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A study of two refractories as mould materials for investment casting TiAl based alloys

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Interfacial reactions between Ti-46Al (at.%) casting and ceramic shell mould made of ZrO_2 and Al_2O_3 were studied using a range of techniques. On the surface of the TiAl casting, a reaction layer as thick as 230 μm was found in the case of the zirconia mould, whereas there was no visible reaction layer for the alumina mould. Electron probe microanalysis indicated that elements of the two kinds of shell moulds diffused into the alloy melt during casting but to different extents. Metallographic analysis, microhardness measurements and composition analysis showed that alumina was stable and suitable for use as shell moulds when casting TiAl based alloys. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Advanced gamma titanium aluminides are one of the most promising intermetallic alloys for high temperature applications owing to their low density, good oxidation and burn resistance, high modulus of elasticity, and high temperature strength retention [1–3]. It is widely recognized that investment casting is the best option for producing complex net or near net shape γ-TiAl components in view of the poor machinability and workability of these alloys [4]. However, the most serious barrier to the use of investment castings is the high reactivity of TiAl alloys in the molten state [5]. They are extremely reactive to refractory oxides during casting, resulting in a reaction layer or oxygen-enriched surface layer, which degrades the properties of the cast parts.

Alumina, as an excellent refractory oxide, has been widely used to make crucibles for melting superalloys, but not for titanium and its alloys because of the high reactivity of titanium melts. Although the high aluminium content of TiAl based alloys may help to lower their reactivity in the molten state [6], only a few investigations have been concerned with casting TiAl alloys using alumina crucibles or shell moulds.

Kuang et al. [7] showed that a TiAl alloy melted in an alumina crucible contained a few inclusions and there was evidence of cracks near the interaction region. The chemical reaction was considered to be a more serious problem. According to Wang et al. [8], there was a reaction layer as thick as 200 μm and a hardened zone about 500 μm thick on the surface of cast TiAl material when an alunima shell mould was used.

In Kuang's research mentioned above, the alumina crucible contained impurity SiO_2, and colloidal silica was used as a binder in Wang's experiment. Since SiO_2 is less stable than the oxides (TiO_2 and Al_2O_3) of the main alloying elements, the reaction between the TiAl and the crucible or shell mould was bound to occur. Kim et al. [9] suggested that the extent of the interfacial reaction between Al_2O_3 mould and titanium castings could be reduced significantly by the proper choice of binder. In this paper, a zirconia sol was used as a binder to make the shell mould with alumina powder. As a comparison, calcia stabilized zirconia shell moulds were also used to cast TiAl. The aim of this work was to study the interactions between alumina moulds and a TiAl alloy in the search for the most suitable refractory for manufacturing shell moulds for TiAl based alloys.

2. Experimental method and procedure

Zirconia sol as a binder was used to prepare ceramic shell moulds with calcia stabilized cubic ZrO_2 ($0.15CaO{\cdot}0.85ZrO_2$) and Al_2O_3 powders using an optimized procedure developed in the authors' laboratory. The ceramic slurries were prepared from refractory fillers and a liquid binder system. Pattern waxes were produced and an assembly was prepared according to the required casting specifications. The assembly was then dipped into the

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slurry, sprinkled with coarse refractory stucco, and dried. The dipping procedure was repeated 7–8 times until the required thickness of shell was built up. Vapour dewaxing method was used to remove the wax pattern. All hollow moulds were sintered at a temperature of 800°C for 2 h before they were placed into a cold hearth induction melting furnace. Centrifugal casting of Ti-46Al (at.%) was then done. The microstructure and alloy chemistry on the cross section and at different depths of the reaction layer were characterized by means of optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), electron probe microanalysis (EPMA) and microhardness measurement.

To identify unambiguously the reaction products at the interface of the mould and TiAl, a special experiment was designed as follows. A block of the TiAl based alloy was cut by electrical discharge machining from the bulk cast alloy and was placed on top of a ceramic plate inside a water-cooled copper crucible of an argon protected furnace. This method had been reported in detail elsewhere [10, 11]. The alloy block was melted by an electric arc using a tungsten electrode and kept molten for 5 min by holding the voltage on the electrode, to ensure sufficient reaction between the melt and the ceramic plate. Specimens taken from the TiAl-mould interface were analyzed using SEM/EDS method.

