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Interactions between  $\gamma$ -TiAl melt and Y<sub>2</sub>O<sub>3</sub> ceramic material during directional solidification process

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Abstract: A  $\gamma$ -TiAl alloy with nominal composition of Ti-47%Al (molar fraction) was directionally solidified in an alumina mould with an Y<sub>2</sub>O<sub>3</sub> protective coating. The effects of processing parameters (melting temperature and interaction time) on the metal-coating interface, microstructure and chemical composition of the alloy were evaluated. The result shows that the Y<sub>2</sub>O<sub>3</sub> protective coating exhibits an effective barrier capability to avoid direct contact between the mould base material and the TiAl melt, although the Y<sub>2</sub>O<sub>3</sub> coating is found to suffer some erosion and be slightly dissolved by the molten TiAl due to the coating-metal interactions. The directionally solidified alloys were contaminated with Y and O, and Y<sub>2</sub>O<sub>3</sub> inclusions were dispersed in the metal matrix. The reason for this metal contamination is the Y<sub>2</sub>O<sub>3</sub> coating dissolution by the TiAl melt. One mode of the interaction between Y<sub>2</sub>O<sub>3</sub> and the TiAl melt is dissolution of yttrium and atomic oxygen in the melt by reaction Y<sub>2</sub>O<sub>3</sub>(s)==2Y (in TiAl melt)+3O (in TiAl melt). Both the extent of alloy contamination and the volume fractions of Y<sub>2</sub>O<sub>3</sub> inclusions depend on the melting temperature and the interaction time.

Key words: TiAl alloys; Y<sub>2</sub>O<sub>3</sub> protective coatings; interactions; directional solidification

## **1** Introduction

TiAl alloys exhibit a large number of outstanding properties, such as high melting point, low density, intrinsic strength retention, high stiffness and creep resistance at elevated temperatures [1–2]. Particularly, it is demonstrated that TiAl alloys with an aligned lamellar microstructure along the growth direction have a good combination of strength and ductility over a wide temperature range [3–4]. However, it is difficult to control the lamellar orientation by simple casting operations. In order to overcome this difficulty, directional solidification has been developed to produce columnar grain material with the lamellar orientation parallel to the growth direction [4–6].

Recently, several refractory materials have been used as mould in directional solidification to produce TiAl alloys [6–7]. Until now, no refractory material is found to be absolutely inert against TiAl melts and some interactions between the refractory crucible/mould and the molten metal always occurs during melting and casting, leading to metal contamination with impurity elements or inclusions from the refractory material [8–12]. When this happens, the microstructure and mechanical properties of directionally solidified (DS) ingots are affected by these elements or inclusions. Taking the Gibbs free energy of formation into account,  $Y_2O_3$  presents the most negative value among common metallic oxides, suggesting that it may have a good stability in contact with molten TiAl alloys [13]. However,  $Y_2O_3$  suffers from two drawbacks, inherently poor thermal shock resistance and high cost. Thus, common oxide crucibles/moulds coated by an  $Y_2O_3$  protective coating seem to be the most effective, stable and less expensive solution [14]. Therefore, it is instructive to directionally solidify TiAl alloys in oxide moulds with an  $Y_2O_3$  coating and to investigate the protection effectiveness of the coating.

In this work, low cost and good thermal shock resistance alumina moulds with an inner coating of  $Y_2O_3$  were used in directional solidification to produce TiAl alloys. The effects of processing parameters (melting temperature and interaction time) on the metal-coating interface, microstructure and chemical composition of the alloy were evaluated. The purpose of this study is to investigate the mechanisms of metal-coating interactions and to discuss the protection

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effectiveness of the Y<sub>2</sub>O<sub>3</sub> coating.

