figure 5-18 (a) Wear debris of Ti/Al-Cr-Fe MMCs and (b) worn surface of the sliding ball.

Figure 5-19 shows the EDX analysis of the worn surface of CS-20, its wear debris and worn surface of the sliding 100Cr6 ball. It can be found that the oxidization of the worn surfaces and wear debris occurs during the sliding tests. Ti is easy to be oxidized and the wear makes the oxidation easier because of the heat generated in the sliding process. Oxidation can have a beneficial effect in reducing wear during sliding of metals and alloys, particularly by preventing metal–metal contact.

Figure 5-19 EDX analysis of (a) worn surface of CS-20, (b) wear debris and (c) worn surface of the sliding ball.

5.4 Discussion

5.4.1 Sintering mechanism

The high sintering pressure can offset the low sintering temperature and shorten the sintering time. In SPS process, the inherent sintering stress caused by reduction of surface area is assisted by an external pressure[190]. The external pressure makes particles rearrange and supplements the inherent sintering stress [191]. Densification rate is high when a high pressure is applied, and this rate dV_d/dt can be related to the applied pressure P_e [192]:

$$\frac{dV_d}{dt} = (1 - V_s)B \left(g \frac{\gamma_{sv}}{x} + P_e \right) \quad (5-1)$$

where V_s is the fractional solid density and $(1 - V_s)$ is fractional porosity, B is a collection of parameters, including diffusivity, temperature, and particle size, γ_{sv} is the solid–vapor surface energy, and g is a geometric term that depends on both the stage of sintering and the way in which x (a sintering stage parameter) is measured. High pressure promotes plastic flow and viscous flow of the powders at elevated temperatures, accelerating sintering process. From the above equation, it can be easily found that higher sintering pressure generates a higher rate of densification. In addition, the driving force for sintering reduces as a result of the application of an external pressure. This leads to a decrease in the sintering temperature and a limitation of grain growth. Thus, the application of a high pressure significantly decreases the temperature required to densify Ti/Al-Cr-Fe MMCs.

The sintering pressure affects not only the density of MMCs but also the composition of Al-Cr-Fe reinforcements. With the increase of the sintering pressure, the composition of Al-Cr-Fe in Ti/Al-Cr-Fe MMCs gets closer to its original value ($\text{Al}_{70}\text{Cr}_{20}\text{Fe}_{10}$). This is because the higher sintering pressure causes more deformation of particles, generating better connections between particles and reducing the current density near the particle contact regions. In the sintering process, the current density near the connection region of two particles is higher than other regions. This means this region is hotter than other regions. When a higher pressure is applied, the connection region becomes bigger, leading to a decrease in the current density and thus the heat generated locally. Therefore, a higher sintering pressure generates a low temperature increase near the connection region and a small hot region, leading to less diffusion of atoms between Ti and Al-Cr-Fe. Therefore, the compositional change of Al-Cr-Fe under higher pressure was reduced.

It is believed that the inter-particle bonding forms as a result of material transfer [77]. Surface diffusion does not bring the particle centers closer together but grain boundary diffusion and volume diffusion can. Surface diffusion has low activation energy and is more active at lower-temperature regimes than grain boundary diffusion or volume diffusion. Thus, a high heating rate tends to reduce the surface diffusion while achieve densification because at higher-temperature regimes all kinds of diffusion are activated. This is useful in reducing the interfacial layer in Ti/Al-Cr-Fe MMCs.

5.4.2 Comparison between SPSed MMCs and HP-SPSed MMCs

The interfacial layer of SPSed Ti/Al-Cr-Fe MMCs, which is about 5-10 μm thick, consists of Ti_3Al phase while the interfacial layer of HP-SPSed Ti/Al-Cr-Fe MMCs,

