Microstructure and Properties of High Temperature Titanium Alloys with a High Si Content Prepared by Powder Metallurgy

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The objective of this paper is to improve the performance of high temperature titanium alloys with a high Si content by powder metallurgy. Firstly Ti-6.5Al-1.4Si-2Zr-0.5Mo-2Sn alloy powders were prepared using two different rotating speeds by plasma rotating electrode process (PREP). Then two sintering temperatures were selected to fabricate titanium alloys by hot isostatic pressing (HIP). The relationship between rotating speed and particle size distribution was investigated. X-ray diffraction, SEM, and OM were used to characterize the phase compositions, morphologies, and microstructures of the powders and titanium alloys. The mechanical properties of titanium alloys were investigated at room temperature, 300°C and 600°C. The results show that high quality titanium alloy powders were prepared by PREP. The mechanical properties of titanium alloy fabricated by powder metallurgy were superior compared to casting. And the strength is higher than typical Ti-1100 high temperature alloy.

\[\text{Keywords: high temperature titanium alloys, microstructure, silicides, plasma rotating electrode process, hot isostatic pressing}\]

1. Introduction

Titanium alloys are widely used in the chemical, pharmaceutical, and aviation industries due to their high specific strength, nonmagnetic properties, high temperature performance, good corrosion resistance, and biocompatibility\textsuperscript{1-4}. High temperature titanium alloys for aero engines are currently under development to replace high temperature steel alloys. Titanium alloys would reduce the engine weight and consequently improve the thrust-to-weight ratio\textsuperscript{5}. The Ukraine National Academy of Sciences has developed a unique design method for high temperature titanium alloy. The developed alloy is based on Ti-Al-Si-Zr system. The alloys were made with a composition of Ti-6.5Al-1.4Si-2Zr-0.5Mo-2Sn (mass%). Preparation by PM consisted of three basic stages, which were (1) production of alloy ingots, (2) powder production by PREP, and (3) hot isostatic pressing (HIP).

The high quality titanium alloy powders were prepared by PREP with rotating speeds of 12000 RPM and 18000 RPM in an Ar atmosphere (99.99%). Figure 1(a) shows a schematic illustration of PREP. Titanium alloy billets were prepared by vacuum arc melting before PREP. During PREP, the atomization chamber was filled with an inert atmosphere (Ar) and the rotating speed of the billet was gradually increased to the desired speed. A plasma torch was used to heat the billet end and molten droplets were dispersed due to the centrifugal force. The small droplets solidified as they travelled towards the chamber walls resulting in fine powders. The powders were divided into different particle size by flapper sample sieve.

HIP was performed using equipment (QIH-15, Sweden, maximum temperature 2000°C, maximum pressure 200 MPa). Powders with particle sizes of 45–150 μm were loaded into the stainless steel can, degassed and sealed tightly. The can was then put into the HIP chamber and vacuum purged with high purity argon (99.99%). The tempera-
ture and pressure of the HIP chamber was then increased to the target settings of 940°C or 980°C and 140 MPa, respectively. The high pressure and temperature were maintained for 4 h. After HIP, the reaction layer which is about 500 μm was removed from the sample.

Prepared powders and processed samples (HIP) were grind, polished, and etched in an etchant solution (HNO₃ 4%, HF 2%, and H₂O 94%) to reveal their microstructures. The chemical composition of the billet and powders was determined by chemical analysis. The oxygen content was determined using a TC600 Nitrogen/Oxygen Determinator (LECO Co., USA). The cross-sectional surface morphologies and phase compositions were investigated by optical microscopy (OM) (Leica DMI3000, Germany), scanning electron microscopy (SEM) (JEOL JXA-8100, Japan), and X-ray diffraction (XRD) (Rigaku D/MAX-RB, Japan). Differential scanning calorimetry (DSC) (NETZSCH STA 449 C, Germany) was used to investigate the phase transition temperature at a heating rate of 20 K min⁻¹ under an Ar atmosphere. The density of HIPed samples was measured by Archimedes method. The tensile properties of HIPed samples were measured at room temperature, 300°C and 600°C using a tension tester (INSTRON 5500, USA) at a strain rate of 5 × 10⁻⁴ s⁻¹. Creep tests were performed using a high temperature creep testing machine (Changchun RSW-100, China) under a stress of 160 MPa at 600°C for 100 h.