# **2** Experimental

## 2.1 Raw materials

y-TiAl alloys with nominal composition of Ti-47%Al (molar fraction) were produced starting from pure elements: titanium sponge (99.76%) and high purity (99.99%) Al ingot. Special care was taken to clean the raw materials, using acetone solution in an ultrasonic bath. After cleaning, they were dried at 150 °C for 120 min. The master alloy was prepared as a button weighing 1 000 g by arc melting under a high purity argon atmosphere using a non-consumable tungsten electrode. The button was melted and turned five times to promote homogeneity (containing an initial oxygen content of 0.06%, measured by the inert gas infrared-thermal conductivity technique). In order to prepare samples that would fit into the moulds, the arc-melted button was cut into master alloy bars with diameter of about 14 mm using electrical discharge machining (EDM). Before the melting experiments, these bars were ground on a lathe, cleaned and dried using the same procedure as described for the raw materials. In this work, the coatings were made from an Y<sub>2</sub>O<sub>3</sub> slurry without alkali metal binders/additives. The slurry consisted of pure  $Y_2O_3$  powder (99.9%), ammonium polyacrylate, polyvinyl alcohol and deionized water. The alumina moulds with an Y2O3 coating were sintered at 1650 °C for 100 h in a resistance heating furnace after dried at 25 °C for 48 h and then at 120 °C for 24 h. The temperature of the furnace was raised slowly at a rate of 1 K/min in order to burn out the additives in the slurry slowly and completely.

## 2.2 Directional solidification operation

The directional solidification was performed using a laboratory-scale Bridgman furnace (LMC, liquid metal cooling technology) equipped with an Y<sub>2</sub>O<sub>3</sub> coated alumina mould (outer diameter of 20 mm, inner diameter of 15 mm, length of (200±20) mm and wall thickness of 15 mm), as shown in Fig. 1. Before each experiment, the furnace chamber was evacuated down to  $6 \times 10^{-3}$  Pa and then backfilled with high purity argon up to 0.05 MPa, in order to reduce the oxygen content to a minimum level and avoid the evaporation of alloy components. After about 40 min since the start of the heating cycle, the temperature reached 1 400 °C, which was measured and controlled by thermocouple A (WRe5-WRe26) shown in Fig. 1. Afterwards, the heating rate was increased in order to reach the desired temperature as fast as possible, and then the melt inside the mould was stabilized at this temperature for different holding time in the furnace and allowed to directionally solidify at a withdrawal rate of 10 mm/min until the entire mould was fallen into the Ga–In–Sn alloy solution. Finally, the mould containing the DS ingot was removed from the furnace at about 50 °C. The selected melting temperatures (*T*) were 1 600 and 1 700 °C, at each temperature, the selected holding times were 1, 10 and 100 min, respectively. Thus, assuming the selected growth rate and the holding time at selected temperature, the interaction time (*t*) between the mould and the melt was calculated to vary from 60 to  $7.2 \times 10^3$  s.



Fig. 1 Schematic diagram of laboratory-scale Bridgman directional solidification furnace equipped with  $Y_2O_3$  coated mould

#### 2.3 Interaction analysis

After directional solidification, the ingots were mechanically separated from the moulds. Electron probe microanalysis (EPMA, JEOL JXA-8100, using backscattered scanning electron microanalysis mode BSE) and transmission electron microscopy (TEM, JEOL JEM-2100F) were used to evaluate the microstructure of the samples. Energy dispersive spectrometry (EDS, Oxford INCAPentaFET-x3) was used to analyze the chemical composition of the samples. Phase identification of the compounds present on the samples surface was performed by X-ray diffraction (XRD, D/max 2200PC) with Cu K<sub> $\alpha$ </sub> radiation. The total Y and O contents of the samples were measured by the inert gas infrared-thermal conductivity technique (IGI, LECO inductively coupled plasma-atomic TC-436) and emission spectrometry technique (ICP-AES, P. E. Plasma 2000), respectively. For each ingot, 2 cylindrical bars parallel to the longitudinal axis of the ingot were taken 4 mm from its surface. After being ground to a final mesh size of 120, cleaned and dried using the same procedure as described for the raw materials, these bars were used for chemical analysis. The volume fractions of inclusions ( $V_{\rm f}$ ) were measured on polished samples by computerized image analysis of at least 15 BSE images for every sample.

