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EXPRESS REGULAR ARTICLE

Effect of Mold Material and Binder on Metal-Mold Interfacial Reaction for Investment Castings of Titanium Alloys

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The aim of the present paper is to investigate the combined effect of mold material and binder for investment casting of titanium and titanium alloys. A plasma arc melting furnace was used for melting titanium alloy, and the interfacial reaction of titanium castings was determined by optical microscope, SEM, EDS analysis and hardness profile. The mold materials examined were ZrO_2, Al_2O_3, $CaZrO_3$ and CaO. Machined graphite mold was examined for comparison. The result shows that the titanium castings produced using ZrO_2 and Al_2O_3 mold had a clear reaction whereas a negligible reaction occurred in the castings in CaO, $CaZrO_3$ and graphite molds. $CaZrO_3$ is regarded as a promising mold material for titanium castings from the viewpoints of thermal stability against molten titanium alloy, sufficient mold handling strength and slurry viscosity control.

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1. Introduction

In today's high technology world, titanium and titanium alloys are increasingly gaining importance in aircraft, atomic generators and chemical plant applications as well as automobile parts due to their unique properties of high specific strength and corrosion resistance.[1–3] Moreover, because of their superior biocompatibility with tissue and excellent corrosion resistance compared with other metallic implant materials, titanium alloys are expected to be used widely for biomedical material applications.[4]

Investment casting is regarded as an economical processing technology for titanium-based net-shaped components owing to the poor machinability and workability of these alloys at ambient temperature.[5,6] But titanium alloys are extremely reactive to refractory oxide molds in the molten state, resulting in surface-level chemical reaction. The interstitial elements from oxide molds have a great tendency to enter into titanium castings during investment casting and cause a deterioration of mechanical properties such as ductility, hardness and toughness.[7]

A number of investigations have already been made on the evaluation of different oxide molds against molten titanium and titanium alloys. Suzuki *et al.* proposed that pure yttria was a strong candidate as a mold for titanium investment casting.[8] However, the use of yttria has been limited by its relatively high cost. The thermal stability of several mold materials against molten titanium and titanium alloys was evaluated by Yoneda *et al.*[9] All these investigations, however, provided little information on the combined effect of binder and mold materials on metal-mold interfacial reaction for investment casting of titanium alloys.

The aim of this work is to optimize and develop a mold material and binder system for investment casting of titanium and titanium alloys from the practical and economic points of view. An attempt was made to investigate the combined effect of mold material and binder on metal-mold interfacial reaction for investment castings of commercially pure titanium (CP Ti) and Ti6Al4V alloy (Ti64) using optical micrograph, SEM and EDS analysis and microhardness measurement.

2. Experimental Procedure

2.1 Mold production

The wax patterns for evaluating the thermal stability of mold materials were made by pouring molten wax into a simple cylindrical metal mold (9 mm in diameter and 30 mm in height) with an integral pouring basin. The wax patterns were then inspected and dressed to eliminate any imperfections resulting from pouring.

Figure 1 shows the standard free energies for the formation of oxides, from which it would appear that ZrO_2, Al_2O_3, CaO and $CaZrO_3$ might show promise as mold materials for investment casting of titanium alloys.[10] Therefore, these were

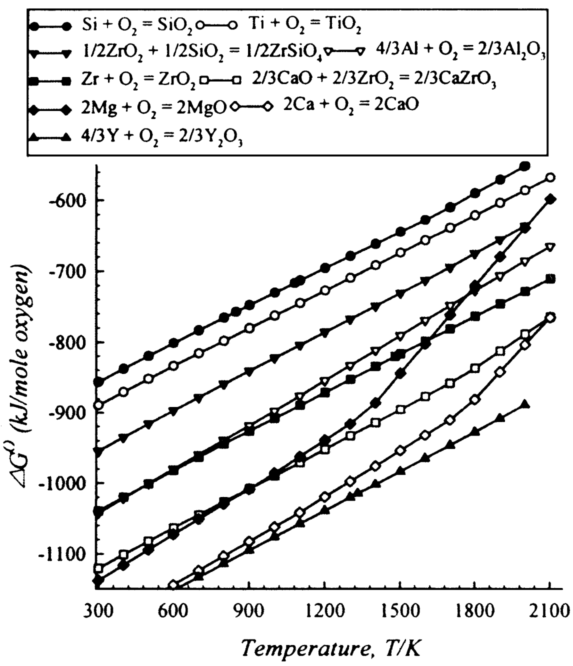

Fig. 1 Standard free energy change of the formation of oxides.

