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**THE EFFECT OF SILICA-CONTAINING BINDERS
ON THE TITANIUM/FACE COAT REACTION**

by

Christian Frueh

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This thesis has been approved on the date shown below:

David R. Poirier
David R. Poirier
Professor of Materials Science and Engineering

2-27-95
Date

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS	6
LIST OF TABLES	10
ABSTRACT	11
1. INTRODUCTION	12
2. BACKGROUND ON MOLD DEVELOPMENT FOR CASTING TITANIUM	16
3. EXPERIMENTAL PROCEDURES	30
3.1 Mold Production	30
3.1.1 Mold with an Alumina/Silica Face Coat	30
3.1.2 Mold with a Ytria/Silica Face Coat	38
3.1.3 Mold with a 100% Ytria Face Coat	38
3.2 Melting Technique	39
3.2.1 Furnace Design	39
3.2.2 Casting Experiments	42
3.2.3 Contact Experiments	44
3.3 Specimen Preparation	47
3.3.1 Mounting/Polishing	47
3.3.2 Etching/Photographic Documentation	48
3.4 Analysis of Castings	49
3.4.1 Microhardness Testing	49
3.4.2 Microprobe Analysis	51
3.4.3 SIMS Analysis	51
3.5 Analysis of Ti-6Al-4V Buttons Resulting from Contact Experiments	52
3.5.1 Microhardness Testing	52
3.5.2 SIMS Analysis	52
3.5.3 Image Analysis	52

TABLE OF CONTENTS — *Continued*

4. RESULTS AND DISCUSSION	54
4.1 Casting Experiments	54
4.1.1 Analysis of Castings Produced in Molds with an Alumina/Silica Face Coat	54
4.1.2 Analysis of Castings Produced in Molds with a Yttria/Silica Face Coat	68
4.1.3 Analysis of Castings Produced in Yttria Crucibles	82
4.2 Contact Experiments	92
4.2.1 Microhardness Analysis of Ti-6Al-4V Buttons Produced in Yttria Crucibles	92
4.2.2 SIMS and Image Analysis of Ti-6Al-4V Buttons Produced in Yttria Crucibles	92
5. CONCLUSIONS	97
APPENDIX	98
REFERENCES	105

LIST OF ILLUSTRATIONS

Figure

1	A schematic of a typical system used for investment casting titanium [courtesy of ASM International] [4]	14
2	Sequence of steps in producing an investment shell mold	17
3	Cross section of a completed investment shell mold prior to pattern removal	19
4	Wax investment used for experimental castings: (a) aluminum die and (b) resulting wax pattern after mounting	36
5	The containerless furnace used to produce castings	40
6	Cross section of a casting and its mold; the arrows point to microhardness traverses	45
7	Cross section of the furnace used for Ti-6Al-4V/Y ₂ O ₃ contact experiments	46
8	Micrograph of a typical Vicker's microhardness traverse across the surface of a Ti-6Al-4V casting	50
9	Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat	55
10	Microhardness profiles of Ti-6Al-4V castings produced in molds having an alumina/silica face coat	56
11	Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in molds having an alumina/silica face coat	59
12	Microstructures from CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C. Etched with Kroll's reagent	60
13	Microstructures from Ti-6Al-4V castings made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C. Etched with 50% glycerin 50% HF	62

LIST OF ILLUSTRATIONS — *Continued***Figure**

- 14 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 63
- 15 20% silicon map of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C 65
- 16 20% aluminum map of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C 66
- 17 Backscattered electron micrographs of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C 67
- 18 Concentrations of aluminum and silicon which have diffused into a CP-Ti casting as a result of its contact with an alumina/silica face coat with no preheat 69
- 19 Concentrations of aluminum and silicon which have diffused into a CP-Ti casting as a result of its contact with an alumina/silica face coat preheated to 800°C 70
20. Microstructure of a CP-Ti casting made in a mold with a yttria/silica face coat, preheated to 800°C. (a) SEM image and (b) a 100% titanium map of the same region 71
- 21 Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat 73
- 22 Microhardness profiles of Ti-6Al-4V castings produced in molds having a yttria/silica face coat 74
- 23 Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in molds having a yttria/silica face coat 75

LIST OF ILLUSTRATIONS — *Continued***Figure**

24	Concentration of yttrium and silicon which has diffused into a CP-Ti casting as a result of its contact with a yttria/silica face coat with no preheat	77
25	Concentration of yttrium and silicon which has diffused into a CP-Ti casting as a result of its contact with an yttria/silica face coat preheated to 800°C	78
26	Microhardness profiles of CP-Ti castings produced in molds preheated to 800°C	80
27	Microhardness profiles of Ti-6Al-4V castings produced in molds, preheated to 800°C	81
28	Microhardness profiles of CP-Ti castings produced in yttria molds	83
29	Microhardness profiles of Ti-6Al-4V castings produced in yttria molds	84
30	Micrograph of Ti-6Al-4V castings produced in yttria molds (a) with no preheat and (b) preheated to 800°C. Etched with Kroll's reagent	85
31	Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in yttria molds	86
32	Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in alumina/silica, yttria/silica, and yttria molds with no preheat	87
33	Concentration of yttrium which has diffused into a CP-Ti casting as a result of its contact with a yttria mold	89
34	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	90
35	Microhardness profiles from Ti-6Al-4V castings produced in either a yttria crucible or a mold having a yttria/silica face coat; molds were preheated to 800°C	91

LIST OF ILLUSTRATIONS — *Continued***Figure**

36	The oxygen concentration gradient, as determined by SIMS, in Ti-6Al-4V buttons melted and held above the liquidus for 15 s and 30 s in yttria crucibles	93
37	Secondary electron micrographs taken of the surface of a Ti-6Al-4V button made in a yttria crucible: (a) distribution of precipitates at grain boundaries and (b) blocky appearance of a large precipitate	94
A1	Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat	98
A2	Microhardness profiles of Ti-6Al-4V castings produced in molds having an alumina/silica face coat	99
A3	Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat	100
A4	Microhardness profiles of Ti-6Al-4V castings produced in molds having a yttria/silica face coat	101
A5	Microhardness profiles of CP-Ti castings produced in yttria molds	102
A6	Microhardness profiles of Ti-6Al-4V castings produced in yttria molds	103
A7	Microhardness profiles of castings (CP-Ti and Ti-6Al-4V) produced in molds, preheated to 350°C, having an alumina/silica face coat	104

LIST OF TABLES

Table

1	Properties of the Binders Used in Making the Investment Shell Mold . . .	31
2	Typical Particle Size Distributions of Fused Silica Used in Face Coat and Backup Coat Slurries	32
3	Stucco Coat Details	33
4	Particle Size Distribution of RG-2	34
5	Particle Size Distribution of 70 Grit Alumina	34
6	Particle Size Distribution of 54 Grit Alumina	35
7	Chemical Analyses of Alloys in Weight Percents	43
8	Chemical Analysis of Ultra High Purity Argon	43
9	Chemical Analysis of Ultra High Purity Helium	47

ABSTRACT

The interactions of CP-Ti and Ti-6Al-4V with investment molds with alumina/silica and yttria/silica face coat systems, and yttria crucibles were studied. It was found that the thickness of the reaction layer (alpha case) was the same, whether a yttria/silica or alumina/silica face coat was used, indicating that it is the silica binder truly which reacts with the titanium. Furthermore, it was found that only the yttria crucible was inert to reacting with titanium when it was used as a mold. When titanium was heated in yttria crucibles, however, and held just above the liquidus for 15 s and 30 s, oxygen and yttrium were found in the resulting samples. This indicates that commercial castings requiring longer solidification times might not be free of the alpha case even when produced in a 100% yttria mold system.

Chapter 1

INTRODUCTION

High strength, low density, and corrosion resistance are desirable properties of titanium alloys in the aerospace, chemical and energy industries. Although titanium alloys were used as early as 1950 [1], titanium investment castings were not used very much for another twenty years [2]. Industry's hesitation to consider titanium castings as a viable alternative to existing materials seems unjustified, especially when one considers that, unlike other alloy systems, titanium castings have a good combination of tensile properties, fracture resistance, and creep strength [3], and they are nearly equal in strength to their wrought counterparts [4]. Impeding the use of titanium castings, however, has been the difficulty associated with producing castings of sufficient quality and low enough cost to allow for their widespread use.

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; (3) obtaining significant amounts of superheat ($> 100^{\circ}\text{C}$) is made impossible by current melting techniques; and (4) it is highly reactive with nearly all gasses, liquids, or solids when at temperatures above 500°C [5]. Although each of these items presents processing difficulties, it is the latter which hinders the capability of titanium casting technology.

Liquid titanium has been termed "the universal solvent" [6] because 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 a fraction of these interstitials is required to destroy its ductility [7,8]. To avoid contamination of the melt, titanium is usually melted in a consumable electrode vacuum arc system, in which a water cooled copper crucible contains the metal in its "skull." Once melting begins, a solid layer of titanium is formed on the inner surface of the crucible which, along with the vacuum, protects the titanium from contamination.

Although a water-cooled copper crucible allows for the melt to be contained, it is difficult to obtain any superheat. Therefore, in order to achieve desired mold fill characteristics titanium foundries compensate for this lack of superheat, by using a centrifugal table, preheating molds, or both [4]. Figure 1 shows a schematic diagram of a typical arrangement used when casting titanium.

Much effort has gone into trying to develop a mold which is resistant to titanium. Typically, the focus has been on the first layers of the mold, known as the face coat. The face coat is comprised of two main components: (1) a binder and (2) a refractory of choice. These two components are mixed in slurry tanks. To date, however, no face coat system exists which prevents the formation of alpha case.

Existing face coat systems react with titanium because commercially available binders are based on colloidal silica. In other words, even if the chosen refractory should, by thermodynamic accounts, be inert to titanium, a reaction still progresses because the face coat has silica in it. Many recent investigations, therefore, have focused on developing a silica free binder material [9-16].

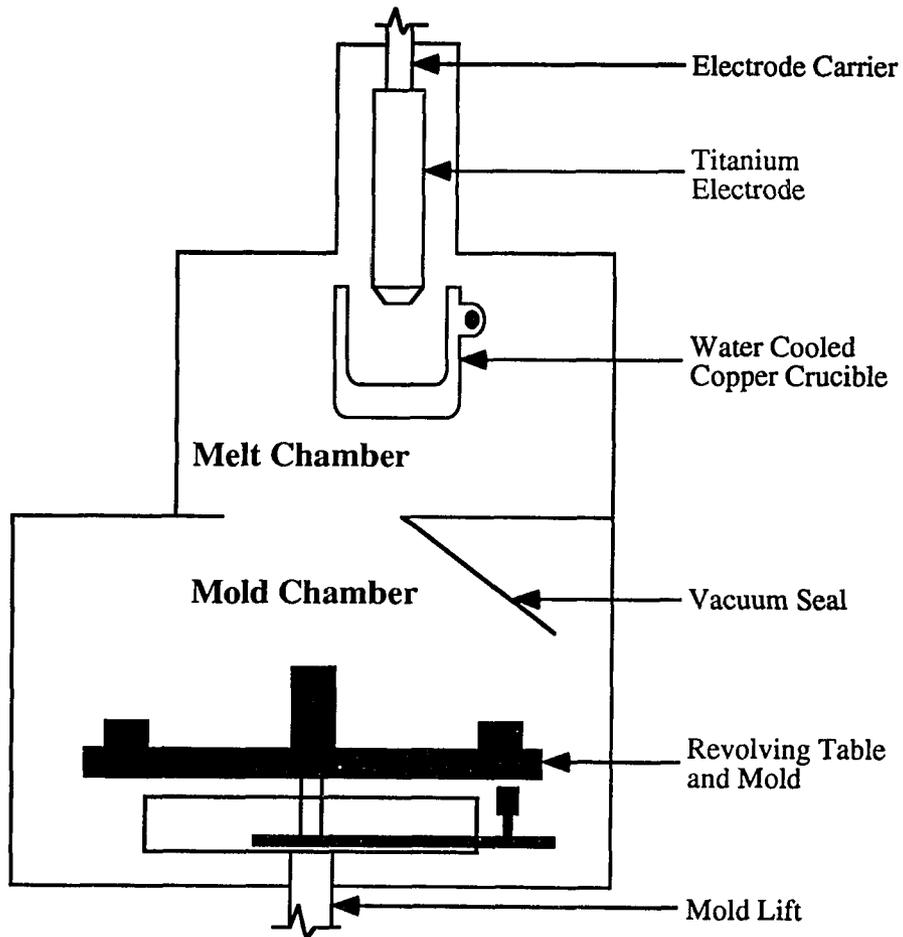


Fig. 1. A schematic of a typical system used for investment casting titanium [courtesy of ASM International] [4].

The main goal of this research is to determine whether silica, used as a binder for investment shell systems, is the prime cause of the reaction between titanium and investment shell molds. Furthermore, it is hoped that this work will convince those in industry that, until silica is eliminated from a shell system, the use of costly refractories such as yttria, zirconia, and hafnia is an unnecessary expense. In this thesis, the effect of a silica containing binder material on the production of CP-Ti and Ti-6Al-4V castings was studied, and the use of yttria as a mold material was investigated.