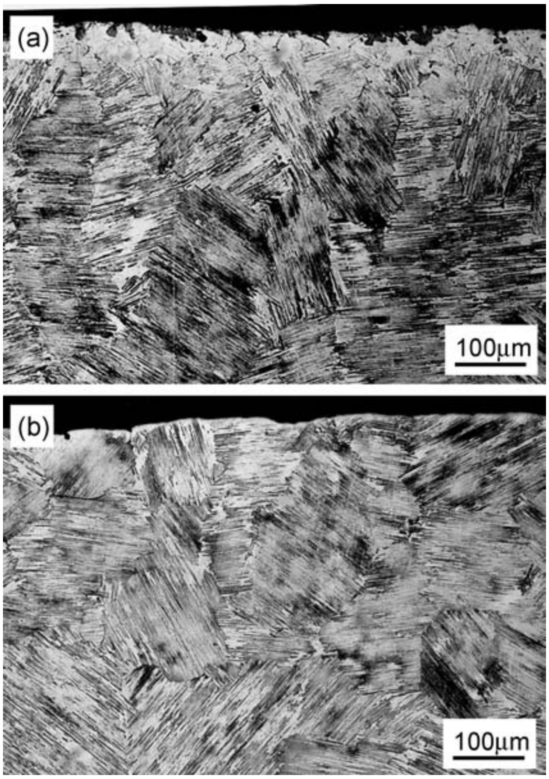

Figure 1 Comparison of optical microstructures of Ti-46Al cast into shell moulds made of (a) ZrO_2 and (b) Al_2O_3. The fully lamellar microstructure can be clearly seen and the mould/metal interface is at the top of the micrographs.

3. Results and discussion

3.1. Metallograph of casting surface

Fig. 1 illustrates the as-cast microstructure of the regions below the surfaces of TiAl investment castings made with different moulds. There appeared a quite clear reaction region between the TiAl casting and the ZrO_2 mould (Fig. 1a). Normally, the grain size of the lamellar TiAl microstructure decreases from the interior (about 200 μm) towards the surface. Some phases distributed mostly along the dendrite boundaries were found to be enriched in Zr using TEM/EDS analysis [10, 11].

It is of interest to note that the casting made with the Al_2O_3 mould consisted of a normal fully lamellar α_2/γ structure and had no visible interaction products. The extent of the fine grain size region on the surface of the casting was not as high as for the ZrO_2 mould, as shown in Fig. 1(b).

SEM examination of the above samples revealed the different depths of the Zr enrichment layer. As shown in Fig. 2(a). Zr clearly diffused into TiAl from both the binder and refractory, whereas the interface between TiAl and the alumina mould (Fig. 2b) was much smoother by comparson.

3.2. Microhardness analysis

Fig. 3 compares the microhardness profiles of casting made with different shell moulds. The surface hardened layer of the casting made with a zirconia mould was about 325 μm thick, in contrast with the alumina shell mould which caused only an increase in hardness less than 20% that for the zirconia mould in a thin surface layer less than 80 μm thick.

When the TiAl melt fills the ZrO_2 mould, the high temperature melt preferentially dissolves the constituents from the mould. The increase of hardness beneath the surface layer is a consequence of the inward diffusion of mould constituents as well as the refined microstructure. Fig. 4 shows the compositions of the reaction products and the concentration profiles of different elements across the reaction zone obtained by electron probe microanalysis. The results from the EPMA show that the contents of elemental Zr and O from the shell mould were relatively high at the surface of casting. The metallic constituents of the mould also significantly influence the surface hardening of the castings made with the ZrO_2 mould. Detailed analyses had been reported elsewhere [10, 11].

For the alumina mould, the microprobe analysis of the alloy casting showed no Al enrichment in the alloy near the surface; but rather a slight decrease. The oxygen concentration in the alloy was somewhat higher near the surface and then became almost constant throughout the alloy. Zr, from binder, was lower near the surface. The magnitude of the above change, however, was trivial compared to the elemental enrichment for the zirconia mould.

Fig. 5 shows the BSE images of the interaction region between the melt and shell mould of the

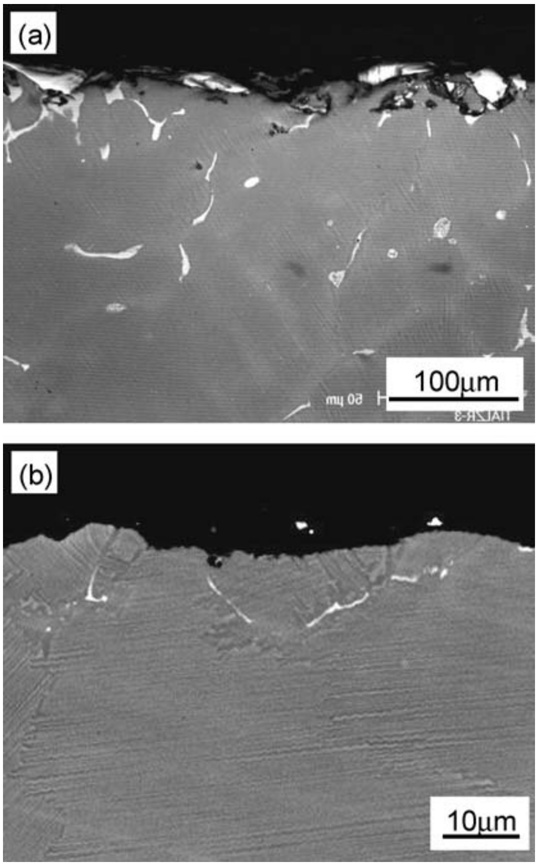

Figure 2 Backscattered electron image of longitudinal section of as-cast Ti-46Al showing its interface with different refractory materials: (a) ZrO_2; (b) Al_2O_3.

