The Effect of Silica-Containing Binders on the Titanium/Face Coat Reaction

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The interactions of CP-Ti and Ti-6Al-4V with investment molds containing alumina/silica and yttria/silica face coat systems were studied. ''Containerless'' melting in argon was employed and small test samples were made by drop casting into the molds. The effects of the face coat material and mold preheat temperatures on the thickness of the alpha case in the drop castings were evaluated with microhardness and microprobe measurements. It was found that the thickness of the alpha case was the same, whether a yttria/silica or alumina/silica face coat was used, indicating that the silica binder can reduce the apparent inertness of a more stable refractory, such as yttria. It was also found that the alloyed titanium castings had a thinner alpha case than those produced from CP-Ti, which suggests that the thickness of the alpha case depends on the crystal structure of the alloy during cooling from high temperatures. Furthermore, the small drop castings made in small yttria crucibles used as molds exhibited little or no alpha case.

I. INTRODUCTION

THREE factors have made the production of quality titanium castings a difficult task: (1) titanium has a high melting point; (2) it has low fluidity at pouring temperatures; and (3) it is highly reactive with nearly all gasses, liquids, or solids at temperatures above 500 °C.[1] Although each factor presents processing difficulties, it is the third which most hinders the capability of titanium casting technology. Liquid titanium has been termed ''the universal solvent,''[2] because violent reactions with gasses, liquids, and solids result in contamination of the titanium. Furthermore, titanium has a high affinity for interstitials such as nitrogen, oxygen, and carbon, and only small concentrations of these interstitials are enough to deleteriously affect its ductility.[3,4]

During solidification, a reaction occurs between a titanium casting and its shell mold. The result of this interaction is an oxygen-enriched surface layer known as the alpha case. If a casting is to be used in a critical application, then this layer must be removed, usually by chemical milling. Because this removal process is waste producing, expensive, and limits the complexity and detail that can be achieved in a casting, much effort has gone into trying to develop a mold material that does not react with titanium. To date, however, no such shell mold has been developed for producing titanium investment castings that are free of the alpha case.

A review of past articles, patents, and reports is given elsewhere.[5] The review also gleans information that resulted from efforts to develop a refractory crucible for containing liquid titanium. This information can be of benefit provided one is not too hasty to eliminate a material from consideration as a mold material because it was shown not to function well as a crucible. For example, Chapin and Friske[6,7,8] investigated the use of various oxides, carbides, borides, a sulfide, carbon, and graphite as possible container materials for titanium. They found that none of the selected materials was inert to titanium. Titanium melted in a thoria crucible was found to contain an average of 5.44 pct thoria; if thoria had been tested as a mold material, however, it is possible that very little or no contamination would have been detected.

Thermodynamics can also help the investigator identify materials which should be tried. An analysis typically involves a comparison of the free energy of formation of the candidate refractory to that of the corresponding titanium phase. This is a rather simplistic approach because, as indicated by Saha et al.,[9] it neglects solution effects. In addition, most commercial binders in ceramic shell molds are made from colloidal silica,[10] so regardless of the chemical stability of a refractory, its effectiveness will be undermined by the presence of the siliceous binder. In this context, Saha et al. evaluated rare earth oxides for use in face coats for investment casting titanium and found yttria to fare the best. It should be noted that work has also been done with sub-stoichiometric yttria.[11,12,13] Although oxygen-deficient yttria was found to be more resistant to titanium than its stoichiometric counterpart, contrary to thermodynamic predictions, its use also resulted in a melt contaminated with yttrium. The authors, however, suggested that further alteration of the stoichiometry of yttria may lead to a refractory which is inert to titanium and would serve as an excellent mold material.[11,12,13]

Assuming an acceptable yttria slurry could be developed, and its use could result in reducing the thickness of the alpha case, one should ask whether it is economical. According to Prigent and Debuigne,[14] the use of yttria would be limited by its ''prohibitive cost.'' Indeed, the $40 to $80/lb[15] price tag for yttria seems very high, especially when compared to the cost of materials such as alumina, silica, and even zirconia. One objective of this work is to determine whether the presence of a siliceous binder drives the Ti/mold reaction, regardless of the refractory used.
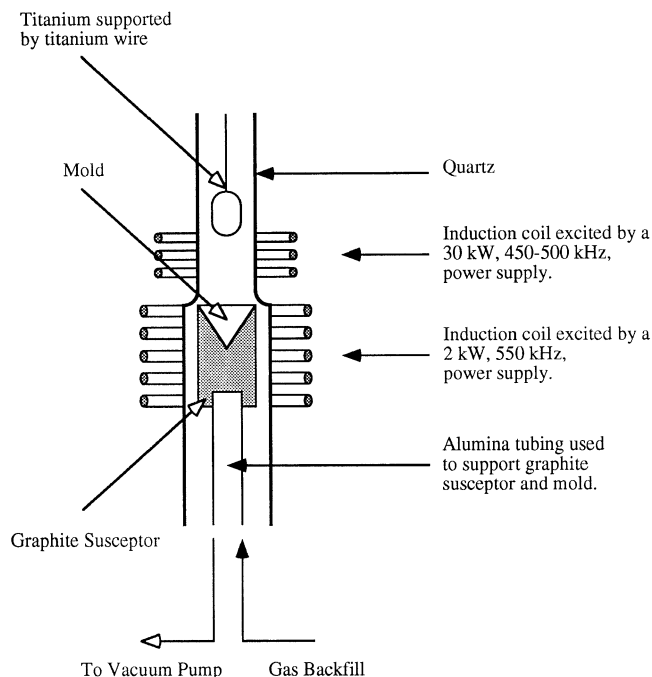
Fig. 1—The containerless melting apparatus used to produce the drop castings.

