Effect of Open Porosity of Y_2O_3 Ceramic on the Apparent Contact Angles and Interactions Between Ti47Al Alloys and Y_2O_3 Ceramic

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Abstract The effect of open porosity of Y_2O_3 ceramic on the apparent contact angle and interaction between molten Ti47Al alloy and Y_2O_3 ceramic substrates under pure Ar was investigated by using a sessile drop method at 1600 °C. As the open porosity increased from 9.6% to 30.3%, the spreading rate of molten Ti47Al alloys on Y_2O_3 ceramic substrates reduced from 2.3 to 1.1°/s; meanwhile, the final equilibrium contact angles increased from 55.8° to 63.6°. The microstructure observations revealed that with increasing the open porosity of the Y_2O_3 substrates, the thickness of sand adhesion at the interfaces of the alloy droplets increased from 5.4 to 15.7 μm, and ceramic particles in the alloy matrix increased as well. The increasing contact area between the molten alloy and the substrate played a dominant role in determining the interaction on TiAl/ Y_2O_3 interface.

KEY WORDS: Contact angle; Yttria; Titanium aluminides; Interaction; Open porosity

1 Introduction

Intermetallic TiAl-based alloys have been found with wide application prospects in the fields of aerospace and automotive due to low density, high-elastic modulus and specific strength [1–3]. Up to date, studies have proposed that directional solidification (DS) technique is effective to

obtain the best combination of microstructure and property of the TiAl alloys [4–6].

When DS of highly reactive TiAl alloys, ceramic materials, such as Al_2O_3 , ZrO_2 , CaO, and Y_2O_3 , have been used as mold materials [7–12]. Among these oxides, Y_2O_3 has been proved to be the most promising material because of its excellent thermal chemical stability [13]. As reported by Lapin et al., the ingots with oxygen content below the technically acceptable upper limit can be prepared when DS of a TiAlNb alloy in a dense Y_2O_3 mold with 0.7 vol% open porosity. Unfortunately, a Y_2O_3 layer with thickness of 30 μm on the surface and a few Y_2O_3 particles in alloy matrix still existed [14]. Zhang et al. [15] showed that when DS of TiAl alloy using Y_2O_3 -coated Al_2O_3 molds containing 30% open porosity, the overall oxygen increment was as low as 0.04 wt%.

Based on the practical application of Y_2O_3 and considering that Y_2O_3 is inherently not thermal shock resistant, a porous Y_2O_3 structure should be preferred [10, 15]. Recently, an improved type porous mold prepared by Tetsui et al. had a better performance compared with the dense one in terms of thermal shock resistance and erosion

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resistance. However, the results showed that interactions between molten TiAl alloys and Y_2O_3 ceramic could not be avoided completely [16].

Poor wettability between the ceramic molds and the molten alloys will be advantage of decreasing the degree of corrosion and erosion of the refractory [17]. However, it may diminish the liquid mobility and thus decrease the mold-fill capability of the alloy melt [18]. Conversely, good wettability guaranteed the mold-fill capability but contributed to the infiltration of the alloy melt through the capillaries on the ceramic mold surface and the occurrence of some reactions, thus leading to contamination and defect of the castings [19, 20]. Therefore, proper wettability between the Y_2O_3 ceramic mold with proper structure and the TiAl alloys is critical to produce high-quality TiAl castings.

Unfortunately, although some efforts began to be made toward structure optimization of Y_2O_3 mold for decreasing the TiAl/ Y_2O_3 interactions, the investigations on the influence of the open porosity of ceramic on the wetting behavior, especially the contact angle and interaction between TiAl alloys and Y_2O_3 ceramic, were very limited. In particular, the determination of wetting behavior for molten TiAl alloys on Y_2O_3 ceramic at high temperature was insufficient. Investigations on the relation between the open porosity of Y_2O_3 ceramic, apparent contact angle and interfacial interaction will not only form a basis for the designing and optimizing structure of Y_2O_3 mold but also control and minimize the degree of interactions between the TiAl alloy melt with high reactivity and Y_2O_3 mold.

Therefore, in this work, the effect of open porosity of Y_2O_3 ceramic on the apparent contact angle and interaction between molten Ti47Al alloys and Y_2O_3 substrates under pure Ar atmosphere was investigated by using a sessile drop method at 1600 °C. The impact mechanisms were also analyzed.