Table 1 Types of oxide and binders examined and mixing ratios.

Oxide	Binder	Oxide vs. Binder
Al_2O_3	Colloidal silica	
$CaZrO_3$	$ZrOCl_2 \cdot 8H_2O$ 1 mol + $(CH_3COO)_2CaH_2O$ 1 mol	1st dipping 3 vs. 1 After 2nd dipping 2.5 vs. 1
CaO	Ethanol 100 g + $CaCl_2$ 4 g	

Table 2 Type of binders for alumina mold.

Oxide	Binder	Oxide vs. Binder
Al_2O_3	Colloidal silica $ZrOCl_2 \cdot 8H_2O$ 1 mol + $(CH_3COO)_2CaH_2O$ 1 mol Aqueous solution (Under development)	1st dipping 3 vs. 1 After 2nd dipping 2.5 vs. 1

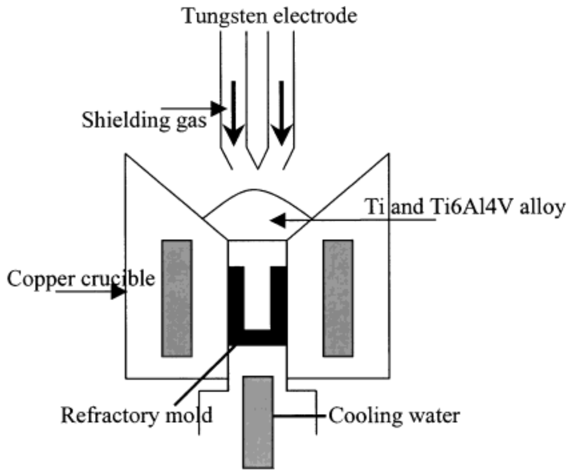

Fig. 2 Schematic diagram of plasma arc melting furnace.

chosen for evaluation. The wax pattern was dip-coated with a primary slurry coat containing very fine oxide powders. It was then underwent stuccoing after draining the excess slurry and given another coat of the same slurry. Later stuccoing procedures were performed with coarser oxide powders and a shell thickness of ~ 5 mm was built by alternately dipping and stuccoing. The oxides and binder used are given in Table 1.

The shell molds were then dried at a controlled temperature (300 ± 2 K) and relative humidity ($50 \pm 10\%$) for at least 4 h. The molds were de-waxed in an autoclave at about 440 K at a pressure of about 0.5 MPa. Subsequently, they were fired at 1273 K for 2 h for hardening and eliminating moisture before introducing them into the plasma arc-melting furnace.

The effect of the binder on the reaction between titanium and the electro-fused Al_2O_3 mold was investigated in order to identify the role in producing alpha case on titanium castings. The binder used for Al_2O_3 mold was conventional colloidal silica, an acetic binder for the $CaZrO_3$ mold and an aqueous solution (still under development). Table 2 presents the binders for the Al_2O_3 mold.

2.2 Melting and casting experiments

Melting and casting experiments were performed in a plasma arc-melting furnace. A direct-current transferred-type torch with a maximum output of 100 kW (1000 A $\times$ 100 V) was used for plasma generation, where the tungsten tip in the torch serves as a cathode and the material to be melted as an anode. Investment casting for metal-mold interfacial reaction was carried out by drop casting procedure after plasma arc melting, as shown in Fig. 2. The pressure of the furnace atmosphere can be controlled in the range of 1.33×10^{-1} Pa (10^{-3} Torr) by a vacuum pump, and then subsequently backfilled with high purity argon to the pressure of 4.9×10^3 Pa (36.7 Torr). Power was then applied until the charge was melted. This cycle of evacuation and flushing with argon was repeated at least two times. When the charge was in a fully molten condition, the arc was directed at the center of the hearth and the current raised to allow the molten metal to flow into a mold positioned below the hearth.