# **3 Results**

## 3.1 Metal-coating interface

Figure 2(a) shows the microstructure of the metal-coating interface of a sample. It can be seen that there is a thin layer of oxide on the sample surface, which is suggested to be yttrium oxide by EDS analysis. Further XRD analysis of the sample surface shown in Fig. 2(b) confirms that the layer is  $Y_2O_3$ . No new phase at the TiAl/Y<sub>2</sub>O<sub>3</sub> interfaces is detected. For every sample, the microstructural observations show that the thickness of the  $Y_2O_3$  layers is 2–10  $\mu$ m and seems to be not affected by processing parameters, as these layers are simply the coating material which adheres to the solidified samples and can be easily removed. These findings indicate that the Y<sub>2</sub>O<sub>3</sub> coating has a good stability in contact with the TiAl melts and exhibits an effective barrier capability to avoid direct contact between the mould base material and the TiAl melt.



Fig. 2 BSE micrograph of  $TiAl/Y_2O_3$  interface (a) and XRD spectrum obtained on sample surface (b)

## **3.2 Microstructure and volume fraction of inclusions** Figure 3 shows the white inclusions dispersed in the

matrix. The microstructural observations of different samples show that every sample is contaminated with white inclusions. EDS quantitative analysis shows that these inclusions are rich in Y and O with molar ratio close to 2:3. The TEM observations and corresponding selected area electron diffraction (SAED) patterns (Fig. 4) show that the white inclusions are  $Y_2O_3$ . Figure 5(a) shows the dependence of the volume fraction of the inclusions on the interaction time at both temperatures. The volume fraction significantly increases with increasing interaction time at both melting temperatures, until a certain interaction time is reached. Subsequently, the volume fraction tends to be a constant value at both temperatures (about 0.40% at 1 600 °C and about 0.52% at 1 700 °C).



Fig. 3 BSE micrographs of metal matrix melt at 1 600 °C (a) and 1 700 °C (b)

#### 3.3 Chemical composition

Figures 5(b) and (c) show the results of chemical analysis of the samples. It can be seen from Fig. 5(b) that every sample shows a slight contamination of yttrium and the yttrium enrichment profiles are found to delineate two distinct regions. In the first region, the yttrium enrichment increases with increasing interaction time at both temperatures, until a certain interaction time is reached. In the second region, the yttrium enrichment is characterized by a constant value (about 0.38% at 1 600 °C and about 0.52% at 1 700 °C, respectively). Besides yttrium, the samples are contaminated with oxygen, as shown in Fig. 5(c). The oxygen enrichment of



**Fig. 4** TEM micrograph (a) and corresponding SAED pattern (b) of Y<sub>2</sub>O<sub>3</sub> particle in sample

the samples varies from 0.03% to 0.09% (mass fraction), for different melting temperatures and interaction time. As in the yttrium enrichment case, the oxygen enrichment is also affected by processing parameters, and tends to be a constant value as the interaction time increases.

# **4** Discussion

In the search for suitable mould materials, the oxide family of materials has received the most attention. The Gibbs free energy diagram of oxides is useful for comparison of the relative stability of oxides, which shows that Y<sub>2</sub>O<sub>3</sub> is thermodynamically much more stable than titanium and aluminium oxides, so no reaction between the  $Y_2O_3$  and molten TiAl should be expected [13]. Nevertheless, it is suggested that the standard Gibbs free energy diagram does not provide a correct picture of the reactivity of oxides with molten metal [15]. In every sample, the presence of Y2O3 inclusions and the enrichment of Y and O contents indicate that the Y<sub>2</sub>O<sub>3</sub> coating is not absolutely inert against the TiAl melt and some interactions occur between them. According to previous studies [16], the most probable reason for the metal contamination with Y and O is the Y<sub>2</sub>O<sub>3</sub> coating dissolution by the TiAl melt. One possible mode of the