Chapter 2

BACKGROUND ON MOLD DEVELOPMENT FOR CASTING TITANIUM

The process of making an investment shell mold begins with a wax replica of the desired part. This replica is then, after cleaning or etching, dipped into a slurry comprised of a finely ground refractory, a liquid vehicle, a binder material, and additives such as wetting agents and green strength promoters. A foundry typically purchases the liquid vehicle, binder material and additives together, packaged as one item called the binder material. So as to follow industrial practice, hereafter these separate items are simply called the binder. The binder is mixed with the separately purchased refractory on site. After dipping in the wet slurry, the pattern is stuccoed with ceramic particles, and then allowed to dry. The sequence of dipping, draining, stuccoing and drying is continued until an investment shell mold of desired thickness and strength is produced. An extra step, known as the prewet, is used by some foundries to add strength to the mold, but it is often omitted because it adds cost to the investment process and can cause delamination of the mold. A flow chart, describing the sequence of events when producing an investment shell mold, is illustrated in Figure 2.

Not apparent in the flow chart are the sizes and composition of the particles used in the stuccos. Typically, the first four layers are stuccoed with particles of progressively coarser grades, which increases the strength of the mold and provides for permeability needed to accommodate the gasses generated during dewaxing and

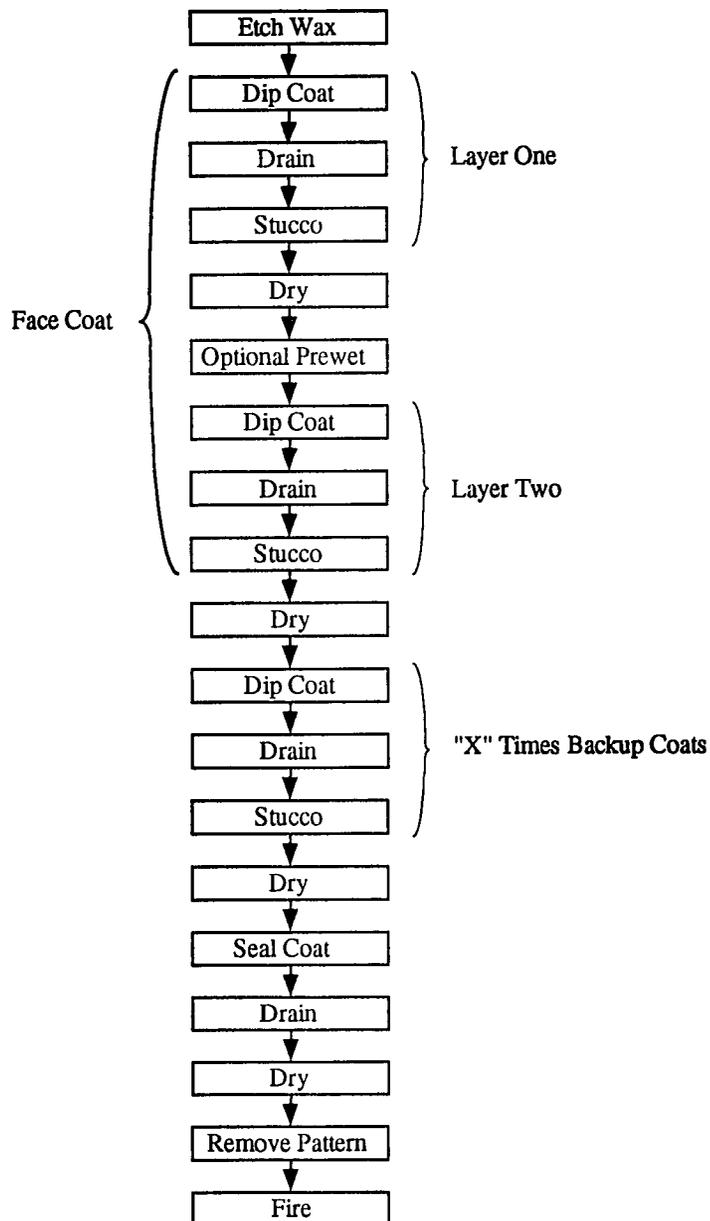


Fig. 2. Sequence of steps in producing an investment shell mold.

casting [17]. Particles used in the outer layers are usually of the same grit size. The composition of the stuccoing material used by foundries is highly varied, but a typical arrangement might use alumina (Al_2O_3) for layers 1 and 2, 50% alumina/50% silica (SiO_2) for layer 3, and silica (SiO_2) for the rest.

The size, concentration, and type of refractory used in the slurry are not the same for all layers. Typically two different slurries are used: a face coat (prime coat) slurry, and a backup slurry. The face coat slurry is specially formulated to eliminate buckling, lifting, cracking, and other casting surface defects and finish problems [18]. The composition of the face coat is unique to a foundry and often proprietary. The remaining layers are known as the backup coats. A cross section of a shell mold prior to removing the wax pattern can be viewed in Figure 3.

Much work has gone into trying to develop a mold which is inert to titanium. To date, however, no shell mold has been developed which when used to produce titanium investment castings eliminates the production of the alpha case. Although the results from a smattering of government sponsored projects have been published, most attempts to develop an inert mold remain proprietary or are published in the form of patent claims.

Past works to develop a nonreactive mold have focused on developing new binder materials and refractories, trying new binder/refractory combinations, and using metal-forming inhibitors in the shell mold.

Most commercial binders are made from colloidal silica [19]. By comparing the free energies of reacting silica with titanium, one can predict that silica is apt to

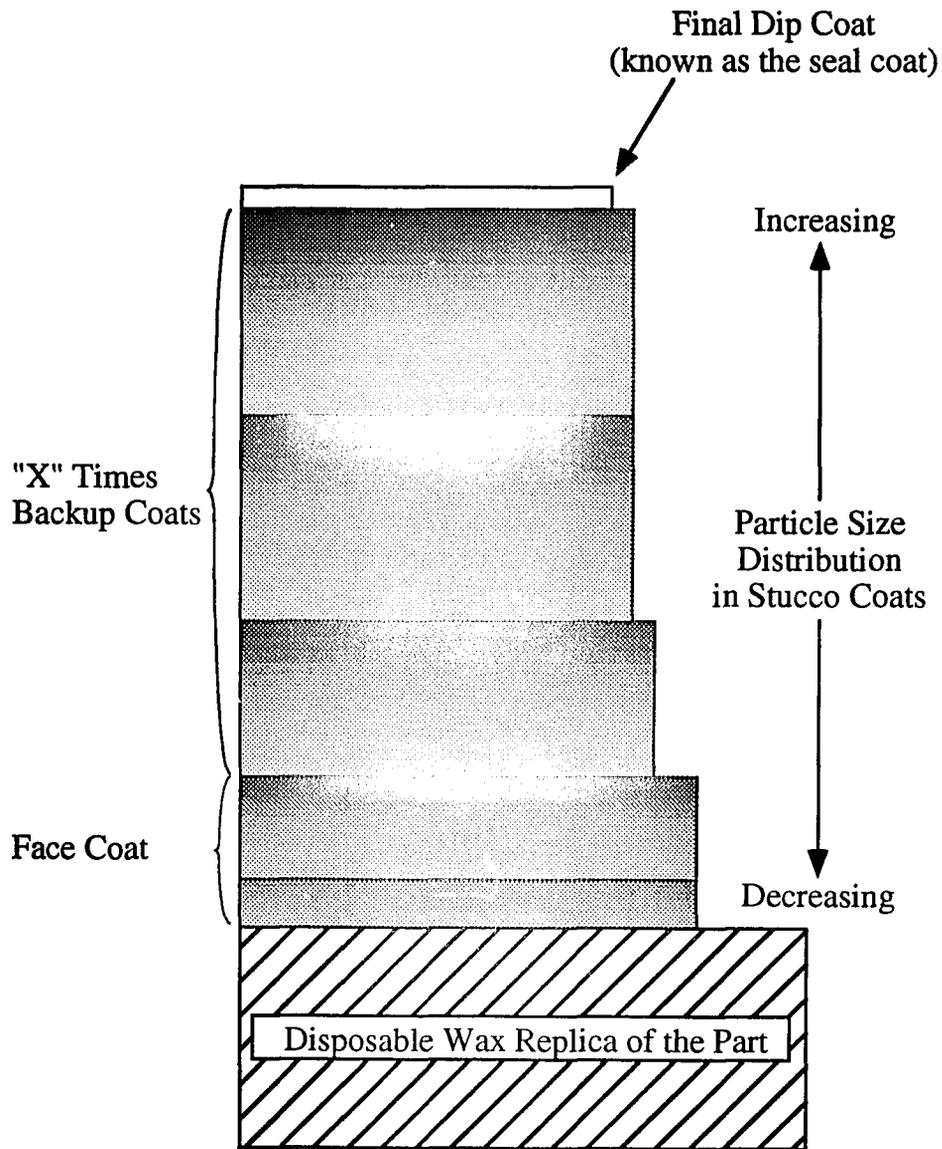


Fig. 3. Cross section of a completed investment shell mold prior to pattern removal.

react with titanium. However, when titanium makes contact with a face coat it must confront not only the binder but the refractory as well; therefore, the true impact of a silica binder on the titanium/face coat reaction is difficult to ascertain. Nevertheless, many concerned with titanium casting have justified their efforts to develop a silica-free binder on the assumption that it is the prime cause of alpha case in titanium.

Feagin used both an acidic zirconia sol [9-11] and a yttria sol [12,13] as a binder for various refractories, particularly zirconia and yttria, and blends thereof. A face coat of 99% yttria resulted in a reaction layer which was less than 3 μm in most regions, the best result offered in any literature on titanium casting [12,13]. There were, however, areas on the casting with an alpha case as thick as 180 μm . Feagin attributed these to "inconsistencies of the process used in making the surface" [12]. It should also be noted that the molds used were small, and no quantitative data were provided concerning the green strength of the mold and slurry shelf life, both important properties of commercial products. For a slurry to be used on an industrial scale, it must remain fluid for long periods of time [19]; in other words it should not gel until it has made contact with the wax. Feagin did acknowledge that gelation was a problem, and states that "several proprietary techniques were used" [13] to prevent this from happening.

A comprehensive work by Calvert [14] used a zirconia forming binder in combination with calcia-stabilized zirconia that resulted in a minimal reaction layer. For example, CP-Ti cast into a zirconia mold, vacuum fired at 1500°C for 2 hours, had a reaction layer between 25 and 75 μm thick. This result is even more

impressive when one considers that the casting was 9 cm in diameter in some portions.

Although not suggested by Calvert, it is possible that by firing the zirconia mold in a vacuum, oxygen is removed from the surface, resulting in a substoichiometric face coat (ZrO_{2-x}) which could be more resistant to titanium than stoichiometric zirconia. By examining a Zr-O phase diagram it is apparent that a nonstoichiometric compound exists in three crystallographic forms [20]. High firing temperatures, however, can adversely affect the dimensional tolerances of the mold. Calvert addresses this issue by stating that: "care was taken to stay below the temperature at which sintering would occur in order to avoid distortion and maintain the close dimensions of the mold," although no further comment was made regarding the dimensional integrity of the produced castings. In reference to Feagin's [13] work, it should be mentioned that yttria was considered by Calvert to be an acceptable face coat except for the "rapid gelation of the slurries and the tendency of the coating to crack or spall during firing." His comment seems to indicate that the surface anomalies on Feagin's casting were not due to a processing error, as suggested, but rather to face coat delamination and titanium reacting with the backing coats.

Schneider [15] attempted to "lock up" the silica present in the binder (colloidal hydrolyzed silicic acid) by mixing it with magnesium carbonate which, when fired, resulted in the production of the more stable forsterite (Mg_2SiO_4). With regard to the performance of the mold material, the only information Schneider gives involves a

chromium-based casting which, he states, "was characterized by an immaculate surface."

Nakamura *et al.* [16] also used a zirconia binder (zirconium oxyacetate) to hold together a face coat of zirconium, and yttria-stabilized zirconia. The zirconium powder controlled mold expansion and served as a barrier to the diffusion of oxygen into the titanium. The alpha case observed by the authors was 200 μm thick, which seems to indicate that the firing techniques employed by Calvert were beneficial since the use of his zirconia face coat resulted in a thinner reaction layer. Also affecting the titanium/mold reaction could be their use of a "commercially available phosphate-bonded material" for the backup coats, unlike Calvert who used the zirconia forming binder throughout. The effect of the backup coat on the metal/mold reaction can be further inferred by examining the work by Taira *et al.* [21]. In this case the experimental methods and the mold material were exactly the same as those used by Nakamura *et al.*, except for the use of titania in the second layer of the face coat instead of zirconia, and the omission of zirconium. The result was an alpha case five times greater than found by Nakamura *et al.*

The impetus for using zirconia sols, such as those mentioned above, in investment molds is likely to have come from the knowledge that they have been used effectively as binder materials for refractory objects such as melting crucibles [22-24]. Much information resulting from past efforts to develop a refractory crucible for containing liquid titanium has in fact proven to be of benefit to those interested in investment casting. Guidance as to which material might be effective in an

investment mold can be extracted from crucible data, providing one remembers that a mold is in contact with a reactive metal for only a short period, unlike a melting crucible which contains a melt considerably longer.