2.3 Evaluation of metal-mold interfacial reaction

The interfacial reaction of mold materials was determined with regard to microstructural characterization of the metal-mold interface by optical microscope and hardness profile. The as-cast specimen were sectioned, polished and examined via an Olympus PME 3 optical microscope to characterize the microstructure after etching using a Keller solution. A hardness test was conducted by utilizing a Microvickers hardness tester (Mitutoyo MVK-H2) measuring at 0.05 mm intervals along the vertical cross section of specimen. The effect of metallic elements and constituents of binder on the interfacial reaction of the Al_2O_3 mold were analyzed using a Philips XL30 ESEM-FEG equipped with an energy dispersing spectrometer.

3. Results and Discussion

3.1 Effect of mold material on metal-mold interfacial reaction

It has been suggested earlier that the relative difference of metal-mold interfacial reaction by microhardness and optical microscopy provides a good index for the relative stability of oxide molds.[11] The hardness profiles of CP Ti and Ti64 alloy rods cast in different mold materials are given in Fig. 3. Figure 4 illustrates the as-cast microstructure of the regions below the surface of the castings. The ZrO_2 mold exhibited the most severe reaction with titanium, resulting in a thick reaction layer, as shown in Figs. 4(a) and (f). Those microstructures were composed of an acicular alpha phase at the surface and equiaxed grains towards the center. However, a negligible reaction with titanium castings occurred in the CaO, $CaZrO_3$ and graphite molds. The results of hardness profiles correspond well with the metallographical observations. The microhardness profiles of Ti64 alloy castings were similar to those of CP Ti, although it did appear that the reaction layers were slightly thicker.

In the present work, the increase of internal hardness in titanium castings was not observed to be influenced by the interfacial reaction. Saha *et al.* proposed that the relative difference of bulk hardness in titanium castings provided a good index for the relative stability of molds.[12] In his work, however, the binder used was colloidal silica regardless of mold

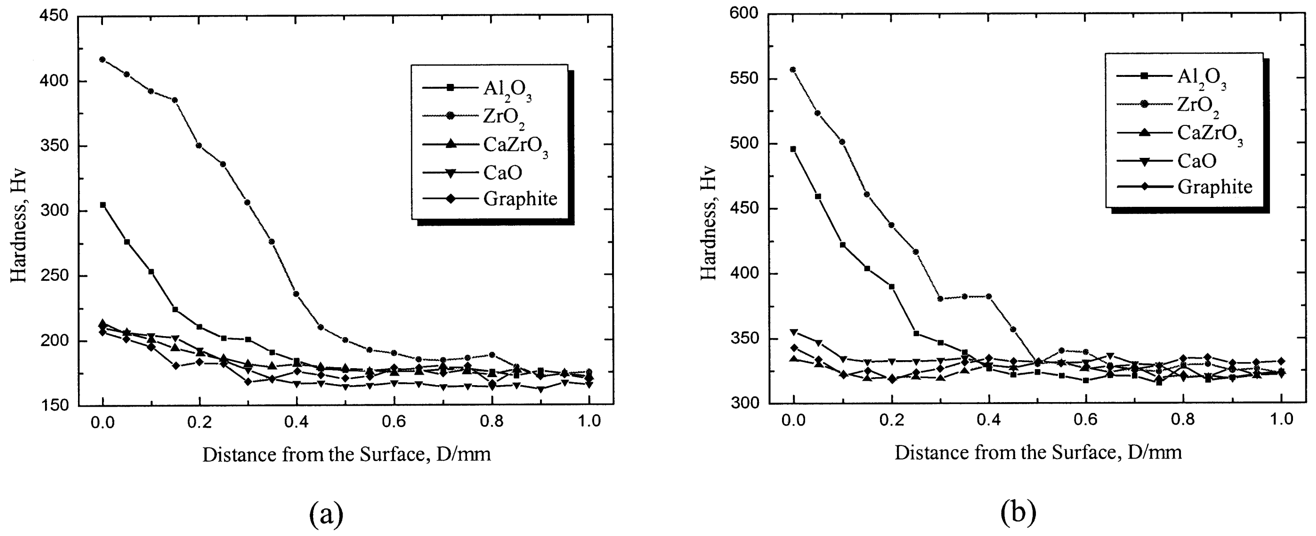

Fig. 3 Effect of mold materials on hardness profiles of (a) CP Ti and (b) Ti6Al4V alloys.