II. EXPERIMENTAL PROCEDURES

A. Mold Production

A face coat slurry and a backup coat slurry were used to make the shell molds. Both slurries used a commercially available binder in conjunction with a refractory. The binders used for the face coat and backup coat were PRIMCOTE* and NYACOL** 830, respectively. For the shell

*PRIMCOTE is a trademark of Ransom & Randolph, Maumee, OH.

**NYACOL is a trademark of PQ Corp., Valley Forge, PA 19482.

system with the alumina/silica face coat, the PRIMCOTE was combined with REMASIL-60* (aluminosilicate) and

*REMASIL 60, RP-1, and RP-2 are trademarks of Remet Corporation, Chadwicks, NY.

RP-1* (fused silica). The powders (−325 mesh) were added in a 10:1 ratio, respectively. The viscosity of the slurry was kept between 20 and 30 seconds and measured in Zahn cup 5; deionized water was added as necessary to adjust the viscosity. The shell system with the yttria/silica face coat used a slurry made in the same manner, except yttria powder was used instead of the REMASIL-60 and RP-1. Although this work did not require slurries with a long ''shelf life,'' it is of interest to note that the yttria slurry gelled much sooner than its counterpart, as was also observed by Calvert.[16] The backup slurry for both molds used NYACOL 830 binder in combination with RP-2* (fused silica).

The molds were built up, around a cone-shaped wax pattern with an opening diameter of 25 mm and a height of 19 mm. Buildup was achieved by dipping the pattern in the appropriate slurry, sprinkling with a stucco, and allowing it to dry in a controlled humidity chamber, as is typical in

an investment casting process. The face coat slurry was used to produce the first two layers, and the backup coat slurry was used for the four succeeding layers and as the seal coat. The composition and particle size distribution of each of the six stucco coats were the same for both types of molds.

The completed shells were dewaxed in a preheated autoclave at 965 kPa and 178 °C and then fired in a furnace at 1000 °C. The resulting product, after firing, was a partially sintered mold, free of organics, ready for casting.

B. Melting Furnace

The reactive nature of titanium places severe restrictions on the type of furnace and crucible which can be used to produce castings. Typically, foundries melt titanium in a water-cooled copper crucible, usually using a consumable arc furnace. It was felt that the use of such a furnace in this project was impractical, considering the large number of samples to be tested. Hence a ''containerless'' system to avoid crucible contamination of the titanium melt was selected.

Figure 1 shows the furnace used to produce the titanium castings. Two induction power supplies were used: a 30 kW, 450 to 500 kHz generator was used for melting and a 2 kW, 550 kHz generator was used for mold preheating through the use of a graphite susceptor. The charge for the melt was hung with titanium wire, and the susceptor/mold fixture was supported with alumina tubing.

As can be seen in Figure 1, melting and casting took place inside a quartz tube. The environment inside the tube was provided by a vacuum system and a gas source. The benefits of using this system were that it provided containerless melting and that melting and casting were done in an inert atmosphere.

C. Casting Experiments

Slugs of CP-Ti (ASTMB-348, Grade 1) and Ti-6Al-4V (AMS-4928M, Grade 5), that weighed 4 g each, were suspended at a fixed distance from the top of the mold with CP-Ti wire. The chamber was evacuated with a mechanical pump to 10^{-1} torr, backfilled with ultra-high-purity argon, and evacuated again. With the mechanical pump still on, the mold was slowly heated to 400 °C and allowed to outgas for 30 minutes. Mold temperature was measured by focusing an optical pyrometer on the face coat. Then the mold was either heated or allowed to cool to a preheat temperature; preheat temperatures of 25 °C, 350 °C, 500 °C, 650 °C, and 800 °C were selected. When the desired preheat temperature was reached, the valve to the mechanical pump was closed and the valve to a turbomolecular pump was opened. After the vacuum stabilized, the chamber was backfilled with argon and evacuated again to a vacuum of $<2 \times 10^{-5}$ torr. Prior to melting, the chamber was backfilled to 17 torr (above ambient pressure) with argon, the mold preheat coil was de-energized, and the melt coil was energized. The chamber was kept at 17 torr with argon during and after the melt.

Because of the position of the slug prior to melting, and the configuration of the coil, the titanium melted from the bottom up. The electromagnetic field and surface tension force held the droplet until the melt pool reached the wire,
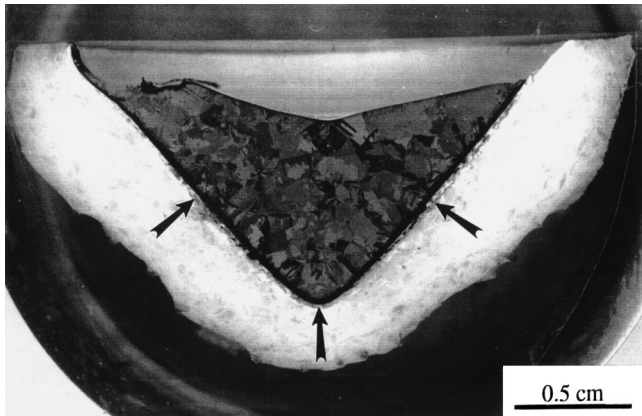
Fig. 2—Cross section of a casting and its mold; the arrows point to microhardness traverses.

when the droplet fell into the mold. Melting took approximately 20 seconds, and the drop casting was kept in the argon until cool. Figure 2 shows a cross section of a casting in its mold.