Consider the comprehensive series of works, by Chapin and Friske [25-27], who investigated the use of various oxides (Al_2O_3 , BeO , ZrO_2 , ThO_2 , Gd_2O_3), carbides (TiC , ZrC , VC , NbC , TaC , WC), borides (TiB_2 , ZrB_2 , CrB_2), a sulfide (CeS), carbon and graphite as possible container materials for titanium. Chapin and Friske found that not one of the selected materials was inert to titanium. Titanium melted in a thoria crucible, for example, was found to contain an average of 5.44% thoria. Because this contamination is deleterious to metal quality the use of thoria as a crucible material is unacceptable; yet, as indicated by Yasrebi, thoria is regarded to be the refractory of choice when making a shell mold because it is "very stable against titanium" [28]. However, it is of interest to note that Precision Castparts no longer uses thoria in its shell systems because its radioactive nature makes disposal very expensive.

It should be apparent that, although useful as a source for ideas and guidance, information from projects which have attempted to develop a refractory crucible for melting titanium can be misleading if one is too hasty to eliminate a material from consideration as a mold material because it did not function well as a crucible.

Others who have been concerned with the development of a refractory to contain liquid titanium include Brace (Al_2O_3 , BeO , ThO_2) [29], Garfinkle and Davis (TiC , ZrC , Cr_3C_2 , TiB_2 , MoB_2 , CrB_2 , TaB_2 , MoSi_2 , CeS) [30], Crandall *et al.* (Zr_3Si , Mo_2Zr , Mo_3Al) [31], and Weber *et al.* (TiC , Ti_2O_3 , $\text{TiO}_{0.42}$, $\text{TiO}_{0.26}$, ThO_2 , ZrO_2

stabilized with MgO, **ZrO₂ stabilized with Ti**) [32]. The materials in bold type in each set were found to perform the best; however, in each case none of the materials tested was found to be inert to liquid titanium.

Eisenberg and Stavrolakis [33] developed oxide crucibles which were stabilized by fluorides. Fluorine seemed appealing because it has little or no solubility in titanium. Some of the oxide-fluoride crucibles included: $\text{La}_2\text{O}_3 \cdot \text{LaF}_3$, $3\text{ZrO}_2 \cdot 2\text{CaF}_2$, and $\text{ZrO}_2 \cdot \text{MgF}_2$. Microhardness tests, however, indicated that a severe reaction took place in each case, and the authors were unable to produce a stable crucible.

Many researchers interested in developing a melting crucible for titanium use thermodynamics to help them identify materials which should be tried. Their analyses typically involve a comparison of the free energy of formation of the candidate material to that of the corresponding titanium phase; for example, CaO vs. TiO, ZrC vs. TiC, and HfO₂ vs. TiO₂. If the free energy of formation of the candidate material at an elevated temperature—typically corresponding to the melting temperature of titanium—is more negative than that of the titanium phase, then it should be considered. This is a rather simplistic approach because, as indicated by Saha *et al.* [34], it neglects to consider solution effects. It is due to a lack of data that such effects are often impossible to evaluate.

Because of its thermodynamic stability, yttria has received considerable attention by crucible developers [35,36]. Yttria does have drawbacks, one of which is its lack of thermal shock resistance, although it should be noted that efforts have been

made to correct this problem [37]. Work has also been done with substoichiometric yttria [38-40]. 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. Yttrium not soluble in the titanium is believed to scavenge oxygen from the solution and precipitate as yttria, resulting in a softening of the titanium matrix. It is because of this softening effect that yttrium has recently received attention as an addition to titanium to render it stronger and more ductile [41]. The authors indicate that further alteration of the stoichiometry of yttria may lead to a yttria crucible which is inert to titanium. They were also of the opinion that the altered yttria would serve as an excellent mold material [38-40].

By examining data from the crucible studies cited above, one is able to get ideas as to which material(s) are the least likely to cause the formation of alpha case in titanium. For example, yttria, substoichiometric yttria and cerium sulfide fared relatively well in melting experiments and should therefore be tried as mold materials. The problem with this information is that it is not directly transferable. Using yttria as an example, when titanium comes in contact with a yttria *crucible* it interacts with a material that is 100% yttria, but when in contact with a yttria *mold* it interacts with, not only yttria, but also the binder. The binder is necessary, because without it the only way to form a robust structure would be to sinter the base material; this is not an option because the dimensional integrity of the mold would be lost to distortion caused during sintering. In commercially available binder materials, based on silica

with a glassy phase, sintering takes place at a lower temperature with less of a tendency for distortion [42].

As discussed above, most binders use silica as a low temperature sintering aid, and many different refractory materials have been combined with them in an effort to develop a shell system for titanium. Schuyler *et al.* [43,44], Richerson and Schuyler [45], and Lassow *et al.* [46], combined yttria with a siliceous binder. The latter reported a 79% average reduction in alpha case when using yttria instead of zirconia. According to Hendricks [42] binding agents based on silica include "conventional colloidal silica, new generation colloidal silica, ethyl silicate and hybrids using ethyl silicate."

Besides the binder and refractory material, researchers have also investigated the effect of metal-forming inhibitors on the titanium/mold reaction. For example Brown [47,48] added a tungsten and/or molybdenum compound "inhibitor-former" to the face coat slurry. This compound is reducible by hydrogen to metallic tungsten or molybdenum, thereby creating a physical barrier which protects the binder from attack by the titanium. Some of the metal-forming inhibitors suggested by Brown include oxides such as MoO_2 , and WO_3 ; acids such as tungstic acid and molybic acid; double salts such as yttrium metatungstate; and alkoxides such as tungsten ethoxide ethylate. Basche [49] also investigated the effect of a metal forming addition, but instead of adding it to the slurry he impregnated the mold by soaking it in an aqueous solution of tungstic acid and ammonium hydroxide. The saturated mold was then fired to convert the tungsten compound to metallic tungsten or tungsten oxide. In this

case a thin continuous tungsten film is present throughout the porous mold, resulting in an electrically conductive mold (which might allow it to be preheated by conventional electromagnetic heating methods). Neither of the studies reported on the effectiveness of these additions on the formation of alpha case in titanium.

The addition of metal powders to ceramics is effective in altering physical properties such as thermal shock resistance [50]. Brown and Brown [51,52] used this technique to increase the resistance of a face coat to reactive metals. Their face coat recipe used metallic columbium, tantalum, or tungsten in combination with refractory metal oxide binders such as colloidal yttria, thoria, hafnia, and zirconia or refractory metal oxide forming binders such as hafnium chloroalkoxides, and zirconium alkoxides.

Graphite [53] has long been relied upon as a mold material when making titanium investment castings and is in fact still used today [54]. Typically used when making larger castings [3,54] graphite has also been suggested for use as an investment mold material. Operhall [55], for example, discussed the use of graphite as an investment mold face coat; Morozov [56] and Zusman and La Voie [57] combined graphite with various resins in an effort to make molds; and Lirones [58-61] made an investment shell mold with a colloidal graphite binder, graphite flour and graphite stucco. It is of interest to note that Lirones [62] also impregnated the molds between layers with various organic resins, which upon firing in an *inert* atmosphere decompose to form a protective carbonaceous coating. The use of graphite, however, is likely to result in an undesirable TiC interface layer [26].

Much of the recent work involving titanium mold development has been encouraged by the dental industry. There has been an ongoing effort in the dental casting industry to find a low cost alternative to the precious alloys currently used in dental applications. Nickel-chromium alloys, for example, have been used in Japan for the past ten years as crown or bridge and porcelain-fused-to-metal restorations instead of gold or silver alloys, although recent questions have been raised concerning their biocompatibility [63]. Titanium offers many advantages over conventional dental casting alloys: low cost, mechanical properties which are in many cases better than those of Type III or IV gold, Ni-Cr, and Co-Cr alloys, excellent corrosion resistance, and low specific gravity [63]. However, once again, the reactivity of titanium discourages its use.

Investigators who have examined metal/mold reactions, specific to the dental industry, include Ida *et al.* [63], Takahashi *et al.* [64], and Wictorin *et al.* [65]. Nakamura [66,67] suggested using a one step method to producing a dental mold for casting titanium. A slurry comprised of silica, alumina, phosphate, and a basic metal oxide is packed into a container with the wax replica of the dental implant. The phosphate causes the slurry to spontaneously harden around the wax, effectively producing an "instant mold" with only one layer, similar to a full mold investment. The results seem to indicate that this recipe could not be used for aerospace castings, however.

Although many materials and techniques have been used in an effort to develop an inert mold, price has been often neglected. For example, Saha *et al.*

[34,68] evaluated rare earth oxides for use in face coats for investment casting titanium and found yttria to fare the best. Assuming an acceptable yttria slurry could be developed and its use resulted in the reduction of the alpha case, one might ask, "Can a foundry afford to use it?" According to Prigent and Debuigne [69], who investigated the use of calcia as a face coat, the use of yttria would be limited by its "prohibitive cost." Indeed, the \$40-\$80/lb [70] price tag for yttria seems very high especially when compared to the cost of materials such as alumina, silica, and even zirconia. However, as indicated by Yasrebi [28], the cost of a mold material is really insignificant when one considers the final price of a titanium casting. He also stated that many of the materials tried by his company, although expensive initially, dropped quickly in price with increased use.

This thesis questions not the expense of materials such as yttria but whether the expense is really necessary if they must be bonded with silica. As mentioned earlier, commercially available binder materials used for producing investment molds contain silica, a material which is known to react with titanium. In this thesis, it is found that the siliceous binder drives the Ti/mold reaction, regardless which refractory is used. Hence, the use of thermodynamically stable materials such as yttria is an unnecessary expense.

Chapter 3

EXPERIMENTAL PROCEDURES

3.1 Mold Production

Three different molds were used for making CP-Ti and Ti-6Al-4V castings; two were true investment shell molds, each with a different face coat, and one was a yttria crucible. The latter represented what might be achievable were a silica free investment mold developed.

3.1.1 Mold with an Alumina/Silica Face Coat

Two slurries, 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; properties of each are given in Table 1. Although both binders are based on colloidal silica and have similar properties, the Primcote is designed to prevent surface defects and finish problems [71].

*Primcote™: Ransom & Randolph, 120 West Wayne St., Maumee, OH 43537.

**Nyacol™: PQ Corporation, PO Box 840, Valley Forge, PA 19482.

Table 1

Properties of the Binders Used in Making the Investment Shell Mold*

Binder	Face Coat Binder: Primcote™	Backup Coat Binder: Nyacol™
Silica, Wt. %	30	30
Particle diameter, μm	10	10
pH @ 25°C	10.5	10.6
Viscosity @ 25°C, cps	8	< 10
Density, lbs/gal	10	9.85
Specific gravity	1.2	1.18
Na ₂ O, Wt. %	0.55	0.48
Particle Charge	Negative	Negative
Color	Greenish Yellow	Opalescent
Price (approx.)	\$0.65/lb	\$0.55/lb

*Properties obtained from data sheets provided by the manufacturer.

For this shell system the Primcote was combined with Remasil-60* (aluminosilicate) and RP-1** (fused silica). The powders (-325 mesh) were added in a 10:1 ratio, respectively; the viscosity of the slurry was kept between 20-30 seconds, No. 5 Zahn cup. Deionized water was added as necessary to reduce the viscosity. By controlling slurry properties, such as density, binder solids content, and pH, a

*Remasil™ 60: Remet Corporation, PO Box 278, Bleachery Place, Chadwicks, NY 13319.

**RP-1: Remet Corporation, PO Box 278, Bleachery Place, Chadwicks, NY 13319.

foundry can increase slurry life [19]. As expected, these properties remained fairly constant (density: 2000 kg m⁻³, solids content: 30%, pH: 10), since the molds were small in size and number. The binder solids content based on the density of the slurry was determined using a formula supplied by the manufacturer [72].

The backup slurry used Nyacol 830 binder in combination with RP-2* (fused silica). The difference between the fused silica in the face coat slurry and that in the backup slurry lies in the size distribution of the particles. A comparison of typical particle size distributions of RP-1 and RP-2 may be found in Table 2.

Table 2

Typical Particle Size Distributions of Fused Silica
Used in Face Coat and Backup Coat Slurries*

Mesh	RP-1	RP-2
+50	n/a	0-0.5
+80	0-0.5	n/a
+100	0-0.5	3-11.5
+140	0-4	7-13
+200	3-9	10-15
+325	13-20	16-23
Pan	69-81	45-55

*Particle size distributions obtained from a data sheet provided by the manufacturer.

*RP-2: Remet Corporation, PO Box 278, Bleachery Place, Chadwicks, NY 13319.

A total of six stucco coats were applied: coats 1-4 were varied in grit size and composition, and coats 4-6 were the same. Table 3 provides information about the stucco coats, and Tables 4-6 give the particle size distributions of Remet RG-2*, Norton 54** grit alumina, and Norton 70 grit alumina, respectively.

