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Characterization of the interaction between molten titanium alloy and Al_2O_3

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Pure titanium and Ti6Al4V alloys with single-crystal Al_2O_3 rod cores were prepared at 1740 °C and 1.2 atm Ar for 30 min. Aluminium diffusion takes place from Al_2O_3 into the titanium region for both Ti/Al_2O_3 and Ti6Al4V/Al_2O_3 interaction couples and results in the formation of an ordered α_2 phase (Ti3Al) in the titanium region adjacent to interfaces, even though there is no visible interaction product at interfaces.

1. Introduction

Titanium alloy is widely used in many areas because of its excellent mechanical properties. However, there is a major concern about clean metals in precision casting because titanium is extremely reactive with ceramic moulds or cores. Alumina (Al_2O_3) is a high-temperature refractory used as moulds or cores in the precision casting process.

The interaction between titanium alloy and Al_2O_3 is a fundamental study in many applications. Studies of the interaction for pure titanium and Ti6Al4V with Al_2O_3 were undertaken and the chemical reaction was addressed, based on the solid state [1, 2]. A visible interaction layer was produced at the interface and determined to be TiO and Ti3Al by X-ray diffraction and reflection electron diffraction techniques. Misra [3] also showed that the reaction products were TiAl and Ti3Al when the Ti/Al_2O_3 couples were hot-pressed at 1200° C for 1 h and then annealed at the same temperature for 100 h. Compared with the sample hot-pressed for 1 h, the alumina was massively consumed owing to the reaction of aluminium with titanium after 100 h diffusion annealing.

In developing semiconductor devices, interactions between the titanium film and the Al_2O_3 substrate have been observed using X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM) [4, 5]. It was found that the thin titanium film consisted of two layers with oxygen in solid solution; Ti3Al adjacent to the Al_2O_3 substrate and titanium at the free surface.

In the case of precision casting, the interaction between highly active titanium alloys and Al_2O_3 is still not well understood. Therefore, the interaction between molten titanium alloys and Al_2O_3 is a fundamental study. The purposes of the present work were to obtain details of the interaction of molten pure titanium and Ti6Al4V with single-crystal Al_2O_3 and to characterize the microstructure of the interaction.

2. Experimental procedure

High-purity titanium and Ti6Al4V powders and single-crystal Al_2O_3 rods were used in the present study. Interaction couples of pure Ti/Al_2O_3 and Ti6Al4V/Al_2O_3 were prepared at 1740 °C with high-purity argon at a pressure of 1.2 atm for 30 min.

Polished sections from the interaction couple were prepared for the microstructural characterization using scanning electron microscopy (SEM). Meanwhile, the energy dispersive X-ray (EDX) analysis was carried out to identify the compositional variation across the Ti–Al_2O_3 and Ti6Al4V–Al_2O_3 interfaces.

Thin cross-section samples of the molten Ti/Al_2O_3 and Ti6Al4V/Al_2O_3 reaction couples were prepared for transmission electron microscopy (TEM) using a dimpler and ion-beam thinner, and subsequently examined in a Jeol 4000FX at 400 kV equipped with energy dispersive analysis of X-rays (EDX) detector.

3. Results and discussion

The microstructural features of the interaction of the molten titanium and Ti6Al4V with single-crystal Al_2O_3 were identified using the SEM. Fig. 1 shows the overall microstructure for the molten Ti/Al_2O_3 and Ti6Al4V/Al_2O_3 reaction couples. Obviously, there are no visible interaction products at the interface between them. EDX analysis was also carried out on the samples in the SEM mode. Typical composition profiles across the Ti–Al_2O_3 and Ti6Al4V–Al_2O_3 interfaces are shown in Fig. 2, excluding oxygen. It can be seen from the composition profiles across the Ti–Al_2O_3 interface that massive aluminium diffuses into the titanium region adjacent to the interface, and titanium diffusion from the pure titanium to Al_2O_3 is negligible. The aluminium concentration is increased to approximately 14 at% in the region of titanium adjacent to the Ti–Al_2O_3 interface. It is very likely that the existence of the high aluminium concentration would lead to the formation of new compounds in the region of titanium adjacent to the interface. Analogously, a relatively high aluminium concentration is