D. Analysis of Castings

Saha et al.[17] confirmed that microhardness profiles can be used to determine the thickness of the alpha case to indicate the diffusion profile of oxygen at the surface of the drop casting. In our work, three Vickers-microhardness traverses were made, using a 100 g load held for 15 seconds on a SHIMADZU hardness tester (Shimadzu Seisakusho Ltd., Kyoto, Japan). The arrows in Figure 2 indicate the locations and directions of the three traverses. Each indentation was made at a specific distance from the surface; for example, if the first indentation in one traverse was 150 μm away from the surface, then the first indentations in the other two traverses were also at 150 μm from the surface. This procedure provided for an average Vickers hardness number (VHN) based on three measurements at a specific distance from the surface.

Figure 3 shows a microstructure and a hardness profile in Ti-6Al-4V that was cast in a mold with an alumina/silica face coat preheated to 500 °C. The thickness of the alpha case is taken as the distance where the hardness value returns to a nominal value. In this example, the nominal value is approximately 380 VHN which, in turn, corresponds to an alpha case with a thickness of 360 μm.

The surfaces of the CP-Ti castings were also evaluated using a microprobe. Area elemental distribution and secondary electron and backscattered electron micrographs were taken with an accelerating voltage of 15 keV. In addition, quantitative analyses were made using software based on the usual corrections for matrix effects. The elements of interest were calibrated with elemental standards, and the analyses were done in 1-μm steps.

III. RESULTS AND DISCUSSION

To gain a perspective on the sizes and cooling rates of the drop castings relative to commercial castings, we calculated their cooling rates after solidification. The analysis is presented in the Appendix. Our calculated results are shown in Figure 4(a) for the five preheat temperatures, as-
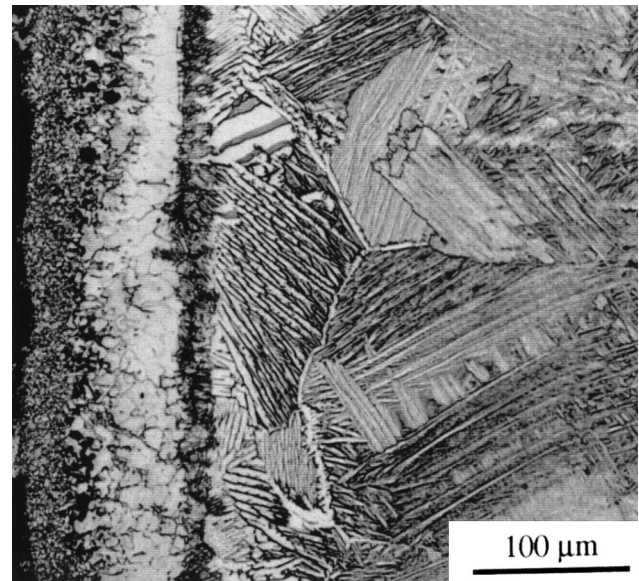
(a)
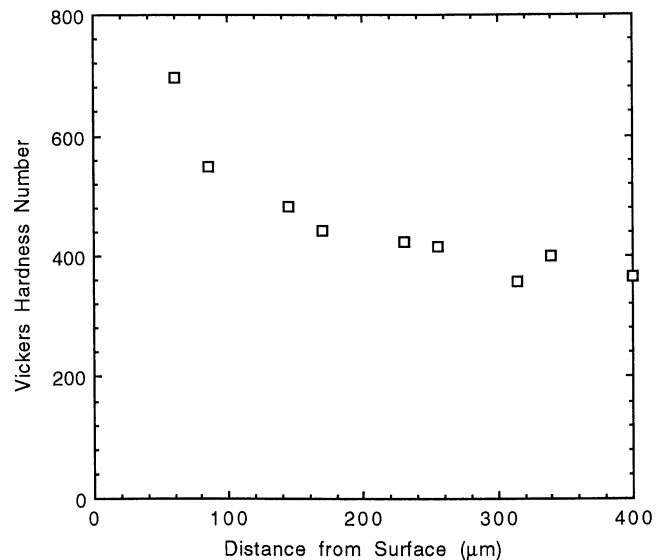
(b)

Fig. 3—Microstructure and hardness profile from a Ti-6Al-4V casting made in a mold with an alumina/silica face coat preheated to 500 °C: (a) microstructure etched with Kroll's reagent and (b) corresponding microhardness plot.

suming that the melting point of Ti is 1958 K. The curves are terminated at 1500 K, because it has been shown by Boettinger et al.[18] that the alpha case grows very little below that temperature. Our calculated results are compared to the cooling after solidification (labeled step casting) of the surface of an experimental investment casting of Ti-6Al-4V; the temperatures have been adjusted upward to the melting point of Ti. The Ti-6Al-4V casting had a variable thickness that varied from 6.4 mm (1/4 in.) to 44.4 mm (1-3/4 in.) in incremental steps of 6.4 mm (1/4 in.).[18] The curve labeled "step-casting" is from the step with a thickness of 6.4 mm, so it is obvious that our drop castings have cooling rates of castings that are less than 6.4 mm in thickness.