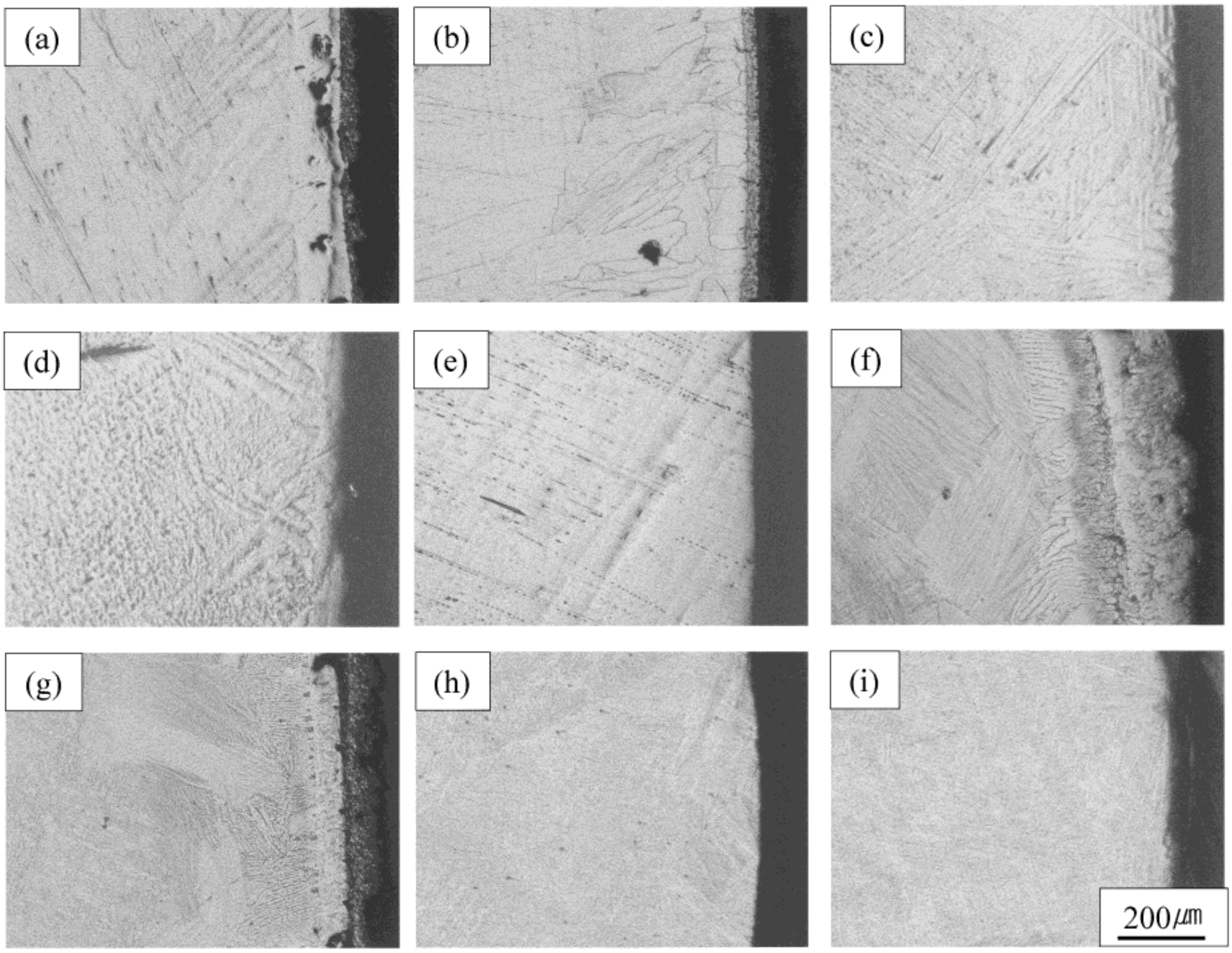

Fig. 4 Photographs showing microstructures of regions below the surface of the as-cast (a) CP Ti in ZrO_2 mold, (b) CP Ti in Al_2O_3 mold, (c) CP Ti in CaO mold, (d) CP Ti in graphite mold, (e) CP Ti in $CaZrO_3$ mold, (f) Ti6Al4V in ZrO_2 mold, (g) Ti6Al4V in Al_2O_3 mold, (h) Ti6Al4V in CaO mold, and (i) Ti6Al4V in $CaZrO_3$ mold, respectively.

materials. Therefore, this could be explained by the fact that the increase of bulk hardness was affected not only by the stability of mold material but also by the effect of binder, colloidal silica.

