Effect of Silicon Addition on Microstructure and Mechanical Properties of Cast Titanium Alloys

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In order to develop a new kind of medical implant material, the microstructure and mechanical properties of cast Ti-Si alloys were investigated using small-size ingots prepared by a dental casting machine. The results show that the addition of silicon significantly changes the microstructure of titanium alloys. The Ti₅Sis intermetallic compound precipitation occurs in the matrix of alpha and beta phases, when the silicon content is over 1.33 mass%. The compound is observed as a netted structure around grain boundaries of the titanium matrix when the silicon content exceeds 2.35 mass%. In addition, the Ti-Si alloys show a good combination of strength and ductility in a wide range of silicon content in contrast to the pure titanium and Ti-6Al-4V alloys. The cast Ti-Si alloys are promising candidates for dental applications because of a good balance between strength and ductility.

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1. Introduction

Titanium and some of its alloys are well known with a high specific strength and good corrosion resistance. Due to these advantages, they have been increasingly attached a great importance and utilization in the aerospace and other industrial markets.¹,²

The titanium alloys are also considered as promising biocompatible metallic materials to be used for creating new medical implant to substitute bioactive hard tissues such as artificial joints and dental roots. However, the titanium alloy implants have a weaker interfacial bonding with a bone comparing to some bioactive materials, such as calcium phosphate ceramics and bioactive glass.³

Li et al.⁴ indicated that the formation of the apatite layer can be induced by silanol which is formed on the surface of the materials such as silica gel, silica glass, and silica ceramics etc. A number of authors⁵-⁷ pointed out that hydrated silica developed on the surface of glass and glass-ceramic plays an important role in forming the surface apatite layer when these materials are implanted into human body. It was proposed that a special type of silanol group is responsible for nucleation and growth of the apatite layer when the silica gels are immersed in the simulated body fluid.

Kitsugi et al.⁸ coated the titanium alloys with titanium silicide (Ti₅Sis) and titanium oxide (TiO₂), and then implanted the specimens into the tibial metaphases of mature rabbits. The results show that the Ti₅Sis and TiO₂ can enhance the early bonding of titanium alloys to bone by inducing a Ca–P layer on the surface of titanium alloys. Recently, Chen et al.⁹ reported that polymethylsiloxane (PDMS)-modified CaO–SiO₂–TiO₂ hybrids prepared by sol–gel process is highly bioactive due to synthesis effect of calcium ion, Si–OH and Ti–OH group.

Besides the bioactive property, silicon plays an important role in modifying the microstructure and mechanical properties of pure titanium having an insufficient strength for the use as an implant material. Silicon is a beta stabilizer and an important element in high temperature titanium alloys. Some investigators¹⁰-¹² have devoted to designing new high temperature titanium alloys by using silicon and indicated that the creep resistance of these alloys is improved by silicide precipitation on mobile dislocations resulting in pinning of these dislocations and inhabitation of their further movement.¹³ In comparison with other alloy systems, it is possible that a small amount of silicon decreases the stacking fault energy of the alloy, and consequently reduces the mobility of dislocations under stress by restricting cross-slip.¹¹

Recently, Suzuki et al.¹⁴ studied the effects of silicon addition on the microstructure and tensile properties for cast Ti–6Al–4V alloys. It was found that the silicon addition was effective for beta-grain refinement and the increase in tensile strength of Ti–6Al–4V alloys. However, the influence of silicon on the mechanical properties and microstructure of cast titanium alloys is not clear yet. Also, the high cytotoxicity of vanadium and tissue response of capsule type due to existence of aluminum¹⁵,¹⁶ urge us to develop a new kind of medical implant material without vanadium and aluminum.

In the present study, the microstructure and mechanical properties of the cast Ti–Si alloys with various silicon contents have been investigated under the condition of a small casting ingot, which is used for dental casting. The results are essential in designing dental implant biomaterials and prostheses, which need both high mechanical strengths and biological affinity.

2. Experiment Procedure

High purity titanium powders (99.9 mass%) were employed as the base metal of materials prepared. The titanium powder was blended with silicon (98 mass%) by ball milling for one hour. The mixed powder was compacted into a cylindrical shape of 55 mm in diameter by a mechanical die with
a press load of 300 kN, weighing about 150 g. Dental casting machine (OAC-T120PT) made by OHARA CO. LTD was used in this study. Laboratory ingots were prepared from the compact by arc melting with a tungsten electrode. The compact was set in a water-cooled copper crucible confined in a vacuum chamber. When an adequate melt quantity has been obtained, the molten pool was superheated for about one minute by adjusting the electric current to maximum value (400 A). Then, the crucible was tilted and the molten titanium was forced into the mold made from MgO–ZrO₂–SiO₂ ceramic powders, with a high pressure of argon gas (0.59 MPa).