**Fig. 5** Volume fraction of Y<sub>2</sub>O<sub>3</sub> particles (a) and Y (b) and O (c) contents of samples with different interaction time

interaction between the  $Y_2O_3$  and the TiAl melt would be the dissolution of yttrium and atomic oxygen in the melt as:

 $Y_2O_3(s) = 2Y(\text{in TiAl melt}) + 3O(\text{in TiAl melt})$  (1)

for which the equilibrium constant is

$$K = \alpha_{\rm Y}^2 \cdot \alpha_{\rm O}^3 / \alpha_{\rm Y,O_3} \tag{2}$$

Thus, if the activity product  $\alpha_{\rm Y}^2 \cdot \alpha_{\rm O}^3$  in the melt is less than *K*, reaction (1) can proceed in the forward direction and Y<sub>2</sub>O<sub>3</sub> can dissolve in the melt. Moreover, whether reaction (1) is feasible or not depends on the combined solubility of Y and O in the melt and the kinetics of that dissolution. From the thermodynamic point of view, it is expected that when the contents of Y and O dissolved in the metal increase to a certain value, the  $Y_2O_3$  coating is not dissolved by the melt and then no dissolution product of the coating (Y and O) can enter into the melt by diffusion, thus reach the dissolution equilibrium of the  $Y_2O_3$ . This is the reason why the enrichment of Y and O contents does not continue to rise in Figs. 5(b) and (c) after a certain interaction time.

The microstructural observations of the samples show that  $Y_2O_3$  inclusions are dispersed in the matrix (Fig. 3). One mechanism contributing to the formation of the inclusions in the melt is the dissolution and diffusion controlled erosion of the grain boundaries resulting in a detachment of grains from the Y<sub>2</sub>O<sub>3</sub> coating. Microstructural evidence for such detachment processes is shown in Fig. 2(a) (marked by arrows) where the outer parts of the Y<sub>2</sub>O<sub>3</sub> layer contact with the melt detach and float into the melt, and very similar detachment events have been reported for the interaction between the Al or Zn-Al melts and the Fe<sub>2</sub>Al<sub>5</sub> layer [17-18]. From the thermodynamic point of view, the erosion is inevitable as a result of the existence of the dissolution phenomenon of  $Y_2O_3$  by the TiAl melt, but it should be noted that Y<sub>2</sub>O<sub>3</sub> particles detached from the coating are also dissolvable in TiAl melt if the concentration of oxygen and yttrium in the melt is lower than the saturation limit. The second mechanism could be a direct precipitation of particles from the melt. At high temperature, Y<sub>2</sub>O<sub>3</sub> is dissolved in molten TiAl, resulting in the increase of Y and O contents in the melt, and subsequently Y2O3 may precipitate from the melt during cooling or solidification, due to the reduction in the solubility of Y and O and the strong binding among Y and O atoms [19-20]. A similar dissolution and precipitation behavior of Y<sub>2</sub>O<sub>3</sub> has been also observed in Y containing Ti alloys [21-22].

Figure 6 illustrates the interactional mechanisms between the Ti-47%Al melt and the  $Y_2O_3$  coating in directional solidification. In Fig. 6, step 1 shows the  $Y_2O_3$  coating dissolving in the TiAl melt by transfer of atoms; step 2 shows the dissolution and diffusion controlled detachment of an  $Y_2O_3$  particle; step 3 shows



Fig. 6 Schematic illustration of interactions between TiAl melt and  $Y_2O_3$  coating

a detached  $Y_2O_3$  particle which is dissolvable in the melt with low concentration of Y and O; and step 4 shows the precipitation of an  $Y_2O_3$  particle from the melt with high concentration of Y and O during cooling or solidification.