In general, the hardening mechanism at the surface of titanium castings is correlated to many factors, including (1) the metal-mold interfacial reaction to evolve oxygen, (2) the absorption of the oxygen into the molten titanium, (3) the diffusion of the oxygen through the surface of castings and (4) the solution hardening by metallic element dissolved from the oxide.[13] In this work, the afore-mentioned second factor was confirmed to be negligibly small because of the intrinsic properties of the plasma arc melting process.

Based on the previous discussion, Fig. 5 shows the hardness distribution of Ti64 castings made in a ZrO_2 mold. The microhardness profile of the surface hardened area was found to delineate two distinct regions, one of which, at a distance of 160 μm, is characterized by the reaction layer (α-case). The following region, the hardening layer of about 400 μm, can be attributed to the diffusion of oxygen into the titanium bulk after metal-mold interfacial reaction.[14] In the first point, when the molten titanium fills the mold, it reacts with the mold and preferentially dissolves the constituents of the mold. This proved that the dissolved metallic element, zirconium, from the oxide preferentially reacted with the molten titanium. It is likely that this increase in oxygen and zirconium levels increased the hardness of the cast titanium. The second region of microhardness profile can be designated as an oxygen diffusion zone, resulting in somehow hardening the bulk titanium. In brief, the increase of the surface hardness is due to the continuation of the diffusion of the mold constituent even after the start of solidification.

It is also of interest to note that the castings produced in a graphite mold have no reaction layer, as shown in Fig. 3(d). A rammed graphite mold, as mentioned by T. Yoneda, reacted violently with molten titanium, resulting in α-case in the surface of the titanium castings.[15] But, there is no reaction layer through metallographic observation and, thus, no increase of the hardness of the titanium castings in the present work. An explanation for this difference could be the large difference in the thermal conductivity of other oxides.[16] Because of its relatively high thermal conductivity, molten titanium in graphite mold rapidly solidified because there was no enough time to react with mold. This result was similar with that of the Ti64 alloy.

The basic conditions for investment molds usually require many factors, such as handling strength, formability, air permeability, cost and collapsiability.[17] However, it is necessary to consider the thermodynamic stability for titanium investment molds because of the extreme reactivity in the molten state.

Although CaO is a promising mold material for titanium investment casting owing to its stable oxide and low cost compared with yttria, unfortunately, it is very difficult to control the viscosity of the slurry and the dispersiveness of the oxide during the dipping and stuccoing process. This is because an ethanol based binder should be used. Moreover, surface defects, such as pinhole and porosity, are likely to appear during the mold making process. In addition, enough handling strength cannot be obtained for investment molds using unhydrated $CaCl_2$.

Therefore, a new material, $CaZrO_3$, is regarded as a promising mold material for investment casting of titanium alloy.[18] It has many merits, including a long-term maintenance of the slurry due to a water based binder, the mold surface is free from defect, it is possible to operate even under vacuum atmosphere, and it also has sufficient handling strength. Moreover, the thermal stability of a $CaZrO_3$ mold is no less than that of a CaO mold, as shown in Figs. 4(e) and (i).

3.2 Effect of binder on metal-mold interfacial reaction

Despite the low thermal stability, as shown in Fig. 4(b), Al_2O_3 has an advantage for being used as investment molds for titanium castings, because of low cost, formability and binder flexibility. The hardness profiles of titanium castings in an Al_2O_3 mold with different binders are given in Fig. 6. Figure 7 illustrates the as-cast regions below the surface of the investment castings with different binders and the results of elemental profiles.

