Microstructure, Metal-Mold Reaction and Fluidity of Investment Cast-TiAl Alloys

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The objective of this study is to investigate the effects of mold preheating temperature on microstructural evolution, metal-mold reaction and fluidity of TiAl alloys. A conventional induction melting furnace was used for melting and casting of TiAl alloys in the present investigation. The previous research showed that metal-mold reaction of titanium castings was inevitable during titanium casting. However, there is no metal-mold reaction of TiAl alloys castings regardless mold materials. These results were supported by the experimental results and thermodynamic calculations. However, the grain size of TiAl alloy castings is gradually reduced with mold preheating temperature due to heterogeneous nucleation near outside of mold and diffusion of metallic element from the mold and binder. A fused Al_2O_3 is promising mold for investment casting of TiAl alloys because of low cost, good strength and thermal stability. The fluidity length of TiAl alloys is increasing gradually with mold preheating temperature. However, it is difficult to predict the accurate applicable limit of preheating temperature of Al_2O_3 mold for investment casting of TiAl alloys due to the relationship between metal-mold reaction and fluidity. Therefore, mold material, binder and mold preheating temperature are the most important process parameter of TiAl alloys investment casting.

(Received July 10, 2003; Accepted December 15, 2003)

Keywords: TiAl alloy, investment casting, metal-mold reaction, microstructure, fluidity, mold preheating, Al_2O_3 mold

1. Introduction

TiAl alloys are receiving significant attention for potential light weight high-temperature structural applications, due to weight savings in combination with their excellent mechanical properties at high temperatures.¹⁾ Despite their unique properties, their industrial applications have been so far limited by poor high-temperature oxidation resistance and relatively low ductility at room temperature. The former problem is recently improved by several techniques such as surface treatment, alloying and composites design.²⁻⁴⁾ TiAl alloys have a difficulty in shaping complex shape parts due to their shortcoming. One approach to solve these difficulties is to through the use of investment casting.^{5,6)}

From the viewpoint of cost-saving process, investment casting route has been received considerable attentions because it is a simpler processing method and, thus has a lower process cost, compared with other approaches such as wrought or powder methods. Unfortunately, TiAl alloys are an inherently difficult material to cast, mainly high activity of molten state and poor fluidity of them, which has two important consequences.⁷⁾ Firstly, ISM and VAR with water-cooled copper crucible are used to prevent contamination, however, these processes generally have lower energy efficiency and low superheating of molten metal, result in being unable to fill a mold satisfactory. First of all, the production of the complex and thin wall castings requires the molten metal having a good filling ability. Besides, it is essential to consider the interfacial reaction between mold and molten metals during casting. As the reaction layer of the castings often behaves as a crack initiation site during the actual usage of castings, the chemical or electrochemical millings are usually required to remove the reaction layer in a sequent process, resulting in increase of process cost and difficulty in control the dimensional tolerance.⁸⁾

Although melting practices of titanium were well devel-

oped, among the melting routes, the benefit of induction melting has been known that the process has handled the material and controlled the atmosphere in the melting process. Especially, the vacuum induction melting process could be profitable in industry if a suitable crucible material is available.⁹⁾ Therefore, how to control the interfacial reactions between titanium and ceramic mold or crucible is of great concern. The present work aimed to discuss the suitability and the thermodynamic consideration of investment mold against molten TiAl alloys, and the effects of mold preheating on metal-mold reaction, microstructural evolution and fluidity of TiAl alloys.

2. Experimental Procedure

2.1 Investment mold preparation for investigating metal-mold reaction

The examined oxides in this study were ZrO_2 (Yakuri Pure Chemical Co. Ltd, Japan), electro-fused Al_2O_3 (UCW-R1, UNION Corp., Korea), CaO stabilized ZrO_2 (Unitec Ceramics, British) and ZrSiO_4 (RZM, Murray Basin Titanium Pty Ltd, Australia). The ceramic shell molds were processed using conventional colloidal silica and an SKKU binder, which is developed the restricted SiO_2 contents as binders a -200 mesh above ceramics was used as slurry filler and a -30 + 80 mesh ceramics were applied as stucco. The molds were built up a wax pattern with an opening diameter of 20 mm and a height of 150 mm. Build-up was achieved by dipping the pattern in the appropriate slurry, sprinkling with stucco, and allowing it to dry in a controlled humidity chamber. The total thickness of ceramic shell mold was kept at 2-3 mm. Subsequently, the shell molds with alternate dipping and stuccoing process were reassembled with one shell mold. The advantage of this technique for a special shell mold is the fact that the critical examination of the thermal stability of mold materials is possible under the same condition; temperature of the melts and mold, melts composition and operating atmosphere. The sequences of

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Fig. 1 Procedures of mold making for investigating metal-mold reaction in the present study.

mold making are summarized in Fig. 1. After that, the mold was dewaxed using high temperature and pressure stream in an autoclave, and then fired at 950°C in a muffle furnace for two hours to burn out the residue of the wax and to increase the strength.