which is about 1 μm thick, consists of mainly AlTi and Al_3Ti . This is because in the HP-SPS process the heating and cooling rate is larger ($200\text{ }^\circ\text{C/min}$) and the holding time is shorter, making Al atoms not have enough time to diffuse into Ti matrix to form Ti_3Al phase. In the Al-Cr-Fe reinforcements of SPSed Ti/Al-Cr-Fe MMCs, no quasicrystals are retained because of excessive atomic diffusion. However, quasicrystals are retained in the Al-Cr-Fe reinforcements of HP-SPSed Ti/Al-Cr-Fe MMCs due to less atomic diffusion. The microhardness and moduli of different regions in the two kinds of MMCs are shown below in Figure 5-20 and Figure 5-21, respectively. The variation of microhardness of Al-Cr-Fe reinforcements in SPSed MMCs is larger than that in HP-SPSed MMCs. This indicates large microhardness difference of the phases which form during the SPS process. The variation of microhardness of Ti matrix of HP-SPSed MMCs is larger than that of SPSed MMCs. This is probably due to the difference of hard working of Ti matrix in different regions during the HP-SPS process. The interfacial layers of the two kinds of MMCs have very close microhardness. The variation of modulus of Al-Cr-Fe reinforcements and Ti matrix in SPSed MMCs is larger than that of HP-SPSed MMCs. However, the variation of modulus of the interfacial layers in HP-SPSed MMCs is larger than that of SPSed MMCs. As elastic modulus is sensitive to composition, such modulus variation difference is probably because the compositional variation is larger in the reinforcements and Ti matrix of SPSed MMCs and in the interfacial layer of HP-SPSed MMCs. Figure 5-22 shows the comparison of wear rate between SPSed Ti/Al-Cr-Fe MMCs and HP-SPSed Ti/Al-Cr-Fe MMCs. It can easily found that HP-SPSed samples exhibit better wear resistance.

Figure 5-20 Comparison of microhardness in different regions of two kinds of MMCs.

Figure 5-21 Comparison of modulus in different regions of two kinds of MMCs.

Figure 5-22 Comparison of wear rate of two kinds of MMCs.

The incorporation of Al-Cr-Fe in the Ti matrix significantly improves the wear resistance. Ti/Al-Cr-Fe MMCs exhibit wear resistance properties equivalent to those of MMCs with other common reinforcements for Ti, such as TiC, TiN and TiB, without regard to the morphology and size of reinforcements. Gu et al. [96] prepared Ti/TiC MMCs by selective laser melting. Their experiments show that the wear rate of Ti can be reduced by around 70% by the incorporation of 15 wt.% TiC. Yazdi et al. [97] reported that the incorporation of about 25 wt.% TiN+TiB into Ti by Tungsten inert gas process can improve the wear resistance by around 75%. Alman et al. [98] also reported that the incorporation of about 20 wt.% TiB₂ into Ti reduced the wear rate by around 70%. It is reported that for the MMCs with micro-sized reinforcements, the wear rate decreased with an increase in the size of reinforcements [193-195]. Thus, it is expected that if the

size of Al-Cr-Fe particles is reduced, the wear rate of Ti/Al-Cr-Fe MMCs can be further improved.

5.5 Conclusions

Ti/Al-Cr-Fe MMCs with Ti as matrix and Al-Cr-Fe powders as reinforcements have been successfully prepared using high pressure spark plasma sintering. As the interfacial diffusion between Ti and Al-Cr-Fe is reduced because of the short sintering time and the high pressure, large Al-Cr-Fe particles can retain their phases, including two quasicrystals, D-AlCrFe, I-AlCrFe, and their two approximants, $\text{Al}_9(\text{Cr,Fe})_4$ and $\text{Al}_8(\text{Cr,Fe})_5$. Interfacial layers form between Ti and Al-Cr-Fe during the sintering process, which mainly consist of Al_3Ti and AlTi , due to the higher diffusion rate of Al atoms. These two phases both have low density, high hardness and good oxidation resistance.

The size of Al-Cr-Fe affects its composition and phases in the composites. The diffusion rate between smaller Al-Cr-Fe particles and Ti matrix is higher, due to the higher specific area and defect density. The probability of preserving quasicrystalline phases in the composites depends on the Al-Cr-Fe size. The larger the Al-Cr-Fe powders are, the higher the probability of preserving quasicrystalline phases in the composites is.

The sintering pressure affects not only the density of the composites but also the compositional changes of Al-Cr-Fe reinforcements. Higher pressure leads to less compositional changes, due to the better rearrangement of particles in the sintering process and the lower interfacial temperature at the inter-particle contact regions. The

dislocation density varies in different regions of the Ti matrix due to the stress difference in the sintering process.