First, the acetic acid binder caused a violent reaction as shown in Fig. 7(b). It is seen from the elemental profiles that the constituent of the binder, carbon was obviously revealed on the metal-mold interfacial area. This could be explained by the fact that the extent of the metal-mold reaction is greatly related to the effect of the binder more than that of the mold material itself. This evidence is in agreement with the hardness profiles, as shown Fig. 6.

Secondly, for the purpose of evaluating the effect of the silica content in the binder on metal-mold reaction, colloidal silica and an aqueous solution, which restricted silica content, were used to investigate the extent of the interfacial area. As shown in Fig. 7(c), the thickness of the alpha case in titanium casings is significantly reduced when compared with

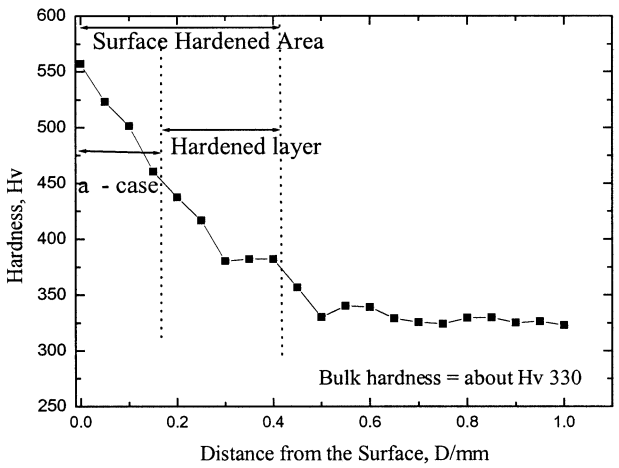

Fig. 5 Hardness distribution of Ti6Al4V alloy castings in ZrO_2 mold.

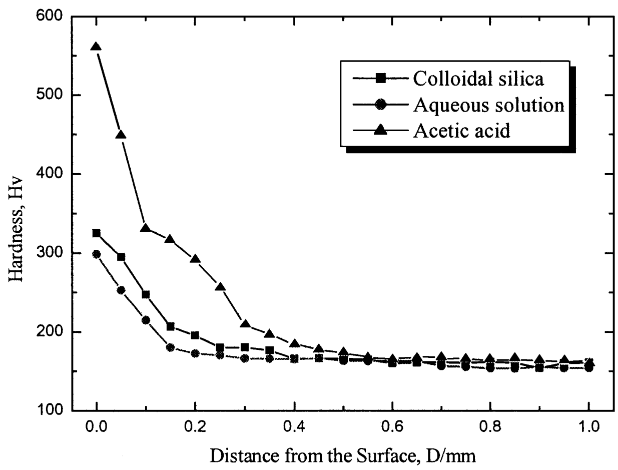

Fig. 6 Effect of the binders on microhardness profile of commercially pure titanium into Al_2O_3 mold.