Table 3
Stucco Coat Details

Stucco	Trade Name	Manufacturer	Material
1	70 Grit Alumina	Norton	Alumina
2	54 Grit Alumina	Norton	Alumina
3	54 Grit Alumina (50%) RG-2 (50%)	Norton Remet	Alumina Fused Silica
4	RG-2	Remet	Fused Silica
5	RG-2	Remet	Fused Silica
6	RG-2	Remet	Fused Silica

*RG-2: Remet Corporation, PO Box 278, Bleachery Place, Chadwicks, NY 13319.

**No. 54 and 70 Alumina: Norton, Worcester, MA 01606.

Table 4

Particle Size Distribution of RG-2*

Mesh (US Standard)	RG-2 (% Retained)
+20	0-1
+30	25-35
+40	34-48
+50	16-32
+80	1-8
Pan	0-0.5

*Particle size distribution obtained from a data sheet provided by the manufacturer.

Table 5

Particle Size Distribution of 70 Grit Alumina*

Mesh (US Standard)	70 Grit Alumina (% Retained)
+45	0
+60	25 max
+70	40 min
+70 and +80	65 min
+100	3 max

*Particle size distribution obtained from the manufacturer.

Table 6

Particle Size Distribution of 54 Grit Alumina*

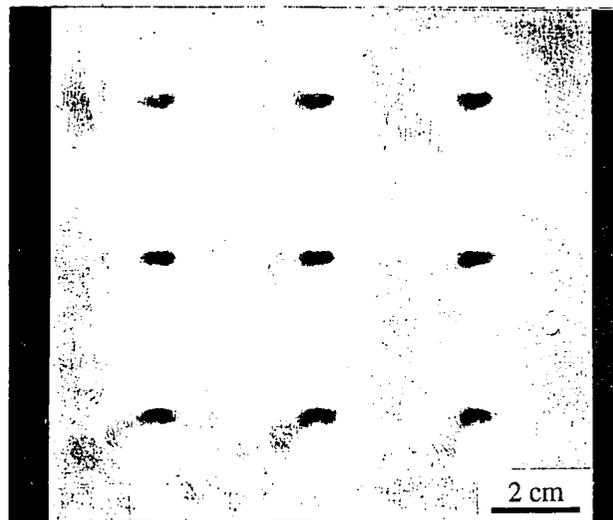
Mesh (US Standard)	70 Grit Alumina (% Retained)
+35	0
+45	30 max
+50	40 min
+50 and +60	65 min
+70	3 max

*Particle size distribution obtained from the manufacturer.

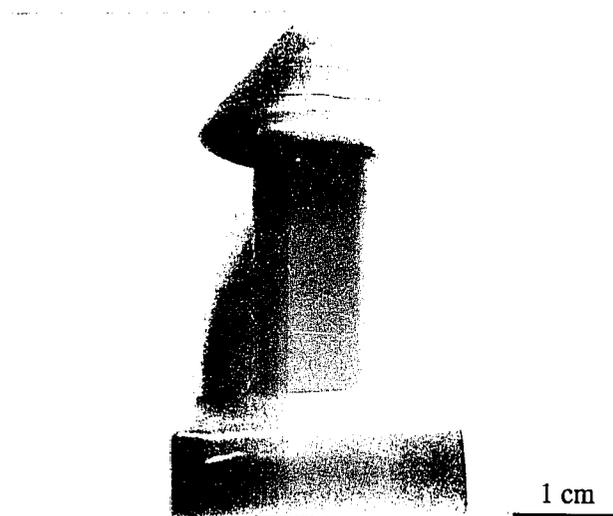
An aluminum plate, with conical depressions (diameter=25 mm, height=19 mm), was used as the die for making the wax patterns. The depressions were filled with melted Yates Red-C* wax using an eye dropper. The resulting cones were then mounted for dipping into a slurry tank. Figure 4 shows the aluminum die and a wax pattern.

Prior to dipping into the face coat slurry, the wax pattern was etched for one minute with trichlorotrifluoroethane solvent. In this case the etch was only used to enhance the adhesion of the ceramic to the wax; in an industrial setting it would also be relied upon to remove the mold release agents from the surface of the wax [73].

*Yates Red-C Wax: Yates, 1615-TW 15th St., Chicago, IL 60608.



(a)



(b)

Fig. 4. Wax investment used for experimental castings: (a) aluminum die and (b) resulting wax pattern after mounting.

The etched pattern was dipped into the face coat slurry and, while still wet, stuccoed with the appropriate grain (see Table 3) using a handheld shaker. The face coat slurry was kept in a beaker which used a stirring plate/bar to keep the mixture stable. To prevent drying cracks in the shell, the pattern was placed in a humidity chamber (50% relative humidity (R.H.)) for 4-6 hours. This drying procedure was used after applying each shell layer to the wax pattern.

Prior to the second dipping, the first layer was immersed into the face coat binder (Primcote) until no air bubbles were visible on its surface; this step is known as the prewet. The prewet strengthens the shell mold by stopping the previous shell layers from absorbing excess binder from the slurry. Excess prewet, however, can cause shell delamination by creating a liquid pocket, which in turn becomes a void when the binder evaporates [74]. Hence, care was taken to properly drain and dry the mold before dipping it into the face coat slurry. After dipping into the face coat slurry, the pattern was stuccoed with the appropriate grain (see Table 3) and dried.

Prior to the third dip, the pattern was prewet with the backup coat binder (Nyacol 830). After drying, the mold was dipped into the backup coat slurry, stuccoed with the appropriate grain and dried. The remaining layers (4-6) were made in a similar fashion, only no prewet was used. After allowing the sixth layer to dry, the mold was sealed using the backup slurry.

A commercial shell mold typically has between 5 to 10 layers depending upon the size of the part; for this work only six were used because the molds were quite small. It should also be noted that a foundry usually dries the molds in environments

at different relative humidities, depending upon the size of the part and the layer. A typical schedule might call for drying layers 1 to 3 at 50% R.H., and layers 4 and greater at 10% R.H. [75]. Although lowering the R.H. causes the shell to dry faster, the probability of shell cracking is increased. The choice of R.H. obviously becomes more critical with larger parts.

The completed shell was dewaxed in a preheated autoclave at pressure of 965 KPa and 178°C (140 psi/353 °F), and then fired in a furnace at 1000°C. The resulting product, after firing, was a "sintered" mold, free of organics, ready for casting.

3.1.2 Mold with a Yttria/Silica Face Coat

To make a mold with a yttria/silica face coat, a face coat slurry made up of Primcote and yttria powder was used. All other aspects of the mold making process were the same as described above (i.e. application procedures, viscosities of face coat and backup coat slurries, backup coat compositions, etc. remained the same).

3.1.3 Mold with a 100% Yttria Face Coat

Initially an effort was made to make a face coat slurry which, after firing, would result in a 100% yttria face coat. Yttrium acetate $[Y(C_2H_3O_2)_3]$ was used as a binder for yttria powder. The acetate converts to yttrium oxide at 489°C. However, three problems were encountered: rapid and instantaneous gelation of the slurry, lack of green strength, and lack of mold strength after firing. Because these problems

could not be solved in a timely fashion, yttria crucibles (22 mm x 27 mm tall, 2 mm wall thickness)* were purchased and represented what might be achievable were a 100% yttria slurry developed. According to the manufacturer, the crucibles were fired to at least 97% of their theoretical density.

3.2 Melting Technique

3.2.1 Furnace Design

The reactive nature of titanium places severe restrictions on the type of furnace and crucible which can be used to produce castings. As discussed before, 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 small size and large number of samples to be tested. Although others involved in the development of shell molds have used miniature VAR furnaces to produce castings [63,65], it was decided that a "containerless" system would be much simpler and just as effective.

Figure 5 shows a cross section of the furnace used to produce the titanium castings. Two induction power supplies were used: a 30 kW, 450-500 kHz, supply was used for melting, and a 2kW, 550 kHz, source was used for mold-preheating. Since the mold materials are not inductive (except when at higher temperatures), preheating was accomplished through the use of a graphite susceptor. The metal slug

*Yttria Crucibles: Custom Technical Ceramics, 8041 W. I-70 #6, Arvada, CO 80002.

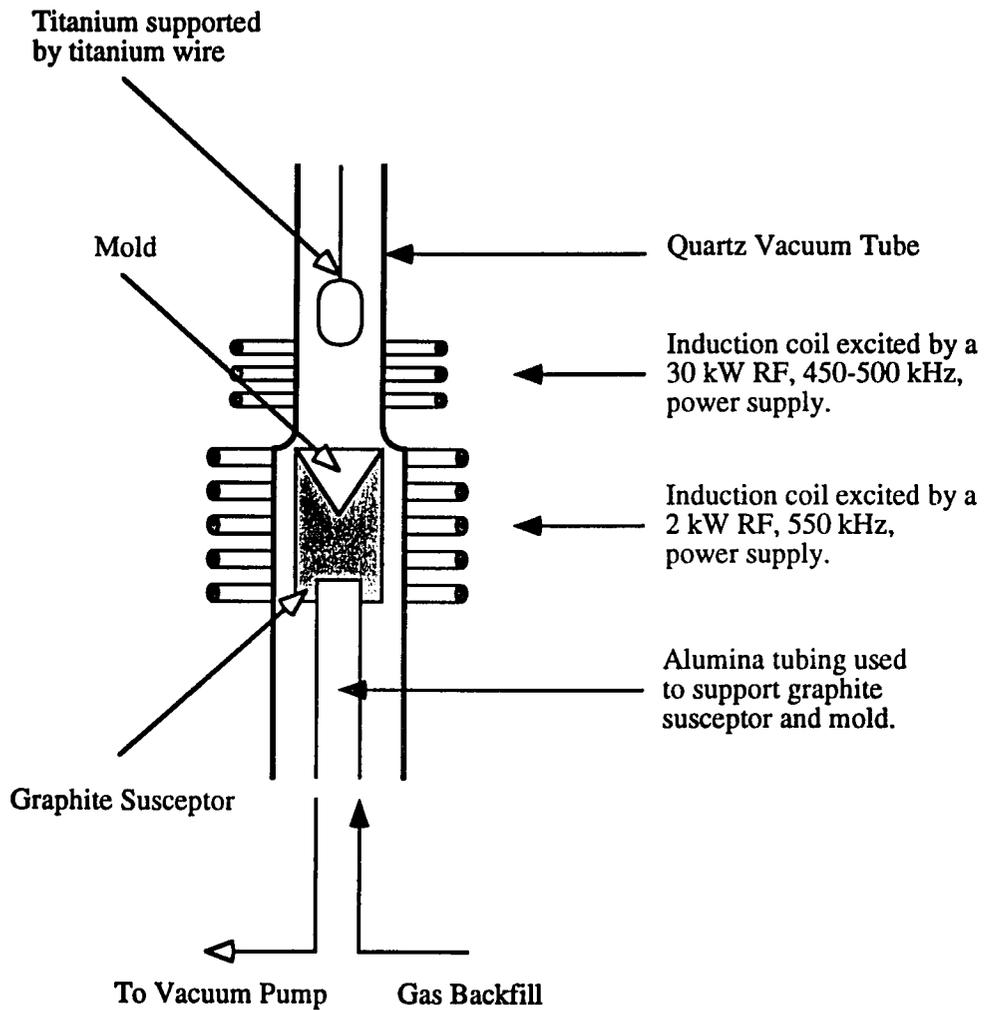


Fig. 5. The containerless furnace used to produce castings.

was hung by titanium wire and the susceptor/mold fixture was supported with an alumina pedestal.

As can be seen in Figure 5, melting and casting took place inside a quartz vacuum tube. The environment inside the tube was controlled by a vacuum system and a gas source. By using a turbomolecular pump, the quartz chamber could be evacuated to less than 10^{-6} torr if desired. The chamber could also be backfilled with a gas of choice. Gas flow was regulated with a flow meter, and chamber pressure was limited by a pressure relief valve set to 1/3 psig. The temperatures of the mold and metal were measured with calibrated optical pyrometers. A two color Ircon* pyrometer was used to measure melt temperature, and a Vanzetti Systems** pyrometer was used to measure mold temperature. The latter, which uses a remote sensing head, was focused on the mold surface by inserting the attached optical cable into a light source, used as a locating beam. Unlike the Vanzetti, the Ircon is a stand-alone sensor, in that it combines sensor and processor functions in a single unit. It was aligned by viewing the object of interest through an eye piece, which is an integral part of the unit. The outputs from both pyrometers were connected to digital recorders.

The benefits of using this system is that it is "containerless" and allows melting and casting to take place in an inert atmosphere. This simplifies matters by

*High temperature pyrometer: Ircon, Inc., 7301 North Caldwell Ave., Niles, IL 60714.

**Low temperature pyrometer: Vanzetti Systems, Inc., 111 Island St., Stoughton, MA 02072.

ensuring that defects found on the surface of the casting are a direct result of the interaction with the mold material.