The addition of Al-Cr-Fe particles into Ti matrix to form MMCs can significantly improve the microhardness and enhance the wear resistance. With the increase of Al-Cr-Fe content, the microhardness of the composites increases, while the wear resistance first increases and then decreases.

Chapter 6   Conclusions and future work

6.1   Conclusions

This thesis is focused on the following subjects: the phases and microstructure of the gas atomized Al-Cr-Fe powders, phases and microstructure of Al-Cr-Fe pellets sintered using SPS, and the preparation of metal matrix composites with Al-Cr-Fe as reinforcements and Ti as matrix. Here are the major conclusions of the research.

1. During the gas atomization process of Al-Cr-Fe, icosahedral phase forms first in dendritic manner and then quasicrystal approximants $\text{Al}_9(\text{Cr,Fe})_4$ and $\text{Al}_8(\text{Cr,Fe})_5$ form in the inter-dendritic regions. The grains in the gas atomized powders are rounded. The lattice for the crystal phases in the gas atomized powders is distorted due to the high cooling rate during the gas atomization process.
2. At about 500 °C the distorted lattice begins to recover to equilibrium state and decagonal Al-Cr-Fe forms. There are four phases in the annealed Al-Cr-Fe powders: $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$, icosahedral Al-Cr-Fe and decagonal Al-Cr-Fe. Grains in the annealed powders possess polygonal morphology.
3. Al-Cr-Fe powders can be sintered into dense pellets using SPS. The sintering temperature has significant influence on the densification of the sintered pellets: as the sintering temperature rises from 650 °C to 800 °C, the relative density of the sintered pellets increases from 70% to 99% while the microhardness increases from Hv 400 to

Hv 810. At the temperature range of 700 °C to 800 °C, the dominant densification mechanism changes from grain boundary sliding to dislocation motion. The SPS process promotes the formation of quasicrystalline phases, especially the decagonal Al-Cr-Fe.

4. There are two quasicrystalline phases, icosahedral Al-Cr-Fe and decagonal Al-Cr-Fe, and two approximants, $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ in the sintered pellets. Icosahedral Al-Cr-Fe is face-centered with its diffraction points inflated by τ and its diffraction points forming pentagons. Decagonal Al-Cr-Fe has a periodicity of about 1.2 nm along its periodic axis. Along its 10 fold axis, the cores of the atomic clusters are imaged as rings with a diameter of approximately 1.5 nm, while the full clusters have a diameter of about 2.10 nm. The HR-TEM images taken along 10 fold axis of decagonal Al-Cr-Fe can be well superimposed with Penrose patterns. $\text{Al}_8(\text{Cr,Fe})_5$ and $\text{Al}_9(\text{Cr,Fe})_4$ are isostructural to binary Al_8Cr_5 and Al_9Cr_4 , respectively.
5. Metal matrix composites with Ti as matrix and Al-Cr-Fe quasicrystal approximants as reinforcement can be sintered using SPS. A Ti_3Al ring forms around each Al-Cr-Fe particle during sintering, which is about 15 μm thick. As the holding time increases, TiAl regions also form at the Al-Cr-Fe boundary. The addition of Al-Cr-Fe particles into Ti matrix significantly improves the microhardness and wear resistance. The holding time has significant influences on the properties of the sintered pellets, with the sample sintered for 10 min exhibiting the highest microhardness (Hv 460) and the lowest wear rate of all the samples tested.

6. After annealing using SPS, the decagonal Al-Cr-Fe content in Al-Cr-Fe powders increases. Ti based metal matrix composites reinforced with Al-Cr-Fe quasicrystals can be sintered using high pressure SPS at a high heating and cooling rate. The interfacial layer between Ti and Al-Cr-Fe is about 1 μm thick, which mainly consists of Al_3Ti and AlTi . Sintering pressure affects not only the density of the pellets but also the composition of Al-Cr-Fe particles in the composites. Higher pressure leads to less compositional change in the sintering process. The dislocation density varies in the different regions of Ti matrix due to the stress difference in the sintering process.
7. Based on the experimental results, the optimal process parameters to consolidate Ti/Al-Cr-Fe MMCs are as follows: The sintering pressure should be over 200 MPa to reduce the compositional changes of Al-Cr-Fe particles. The heating and cooling rate should be as high as 200 $^{\circ}\text{C}/\text{min}$ without holding time to reduce the diffusion and retain Al-Cr-Fe quasicrystals.
8. The incorporation of Al-Cr-Fe particles into Ti matrix significantly improves the microhardness and wear resistance. The microhardness of the composites increases with the Al-Cr-Fe content while the wear rate of the composites first decreases and then increases.