3. Results and Discussion

3.1 The relationship between rotating speed and particle size, chemical composition

In recent years, PREP has become the hot research topics in the titanium alloy powder preparation. The quality and properties of the powders are determined by the experimental parameters including the melting rate, billet diameter, rotating speed, and plasma gas composition. These parameters are interrelated by the following equation:

\[
d = k \left( \frac{\sigma}{D \cdot \rho} \right)^{(1/2)} \cdot \frac{30}{\pi n}
\]

Where \( k \) is a coefficient, \( d \) is the average particle size, \( D \) is the billet diameter, \( \sigma \) is the surface tension, \( n \) is the rotating speed, and \( \rho \) is the density.

The rotating speed has the largest influence on the powder particle size distribution. The particle size distribution of powders prepared by two different rotating speeds is shown in Fig. 1(b)–(c). The average particle size decreases with increasing rotating speed. Both kinds of powder particle size is mainly distributed in 44–250 μm. At 12000 RPM more than 95% of particles are distributed between 74 and 250 μm. Whereas, at 18000 RPM the size of the powders was mainly distributed between 44 and 150 μm, suggesting that the particle size decreased significantly. This illustrates that it is hard to prepare fine particles smaller than 44 μm during PREP.

Oxygen contamination influences the mechanical properties of titanium alloys. Small increase in oxygen content in HIP prepared samples can lead to a significant decrease in elongation. Therefore, to ensure that the titanium alloys have better mechanical properties, the oxygen increment should be strictly controlled during powder preparation. The chemical compositions of the original ingot and alloy powders with different size ranges are listed in Table 1. The results show that with decreasing particle size, the content of...
elements such as Al, Sn, Zr, Si, Mo, and O increase. Due to the high temperature and vacuum within the atomization chamber during PREP, low boil elements such as Al, Si, and Sn can easily vaporize. Fine powders are more liable to oxygen absorption due to their larger specific surface areas. Table 1 shows that the oxygen content of all powders is less than 0.1 mass%. Therefore, the subsequent high quality titanium alloy powders can improve the mechanical properties of HIPed samples.

3.2 Microstructures of alloy powders

Figure 2 shows SEM and OM micrographs of the surfaces and cross-sectional areas for the titanium alloy powders prepared by PREP. The powders have spherical morphologies. There are no satellite ball and hollow powder as shown in Fig. 2(a) and Fig. 2(c). There are two key methods for fabricating high quality titanium alloy powders, which are PREP and gas atomization (GA). The use of GA can lead to satellite ball and hollow powder\(^{15}\), which can be detrimental to subsequent shaping such as HIP, 3D printing. Therefore, titanium alloy powders prepared by PREP can meet the processing requirements for HIP. Two different surface morphologies for the powders were observed, as seen in Fig. 2(b). The main morphology is cellular but there is also a lamellar structure. The cross-sectional micrographs are shown in Fig. 2(d), the microstructure consists of equiaxed grains with a continuous lamellar structure within the grain. The grains in the core of the powder are coarser than that in the edge, as the cooling rate in the edge is faster than that in the core. The fast cooling rate can inhibit grain growth in the edge.

All three sizes of powder consist of $\alpha'$ martensitic phase. During PREP, the plasma temperature is much higher than the $\beta$ phase transition temperature. Therefore, the molten metal droplets occur $\beta/\alpha'$ phase transition during cooling. However, the $\beta$ phase cannot transform into $\alpha$ phase due to the high undercooling and metastable $\alpha'$ phase is formed, which has a close-packed hexagonal structure. The $\alpha'$ phase is a non-equilibrium phase and can transform into $\alpha + \beta$ at high temperature. With decreasing particle size, the intensity of the diffraction peak gradually decreases and the width increases due to the reduction in grain size.

<table>
<thead>
<tr>
<th>Particle size(μm)</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
<th>Zr</th>
<th>Mo</th>
<th>Sn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingot</td>
<td>/</td>
<td>87.49</td>
<td>6.46</td>
<td>1.38</td>
<td>2.04</td>
<td>0.55</td>
<td>2.02</td>
</tr>
<tr>
<td>178–250</td>
<td>87.84</td>
<td>5.99</td>
<td>1.35</td>
<td>1.72</td>
<td>0.50</td>
<td>1.52</td>
<td>0.052</td>
</tr>
<tr>
<td>Powders</td>
<td>150–178</td>
<td>88.06</td>
<td>6.08</td>
<td>1.41</td>
<td>1.84</td>
<td>0.50</td>
<td>1.60</td>
</tr>
<tr>
<td>44–74</td>
<td>88.04</td>
<td>6.13</td>
<td>1.44</td>
<td>1.91</td>
<td>0.68</td>
<td>1.68</td>
<td>0.077</td>
</tr>
</tbody>
</table>