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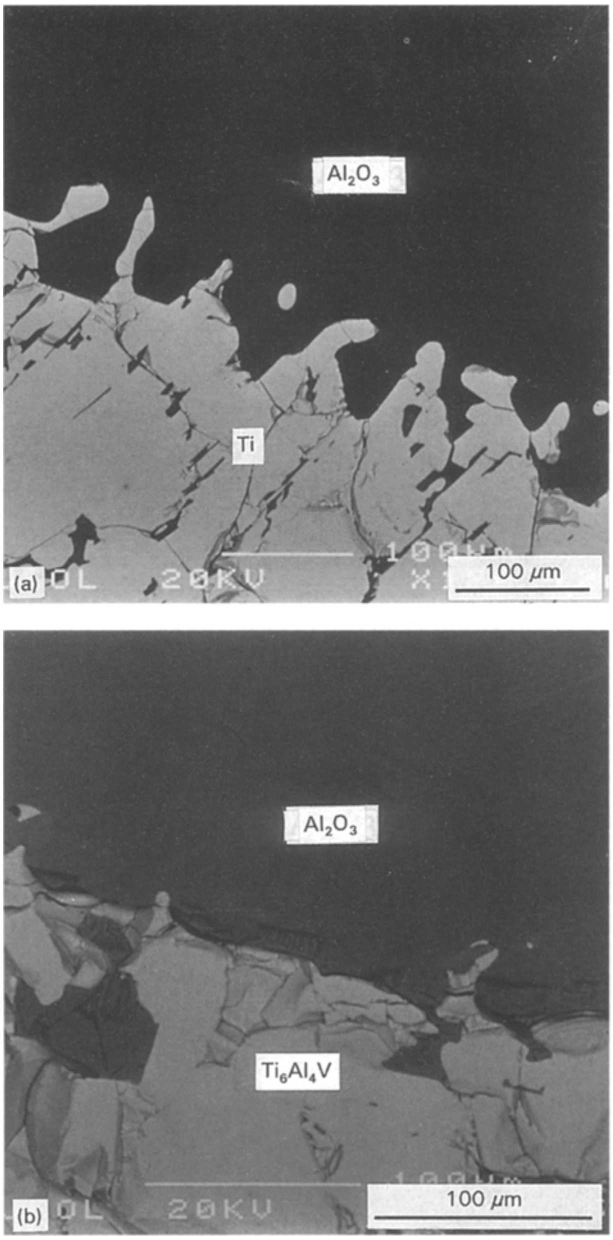

Figure 1 Backscattered electron micrographs showing the overall microstructure of titanium-based alloys with single-crystal Al_2O_3: (a) Ti/Al_2O_3 interaction couple, (b) $Ti6Al4V/Al_2O_3$ interaction couple.