In the present work, the  $Y_2O_3$  coating is not densely sintered and its porosity is relatively high, which ensures a good thermal shock resistance and also provides a direct pathway for liquid metal to be drawn into the coating structure. When the metal reaches the liquid state and its fluidity is high enough, it can easily penetrate the interstices between the Y<sub>2</sub>O<sub>3</sub> grains of coating, which increases the rate of the coating erosion and alloy contamination. These findings suggest that the porosity of the Y<sub>2</sub>O<sub>3</sub> coating should be decreased and the erosion resistance should be improved. However, a low porosity may lead to a reduction of the coating thermal shock resistance. Therefore, a balance between the thermal shock resistance and porosity of the coating is necessary to reduce the erosion effect and the alloy contamination to a minimum level. A coating with ceramic structure and a porous inner and dense surface is probably an effective solution.

## **5** Conclusions

1) A Ti-47%Al alloy is directionally solidified in an alumina mould with an  $Y_2O_3$  protective coating. The  $Y_2O_3$  protective coating exhibits an effective barrier capability to avoid direct contact between the mould base material and the TiAl melt. The  $Y_2O_3$  coating is found to suffer some erosion and is slightly dissolved by the molten alloy, and the mechanism contributing to such interaction is the dissolution of yttrium and atomic oxygen in the melt.

2) The extent of dissolution and consequent alloy contamination with yttrium and oxygen depends on both melting temperature and interaction time. As the interaction time increases, both the volume fractions of  $Y_2O_3$  inclusions dispersed in the metal matrix and the impurity contents of the alloys tend to be constant.

## References

- BOYER R R. An overview on the use of titanium in aerospace industry [J]. Materials Science and Engineering A, 1996, 213(1-2): 103-114.
- [2] KIM Y W. Gamma titanium aluminides: Their status and future [J]. JOM, 1995, 47(7): 39–41.
- [3] JOHNSON D R, MASUDA Y, INUI H, YAMAGUCHI M. Alignment of the TiAl/Ti3Al lamellar microstructure in TiAl alloys by directional solidification [J]. Materials Science and Engineering A, 1997, 239(6): 577–583.
- [4] JOHNSON D R, INUI H, OH M H, WEE D M, YAMAGUCHI M. A composition window in the TiAl-Mo-Si system suitable for lamellar structure control through seeding and directional solidification [J].

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Materials Science and Engineering A, 2002, 329-331: 19-24.

- [5] YAMAGUCHI M. JOHNSON D R, LEE H N, INUI H. Directional solidification of TiAl-base alloys [J]. Intermetallics, 2000, 8(5–6): 511–517.
- [6] JOHNSON D R, INUI H, MUTO S, OMIYA Y, YAMANAKA T. Microstructural development during directional solidification of α-seeded TiAl alloys [J]. Acta Mater, 2006, 54(4): 1007–1085.
- [7] LAPIN J, ONDRÚŠ Ľ, BAJANA O. Directional solidification of intermetallic Ti-46Al-2W-0.5Si alloy in alumina moulds [J]. Materials Science and Engineering A, 2003, 360(10): 85–95.
- [8] CHEN Yu-yong, XIAO Shu-long, KONG Fan-tao, WANG Xue. Microstructure and interface reaction of investment casting TiAl alloys [J]. Transactions of Nonferrous Metals Society of China, 2006, 16(S): s1910–s1914.
- [9] LUO Wen-zhong, SHEN Jun, MIN Zhi-xian, FU Heng-zhi. Investigation of interfacial reactions between TiAl alloy and crucible materials during directional solidification process [J]. Rare Metal Materials and Engineering, 2009, 38(8): 1441–1445. (in Chinese)
- [10] LI Bang-sheng, LIU Ai-hui, NAN Hai, BI Wei-sheng, GUO Jing-jie, FU Heng-zhi. Wettability of TiAl alloy melt on ceramic moulds in electromagnetic field [J]. Transactions of Nonferrous Metals Society of China, 2008, 18(3): 518–522.
- [11] JIA Qing, CUI Yu-you, YANG Rui. A study of two refractories as mould materials for investment casting TiAl based alloys [J]. Journal of Materials Science, 2006, 41(10): 3045–3049.
- [12] LIU Ai-hui, LI Bang-sheng, NAN Hai, SUI Yan-wei, GUO Jing-jie, FU Heng-zhi. Study of interfacial reaction between TiAl alloys and four ceramic molds [J]. Rare Metal Materials and Engineering, 2008, 37(6): 956–959. (in Chinese)
- [13] KOSTOV A, FRIEDRICH B. Predicting thermodynamic stability of crucible oxides in molten titanium and titanium alloys [J]. Materials

Science and Engineering A, 2006, 38(2): 374–385.