2 Experimental

The master alloy with nominal compositions of Ti–47Al (wt%) was prepared with a vacuum non-consumable arc-melting furnace using commercial Ti sponge (99.76%) and high-purity Al ingot (99.99%) as raw materials. The master alloy was cut into 3 mm × 3 mm × 3 mm cubic samples. Then, the alloy samples were polished to remove the oxide. Y_2O_3 ceramic substrates with different open porosities were fabricated by dry pressing method. The open porosity for Y_2O_3 substrates is listed in Table 1. Before the wetting experiments, both the Y_2O_3 substrates and the TiAl samples were ultrasonically cleaned in acetone.

The wetting experiments were carried out in a sessile drop apparatus. Schematic illustration of the apparatus is

Table 1 Open porosity of Y_2O_3 ceramic substrates

Specimens	Y_2O_3 -A	Y_2O_3 -B	Y_2O_3 -C
Open porosity (%)	9.6	13.8	30.3

shown in Fig. 1. The ceramic substrate was placed in the middle of the furnace and adjusted to a horizontal position. The cubic alloy samples were stored in the Al_2O_3 tube. After that, the chamber was firstly evacuated to about 9.9×10^{-4} Pa, then heated to 1200 °C at a rate of 20 °C/min, and then filled with 1.1–1.2 atm Ar (99.999%) in order to prevent the elements in the alloy from evaporation. Thereafter, the chamber was heated at a rate of 10 °C/min. When the temperature reached 1600 °C, the alloy cubic dropped from the Al_2O_3 tube onto the Y_2O_3 ceramic substrate and optical images were obtained by using a digital camera. When the alloy completely melted, the moment was defined as the zero time, at which the molten alloy started to spread. After 20-min isothermal holding at 1600 °C, the furnace was cooled down to room temperature.

The contact angle was analyzed by using a professional drop shape analysis program. After cold embedding in resin, the alloy droplets and substrates were cut perpendicular to the interface and then polished. Microstructure was observed by scanning electron microscopy (SEM, APOLLO 300, UK). Elemental compositions were analyzed by energy-dispersive spectrometer (EDS, Oxford INCA PentaFET-x3). The thickness of the interfacial interaction layer was determined by averaging the measured values from >10 different locations. The volume fraction of the ceramic particles in the alloy matrix was measured by Image J software.

3 Results

3.1 Microstructure of Y_2O_3 Ceramic

Figure 2 shows the microstructure of Y_2O_3 ceramic substrates. Closed pores formed inside the Y_2O_3 -A substrate with 9.6% open porosity, and the size range of the pores was 7–28 μm, as shown in Fig. 2a, b.

When the open porosity of the ceramic substrate increased up to 13.8% (Y_2O_3 -B), the size of the closed pores increased and the range was 7–55 μm. Moreover, open porosity appeared at the same time (Fig. 2c, d). For the Y_2O_3 -C substrate with 30.3% open porosity as shown in Fig. 2e, f, the ceramic particles arranged loosely and there were large number of open porosities between the ceramic particles. Moreover, according to the cross-sectional images, smooth substrate surface (Fig. 2b) became

Fig. 1 Schematic illustration of the sessile drop apparatus

Fig. 2 SEM images of Y_2O_3 substrates: **a**, **c**, **e** surface images of Y_2O_3 -A, Y_2O_3 -B and Y_2O_3 -C substrates, respectively; **b**, **d**, **f** cross-sectional images of Y_2O_3 -A, Y_2O_3 -B and Y_2O_3 -C substrates

Fig. 3 Images of sessile droplets of molten Ti47Al samples on Y_2O_3 substrates with different open porosities at 1600 °C

uneven when open porosity of substrates increased (Fig. 2d, f).

3.2 Apparent Contact Angle

Figure 3 displays the images of the sessile drops of alloy melts on the Y_2O_3 substrates with three kinds of open porosities. It can be seen that droplets with axisymmetric shape were formed on all substrates. The spreading time when the alloy melts spread completely was approximately 22, 37, and 40 s, respectively, for the A, B, C substrates.