specially-prepared couple. The bright phases in both micrographs are rich in Zr as revealed by EDS analysis. The TiAl alloy melts tended to react more actively with the zirconia mould. This is demonstrated in the special reaction layer (Fig. 5(a)) that is extended to as much as several mm deep, though not shown here. The Zr was dissolved from the ZrO_2 refractory as well as the ZrO_2 sol binder for the zirconia mould, while the Zr that formed the bright phase particles in Fig. 5(b) for the alumina mould came from the zirconia binder. From Fig. 5(b), the reaction zone was about 100 μm thick and the Zr-rich phases were located along the dendrite boundaries. The reaction between the molten TiAl alloys and Al_2O_3 is expected to be further reduced if the binder is free of Zr.

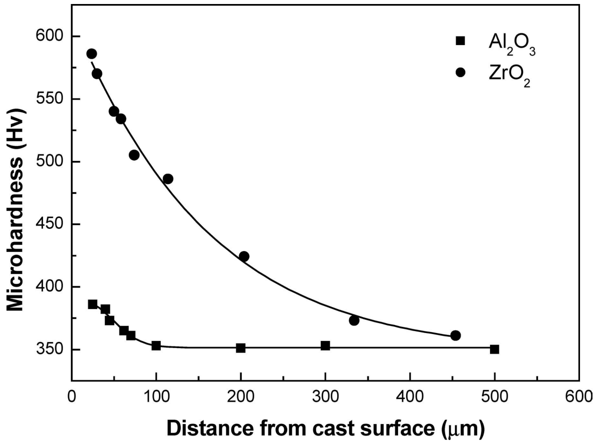

Figure 3 Hardness profiles of the hardened layer at the surface of Ti-46Al cast into different shell moulds.

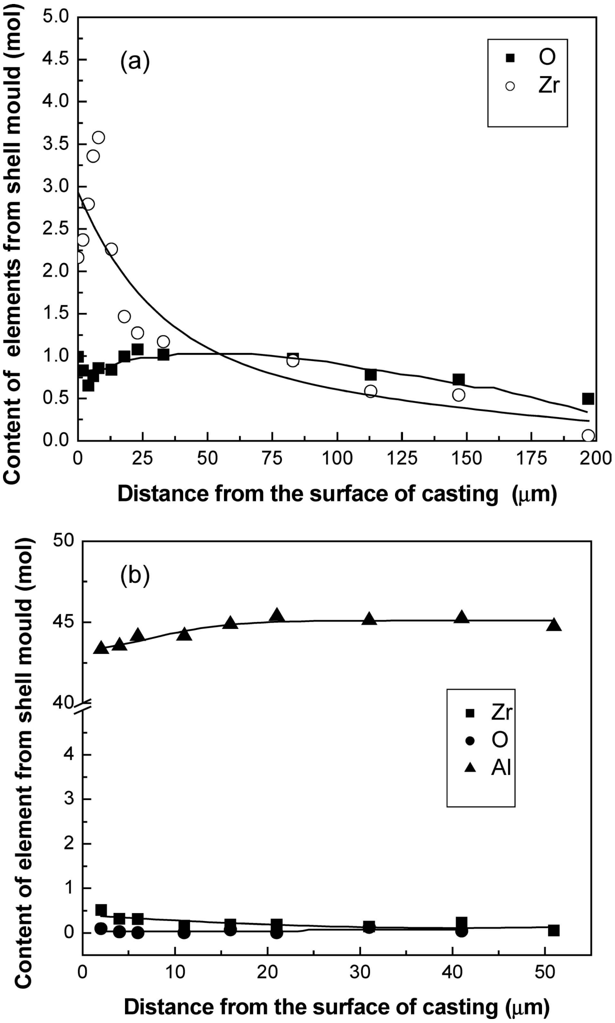

Figure 4 Depth profiles of elements from the casting surface obtained by EPMA quantitative microanalysis: (a) ZrO_2 mould; (b) Al_2O_3 mould.

3.3. Mechanism of reaction

The above results show that the interface reaction of TiAl with ZrO_2 shell mould is more severe than that with an Al_2O_3 mould. The concentration gradient of Zr at the interface of the ceramic shell mould and the alloy melt resulted in Zr diffusing into the melt. Zr segregates at the dendrite boundaries during solidification [11]. Al is liable to form compound with Zr according to theoretical results obtained with the Miedema model [12, 13]. The enthalpy of formation of compounds in the Al-Zr system is more negative than Al with other elements in the present alloy system [14].