3.2.2 Casting Experiments

Both CP-Ti (ASTM-B-348, Grade 1)* and Ti-6Al-4V (AMS-4928M, Grade 5)** were cast; the metal was purchased as 1.3 cm diameter barstock, and machined in the form of 4 gram slugs. Table 7 shows the chemical analyses of both purchased alloys. The slugs were centered and supported a fixed distance (5.1 cm) from the top of the mold with CP titanium wire.

The chamber was evacuated with a mechanical pump to 10^{-1} torr, backfilled with ultra high purity argon[†] (Table 8), 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 the optical pyrometer on the face coat. Then the mold was either heated or allowed to cool to the desired preheat temperature; preheat temperatures of 25, 350, 500, 650, and 800°C were selected. When the preheat temperature was reached, the valve to the mechanical pump was closed and the valve to the turbomolecular pump was opened. After the vacuum stabilized, the chamber was backfilled with argon, and evacuated again. This procedure was continued until the desired vacuum ($<2 \times 10^{-5}$ torr) was reached.

*CP Ti: President Titanium, 243 Franklin St. (Rt. 27), Hanson, MA 02341.

**Ti-6Al-4V: Titanium & Alloys Corp., 21601 Hoover Rd., Warren, MI 48089.

†Ultra High Purity Argon: Tri-Gas Inc., 8200 Washington NE, Albuquerque, NM 87113.

Table 7

Chemical Analyses of Alloys in Weight Percents*

Element	CP Ti	Ti-6Al-4V
N	0.010	0.01
C	0.006	0.01
O	0.12	0.19
Fe	0.13	0.21
H	0.008	0.0007
Ti	Balance	Balance
Al	—	6.54
V	—	4.14
Y	—	<0.001

*Information provided by the manufacturer.

Table 8

Chemical Analysis of Ultra High Purity Argon*

Impurity	Amount Present (ppm)
O ₂	< 10
H ₂ O	< 1
CH ₄	< 0.2
N ₂	< 5

*Information provided by the manufacturer.

Prior to melting, the chamber was backfilled with argon, the mold preheat coil was de-energized, and the melting coil energized. The chamber was kept at 1/3 psig 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 top of the sample when it broke free from the wire and fell into the mold. Melting took approximately 20 s. The casting was kept in the argon filled chamber until cool. Figure 6 shows a cross section of a casting and the mold.

3.2.3 Contact Experiments

The time during which a reaction occurs between a poured casting and its mold is dependent upon the size of the casting. Because the castings produced in these experiments were rather small, the solidification rates were relatively high. In order to simulate the effect of a larger casting on the stability of a yttria mold, titanium/yttria contact experiments were run. Figure 7 shows a cross section of the furnace used for these experiments.

After placing a 10 gram slug of the alloy into the yttria crucible, the melt chamber was evacuated and backfilled with ultra high purity helium* (Table 9). The evacuation/backfill process was continued until a satisfactory vacuum was obtained

*Ultra High Purity Helium: Tri-Gas Inc., 8200 Washington NE, Albuquerque, NM 87113.

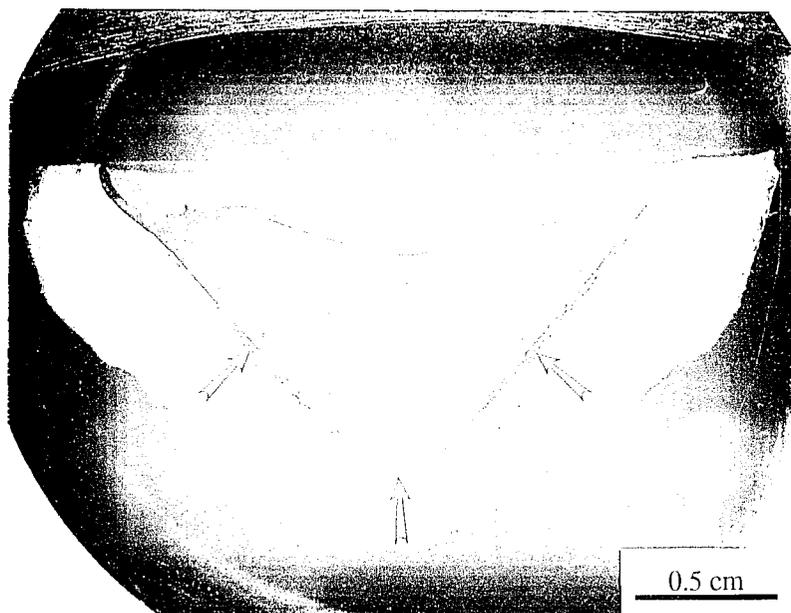


Fig. 6. Cross section of a casting and its mold; the arrows point to microhardness traverses.

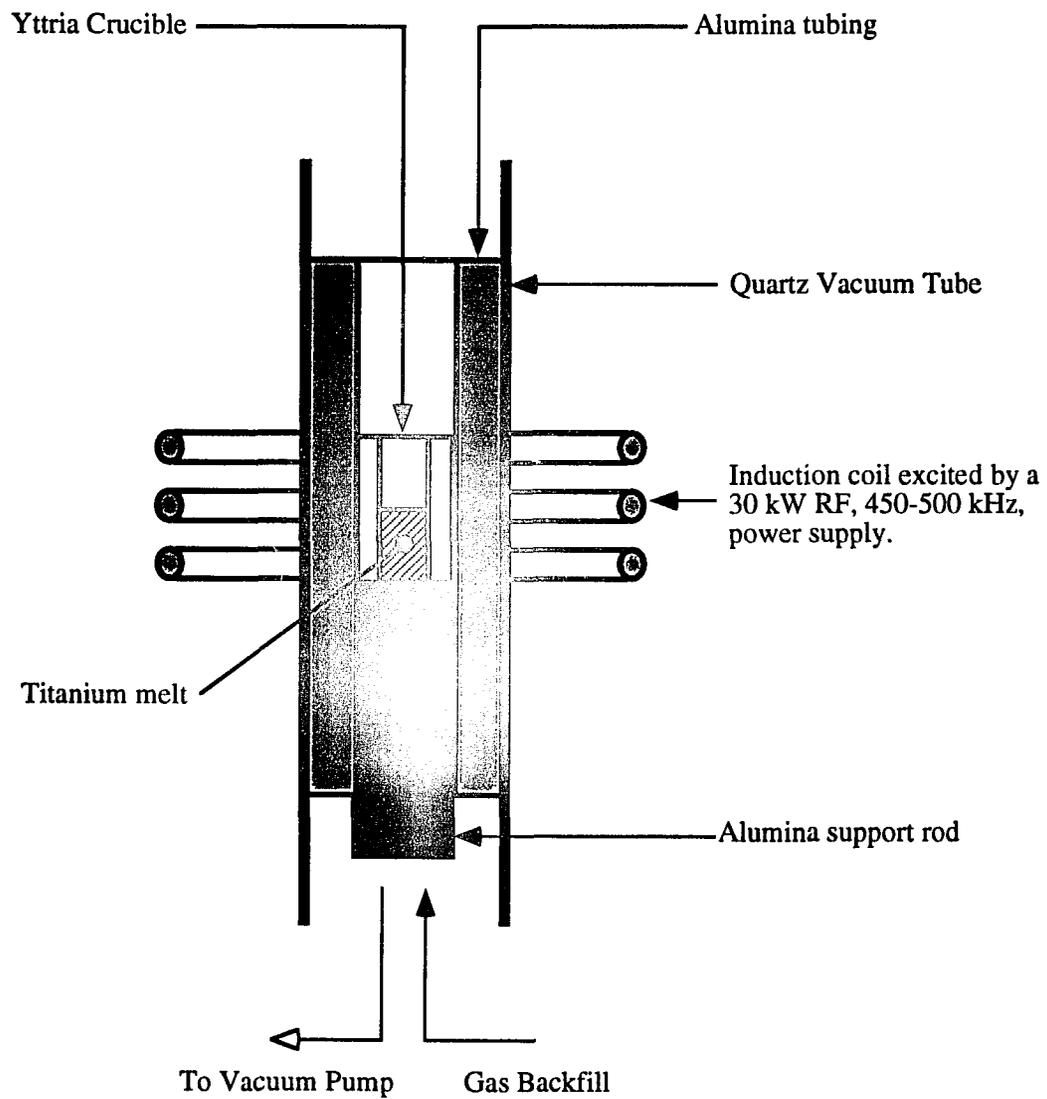


Fig. 7. Cross section of the furnace used for Ti-6Al-4V/Y₂O₃ contact experiments.

Table 9

Chemical Analysis of Ultra High Purity Helium*

Impurity	Amount Present (ppm)
O ₂	< 3
H ₂ O	< 3
CH ₄	< 1
N ₂	< 5
H	< 1
Neon	< 23

*Information provided by the manufacturer.

(<2x10⁻⁵ torr). The chamber was then backfilled to a pressure of 1/3 psig with helium. Then the alloy was slowly heated until melting occurred; the temperature was observed from above using an optical pyrometer. The melt was kept in contact with the crucible for either 15 s or 30 s to simulate longer cooling periods of larger castings.

3.3 Specimen Preparation

3.3.1 Mounting/Polishing

After sectioning the samples with a slow speed saw, they were mounted in filled epoxy using a hot press mount. Six or seven samples were then ground with a force of 150 N at 300 rpm, with 240 grit SiC paper, followed by polishing with a

force of 225 N at 150 rpm for 7 minutes on a 15 μm diamond cloth that was periodically sprayed with an alcohol based lubricant. The final step consisted of polishing the samples with a force of 50 N at 150 rpm for 5 minutes on a cloth, sprayed with a mixture of 96 ml OP-S,* 2 ml hydrogen peroxide, and 2 ml ammonium hydroxide.

3.3.2 Etching/Photographic Documentation

All specimens were etched with Kroll's reagent (1.5 ml HF, 3.5 ml HNO₃, and 95 ml DI H₂O). Light micrographs were taken to document the thickness of the alpha case. Originally, it was hoped that these optical micrographs could be used to accurately determine the thickness of the alpha case; this, however, proved not to be the case because often there was no distinct border on the oxygen rich layer.

Although other tests (e.g., microhardness testing and SIMS) were used to firmly establish the thickness of the reaction layer, the use of color microscopy as a way to determine alpha case thickness was also explored.

In color microscopy, the CP-Ti castings were repolished and etched with 50 ml glycerine and 50 ml HF. Color micrographs were then taken for the purpose of determining alpha case thickness; these data were compared to data from either microhardness tests or SIMS.

*OP-S: Struers USA, 26100 1st St., Weslake, OH 44145.

3.4 Analysis of Castings

3.4.1 Microhardness Testing

Because of the effect of interstitials on the mechanical properties of titanium [7,8], it would seem that one should be able to correlate the concentration of an interstitial with a mechanical property. Saha *et al.* [68], for example, confirmed that microhardness profiles can be used to determine the thickness of the alpha case, or more specifically they can be used to determine the diffusion profile of oxygen at the surface of a casting.

For this work three Vickers microhardness traverses were made using a 100 g load held for 15 s on a Shimadzu* hardness tester. Figure 6 shows a cross-section of a casting and its mold with arrows indicating the location and direction of the three traverses (note that each traverse is perpendicular to the surface). Figure 8 is a micrograph of one microhardness traverse. Each indentation was made at a specific distance from the surface; for example if the first indentation in traverse I of Figure 6 was made 150 μm away from the surface, then the first indentations in II and III were also made 150 μm from the surface. Although tedious, this procedure provided for an average Vickers hardness number (VHN) at a specific distance from the surface. In this example, the hardness numbers from the first marks of traverses I, II, and III were averaged to get the VHN at a distance of 150 μm from the edge.

*Shimadzu Seisakusho Ltd., Kyoto, Japan.



Fig. 8. Micrograph of a typical Vicker's microhardness traverse across the surface of a Ti-6Al-4V casting.

3.4.2 Microprobe Analysis

The surfaces of the CP-Ti castings were evaluated using a JEOL* JXA-8600 Superprobe. The system was run by Sandia TASK 8 software working in conjunction with a Noran** automation package [76]. Identical area elemental distribution (EDPMs), secondary electron (SEM) and backscattered electron (BES) micrographs were taken near the edge with an accelerating voltage of 15 keV and a beam current between 25 and 30 mA. In addition, quantitative analyses were made using the $\phi(\rho z)$ correction parameter for matrix effects. The elements of interest were calibrated against pure element standards. The elements quantified in the castings produced by the yttria molds, molds with an alumina/silica face coat, and molds with a yttria/silica face coat were Y, Al and Si, and Y and Si, respectively. The analyses were done in 1 μm steps from the center to the edge.

3.4.3 SIMS Analysis

A Cameca IMS-4f*** secondary ion mass spectrometer was used to determine oxygen profiles of the samples. These profiles were used to confirm the results of the microhardness tests. The castings were sectioned, mounted, polished, and coated with a 0.3 nm thick layer of gold. Oxygen concentration profiles were produced by analyzing the sample in a stepwise fashion from the edge inward. At

*JEOL JXA-8600: JEOL USA Inc., 11 Dearborne Rd., P.O. Box 6043, Peabody, MA 01961-6043.