Again, using results from Boettinger et al.,[18] the times to cool to 1500 K for step thicknesses from 6.4 to 25.4 mm
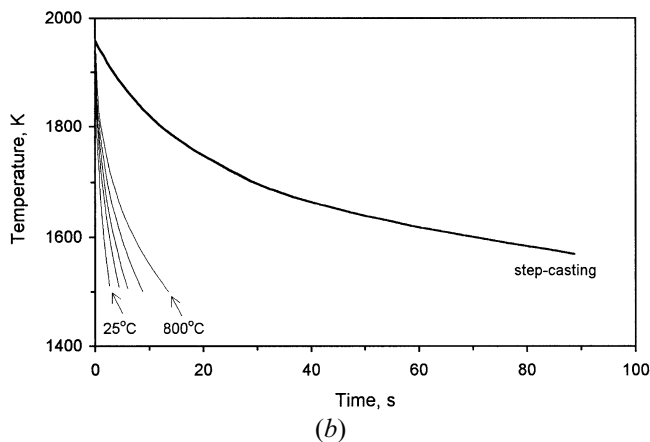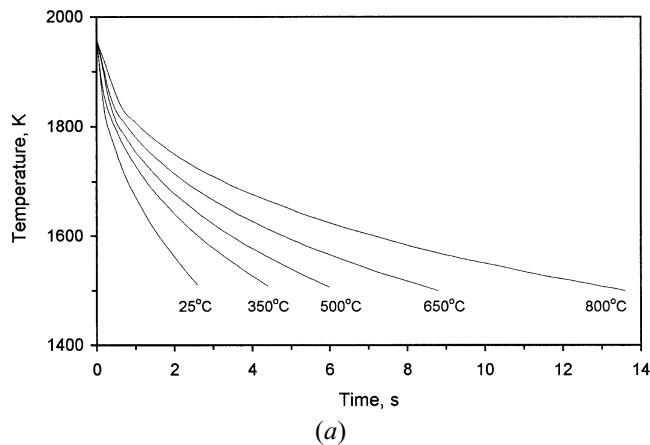
Fig. 4—Calculated curves of cooling after solidification: (a) cooling in molds with different preheats; and (b) the cooling curves compared to the cooling of a surface of section of 6.4-mm thickness (labeled step casting).
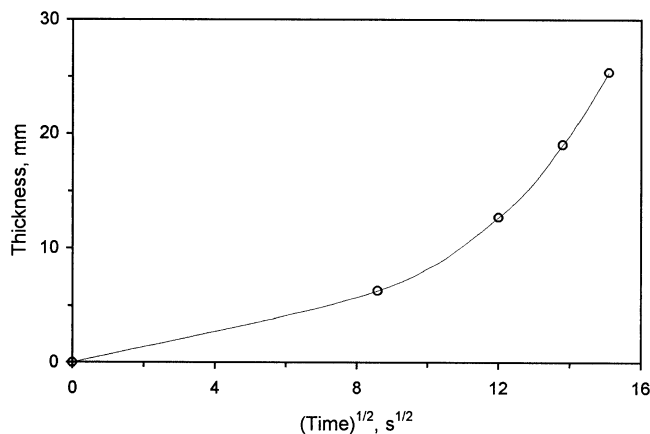

Fig. 5—Time to cool to 1500 K for various section thicknesses.[18]

are plotted in Figure 5. Interpolations based on our times to cool to 1500 K from Figure 4(a) indicate that the drop castings studied herein are equivalent to investment castings that are 1.2- to 2.6-mm (0.05- to 0.10-in.) thick, depending on the preheat.

A. Microhardness Results

Figure 6 shows microhardness profiles of the CP-Ti castings made in molds with an alumina/silica face coat. Castings were produced in molds at room temperature (RT) and
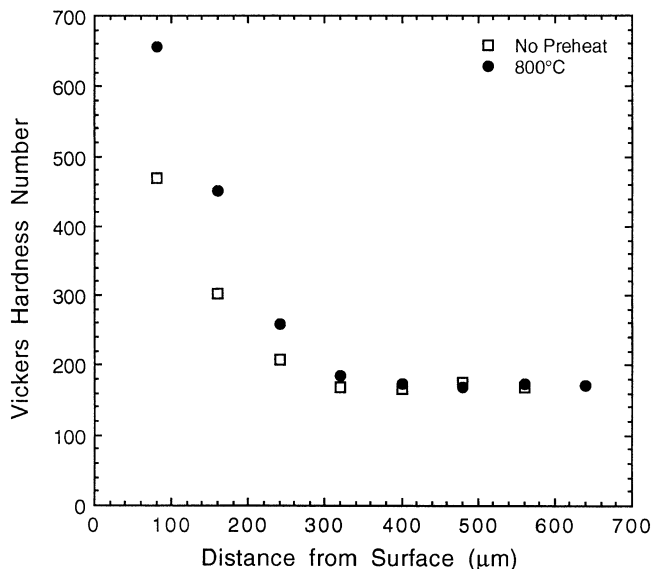