6.2 Novelty

1. The porosity of SPSed Al-Cr-Fe samples significantly decreases when the sintering temperature increases to 700 °C from 650 °C. This implies that sintering temperature is a very important parameter for consolidating quasicrystal powders using SPS.
2. SPS annealing can yield higher content of decagonal Al-Cr-Fe quasicrystals than vacuum oven annealing. This implies that SPS process promotes the formation of decagonal Al-Cr-Fe.
3. Sintering pressure affects the composition of Al-Cr-Fe reinforcements in MMCs prepared using high pressure SPS. As the sintering pressure increases, the composition of reinforcements gets close to their original value.
4. Al-Cr-Fe quasicrystals can be retained in Ti/Al-Cr-Fe MMCs using high pressure SPS with a high heating and cooling rate of 200 °C/min under a high sintering pressure of 250 MPa.

6.3 Future work suggestion

1. The comparison of XRD patterns of the SPSed powders and annealed powders indicates that SPS process can promote the formation and growth of Al-Cr-Fe quasicrystals, especially decagonal Al-Cr-Fe. However, the mechanism for such promotion still needs further investigation. In particular, the role of electrical field in this process needs further study. Moreover, it is probably the case for other quasicrystals. Experiments should be performed to check whether or not SPS can promote the formation of other quasicrystals like icosahedral Al-Cu-Fe and decagonal

Al-Ni-Co. In addition, theoretical models should be built to illustrate how the formation of decagonal Al-Cr-Fe is promoted.

2. Evident grain morphology differences between the as-received and annealed Al-Cr-Fe powders can be observed using TEM. However, the microstructural evolution and phase segregation in the annealing process of gas atomized Al-Cr-Fe powders still need further investigation. The mechanism for the morphology changes and phase segregation also needs further study to reveal the nature of microstructural evolution. This includes the driving forces of the evolution, the diffusion process, and also the activation energy for the phase segregation. In addition, the possible crystallographic orientation relationship between these phases needs further study. Structural models for the quasicrystalline phases also should be built to demonstrate the structure of these phases.
3. As the sintering parameters determine the porosity of the sintered pellets, it is expected that quasicrystals used for hydrogen storage and for catalysis with appropriate porosity can be sintered using SPS by choosing suitable sintering parameters. Similarly, it is expected the quasicrystals used for optical and magnetic applications can be sintered using SPS.
4. Metal matrix composites with Al-Cr-Fe quasicrystals as reinforcements and Ti as matrix can be prepared using high pressure spark plasma sintering by choosing appropriate sintering parameters and Al-Cr-Fe powder size. Due to the unique sintering

mechanism of SPS, it is reasonable to infer that some other metals can also be sintered at a relatively low temperature and thus used as matrix for the metal matrix composites. Likewise, some other quasicrystals may be also used as reinforcements in the composites. Therefore, some other metals, such as Fe, Ni, and other quasicrystals, such as decagonal Al-Ni-Co, icosahedral Al-Mn may be combined to form composites with various attractive properties. In addition, functionally gradient materials, which can make full use of the unique properties of quasicrystals for some special functional applications, are expected to be prepared by SPS because of the low sintering temperature and short sintering time of SPS.

5. It is found that the high heating rate and sintering pressure can reduce the diffusion between Ti matrix and Al-Cr-Fe reinforcements. However, the range of heating rate and sintering pressure in our previous experiments were limited. Whether or not the higher heating rate and sintering pressure can further reduce the interfacial diffusion and reaction still needs more experiments.
6. The wear resistance properties of Ti/Al-Cr-Fe MMCs should be tested under different conditions to simulate the real applications. For example, different load and different sliding velocity should be chosen. The influences of particle size on the wear resistance properties need to be investigated as well.

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