**Noran Automation System: Noran Instruments Inc., 2551 W. Beltline HW, Middleton, WI 53562.

*Cameca IMS-4f: Cameca USA, 2001 W. Main St., Stamford, CO 06902.

each step, prior to analysis, the surface was cleaned using a $50\ \mu\text{m} \times 50\ \mu\text{m}$ raster pattern of Cs^+ ions accelerated to 14.5 kV with a primary current of 63 nA. Then, using the same voltage and current settings, the beam was focused to analyze an area of $8\ \mu\text{m}$, Cs^+ bombardment was continued, and negative secondary ions of oxygen and titanium were collected and counted. Software used in conjunction with the IMS-4f was made by Charles Evans & Associates.*

3.5 Analysis of Ti-6Al-4V Buttons Resulting from Contact Experiments

3.5.1 Microhardness Testing

Same as in Section 3.4.1.

3.5.2 SIMS Analysis

The procedure was similar to that described in Section 3.4.3, however, only two areas were analyzed (one at the edge and one 5 mm from the edge).

3.5.3 Image Analysis

After sectioning, mounting, and polishing the Ti-6Al-4V specimens from samples in the contact experiments, it was observed that yttria had precipitated along the prior β grain boundaries. Image analysis was done to determine the area fraction

**Software: Charles Evans & Associates, 301 Chesapeake Dr., Redwood City, CA 94063.

of these precipitates. Images were captured with Adobe Photoshop* in 24 bit color (3 bytes per pixel) and then converted to a 640 x 480 black and white pixel image. The captured image was thresholded and used to determine the area fraction of the precipitates in PrismView.** Twelve images were taken on each sample, with each image representing an area of 3.1 mm².

*Adobe Photoshop: Adobe Systems Inc., 1585 Charleston Rd., Mountain View, CA 94039-7900.

**PrismView: Dapple Systems, 355 W. Olive Ave., Suite 100, Sunnyvale, CA 94086.

Chapter 4

RESULTS AND DISCUSSION

4.1 Casting Experiments

4.1.1 Analysis of Castings Produced in Molds with an Alumina/Silica Face Coat

Figures 9 and 10 show microhardness profiles on the CP-Ti and Ti-6Al-4V castings made in molds with an alumina/silica face coat. Castings were produced in molds at room temperature (RT), 350, 500, 650 and 800°C, but only profiles at RT and 800°C are plotted in order not to overload the plots with data (complete plots for all casting experiments can be viewed in the Appendix). In both cases, it can be observed that as the mold preheat temperature rises the hardness increases. It is of interest, however, to note that the preheat temperature does not greatly influence the apparent thickness of the alpha case. Using the results in Figure 9 as an example, at 80 μm from the interface the VHN is 470 for the casting produced in the mold at RT and 660 in the mold preheated to 800°C. The alpha case thickness, however, varies at most by 80 μm : 320 μm for the RT case vs. 400 μm for the 800°C case.

Although it is rather difficult to discern where the alpha case actually ends in Figure 10, it appears that the preheat temperature does not influence the thickness of the alpha case at all.

By comparing Figure 9 to 10, it appears that the reaction layer is thicker for the unalloyed case (please note Figure A7 as it better supports this observation).

Although differences in melting points could affect the extent of a metal/mold

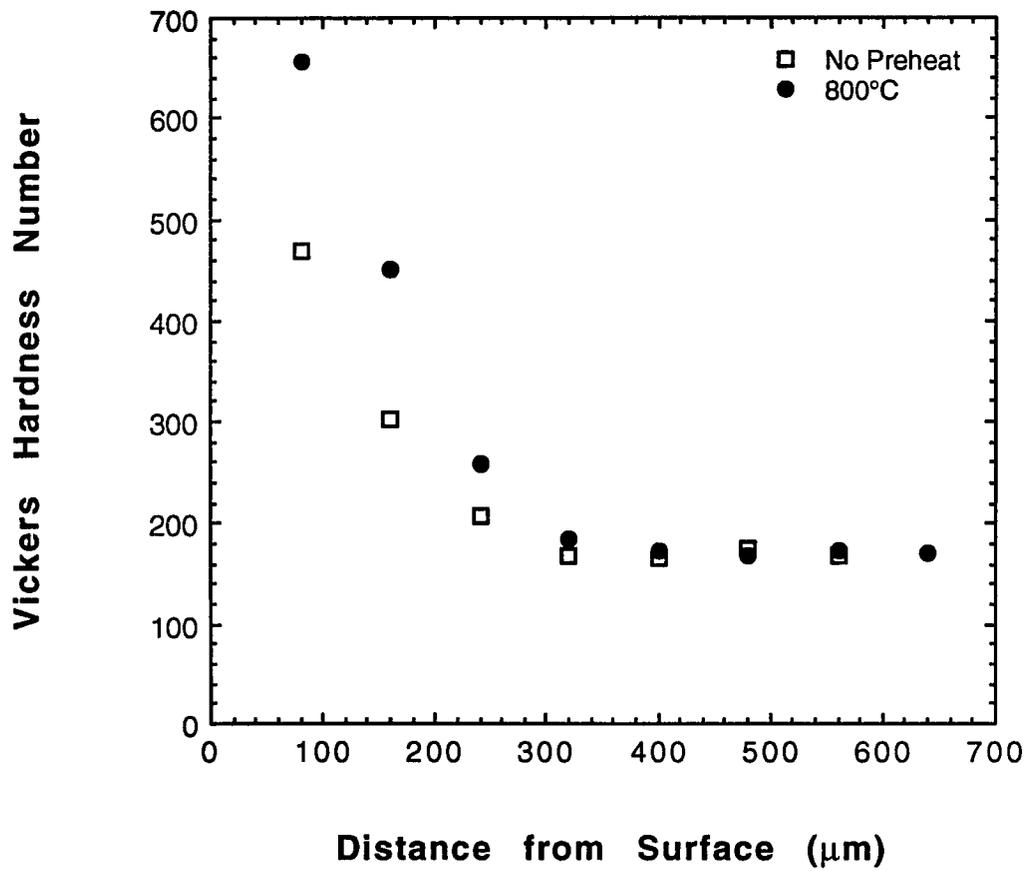


Fig. 9. Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat.

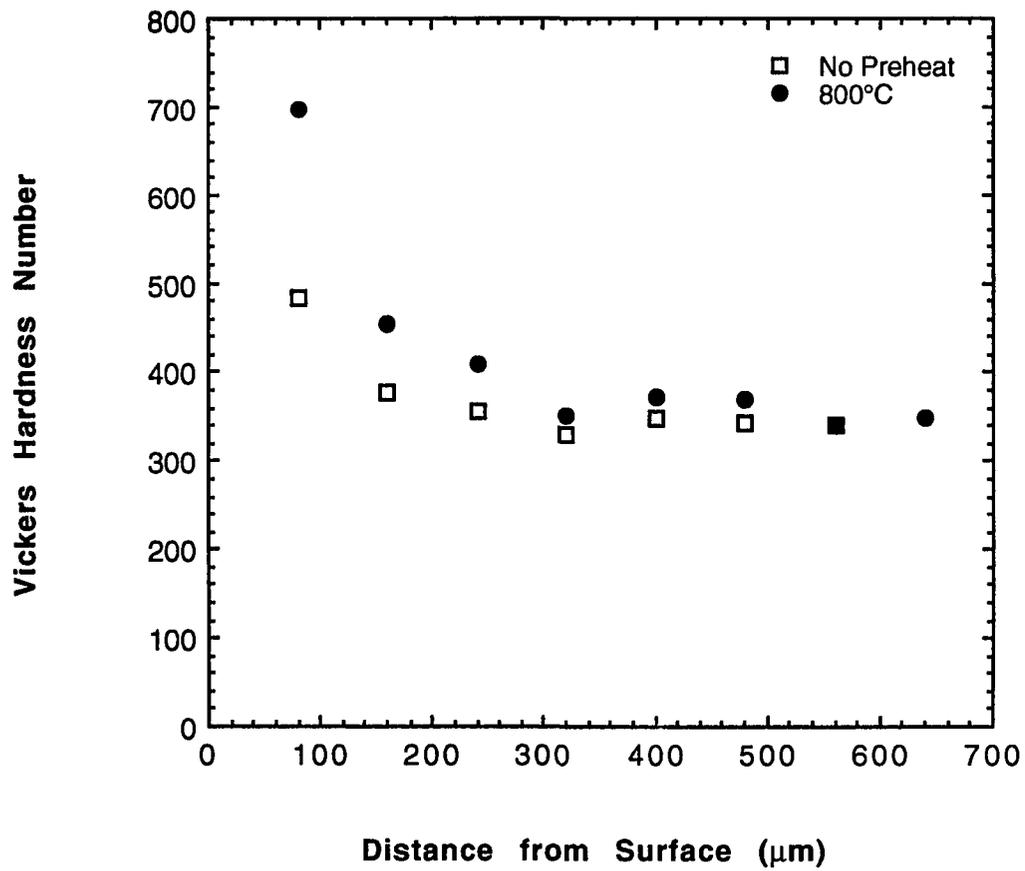


Fig. 10. Microhardness profiles of Ti-6Al-4V castings produced in molds having an alumina/silica face coat.

reaction, in this case the melting points are similar. It is feasible that the allotropic nature of titanium affects the results. Upon cooling CP-Ti undergoes a transformation from a body-centered cubic structure (the beta phase) to its hexagonal close-packed phase (the alpha phase) at 882°C. The addition of aluminum to titanium raises the beta transus to 980°C [4]. Because interstitials, in this case oxygen, are able to diffuse more readily in a body-centered cubic lattice [77], more oxygen is able to diffuse into the CP-Ti because it retains its BCC structure longer.

Taira *et al.* [21] found the alloys in order of increasing alpha case are Ti-15V, Ti-30Pd, Ti-20Cu, Ti-6Al-4V, and CP-Ti. As expected, because their melting points are significantly lower than the rest (nearly 1400°C vs. over 1600°C), the alloys with Pd and Cu had the thinnest cases. By considering the difference between the melting point and the temperature at which no β remains, one finds that all of the alloys, except one, follow the pattern described above [21]. Ti-15V, which should have had the thickest alpha case, was the only alloy to deviate from the proposed pattern. In order to explain this deviation, one should examine the effect of vanadium on interstitial diffusion. Although Collins [78] states that the addition of transition elements such as vanadium to titanium results in an increase of the electron density in a titanium alloy, this statement cannot be used to explain the effect of vanadium on oxygen diffusion since it is not duplicated in titanium alloys containing the transition elements copper and lead. Therefore, based on Taira *et al.*'s results, one could suggest that vanadium acts as a barrier to oxygen; however, it was not possible to

support this hypothesis at the time of this writing as no Ti-V diffusion data could be found by the author.

Figure 11 shows the results of the secondary ion mass spectrometry (SIMS) analyses performed on the CP-Ti castings. In this figure the intensity of the oxygen signal, normalized by the titanium signal, is plotted against distance. Unlike the profiles determined by microhardness testing, these indicate that the alpha case is thicker with increasing preheat temperatures. Figure 11 indicates that the alpha case is 200 μm and 400 μm for the castings produced in molds at RT and 800°C, respectively. Furthermore, it is observed that at the higher preheat temperature, the amount of oxygen which diffuses into the sample is increased. Microhardness results were similar in this respect, although it is difficult to see differences past the point where the plot indicates that the alpha case ends in Figures 9 and 10.