Ingot cooling took place in an argon atmosphere until the mold was safely removed to air without oxidation of the titanium alloys. The resulting ingot had a dimension of approximately 45 × 20 × 12 mm³. The test specimens were cut from the ingot for the measurements of tensile strength, elongation, and hardness and microstructure observation. The dimension of tensile specimens is shown in Fig. 1. The tensile test was performed at an initial strain rate of 5 × 10⁻⁴ s⁻¹ at room temperature. The Vickers microhardness was tested with a load of 9.807 N and holding time of 15 s at room temperature. The specimens for metallographic examination were ground with silicon carbide paper from 220 to 2400-grit, and polished with nylon or silk cloth and a 6- to 1-μm diamond spray. After being cleaned with acetone and ethanol using an ultrasonic washer, the specimens were etched with an etchant containing 5 mL HF, 20 mL HNO₃ and 75 mL H₂O. The microstructure of titanium alloys was examined by optical microscopy, X-ray diffraction (XRD) and an electron probe microanalyzer (EPMA). The fracture surface was observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Effect of silicon on the microstructure

The chemical compositions of cast titanium alloys are shown in Table 1. Figure 2 shows the optical microstructure of the cast titanium without silicon addition. The microstructure consists of large grains of the matrix alpha phase with a dispersion of black particles of the beta phase due to the presence of tramp iron. The variation of microstructure of Ti–Si alloys with addition of silicon is given in Fig. 3. As the silicon content increases from 0.46 to 2.75 mass%, the microstructure is changed to acicular, lamellar and serrated alpha mixed with beta phase. The relation between the prior beta grain size and silicon content is shown in Fig. 4. The result indicates that silicon is effective in prior beta grain refinement during the process of ingot solidification.

When the silicon content exceeds 1.33 mass%, the plate-like compounds are observed either on the prior beta grain boundaries or within the grains. Figure 5 shows the results of backscattered electron and X-ray images of the compound measured by EPMA. Obviously the compound mainly consists of silicon and titanium. It is deduced that the compound is a kind of titanium silicide. The results examined by X-ray diffraction certified that the silicide is Ti₅Si₃ intermetallic compound. The morphology and distribution of the silicide change with increasing silicon concentration. When silicon content is about 1.33–1.82 mass%, some fine plate-like and laminate silicides are observed near the prior beta grain boundaries, as shown in Figs. 3(c) and (d). As silicon is added to 2.35 mass%, the network silicide is precipitated on the prior beta grain boundaries and many blocky-like silicide particles are dispersed within the grain as shown in Figs. 3(e) and 5(a). However, with extending silicon content up to 2.75 mass%, the thickness of the netted silicide increases and the blocky-like silicide particles disappear from grain interior as illustrated in Figs. 3(f) and 5(b). It is inferred that the network silicide is formed from residual molten at the prior beta grain boundary due to segregation of silicon during ingot solidification. The titanium silicide of lamellar structure should be formed by eutectic reactions from liquid to beta and Ti₅Si₃. The fine blocky-like silicide particles are precipitated from beta phase under the temperature of beta transus. The reason that the silicide particles are precipitated predominantly near the grain boundary or sub-grain boundary is that...

<table>
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<tr>
<th>Alloy*</th>
<th>Si</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>Fe</th>
<th>Ti</th>
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<td>0.46</td>
<td>0.030</td>
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<td>0.0042</td>
<td>0.03</td>
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<td>BAL.</td>
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<tr>
<td>TS15</td>
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<td>0.35</td>
<td>0.0044</td>
<td>0.03</td>
<td>BAL.</td>
</tr>
<tr>
<td>TS20</td>
<td>1.82</td>
<td>0.032</td>
<td>0.36</td>
<td>0.0040</td>
<td>0.03</td>
<td>BAL.</td>
</tr>
<tr>
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<td>0.35</td>
<td>0.0043</td>
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<td>BAL.</td>
</tr>
<tr>
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<td>0.34</td>
<td>0.0039</td>
<td>0.04</td>
<td>BAL.</td>
</tr>
</tbody>
</table>

* T: titanium, S: silicon.
the grain boundaries are high-energy areas and hence are preferred sites for nucleation. The decrease of grain size due to increase of silicon content reduces the diffusion distance of silicon to the pre-precipitated network silicide. Thus, the silicide precipitated from beta phase may nucleate and grow on the face of network silicide, which will cause the size of the netted silicide to be larger and silicide particles to disappear from grain interior area.