3.3 Relative density and microstructure of HIPed titanium alloys

Generally, the HIP temperature is slightly lower than the $\beta$-phase transition temperature. The $\beta$-phase transition temperature is defined by the first order derivative of the DSC curve\(^{22,23}\). Figure 3 shows that the $\beta$-phase transition temperature of the powder is 997.9°C. To investigate the effects of HIP temperature on the microstructure and properties, HIP was performed at 940°C and 980°C at a pressure of 140 MPa for 4 h.

The properties of HIPed samples were evaluated by the homogeneity and relative density. The key parameters during the HIP process are temperature, pressure and time. However, temperature has the greatest influence on the homogeneity and density\(^{22}\). The results show that the density increases when the HIP temperature is increased from 940°C to 980°C. A density of 4.31 g cm\(^{-3}\) was measured for the sample sintered at 940°C with a relative density of 96.9%, based on the ingot density (4.45 g cm\(^{-3}\)). The density of the
sample sintered at 980°C was 4.44 g cm$^{-3}$ with a relative density of 99.7%. It can also be reflected in the metallographic image free of etching. The low-density sample contained lots of small pores as shown in Fig. 4(a). As the density increased fewer pores were observed (Fig. 4(b)). Before HIP, powders should be loaded into a can, degassed and sealed tightly. It has been reported that densification of powders cannot be performed completely when the thickness of the can is greater than 5 mm$^{24}$. In this study, the can is made from low carbon steel and has an average thickness of 2 mm. Figure 4(c) shows that the thickness of the reaction layer between the titanium alloy and low carbon steel is 200 μm.

Microstructures of the HIPed samples sintered at 940°C and 980°C are shown in Fig. 5(a)–(d). The particle profiles are clear for samples sintered at 940°C (Fig. 5(a)). When the temperature was increased to 980°C, the microstructure consists of homogeneous equiaxed grain (Fig. 5(b)). XRD analysis (Fig. 5(e)) revealed that the HIPed titanium alloys consist of α-Ti phase and Ti$_5$Si$_3$ silicide. The maximum solid solubility of silicon in α-Ti is 0.45%. The silicon content for the alloy presented here is 1.4% and it can exist in either the solid solution (α-Ti phase) or in the silicide phase (Ti$_5$Si$_3$). It can be seen from Fig. 5(c)–(d) that the alloy matrix is composed of α-Ti phase (Represented with A). There is also striped phase (Represented with B) and dot-like phase (Represented with C) which is the precipitated Ti$_5$Si$_3$ silicide. The distribution of the Ti$_5$Si$_3$ silicide is homogeneous. Such structure is representable as a natural composite (in situ composite), where the hardening Ti$_5$Si$_3$ phase is formed in the process of eutectic crystallization$^{10}$. It can be found the size of the striped structure grows with increasing temperature. The different areas were analyzed by EDS to identify the phase compositions and the results are listed in Table 2. The striped and dot-like phases have a high Si and Zr content. The result of EDS analysis is affected by the surrounding phases. Moreover, the depth of the phases B and C must be only several micron meters at most. The X-rays used for EDS analysis come from much larger area beneath the surface. So the content of Si in phase B and C is only 3–8%, less than that in Ti$_5$Si$_3$ phase which is 37.5%. Researchers have studied in detail the phase equilibrium and structure in the Ti-Si system. It has been highlighted that the Ti$_5$Si$_3$ silicide is only observed in binary alloys and its stability depends strongly on the oxygen and carbon content$^{25}$. And the Ti$_5$Si$_3$ silicide exists in binary and multicomponent alloys. When the content of Zr is increased about 5%, partial Ti is substituted by Zr to form a more dispersed (Ti, Zr)$_5$Si$_3$ phase.