2.2 Induction melting and casting process

TiAl material of nominal composition Ti-47Al(at%) specimen has been prepared by plasma arc melting furnace under argon atmosphere. The 1000 g charge of TiAl alloy was melted in a graphite crucible using a high frequency induction furnace. The charge materials were offcuts from ingots of Ti-47Al prepared in the plasma arc-melting furnace. The pressure of the furnace atmosphere can be controlled in the range 1.33×10^{-1} Pa by vacuum pump, and then subsequently backfilled with high purity argon at a pressure of 4.9×10^3 Pa. This cycle of evacuation and flushing with argon was repeated at least two times. The shell molds were rapidly preheated by halogen lamp to 400, 600 and 800°C. The furnace was switched on and the temperature was gradually increased until the charge was melted. The power was turned off 60 s after complete melting as judged by the visual inspection and the melt was poured into the preheated mold by tilting the crucible.

2.3 Determination of metal-mold reaction

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. Hardness test was conducted by utilizing Mitutoyo MVK-H2 Microvickers hardness tester, measured at 0.05 mm intervals on the vertical cross section of the solidified specimen with 200 g-load time and a load time 10 s. The metallic element and constituent of binder on interfacial reaction of as-cast specimen have been analyzed using Philips XL30 ESEM-FEG equipped with electron probe microanalyzer (EPMA).

2.4 Spiral fluidity measurement

As mentioned above, the spiral fluidity mold is applied in the fluidity test of TiAl alloys using the lost-wax process. It is important to secure a good fluidity and a longer fluidity length. The mold is designed to remove the majority of entrapped oxides and slags and to introduce the TiAl melts into mold as smoothly as possible, so that it just fills the cross-section at all times and does not react excessively with the atmosphere or the mold. After complete melting of TiAl alloys with holding time, 1 minute, and then, the melt was poured into the preheated mold by tilting the crucible. The spiral mold is preheated to 400 and 600°C. Additionally, an attempt was made to compare with the fluidity of pure aluminum under same condition. Then, TiAl alloys are cast into the spiral mold, and air cooled to room temperature. The as-cast spirals were then sectioned, polished, and examined using an Olympus PME 3 optical microscope to investigate the mode of solidified TiAl alloys.

3. Results and Discussion

3.1 Metal-Mold reaction and microstructure

The key requirements of an investment casting mold usually require many factors, such as sufficient green/fried strength, formability, mold permeability, cost, high thermal shock resistance and collapse-ability.^{10,11)} However, it is essentially necessary to consider the thermodynamic stability of investment mold because TiAl alloy is very reactive in the molten state, easily oxidized, and reacts with the crucible and mold materials. Previously, Kuang *et al.* already investigated suitability of different refractory as mold and crucible for melting and casting of TiAl alloy.¹²⁾ However, their study showed that the interaction between the TiAl and candidate refractories was only attributed to their mutual wettability.

It has been proposed previously that the relative difference of metal-mold reaction by microhardness and optical microscopy provides a good index for the relative stability of refractories.¹³⁾ Figure 2 illustrates the as-cast microstructure

Fig. 2 Photographs showing the as-cast microstructure of the regions below the surfaces of the castings with different mold materials with no preheat; (a) Al_2O_3 , (b) ZrSiO_4 , (c) ZrO_2 and (d) CaO stabilized ZrO_2 mold.

Fig. 3 The hardness profiles of TiAl alloy rod cast into investment mold with different molds at room temperature; (a) colloidal silica and (b) SKKU binder.

of the regions below the surface of the castings with different mold. As shown in Figs. 2(a)–(d), there are no clear strange microstructure nearby metal-mold interface regardless mold materials. These results are also consistent with the hardness distribution of TiAl castings surface (Fig. 3). It should be noted here that the thickness of hardness increase of TiAl alloy castings is significantly smaller than that of pure Ti and Ti-6Al-4V alloy under same experimental conditions.¹⁴⁾ Because TiAl alloy was conventionally known as reactive metal in the molten state, the proper investment mold is serious matter in the previous study. Besides, regardless of the kind of the binder, the TiAl melts were not reacted with mold materials, as shown in Figs. 3(a) and (b). However, SKKU binder, which restricted silica contents, has disadvantages with low strength of the investment mold, difficulty in making slurry due to the phenomenon of easily foaming and the dimensional tolerances of castings surface. And then, this may be the main reason why TiAl alloys is more thermodynamically stable with different mold material compared with conventional titanium alloys, these results were explained by the thermodynamic considerations. For example, we consider the thermodynamic data between TiAl and Al_2O_3 . When TiAl melts poured into Al_2O_3 mold, the reaction was the followings;¹⁵⁾

If reactions (1), (2) and (3) are combined, the reaction is the following.