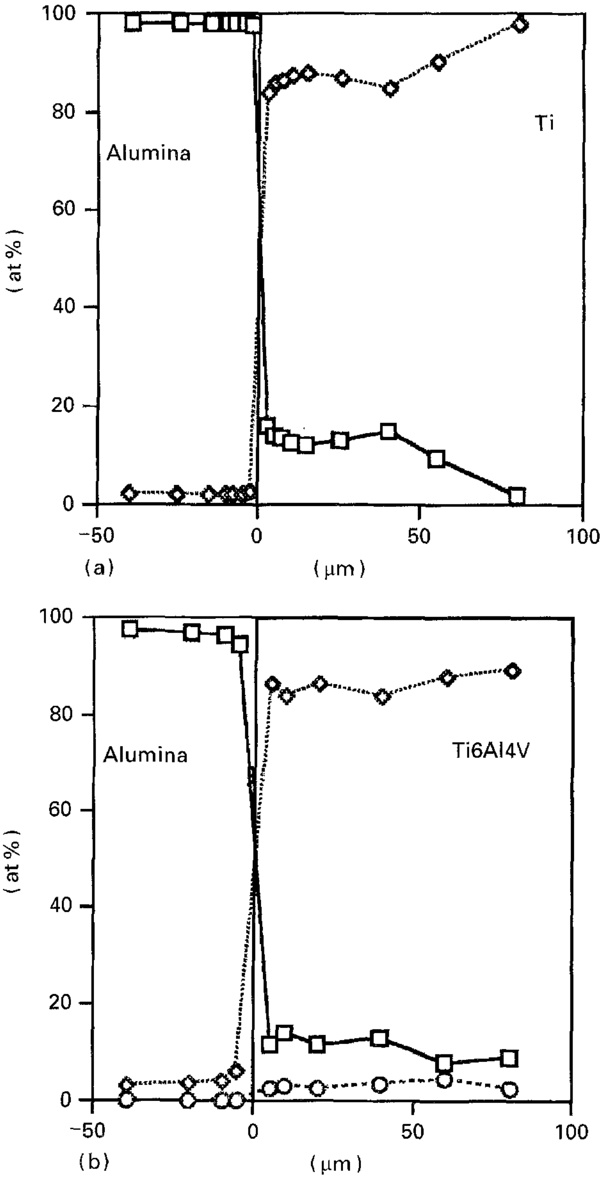

Figure 2 Composition profiles across interfaces obtained from Ti/Al_2O_3 and $Ti6Al4V/Al_2O_3$ interaction couples (excluding oxygen), (a) across the $Ti–Al_2O_3$ interface, (b) across the $Ti6Al4V–Al_2O_3$ interface. (–□–) Al, (---◇---) Ti, (--○--) V.

also found in the region of Ti6Al4V adjacent to the interface.

It is very significant to study the interaction between titanium-based alloys and Al_2O_3 using transmission electron microscopy. Typical transmission electron micrographs taken from the samples of molten pure titanium and Ti6Al4V with single-crystal Al_2O_3 are shown in Fig. 3a and b, respectively. Clearly, there is no visible new phase in either reaction couple. Fig. 4a and b are typical transmission electron micrographs taken from molten pure titanium and Ti6Al4V adjacent to the interfaces with inserted selected-area diffraction patterns. The selected-area diffraction pattern as shown in Fig. 4a is indexed as a disordered hexagonal α phase in the direction of $[0001]_\alpha$. Meanwhile, it is noted that there are added spots in the diffraction pattern. These added spots are indexed as the ordered hexagonal superlattice spots corresponding to the presence of an α_2-type phase [Ti3Al] in the direction of $[0001]_{\alpha_2}$. Correspondingly, the selected-area diffraction pattern in Fig. 4b is indexed as a disordered hexagonal α phase in the direction of $[01\bar{1}0]_\alpha$ with ordered hexagonal α_2 phase. Obviously, the aluminium diffusion from Al_2O_3 into titanium gives rise to the formation of Ti3Al. In terms of the phase diagram of the Ti–Al system as shown in Fig. 5, it is known that a titanium alloy containing 0–12 at% Al will be in the α-phase region and from 12–25 at% Al will be in a two-phase region ($\alpha + \alpha_2$). Generally, the Ti–Al alloy in the α-phase region is rather featureless and typical of a single-phase alloy [6]. In the case of the molten pure titanium with Al_2O_3, the aluminium diffusion takes place from Al_2O_3 into titanium and the aluminium content is approximately up to 14 at%. The relatively high aluminium concentration in the titanium region adjacent to the interface will lead to the transformation of a disordered α phase to ordered α_2; neverthe-