The evolution of the contact angle vs the time for the three substrates is represented in Fig. 4. It can be clearly observed that the contact angle curves exhibited two different characteristic regions with time. In the first region, the contact angle decreased rapidly with increasing time. The average spreading rates were 2.3, 1.5, and 1.1°/s, respectively, for the molten alloy on A, B, and C substrates. The results indicated that with the increase in the open porosity of the Y_2O_3 substrates, the spreading rate slowed down. The other region was constant where the value of the contact angle θ was nearly stable. The final equilibrium

Fig. 4 Variation in contact angle of molten TiAl alloy with time on Y_2O_3 substrates with different open porosities

contact angles on Y_2O_3 -A, Y_2O_3 -B, and Y_2O_3 -C substrates were 55.8°, 58.1°, and 63.6°, respectively. Obviously, the equilibrium contact angles increased with increasing open porosity of the substrates as shown in Fig. 5.

Fig. 5 Equilibrium contact angles of molten Ti47Al droplets on Y_2O_3 substrates with different open porosities

3.3 Interaction

Micrographic observations on the cross section perpendicular to the interface of the alloy droplets are presented in Fig. 6. It demonstrated that there were sand adhesion layers for all samples. With increasing the open porosity of the substrates, the sand adhesion transformed from discontinuous (Fig. 6a) to continuous (Fig. 6b, c). Moreover, the dense sand adhesion layer (Fig. 6a, b) became loose (Fig. 6c).

As shown in Fig. 7, the thickness of the sand adhesion was 5.4, 8.1, and 15.7 μm for the Y_2O_3 substrates with open porosity of 9.6%, 13.8%, and 30.3%, respectively.

The EDS analysis of cross section at the metal–ceramic interfaces for Y_2O_3 -A, Y_2O_3 -B and Y_2O_3 -C systems is illustrated in Fig. 8. As shown in Fig. 8, no new phases were detected at the interface. Furthermore, it was indicated that when Y_2O_3 contacted TiAl alloys at high temperature, the different apparent contact angles of the molten Ti47Al alloys on Y_2O_3 ceramic substrates caused by the change in the open porosity of the substrates had no

Fig. 7 Thickness of sand adhesion of the TiAl droplets resting on different open porosities Y_2O_3 substrates

significant influence on the high thermodynamic stability of Y_2O_3 .

Figure 9 demonstrates the microstructure images of the matrix of the alloy droplets. White Y_2O_3 particles present in all the three alloy droplets. Figure 10 illustrates the volume fraction of Y_2O_3 particles in the alloy matrix for the three systems. The statistical results obtained by using the Image J software indicated that the content of ceramic inclusions increased with increasing the open porosity of the substrates. The volume fraction of the Y_2O_3 particles in the alloy droplets matrix was 0.091, 0.137, and 0.253 for the alloy droplets on the substrates with open porosity of 9.6%, 13.8%, and 30.3%, respectively.

4 Discussion

With the increase in the open porosity of the Y_2O_3 substrates, the equilibrium contact angle increased; meanwhile, the spreading rate of molten Ti47Al alloy on Y_2O_3 ceramic substrate decreased. Dissolution of the substrate into the alloy melt could significantly promote the

Fig. 6 SEM micrographs of the cross section perpendicular to the interface of the alloy droplets: **a** Ti47Al/ Y_2O_3 -A system; **b** Ti47Al/ Y_2O_3 -B system; **c** Ti47Al/ Y_2O_3 -C system

Fig. 8 Map analysis of Ti, Al, Y, and O elements of the interface of the solidified alloy droplets: **a** Ti47Al/Y₂O₃-A system; **b** Ti47Al/Y₂O₃-B system; **c** Ti47Al/Y₂O₃-C system

Fig. 9 Backscattered electron images of the matrix of alloy droplets for **a** Ti47Al/Y₂O₃-A system; **b** Ti47Al/Y₂O₃-B system; **c** Ti47Al/Y₂O₃-C system

Fig. 10 Volume fraction of Y₂O₃ particles in alloy droplets on Y₂O₃ substrates with different open porosities

spreading of the molten alloy on the substrate. The effect of open porosity of Y₂O₃ substrate on contact angle may be explained through the influence of substrate roughness and open porosity. Figure 11 demonstrates the schematic diagram of molten Ti47Al alloys resting on Y₂O₃-A, Y₂O₃-B,

Y₂O₃-C substrates. Roughness of the substrates, Ra, measured by a contact roughness tester indicated that Ra increased from 1.02 to 4.12 μm when the open porosity of Y₂O₃ substrates increased from 9.6% to 30.3%, as shown in Fig. 12. Consequently, the spreading of the liquid was impeded due to the pinning to the triple line by ceramic edges and thus increased the equilibrium contact angle [21]. Moreover, the resistance arriving from the surface of substrates enlarged with increasing the open porosity, which can be confirmed by the decrease in spreading rate of the molten alloy as mentioned above.