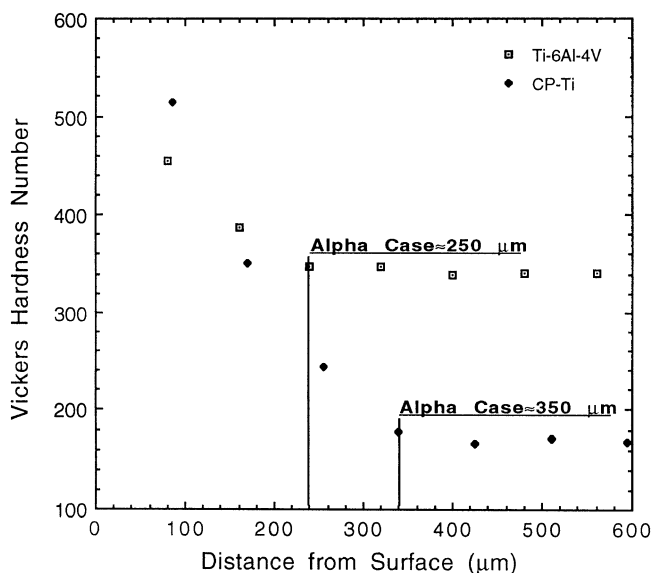Fig. 6—Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat.

Fig. 7—Microhardness profiles of castings (CP-Ti and Ti-6Al-4V) produced in molds, preheated to 350 °C, having an alumina/silica face coat.

in molds preheated to 350 °C, 500 °C, 650 °C, and 800 °C, but only profiles at RT and 800 °C are plotted in order not to overload the plots with data. In Figure 6, it can be observed that as the mold preheat temperature rises, the hardness increases, an indication of more contamination resulting from preheating. Note, however, that the preheat temperature does not greatly influence the apparent thickness of the alpha case.

The microhardness profiles in the Ti-6Al-4V castings were similar to those in Figure 6, although it did appear that the reaction layers were slightly thinner. Figure 7 illustrates this by comparing drop castings made in molds preheated to 350 °C. An explanation for the difference could be the allotropic nature of titanium. Upon cooling, CP-Ti undergoes a transformation from a body-centered cubic structure (the beta phase) to its hexagonal close-packed
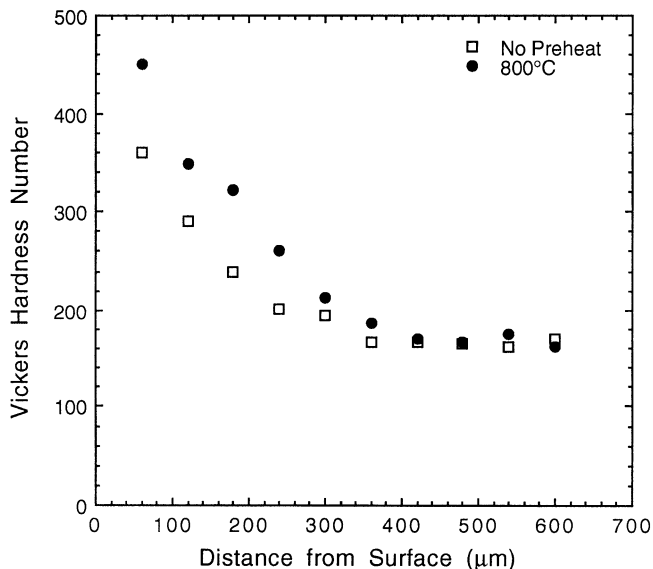
Fig. 8—Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat.
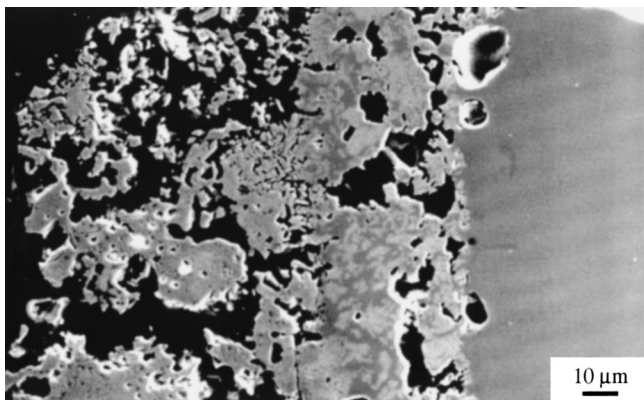