According to the eq. (4), the reaction for producing TiO_2 is very difficult due to positive value of free formation energy. As mentioned above, there is no metal-mold reaction between TiAl alloys and Al_2O_3 mold, as shown in Fig. 2(a) and Fig. 3. Moreover, the thermodynamic consideration of other refractories, eg. ZrO_2 and ZrSiO_4 , is alike result.¹⁵⁾ In the similar investigation, Meada *et al.* supported the above reason by the fact that the activity of Ti-50Al alloy was smaller to one tenth than that of pure titanium at 1800°C by integration of the Gibbs-Duhem equation.¹⁶⁾ In this case, it is impossible to form alpha case in the surface of TiAl castings because titanium lattices were connected strongly with aluminum ones. Larsen *et al.* already showed that the high aluminum contents in XD near gamma alloys, compared with conventional titanium alloys, helped to lower the reactivity of the molten alloy with ceramic mold material.¹⁷⁾ According to studies of Zalar *et al.* and Misra, the reaction products were not TiO_2 but Ti_3Al and TiAl between Al_2O_3 and TiAl during the diffusion couple.^{18,19)} They showed that the diffusivity of oxygen, result from decomposition of Al_2O_3 , was also decreased suddenly with aluminum content in titanium alloys.

Besides, the mold preheating is important process parameter in the investment casting of TiAl alloy, if not, insufficient preheating, results in casting defects such as misrun, shrinkage and porosity, etc. However, the excessive preheating accelerates metal-mold reaction of titanium castings. According to the optical microscope and hardness profiles of metal-mold reaction with different refractories, we chose the conventional investment mold, Al_2O_3 and ZrSiO_4 so as to investigate the effect of mold preheating on metal-mold reaction of TiAl alloys. Figure 4 show the as-cast microstructure of the regions below the surfaces of TiAl castings with colloidal silica bonded ZrSiO_4 and Al_2O_3 mold on mold preheating temperature. The castings was refined in the region adjacent to the mold but became coarse towards the center of the ingot. As shown in Fig. 4, as the grain size of TiAl alloy castings is gradually refined with mold preheating temperature, regardless of mold materials. In general, the grain size of solidified structure is dominated by temperature gradient (G) and solidification velocity (V). However, this tendency of the castings grain refining in the present study is addressed by the following reasons.

Figure 5 are EPMA elemental profiles of the TiAl castings into colloidal silica bonded ZrSiO_4 and Al_2O_3 mold with mold preheating temperature. In the case of TiAl castings

Fig. 4 Photographs showing the as-cast microstructure of the regions below the surfaces of the castings; (a) Al_2O_3 , 400°C, (b) Al_2O_3 , 600°C, (c) Al_2O_3 , 800°C, (d) ZrSiO_4 , 400°C, (e) ZrSiO_4 , 600°C, and (f) ZrSiO_4 , 800°C.

Fig. 5 EPMA elemental profiles of TiAl alloy castings produced in (a) ZrSiO_4 and (b) Al_2O_3 mold with preheating temperature.

into ZrSiO_4 mold, as shown in Fig. 5(a), when the difference in the temperature between the molten metal and mold decreases, the heat transfer is decelerated and then, the solidification time increases. This results in the increase of the available time for the diffusion within the liquid of the element come from investment mold. The EPMA line profiles, in particular, that of silicon and zirconium, supported that the mold materials and binder element diffused outwardly toward the outermost the surface of the castings, being greater with the increasing extent of mold preheating. The diffusion tendency of these elements is accelerated with mold temperature, showing the peak silicon and zirconium in the Fig. 5(a). On the other hand, as shown in Fig. 5(b), that of

TiAl casting into Al_2O_3 mold showed that there is a little silicon diffusion at mold temperature, 800°C. This may be due to the element dissolution of the binder constituent. Frueh *et al.* previously suggested that the binder influence directly metal-mold reaction of titanium castings in the case coat yttria/silica face coat with mold preheating.²⁰⁾ It should be noted that from the elemental profiles, these elements, zirconium and silicon in the TiAl castings were helpful to refine the grain size, as shown in Fig. 4. Besides, Fig. 6 also shows the effect of the hardness distribution of TiAl castings surface on the mold preheating temperature. The hardness increase of the internal casting as well as castings surface depended strongly on the diffusion of revealed elements even after the start of solidification. In additional, the more increasing mold preheating temperature are, the greater possibility of heterogeneous nucleation of the preheated mold surface are, resulted in the refining the grain of the castings.²¹⁾ R. Yang *et al.* also revealed that the hardness increase of TiAl castings surface is attributed to the refined grain and the decomposition of mold constituent.²²⁾ From the above discussion, a fused Al_2O_3 is regarded as a promising investment mold of TiAl alloy. It offers advantages over thermal stability, the low cost, sufficient mold strength and flexibility of binder choice.