3.2 Effect of silicon on the mechanical properties

Figure 6 shows the variation of hardness with the silicon contents. The hardness of the titanium alloys increases with increasing silicon content. Figure 7 represents the relation between the tensile strength and elongation of titanium alloys with variation of silicon addition. Fracture surfaces of the tensile tested specimens are given in Fig. 8.
It can be seen that for the Ti–Si alloy the tensile strength increases rapidly from 371 to 733 MPa with silicon addition from 0 to 0.46 mass%. At the same time, the elongation of the alloy increases from 7.68 to 8.32%. Fractograph of the specimen with 0.46 mass% Si, as shown in Fig. 8(a), indicates very ductile and transgranular fracture with extensive dimple formation and tear ridges. The microstructure of the alloy is a mixture of lamellar and serrated alpha and beta phases without silicide precipitation. It can be deduced that tensile strength and ductility are enhanced by the grain refinement and solution strengthening by silicon.

The tensile strength continuously increases and the elongation decreases up to the addition of silicon of 1.82 mass%. However, the elongation decreases slightly and keeps in a relatively good level of 6.7–7% when the silicon content is 0.89–1.82 mass%. Increasing the content of silicon results in refinement of grain size, rising of beta phase and silicide precipitation, which causes the strength and hardness of the alloys to increase and the ductility to decrease. However, the ductile properties could be maintained at a relatively stable level, because the distribution and morphology of silicides are not continuous or in network-state yet. The improvement in tensile ductility is consistent with the change in the fracture mode as shown in Figs. 8(b), (c) and (d). It should be noted that all the fractures are transgranular and ductile but the size of tear ridges becomes smaller with the increase of silicon content.

When the silicon content exceeds 2.35 mass%, there is a small loss in tensile strength but a significant loss in tensile ductility; the total elongation is nearly 0%. The drop in ductility is due to the occurrence of intergranular fracture as shown in Figs. 8(e) and (f), which results from the continuous pre-
The Ti–Si alloys show a good combination of strength and ductility in contrast to the pure titanium and Ti–6Al–4V alloy. When the silicon content is around 0.46–1.82 mass%, the tensile strength is about 733–1031 MPa which is 2–2.8 times higher than that of pure titanium and the tensile elongation is about 8.3–6.7% which is increased by 86–50% compared to the Ti–6Al–4V alloy. From Fig. 9, it can be seen that the different good combinations of strength and ductility are obtained by adjusting the content of silicon in a wide range to meet different requirements. The Ti–Si alloys can be expected to be useful as new bioactive materials due to their good mechanical properties. However, the fatigue strength may be reduced by much silicide precipitation in the matrix as the silicon content exceeds 1.33 mass%. Because the present experiment was done with a small-sized ingot, the microstructure and mechanical properties are considered to be affected by the cooling rate. Thus, the results are suitable for developing the titanium alloy used for small-scale castings such as dental prostheses etc. Further investigations should be done to determine how the silicon addition influences the biocompatibility of titanium alloys as well as the mechanical properties of cast titanium alloys with a thicker dimension.

4. Conclusions

(1) The microstructure of the cast Ti–Si alloys is the acicular, lamellar and serrated alpha phase mixed with beta phase. The plate-like silicide Ti5Si3 intermetallic compounds are precipitated, as the silicon content is over 1.33 mass%. When silicon content exceeds 2.35 mass%, network silicide is observed around grain boundaries. The silicon addition is effective in prior beta grain refinement during the process of precipitation of grain boundary silicides.

In order to compare the mechanical properties of the cast Ti–Si alloys with that of the cast Ti–6Al–4V alloy - the most widely used titanium alloy - the cast Ti–6Al–4V alloy was prepared by the same method. Figure 9 shows the result. It should be noted that the Ti–6Al–4V alloy possesses the highest hardness and tensile strength but has the smallest ductility among the cast titanium alloys prepared in this experiment. The microstructure of the cast Ti–6Al–4V alloy obtained from this experiment is a mixture of plate-like acicular alpha and beta phase with large beta grains, as shown in Fig. 10. This kind of microstructure is detrimental to tensile elongation due to existence of many brittle beta phases.13

Fig. 9 Mechanical properties of various cast titanium alloys. Pure Ti and Ti–6Al–4V were prepared under the same casting condition as Ti–Si alloys.

Fig. 10 SEM image and optical micrograph of the cast Ti–6Al–4V alloy. a: fracture surface after tensile test, b: microstructure.
solidification.

(2) When the silicon content is below 1.82 mass%, Ti-Si alloys show a good combination of strength and ductility in contrast to the pure titanium and Ti–6Al–4V alloy. The tensile strength is about 733–1031 MPa, which is 2–2.8 times higher than that of pure titanium, and the tensile elongation is about 8.3–6.7%, which is increased by 86–50% compared to the Ti–6Al–4V alloy prepared under the identical condition. The cast Ti–Si alloys can be expected to be promising bioactive materials.

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REFERENCES