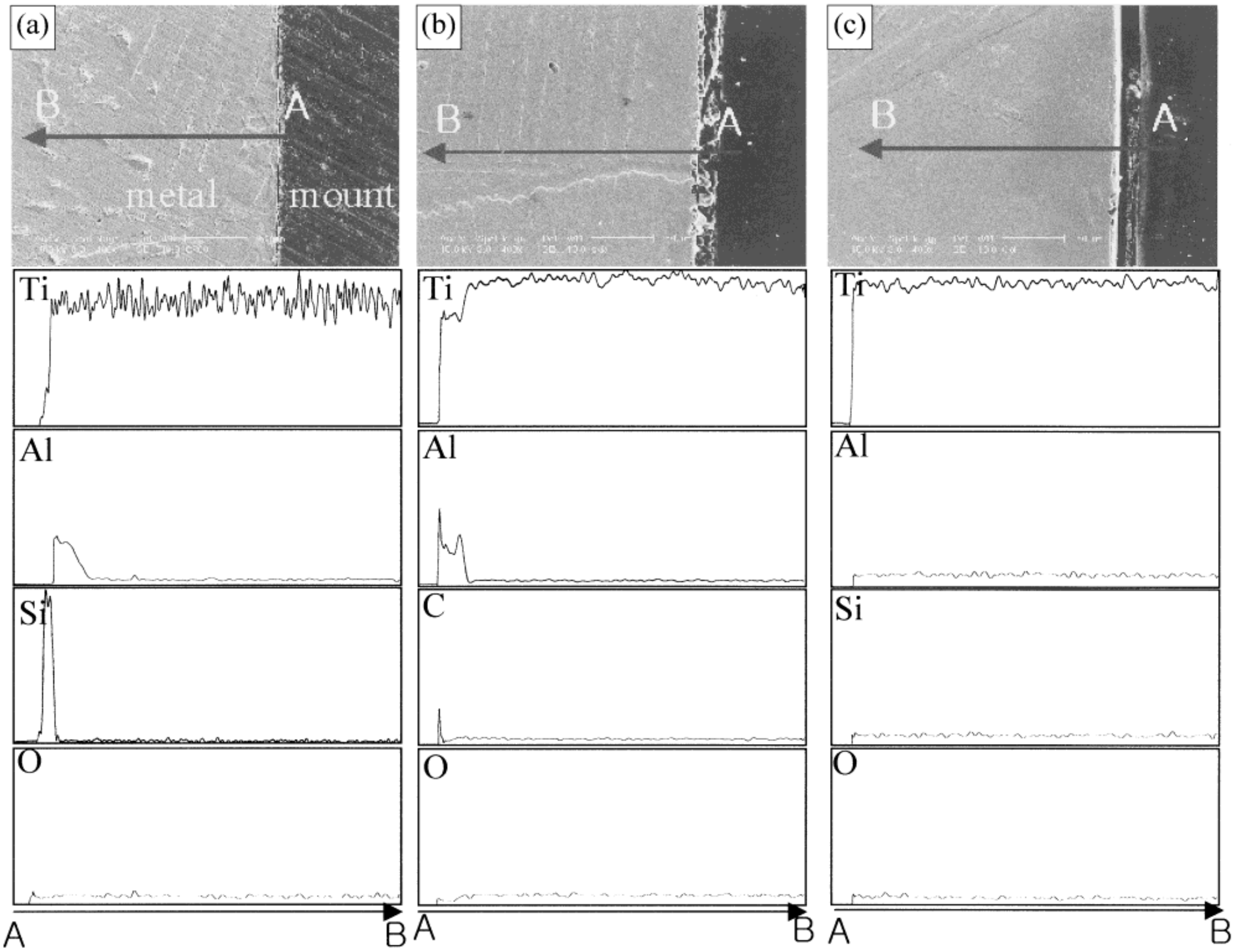

Fig. 7 Results of EDS line scanning of the regions below the surface of the castings with different binders; (a) colloidal silica, (b) acetic acid, and (c) aqueous solution.

other candidate binders as shown in Figs. 7(a) and (b). This is related to the silicon content in the binder, which caused a violent reaction between silicon and molten titanium.[19] In a similar study, Yoneda *et al.* concluded that the silicon content in the binder using a CaO mold influenced the effect of the binder on the metal-mold interaction.[9] The hardening effect observed at the surface of the casting may depend on the presence of oxygen and silicon in the reaction zone. When the values of oxygen and silicon contents increased, the hardness levels were correspondingly higher, as shown in Fig. 7.

By comparing the data of the Al_2O_3/colloidal silica interaction to that of the Al_2O_3/aqueous solution interaction from Figs. 6 and 7, it appears that the reduction of the reaction layer could be gained through the incorporation of a more thermodynamically stable binder. Therefore, it would be preferable if the use of silica, in free or combined form, either as a binder or as a mold constituent, could be minimized to decrease the tendency of metal-mold interface.

4. Conclusions

In order to develop and optimize the mold material for the investment casting of titanium alloys, from the practical and economic views, a metal-mold interfacial reaction was performed by using the plasma arc melting process. The conclusions are summarized as follows.

(1) The thermal stability of mold materials against molten titanium alloy is estimated by the thickness of the reaction layer and hardness profiles.

(2) A $CaZrO_3$ is regarded as a promising mold material for investment castings of titanium alloys because of high-temperature thermal stability, good handling strength and the easy control of the slurry.

(3) The metal-mold interfacial reaction of titanium castings is related not only to the thermodynamic stability of the mold material, but it is also quite dependent on the binder.

(4) It is necessary to take thermal stability, flexibility and handling strength into consideration when developing mold materials and binders for the investment casting of titanium.

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