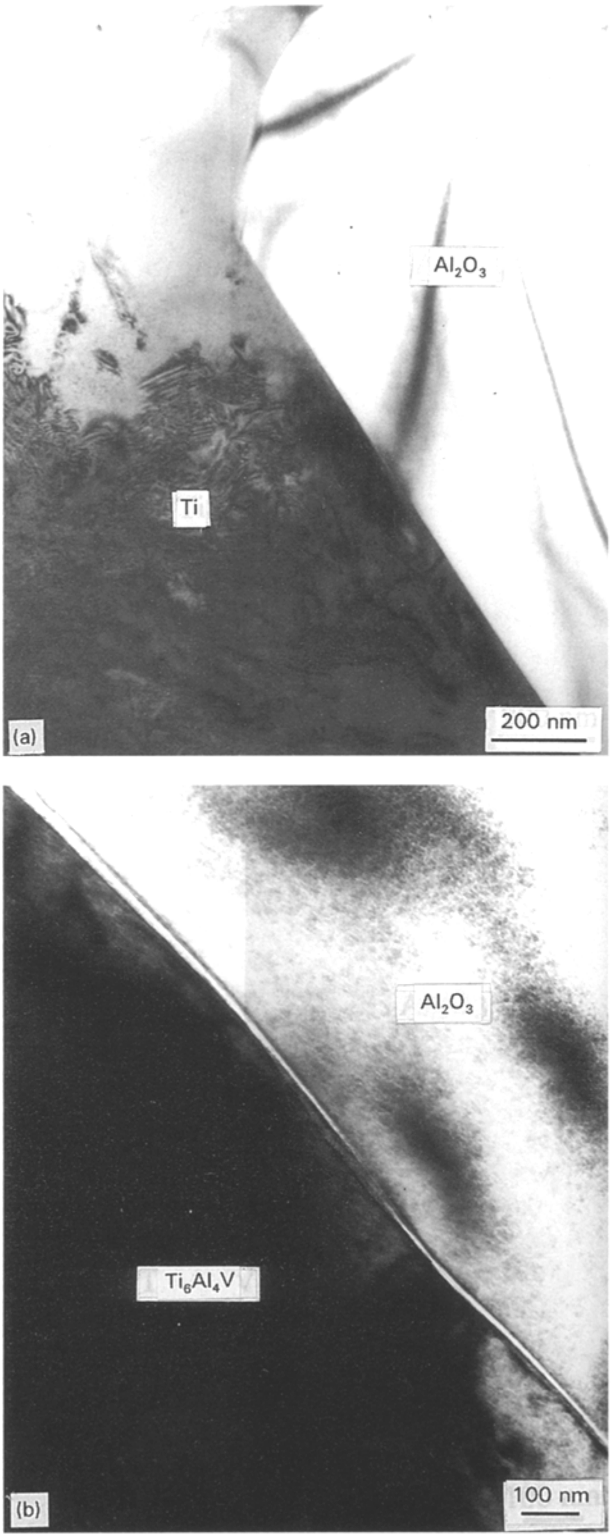

Figure 3 Typical transmission electron micrographs showing interfaces in the (a) Ti/Al_2O_3 interaction couple, (b) Ti6Al4V/Al_2O_3 interaction couple.

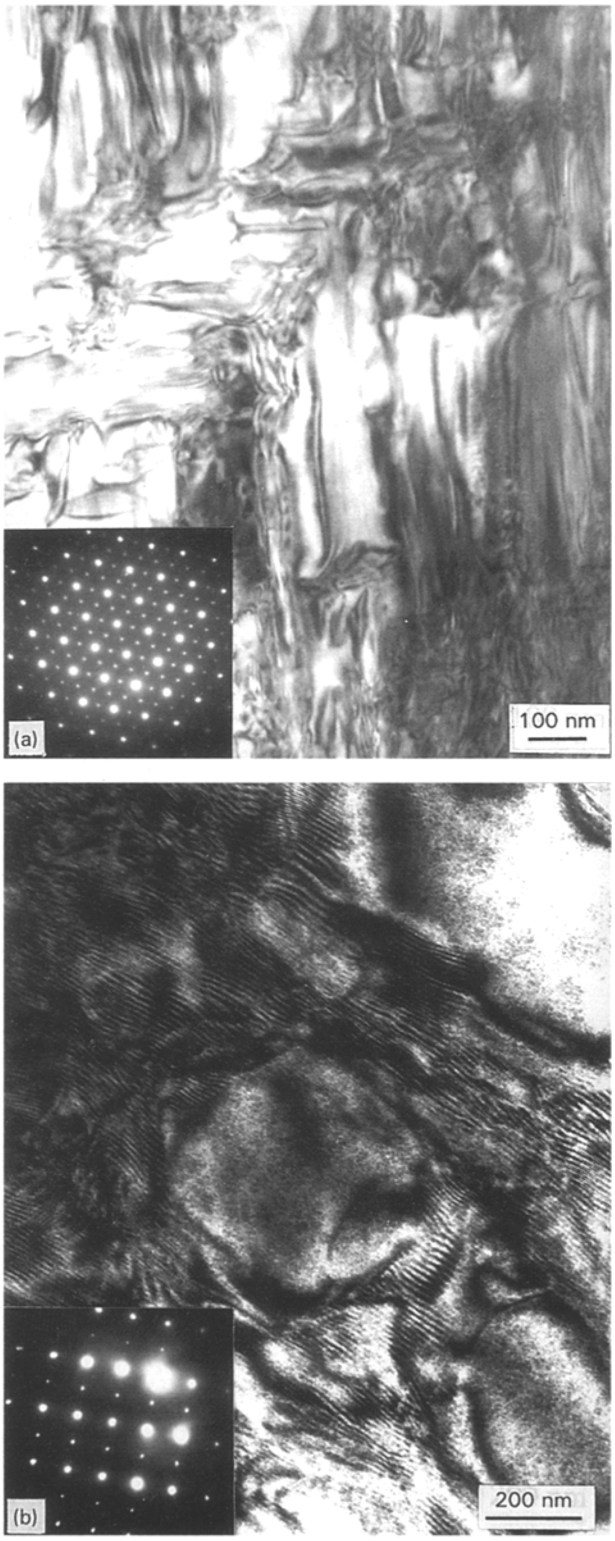

Figure 4 Transmission electron micrographs taken from the titanium region adjacent to the interface, inserted with corresponding selected-area diffraction patterns: (a) the pure titanium region, (b) the Ti6Al4V region.