Figure 12 shows micrographs taken near the surface of two CP-Ti castings made in molds at RT and 800°C, with an alumina/silica face coat. The lighter region is the oxygen enriched alpha case. It is evident from these micrographs that the reaction layer is not of a constant thickness; in fact, the thickness appears to vary by as much as 50%. These results are not unusual. Feagin [12,13] shows a micrograph of a Ti-6Al-4V casting made in an investment mold, with a yttria face coat, which has an isolated spot of alpha case surrounded by a large region free from any surface anomalies. It is, therefore, possible that a test (SIMS or microhardness testing) could give inaccurate results if a trace is across a region containing an atypical amount of oxygen. It could be suggested that, because only one SIMS trace was done on each

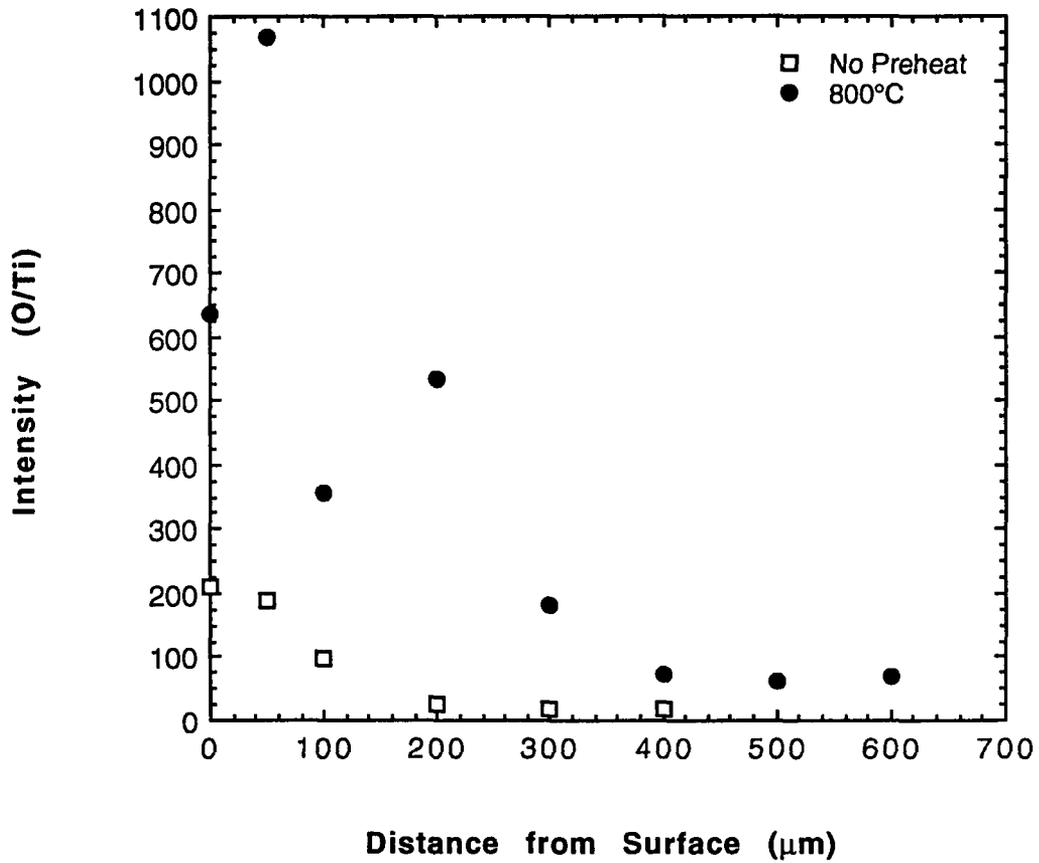
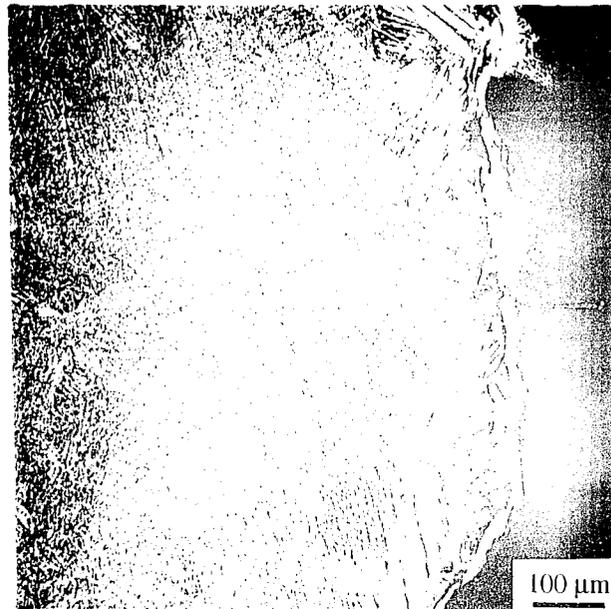
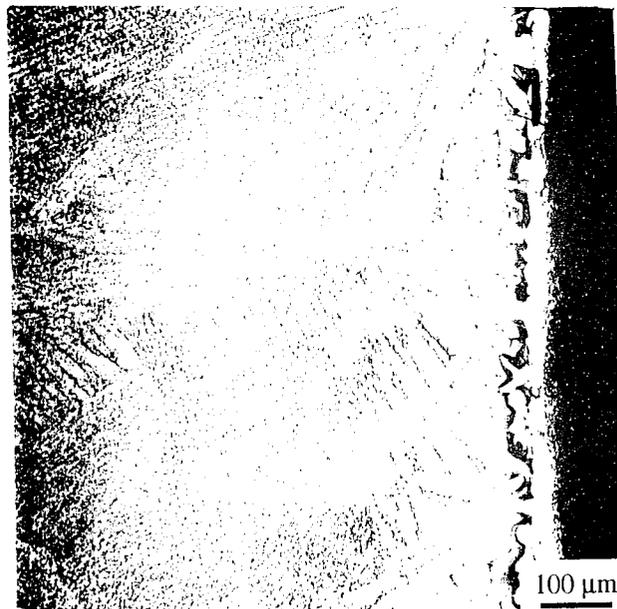


Fig. 11. Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in molds having an alumina/silica face coat.



(a)



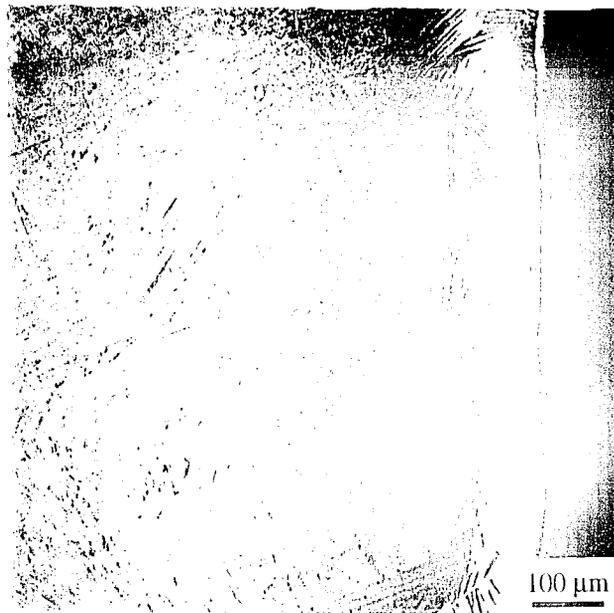
(b)

Fig. 12. Microstructures from CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C. Etched with Kroll's reagent.

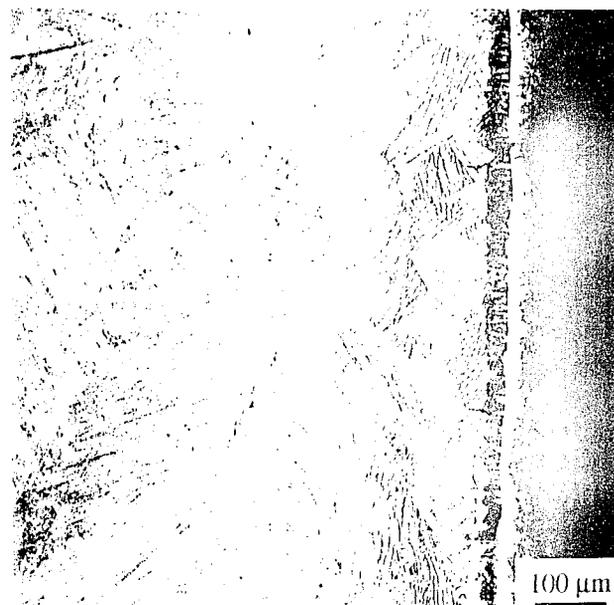
sample (versus the microhardness traces), it was inappropriate to compare SIMS data to microhardness data; however, the disparity mentioned is also visible when comparing data (SIMS vs. microhardness) obtained from the castings produced in molds with a yttria/silica face coat. An explanation for the disparity is offered later.

By viewing Figure 12 one is left with the impression that optical metallography may in fact serve as a useful technique for determining alpha case thickness. One is able to quickly determine that the alpha case is approximately 200 μm in Figure 12(a) and 350 μm in Figure 12(b), which compare favorably with Figure 11. However, the success of this particular example is deceptive because the appearance of the reaction layer was in fact difficult to control during etching. Figure 13 for example shows two Ti-6Al-4V castings made in molds with an alumina/silica face coat at room temperature and at 800°C. Because the samples were etched for different periods, the impression is given that the alpha case is lessened as the mold preheat temperature is raised. Although the castings in Figure 13 were etched with a 1:1 solution of glycerin and concentrated HF to exaggerate the effect, one can also see in Figure 14(a), which shows a Ti-6Al-4V casting made in a mold with an alumina/silica face coat preheated to 500°C, that even when the appropriate reagent is used it is difficult to determine the thickness of the reaction layer. Figure 14(b) shows the corresponding microhardness plot which indicates an alpha case thickness of 350 μm .

It was mentioned earlier that some efforts were made to see whether color prints could be used in determining alpha case thickness, using an etchant comprised



(a)



(b)

Fig. 13. Microstructures from Ti-6Al-4V castings made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C. Etched with 50% glycerin 50% HF.

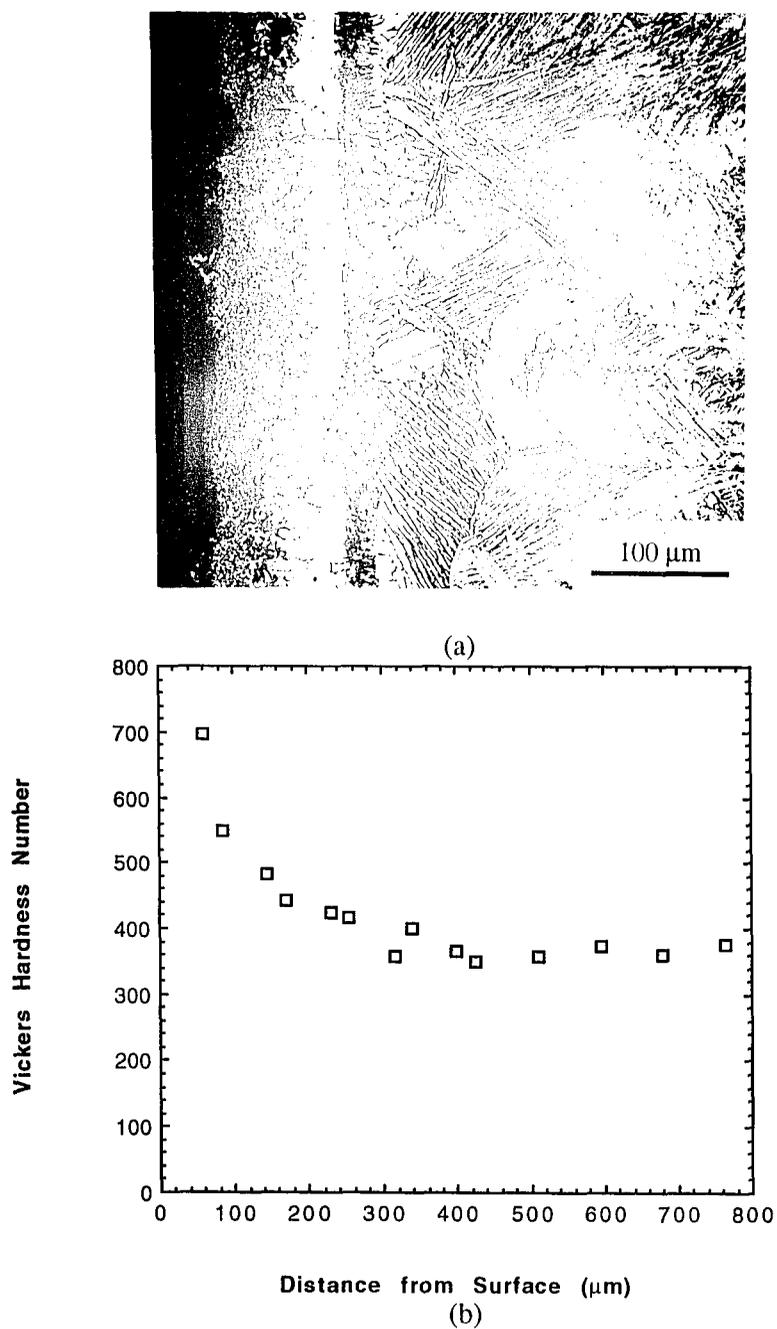
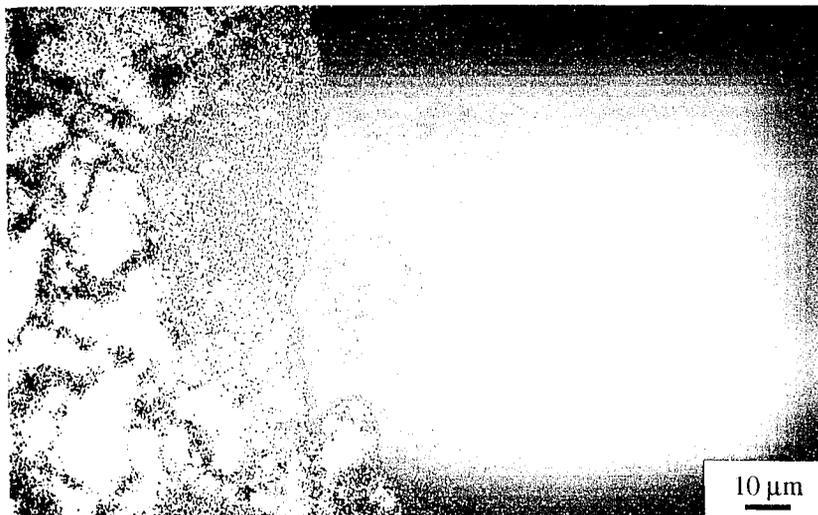


Fig. 14. Microstructure and hardness profile from a Ti-6Al-4V casting made in a mold with an alumina/silica face coat preheated to 500°C. (a) Microstructure etched with Kroll's reagent and (b) corresponding microhardness plot.

of 50% glycerin and 50% concentrated HF. Although the alpha case was distinctively white and easily distinguished from the sea of colors representing the unaffected portion of the alloy, the appearance was difficult to control. In fact, in many cases the specimens did not have a predictable color scheme. The appearance of the etched surface seemed especially sensitive to time. Furthermore, etching was complicated by the rapidly changing properties of the solution. If an etching solution with a longer shelf life could be developed, then it is possible that color microscopy could be a viable technique for determining alpha case thickness.