### 3.4 Mechanical properties

The mechanical properties of alloys based on the Ti-Al-Si-Zr system are primarily determined by the content of silicon and the morphology and distribution of the silicide$^{11}$. During casting, the hardening phase forms a rod skeleton and difficult to be deformed, causing brittle fracture on a macroscale. For this reason, it is advantageous to improve the properties of the cast metal by two methods. One is refining the grains. Another is decreasing the size of the hardening phases in order to increase the interface area, so that the randomness of the crack propagation path is greatly increased. The mechanical properties of cast and HIPed alloys at different temperatures are presented in Table 3. The data shows that both the tensile strength and yield strength of cast alloy ($\sigma_b$: 683 MPa, $\sigma_s$: 628 MPa at room temperature) are lower than that of HIPed alloys ($\sigma_b$: 1003 MPa, $\sigma_s$: 912 MPa at room temperature when HIPed at 980°C). The plasticity
of cast alloy is insufficiently high. The mechanical properties of cast alloy are worsened due to the heterogeneous silicide distribution and coarse grains. In addition, mechanical properties of HIPed alloys were compared with Ti-1100 (Ti–6Al–2.75Sn–4Zr–0.4Mo–0.4Si) which is a typical high temperature titanium alloy in Table 3. The strength of HIPed alloys is higher than that of Ti-1100 alloy, but the plasticity needs to be improved.

During the HIP process, when the sintering temperature is raised to 980°C, densification of powders occurs more readily. Previous studies show the bigger the hard precipitated phase, the lower of the plasticity for SiC/Cu composite. For samples treated at 980°C, though the size of silicide increases, but its strength and plasticity are improved compared to samples treated at 940°C. This is due to its large relative density and homogeneous microstructure. The dispersive distribution of Ti₅Si₃ silicide can improve the mechanical properties, specifically the plasticity. M. Barmouz et al. have previously demonstrated that a homogeneous Ti₅Si₃ silicide phase with a size less than 1 μm is beneficial for mechanical properties. When the Ti₅Si₃ silicide phase is larger than 1 μm or aggregated in the matrix, the mechanical properties are reduced. Figure 5(c)–(d) shows that the size of the striped Ti₅Si₃ silicide is 5–10 μm. Further studies are underway to optimize the mechanical properties of the HIPed alloys, such as thermomechanical processing to reduce the size of the silicide.

The creep strain behavior was investigated at 600°C at
the content of Si of research alloy is nearly four times than that of Ti-1100 alloy, but the creep strain was slightly higher than that of Ti-1100 high temperature titanium alloys due to higher silicon content. Previous study shows the Si element in solid solution or in silicide shows creep resistant effect, and the former is the dominating condition of Si element\(^{(29)}\). The content of Si does not affect the Si element in solid solution, so it has not much impact on the creep performance.

Figure 6 shows SEM images of the fractured surface for the HIPed titanium alloys. The fractured alloys HIPed at 940°C and 980°C exhibit apparent dimple characteristics (Fig. 6(a)–(b)). Cleaved facets for alloys HIPed at 940°C can also be observed (Fig. 6(a)). The crack appears to have propagated along prior particle boundaries. There were no obvious crack initiation sites in samples HIPed at 980°C (Fig. 6(b)). This further confirms that the mechanical properties of alloys HIPed at 940°C are inferior to those HIPed at 980°C.

4. Conclusions

High quality titanium alloy powders were prepared at different rotating speeds by PREP. The particle size is mainly distributed between 44–250 \(\mu m\), with a spherical morphology. As the rotating speed increased, the proportion of small particles increases. The composition of alloying elements in powders is changed after processing in comparison to the original composition. The loss of low boiling point elements such as Al and Sn is relatively large. With decreasing particle size there is increasing oxygen content, but the oxygen content does not exceed 0.1 mass%. The alloy powder is mainly composed of \(\alpha'\) martensitic phase. The microstructure of the HIPed alloys is composed of Ti\(_5\)Si\(_3\) silicide surrounded by \(\alpha\)-Ti matrix. The mechanical properties of the alloys prepared by HIP are better than that of the cast alloy. The strength and ductility of samples HIPed at 980°C are superior to those HIPed at 940°C, at condition of room temperature, 300°C and 600°C.

**Acknowledgments**

This work was supported by the the National Natural Science Foundation of China (No. 51504072), the International Cooperation Program of Guangzhou City (No. 2014J4500024), the International Cooperation Program of Guangdong Province (No. 2014B050503003), the Basic Research Program of Guangdong Province (No. 2015A030310193), the Major Program of Guangdong Province (No. 2015B010122004), the Project for Research Environment and Capacity Building of Guangdong Academy of Sciences (No. 2016GDASPT-0209, NO. 2016GDASPT-0102), the Project of Industry-university-research Institute Collaborative Innovation of Guangzhou City (No. 201604040006) and the Project for Public welfare research and Capacity Building of Guangdong Province (No. 2017A070702019).

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