less it failed to reveal the presence of an ordered α_2 (Ti3Al) region. Analogously, the Ti6Al4V–Al_2O_3 interaction couple appears as a similar feature as the Ti–Al_2O_3 interaction couple.

A possible mode of reaction for titanium and Ti6Al4V with Al_2O_3 would be dissolution of aluminium and atomic oxygen in titanium by the reaction

$$Al_2O_3 \rightarrow 2Al + 3O \qquad (1)$$

Consequently, the dissolution of aluminium in the titanium matrix would result in the precipitates of ordered Ti3Al by heterogeneous nucleation. The formation of Ti3Al for both reaction couples is controlled by aluminium diffusion. Obviously, the aluminium diffusion is a rate-controlling step; the considerable aluminium content in the Ti6Al4V could accelerate the reaction. Pure titanium can dissolve large amounts of oxygen. However, limited numbers of

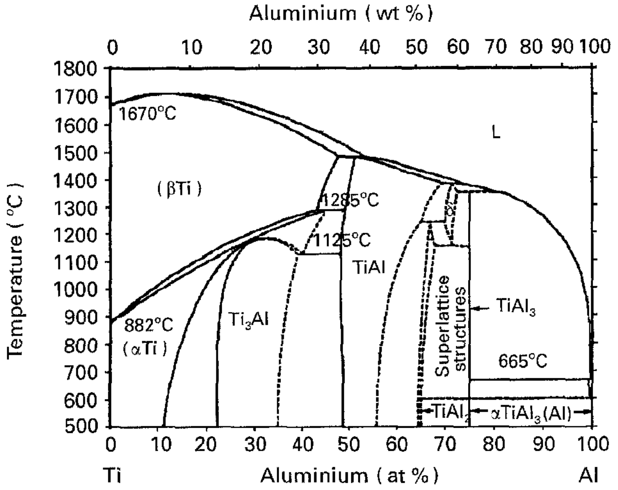

Figure 5 Phase diagram of the Ti–Al system.

Ti^0 and Ti^{2+} can substitute for aluminium in the Al_2O_3 lattice [4].

Initially, the fine particles of α_2 phase precipitates are produced in the titanium region adjacent to the interface by heterogeneous nucleation. The growth of the α_2 phase precipitates will occur due to further diffusion of aluminium into the titanium matrix and will gradually form visible particles. From the investigation of the thin titanium film on Al_2O_3 reported by others, it was found that there was an interaction layer of Ti3Al produced at the interface between titanium films and Al_2O_3 substrates when the sample was annealed below 1000 °C for a considerable time in vacuum [4]. Apparently, when both Ti/Al_2O_3 and $Ti6Al4V/Al_2O_3$ interaction couples were prepared at 1740 °C for 30 min, the aluminium diffusion from Al_2O_3 to the titanium or Ti6Al4V region takes place at the interfaces and results in the formation of ordered Ti3Al phases in the titanium region adjacent to the interfaces. Therefore, the precipitates of ordered Ti3Al would be formed at the initial stage and be so small that the precipitates could not be revealed by transmission electron microscopy.

4. Conclusion

The interaction between molten titanium alloys and Al_2O_3 prepared at 1740 °C and 1.2 atm Ar for 30 min has been determined. There is no visible interaction layer. However, the massive aluminium diffusion from Al_2O_3 to titanium takes place and results in the high aluminium concentration in the titanium region adjacent to the interface. Based on the TEM observations, it is found from the sample of the pure $Ti–Al_2O_3$ couple that the precipitation of Ti3Al occurs in the titanium region adjacent to the interface, due to the high aluminium concentration. Analogously, the $Ti6Al4V–Al_2O_3$ interaction couple reveals similar features to the $Ti–Al_2O_3$ interaction couple.

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