- [14] SMEACETTO F, SALVO M, FERRARIS M. Protective coatings for induction casting of titanium [J]. Surface and Coatings Technology, 2007, 201(24): 9541–9548.
- [15] SAHA R L, NANDY T K, MISRA R D K, JACOB K T. On the evaluation of stability of rare earth oxides as face coats for investment casting of titanium [J]. Metallurgical and Materials Transactions B, 1990, 21(3): 559–566.
- [16] BARBOSA J, RIBEIRO C S, MONTEIRO A C. Influence of superheating on casting of γ-TiAl [J]. Intermetallics, 2007, 15(7): 945–955.
- [17] ZHANG K, TANG N Y, GOODWIN F E. Reaction of 316L stainless steel with a galvanizing bath [J]. Journal of Materials Science, 2007, 42(23): 9736–9745.
- [18] EGGELER G, AUER W, KAESCHE H. Attack of molten aluminum on low alloy steel [J]. Materials and Corrosion, 1987, 38: 351–355.
- [19] WU Y, HWANG S K. Microstructural refinement and improvement of mechanical properties and oxidation resistance in EPM TiAl-based intermetallics with yttrium addition [J]. Acta Mater, 2002, 50(7): 1479–1493.
- [20] WU Y, HWANG S K, NAM S W, KIM N J. The effect of yttrium addition on the oxidation resistance of EPM TiAl-based intermetallics [J]. Scripta Materialia, 2003, 48(12): 1655–1660.
- [21] XU D, LU W J, YANG Z F, QIN J N, ZHANG D. In situ technique for synthesizing multiple ceramic particulates reinforced titanium matrix composites (TiB + TiC + Y<sub>2</sub>O<sub>3</sub>)/Ti [J]. Journal of Alloys and Compounds, 2005, 400(1–2): 216–212.
- [22] de CASTRO V, LEGUEY T, MUÑOZ A, MONGE M A, PAREJA R. Microstructure and tensile properties of Y<sub>2</sub>O<sub>3</sub>-dispersed titanium produced by arc melting [J]. Materials Science and Engineering A, 2006, 422(1–2): 189–197.

# γ-TiAl 合金定向凝固过程中与氧化钇陶瓷材料的界面反应

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摘 要:研究液态金属冷却定向凝固条件下,Ti-47%Al 合金与 Y<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 双层结构陶瓷管内层 Y<sub>2</sub>O<sub>3</sub>的相互作用。 分析熔体温度和相互作用时间对界面反应、合金组织和成分的影响。结果表明:虽然 Y<sub>2</sub>O<sub>3</sub> 层受到一定程度的侵 蚀和溶解,但 Y<sub>2</sub>O<sub>3</sub> 层有效地阻隔化学稳定性较差的 Al<sub>2</sub>O<sub>3</sub> 外层与 TiAl 合金熔体接触,避免 Al<sub>2</sub>O<sub>3</sub> 与 TiAl 之间的 化学反应。合金熔体受到一定程度的污染且含有少量夹杂物。在一定保温时间内,合金中的杂质含量(Y 和 O)和 夹杂物(Y<sub>2</sub>O<sub>3</sub>)体积分数均随着过热温度的提高而增加,但随着保温时间的进一步延长,杂质含量和夹杂物体积分 数趋于恒定值,不再显著变化。

关键词: TiAl 合金; Y<sub>2</sub>O<sub>3</sub>保护涂层; 相互作用; 定向凝固

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