Fig. 9—Microstructure (SEM image) of a CP-Ti casting made in a mold with a yttria silica face coat, preheated to 800 °C.
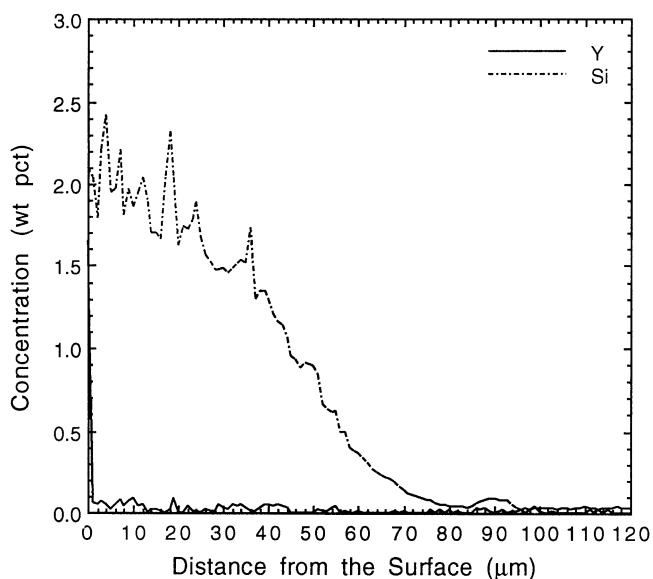

Fig. 10—Concentrations of yttrium and silicon which have diffused into a CP-Ti casting as a result of contact with a yttria/silica face coat with no preheat.

phase (the alpha phase) at 882 °C. The addition of aluminum to titanium raises the beta transus to 980 °C.[19] Because interstitials, in this case oxygen, are able to diffuse more readily in a body-centered cubic lattice,[20] more oxygen is able to diffuse into the CP-Ti because it retains the beta structure longer.

Figure 8 shows the effect of mold preheat temperature on the reaction between CP-Ti and the yttria/silica face coat. The results are similar to those seen in Figures 6 and 7, in that the higher mold preheat temperature resulted in higher hardness in the alpha-case layer. Once again, the results obtained from the alloyed titanium were similar to those from the CP-Ti, with the exception that the thickness of the alpha case was greater on the CP-Ti castings than on the Ti-6Al-4V castings.

It is of interest to note that the castings produced in molds with an alumina/silica face coat stripped cleanly from their molds, whereas those produced in the molds with a yttria/silica face coat adhered to the molds and caused the face coat to spall off upon separation from the casting. Figure 9 shows a secondary electron micrograph of the surface of a CP-Ti casting made in a preheated mold (800 °C) with a yttria/silica face coat. From the figure, it can be determined that titanium has penetrated the face coat, possibly because the yttrium oxide refractory did not sinter enough. Calvert[16] found that firing temperatures of at least 1200 °C were required; in fact, the best results came from a mold which was fired in a vacuum furnace at 1500 °C.

The thickness of the metal penetration shown in Figure 9 varied between 30 and 50 μm, depending on the mold preheat temperature. Castings produced in molds at RT had layers which were approximately 30 μm; castings produced in molds at 800 °C had layers closer to 50 μm. All other castings had layers that were between 30- and 50-μm thick.

By comparing data of the titanium-yttria/silica face coat interaction to data of the titanium-alumina/silica face coat interaction, it appears that no significant benefit was gained through the incorporation of the more thermodynamically stable yttria within the face coat. Even though the plots show that the yttria/silica face coat resulted in somewhat lower hardnesses in the alpha case, the thickness of the alpha case and the hardnesses beyond the alpha case are the same as those resulting from casting against an alumina/silica face coat.

B. *Microprobe Results*

In order to explain why the incorporation of a more stable refractory in the face coat did not reduce the thickness of the alpha case, microprobe analyses were carried out. From Figure 10, it is apparent that the reaction between a titanium casting and a yttria-rich face coat is fueled by the oxygen resulting from the decomposition of silica, not yttria. Figure 10 shows that only silicon has diffused into the casting, indicating that the yttria was left intact.

In drop castings made in molds with alumina/silica face coats, aluminum along with silicon was dissolved in the alpha-case layer. This is observable in Figure 11(b), which shows a significant amount of Al in a CP-Ti casting made in a mold with an alumina/silica face coat preheated to 800 °C. Figure 11(a), a backscattered electron micrograph of the mapped region, is provided to ensure that the metal/mold interface is recognizable. The cracks should also be noted,
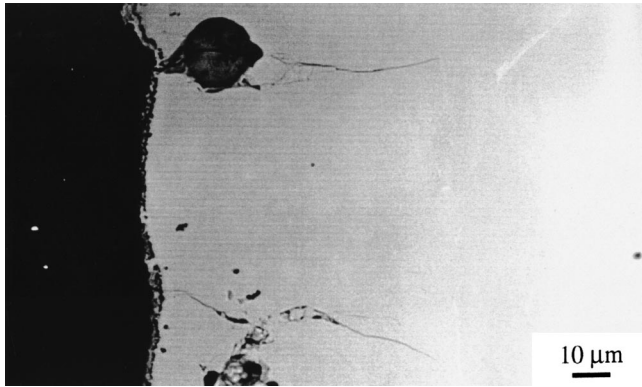
(a)

(b)
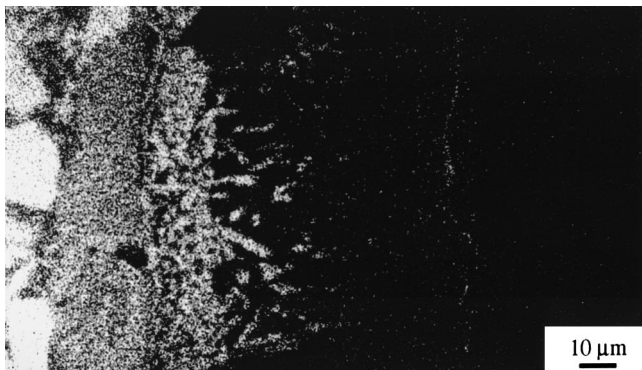
(c)