One possible mode of reaction between Ti–Al alloys and Al_2O_3 would be dissolution of Al and atomic oxygen

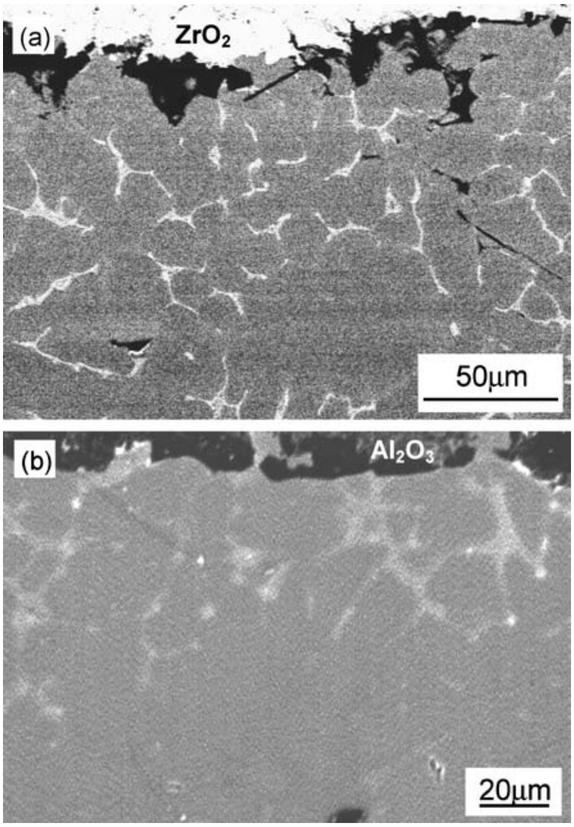

Figure 5 Backscattered electron image of the cross section of the specially-prepared reaction zone showing different depth for different shell moulds: (a) ZrO_2; (b) Al_2O_3.

in the alloy by the reaction [15]

$$\begin{aligned} Al_2O_3 = {} & 2\mathrm{Al}(\text{liquid, in Ti-Al alloy}) \\ & + 3\mathrm{O}(\text{mass pct, in Ti-Al alloy}) \qquad (1) \end{aligned}$$

for which the equilibrium constant is expressed as follows:

$$K = \frac{a_{\mathrm{Al}}{}^2 \cdot (f_{\mathrm{o}}[\mathrm{masspctO}])^3}{a_{\mathrm{Al_2O_3}}}$$

where a_i is the activity of component i relative to the pure substance, f_0 is the activity coefficient of oxygen in molten metal, and [mass pct O] is the oxygen content of molten metal in mass pct. Since solid Al_2O_3 is equilibrated with molten metals, $a_{\mathrm{Al_2O_3}}$ is unity. Because of the low oxygen contents in molten metals, the activity coefficient of oxygen is assumed to be unity. Therefore, the equilibrium constant of reaction (1) becomes

$$K = (a_{\mathrm{Al}})^2 \cdot [\text{mass pct O}]^3$$

Thus, if the activity product, $\{(a_{\mathrm{Al}})^2 \times [\text{mass pct O}]^3\}$, in the alloy is less than K, Al_2O_3 can be dissolved in the alloy by reaction (1). Of course, whether reaction (1) is feasible or not would depend on the solubility of oxygen in the TiAl based alloys. Pure molten Ti can dissolve large amounts of oxygen, so the concentration gradient of O is formed at the interface of alumina and Ti, which would accelerate reaction (1), resulting in the formation of TiO and Ti_3Al in solid solution [16, 17]. However, the presence of Al in TiAl results in a lower solubility for oxygen compared to pure Ti, Kobayashi and Tsukihashi [18] reported that the oxygen contents of molten Ti-54Al alloys equilibrated with solid Al_2O_3 at 1873 K were about 0.7 [mass pct O]. Although the oxygen content increases with decreasing aluminum contents of the alloy, the contact time during casting is very short because of the fast solidification. The EPMA results in this experiment showed that the oxygen content of a TiAl casting produced in Al_2O_3 mould was lower than that made in a ZrO_2 mould. So the reaction between the Al_2O_3 mould and molten TiAl would be decreased accordingly.

4. Conclusion

The results of microhardness profiling, metallographic observations and designed experiments to accelerate the interface reaction all showed that the ZrO_2 shell mould reacted severely with TiAl alloy, but that the reaction with the Al_2O_3 mould was relatively insignificant due to their thermodynamic properties and chemical compatibility. The Al_2O_3 mould can be a good candidate for investment casting of TiAl based alloys, but the binder, Zr sol, which is liable to react with TiAl melt needs to be improved.

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