Furthermore, as illustrated by the 3D morphology of the surface in Fig. 13, the surface of the substrates was porous, so inevitably the molten TiAl alloy connected with the vapor entrapped in the open pores of the substrates when spreading. Consequently, composite surface formed at the liquid/solid interface as shown in Fig. 11, and the equation proposed by Cassie and Baxter [22] may be effective to explain the variation of the apparent contact angle of the droplets. The apparent contact angle was assumed to meet the following formula [23]:

$$\cos \theta_D = f_1 \cos \theta - f_2 \quad (1)$$

Fig. 11 Schematic configurations of sessile drops resting on the substrates with different open porosities

Fig. 12 Surface roughness and contact angle versus open porosity of Y_2O_3 substrates

Fig. 13 Typical 3D surface morphology of the porous ceramic substrate

where θ_D is the apparent contact angle, θ is the intrinsic contact angle, and f_1 and f_2 are the solid–liquid contact area and vapor–liquid contact area per superficial area of the

interface, respectively. Thus, the high ratio of f_2 to $f_1(F)$ caused by the open porosity of the substrates resulted in a relatively larger apparent contact angle.

Furthermore, with increasing the open porosity, vapor entrapped in the surface increased, which will increase the vapor–liquid contact area f_2 , and then the value of F may increase as well. Thus, it may be reasonable that contact angle of molten TiAl increased when increasing the open porosity of the Y_2O_3 ceramic.

Moreover, the main mechanism of the interaction between TiAl alloys and Y_2O_3 ceramic was the dissolution of the substrates to the alloys. With increasing the open porosity of the Y_2O_3 substrates, the open porosity which provided path for the alloy melt to penetrate into the substrate increased. Additionally, owing to the wetting tendency of the alloy melt and capillary force imposed on the alloy melt, penetration of the molten alloys into the substrates occurred. Therefore, the increasing open porosity and complex surface morphology eventually increased the contact area between the liquid alloy and ceramic substrate. As shown in Fig. 11, the permeation alloy melt (marked in red) increased due to the increase in open porosity. The increasing contact area further promoted the dissolution rate of the substrates to alloy melts and increased the dissolution of ceramic into alloy matrix, as illustrated in Fig. 10. Chaney and Varker have drawn the similar conclusion that the high surface-to-volume ratio of porous material (e.g., silicon carbide and silicon nitride) promoted the dissolution of the solid to the liquid (molten silicon) [24]. With increasing the open porosity of the Y_2O_3 substrates, the bond strength between ceramic particles weakened and the increase in dissolution of the substrates accelerated the intergranular corrosion of the ceramic particles.

Moreover, the increasing contact area between alloy melt and ceramic particles further enhanced the bond strength of the molten alloy to the ceramic particles due to the increase in metal–oxide chemical bonds and metal–oxygen chemical bonds [25]. Consequently, the sand adhesion at the interface of alloy droplet increased as shown in Fig. 6.

5 Conclusions

1. As the open porosity increased from 9.6% to 30.3%, the spreading rate of molten Ti47Al alloys on Y₂O₃ ceramic substrates slowed down from 2.3 to 1.1°/s and the final equilibrium contact angles increased from 55.8° to 63.6°.
2. The increasing contact area between the molten alloy and the substrate played a dominant role in determining the interaction on TiAl/Y₂O₃ surface. With increasing the open porosity of the Y₂O₃ substrates, the thickness of sand adhesion at the alloy–ceramic interfaces increased from 5.4 to 15.7 μm, and the precipitated ceramic particles in the alloy matrix increased as well.
3. Although the variation in the open porosity of the Y₂O₃ substrates caused difference contact angle of Ti47Al melts on the Y₂O₃ substrates, the Y₂O₃ ceramic substrates showed a good thermodynamic stability.

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