Fig. 11—The alpha case of a CP-Ti casting made in a mold with an alumina/silica face coat preheated to 800 °C. (a) Backscattered electron micrograph; (b) 20 wt pct aluminum map; and (c) 20 wt pct silicon map. The large silicon-rich particles in (c), located to the left side, are glass particles in the epoxy mounting material.

as they indicate the brittle nature of the alpha case. Figure 11(c) is included to illustrate that the silicon diffused into the casting in a different manner than the aluminum. While the aluminum is evenly dispersed, the distribution of Si has fingers ahead of the overall diffusion layer. This suggests the formation of a low-melting eutectic or grain boundary diffusion. Saha and Misra[21] indicated the formation of the low-melting Ti_5Si_3 + Ti eutectic at the metal mold interface during the casting of Ti in zircon ($ZrSiO_4$) sand molds. Although it was not determined whether this phase was a result of the interaction of titanium with free silica or silica derived from the zircon sand, their results did indicate that
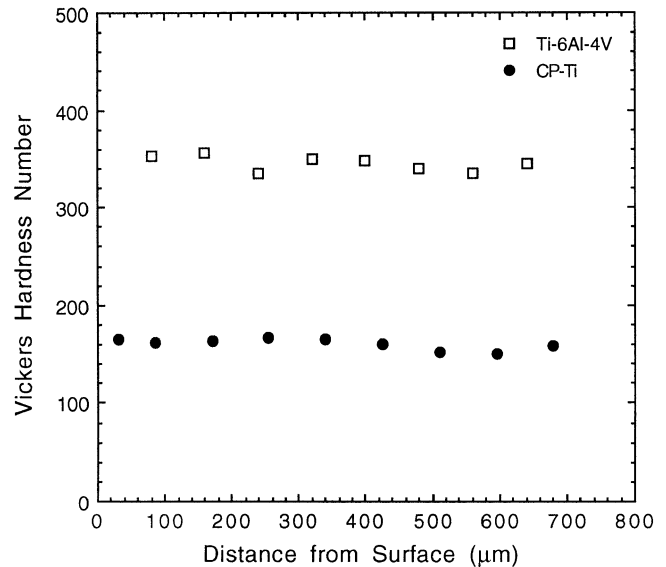

Fig. 12—Microhardness profiles of CP-Ti and Ti-6Al-4V castings produced in yttria crucibles preheated to 800 °C.

if the amount of free silica was lessened, then the Ti/mold reaction was likewise lessened.

C. *Analysis of Castings Produced in 100 Pct Yttria Molds*

Based on the results in Section B, it appears that the concentration of oxygen at the Ti/mold interface is set by the partial pressure of oxygen resulting from the reduction of silica. Therefore, in order to realize the benefit of using yttria, one must eliminate the silica. To determine whether this was indeed the case, an effort was made to make a face-coat slurry from yttria particles and yttrium acetate as the binder. Yttrium acetate converts to the oxide at elevated temperatures. Three problems were encountered: rapid and instantaneous gelation of the slurry, lack of green strength, and lack of mold strength after firing. We were not able to overcome these problems, so yttria crucibles (22 mm in diameter, 27-mm tall, and 2 mm in wall thickness with a porosity of less than 1 pct) were purchased and used as molds.

Figure 12 shows microhardness plots of CP-Ti and Ti-6Al-4V castings produced in crucibles preheated to 800 °C. As indicated by the plots, yttria appears to be an excellent mold material for titanium, as there is no indication of an alpha case. Figure 13, which shows an optical micrograph of the surface of a Ti-6Al-4V casting solidified in a yttria mold, further supports this observation, especially when it is compared to Figure 3(a). One should keep in mind, however, that the yttria crucibles were almost fully dense. Hence, the thermal conductivity of the crucibles must have been significantly greater than that of the shell molds, and the cooling rate was likewise greater. Indeed, the Widmanstätten microstructure of the drop casting in Figure 13 indicates that a relatively high cooling rate was achieved. However, even with the yttria crucible preheated to 800 °C, no evidence of an alpha case was seen.