3.2 TiAl Fluidity

In general, the fluidity of molten metal is affected by two major factors: the intrinsic fluid properties of molten metal and the casting conditions.²³⁾ The latter includes casting equipment, casting temperature, the mold temperature, the permeability of the investment material, speed of the molten metal flow resulting from the casting force, the wettability of the mold components to molten metal, and the spruing configuration. In order to avoid the casting parameter in the present work, except for mold temperature, we adapt the same casting condition; the pouring height, heating profiles for melting and melt holding time, etc. It could be seen from Fig. 7 that the influence of mold temperature on the fluidity of TiAl alloy is remarkable. Especially, the fluidity of TiAl

Fig. 6 The effect of hardness profiles of TiAl alloy castings produced into (a) ZrSiO₄ and (b) Al₂O₃ mold on preheating temperature.

Fig. 7 Spiral fluidity length of TiAl alloys with mold preheating temperature.

alloy, at preheated 600°C mold, is correspondent with that of pure aluminum, at superheating 50°C. The fluidity length of alloy is inversely proportional to the difference of pouring and mold temperature, so the fluidity increases with increasing of mold temperature. Conventional, fluidity, L_f can be expressed by the distance that molten metal has flown during filling and solidification. It is the product of filling speed, V ,

Table 1 The mixing ratio of slurry and their viscosity.

Oxide	Binder	Slurry viscosity (Zhan cup #4)
ZrO ₂		
ZrSiO ₄	Colloidal silica,	1st 45 ~ 55 s.
Al ₂ O ₃	SKKU binder	2nd 30 ~ 35 s.
CaO stabilized		3rd 23 ~ 25 s.
ZrO ₂ .		

and filling time, t_f , before molten metal stop filling, then we have the flow distance the following,²⁴⁾

$$L_f = V \cdot t_f \quad (5)$$

During solidification of the melts as it flows into the mold, this mushy volume is likely to form on the metal initially solidifying on the inner walls of the mold. There is no doubt that if this mushy volume forms, there is greater resistance to the flowing metal, increasing the apparent viscosity and reducing the total fluidity of the metal. The direct relationship between fluidity and mold temperature also means that anything that increases solidification time, t_f , will increase fluidity, as like eq. (5).²⁵⁾ Finally, there is a much smaller temperature difference between the fusion temperature and the mold temperature when preheating mold, compared to unpreheated mold. This smaller temperature difference prolongs the time the preheating mold is its liquid state because of a lower temperature gradient in the molten metal near the mold.

Figure 8 show the microstructure of polished cross-section of solidified TiAl alloys in Al₂O₃ spiral mold. The all specimen were same solidification mode, long freezing range alloy. This is expected that the fluidity is inferior to that of pure titanium and aluminum. As shown in Fig. 7, however, the increase in the solidification time is major factor that determine the spiral fluidity of the TiAl alloy in the present investigation. Moreover, the cause of increasing fluidity of TiAl alloy is supported that they have a peritectic reaction which appears in the form of envelopment, surrounding each particles of the primary constituent during solidification. The work of Portevin *et al.* showed that the fluidity of Sb-Cd binary system, as like the occurrence of peritectic reaction, showed the extremely sharp maximum for definite range with constant degree of overheating due to solidification range and solidification mode.²⁶⁾

4. Conclusions

Using conventional induction melting furnace, the present works were focused on the effect of mold preheating temperature on microstructure evolution, metal-mold reaction and the fluidity of TiAl alloys. The conclusions were drawn the followings;

- (1) Unlikely metal-mold reaction of conventional titanium alloys, there is no metal-mold reaction of TiAl alloy during casting regardless mold materials. These phenomena were supported by the experimental results and thermodynamic calculations.
- (2) A fused Al₂O₃ is a candidate for investment mold of TiAl alloy because of the thermal stability, enough strength of

Fig. 8 Photographs of polished cross section of solidified TiAl alloys in spiral mold with mold preheating temperature; (a) room temperature, (b) 400°C, and (c) 600°C.

mold handling and flexibility for making slurry.

(3) As the greater the mold preheating temperature, the grain of TiAl alloys is refined due to the diffusion of the binder elements and the heterogeneous nucleation of the preheated mold surface.

(4) The spiral fluidity of TiAl alloys is directly related to the mold preheating temperature. This could be explained by the fact that the increase in the solidification time is major factor that determine the spiral fluidity of the TiAl alloy.

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