By comparing microhardness data from castings produced in yttria crucibles with data from castings produced in molds with yttria/silica face coats (Figure 14), it becomes apparent that the benefits of yttria are not realized when it
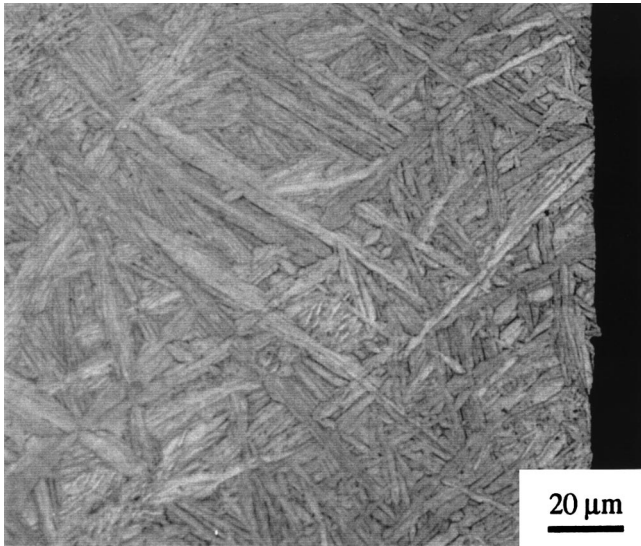
Fig. 13—Micrograph of Ti-6Al-4V casting produced in a yttria mold preheated to 800 °C. Etched with Kroll's reagent.
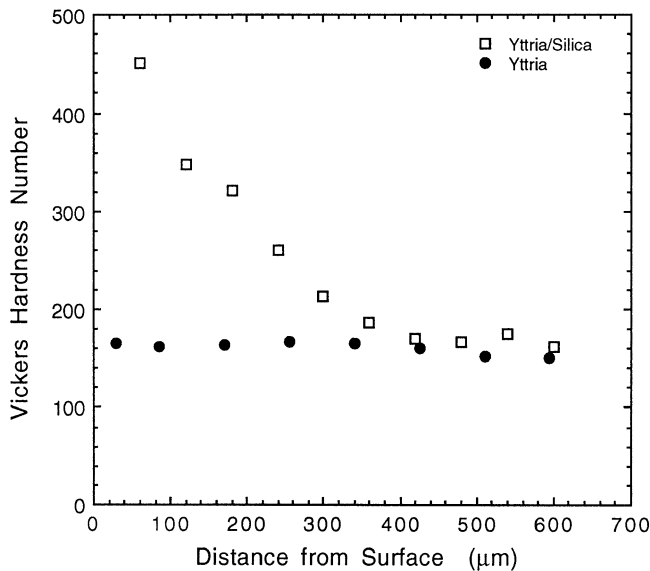

Fig. 14—Microhardness profiles from CP-Ti castings produced in either a yttria crucible or a mold having a yttria/silica face coat; molds were preheated to 800 °C.

is combined with a silica binder. Furthermore, these data indicate that if a silica-free yttria face coat were developed, then the alpha case might be reduced significantly or perhaps even eliminated in relatively small castings. Feagin,[22,23] however, reported encouraging results when he cast Ti-6Al-4V in molds, with a near 100 pct yttria face coat. His test castings were larger than our drop castings, albeit not necessarily typical in size of commercial castings, and had an alpha case of less than 3 μm.

IV. CONCLUSIONS

In this research, the effect of face coat composition on the reaction between titanium and an investment shell mold was investigated in order to identify the culprit responsible for the production of alpha case on titanium castings. The major conclusions of this research are the following.

1. Silica, used as a binder for the investment shell mold, drives the Ti/mold reaction regardless of the refractory used.
2. The use of a thermodynamically stable refractory, such as yttria, in a face coat might be an unnecessary expense when combined with a silica binder.
3. The benefit of using yttria as a face coat material to reduce the alpha case could be further enhanced, if a silica-free binder is developed.
4. Ti-6Al-4V castings had thinner alpha cases than those produced from CP-Ti.

APPENDIX
Estimation of cooling of drop castings

This analysis accounts for the cooling of the drop castings after they have solidified. The thermal thickness of the molds is much greater than the thickness of the mold, so that at least for the period to cool to 1500 K, we can assume that the mold behaves as a semi-infinite solid. Since a drop casting is relatively small and metallic, we assume that its temperature is uniform during cooling.

The loss of energy by radiation (J s^{-1}) from the drop casting is

$$Q_R = A_T \sigma \varepsilon (T^4 - T_s^4) \qquad [A1]$$

where A_t is the area of the top surface of the casting; σ is the Stefan–Boltzmann constant; ε is the emissivity; T is the temperature of the casting; and T_s is the temperature of the surroundings. The loss of energy by conduction from the casting and into the ceramic shell mold is

$$Q_M = \frac{A_s k (T - T_0)}{(\pi \alpha t)^{1/2}} \qquad [A2]$$

where A_s is the area of the conical side of the casting; k, α, and T_0 are the thermal conductivity, thermal diffusivity, and temperature, respectively, of the ceramic shell mold; and t is the time. Equation [A2] is strictly applicable to the case where T is constant, but here, we use Eq. [A2] as an approximation updating T with time as the drop casting cools.

The casting cools according to

$$\rho' V C_\rho' \frac{dT}{dt} = Q_R + Q_M \qquad [A3]$$

where ρ' and C_ρ' are the density and specific heat of the casting and V is its volume. Numerical solutions of Eqs. [A1] through [A3] were obtained by calculating T after small time-steps of 5×10^{-4} s. The cooling curves shown in Figure 4(a) were calculated in this way. Since perfect thermal contact between the casting and the mold was assumed, the calculations overestimate the cooling rates.

The following properties and dimensions were used in the calculations: $A_s = 3.42 \times 10^{-4}$ m²; $A_T = 2.27 \times 10^{-4}$ m²; $V = 7.3 \times 10^{-7}$ m³; $\rho' = 4510$ kg m⁻³; $\varepsilon = 0.2$; $k = 0.7$ J m⁻¹ K⁻¹ s⁻¹; $C_\rho = 1100$ J kg⁻¹; $\rho = 1800$ kg m⁻³; and $C_\rho' = 414 + 0.166\, T$, J kg⁻¹.

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