To further characterize the samples, microprobe analyses were carried out. Figures 15 and 16 show elemental distribution maps for Si and Al, respectively, in CP-Ti castings made in molds with an alumina/silica face coat at RT and 800°C. To ensure that the metal/mold interface is easy to recognize, backscattered electron micrographs of the mapped regions are provided in Figure 17. An interfacial layer, darker than the bulk sample, makes it easy to identify the metal/mold interface. It is likely that the reason for the altered color of the interface is due to a limited solid solution of titanium in the oxide face coat [79]. The cracks in Figure 17(b) should also be noted, as they indicate the brittle nature of the alpha case.

Figure 15 shows two silicon maps, next to the metal/mold interface, for castings produced in molds at RT and 800°C. [It should be noted that the large (~10-15 μm) irregularly shaped silicon rich particles, located on the left side of the map, are glass particles in the epoxy mounting material; the particles help to preserve the edge of the sample during polishing.] It is evident that as the preheat temperature



(a)

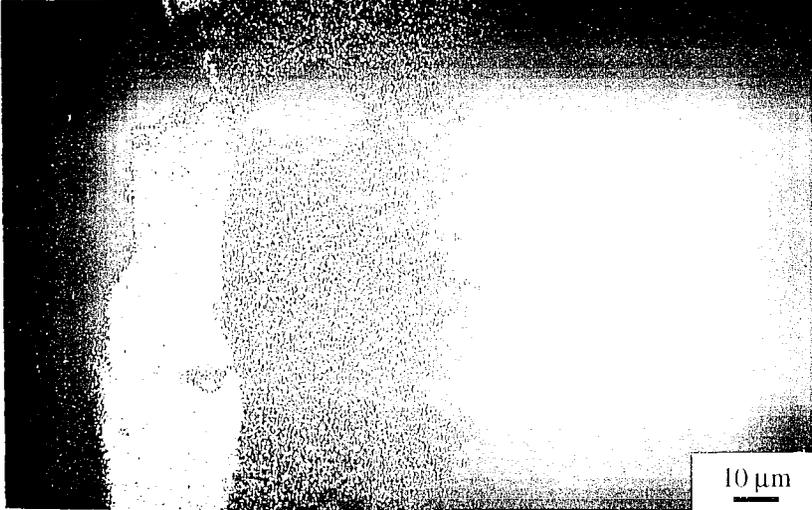


(b)

Fig. 15. 20% silicon map of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C.

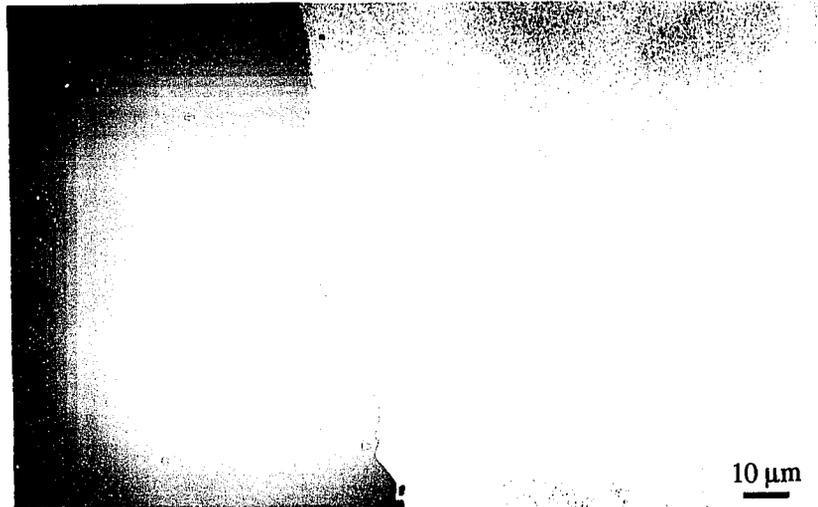


(a)



(b)

Fig. 16. 20% aluminum map of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C.



(a)



(b)

Fig. 17. Backscattered electron micrographs of a CP-Ti casting made in a mold with an alumina/silica face coat (a) with no preheat and (b) preheated to 800°C, respectively.

increases the amount of silicon which diffuses into the metal increases. In Figure 15(b) the diffused silicon has a structure with fingers ahead of the overall diffusion layer. The structure is unique to the high mold preheat case and suggests the formation of a low-melting eutectic or grain boundary diffusion. Saha and Misra [80] 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 if this phase was a result of the interaction of titanium with free silica or silica derived from the zircon sand, the results did indicate that if the amount of silica was lessened, then the Ti/mold reaction could be minimized.

Figure 16 shows aluminum maps, adjacent to the metal/mold interface, in castings produced in molds at RT and 800°C. It is apparent that as the preheat temperature was increased the amount of aluminum diffused into the metal increased. Unlike silicon, the aluminum is evenly dispersed in both the low and high mold preheat cases. By comparing Figure 15 to Figure 16, it appears as if the extent of diffusion of Si is greater than the extent of diffusion of Al. Figures 18 and 19 are plots that confirm this by quantifying the amount of diffused silicon and aluminum for the RT and 800°C mold preheat cases, respectively.

4.1.2 Analysis of Castings Produced in Molds with a Yttria/Silica Face Coat

Unlike the castings produced in molds with an alumina/silica face coat, 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 20(a) shows a

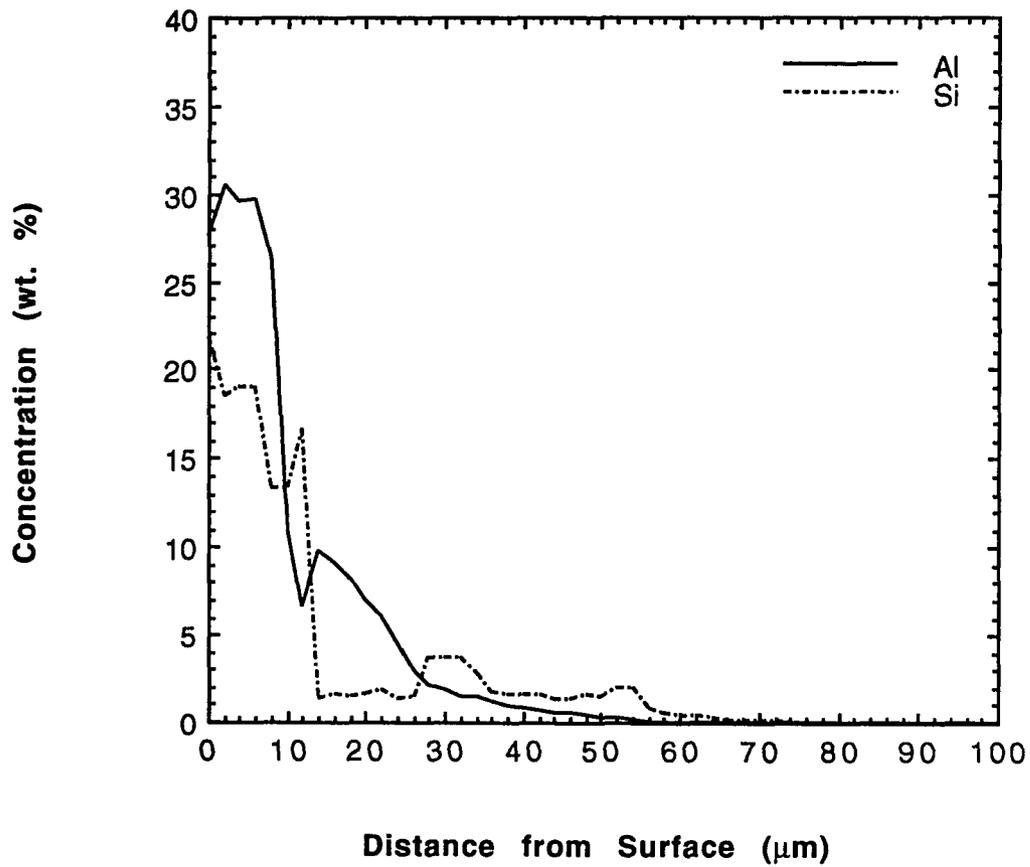


Fig. 18. Concentrations of aluminum and silicon which have diffused into a CP-Ti casting as a result of its contact with an alumina/silica face coat with no preheat.

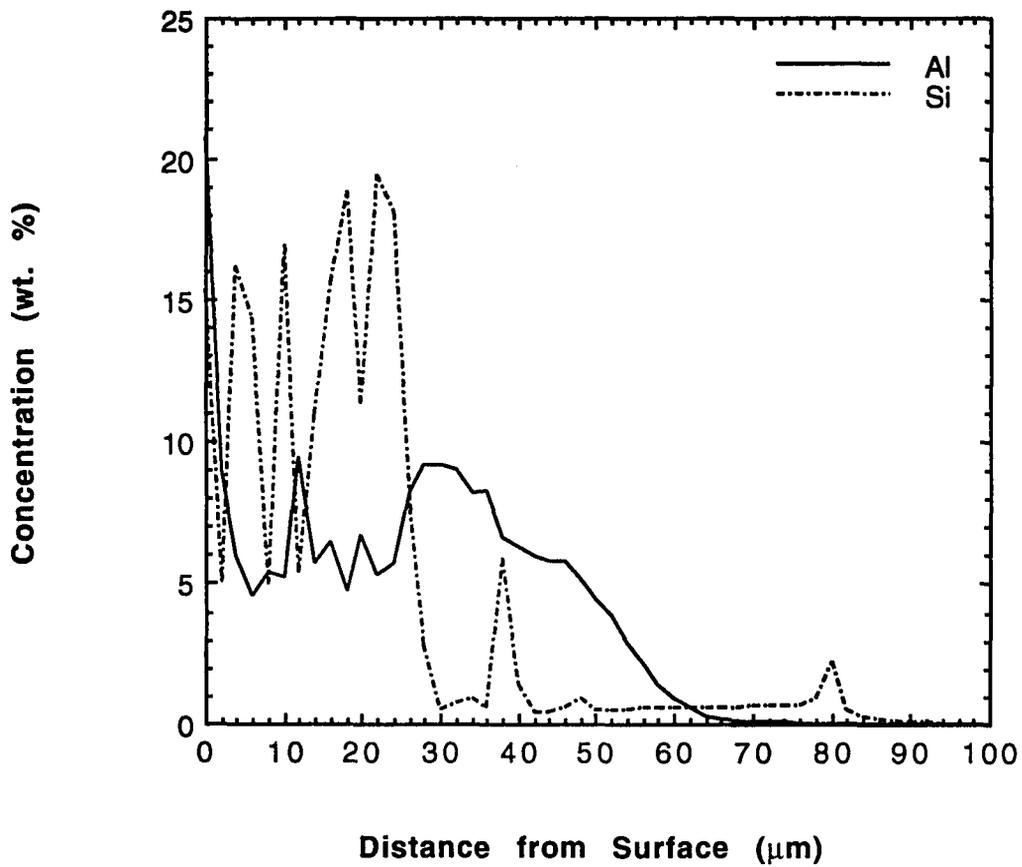
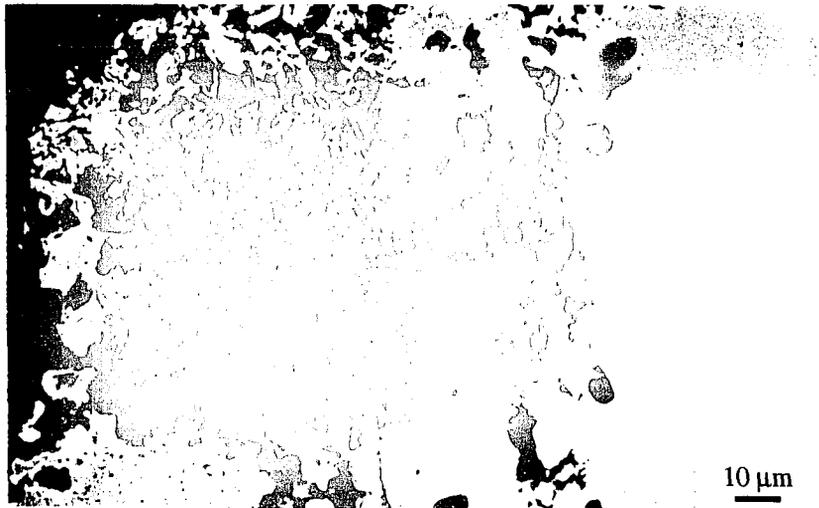
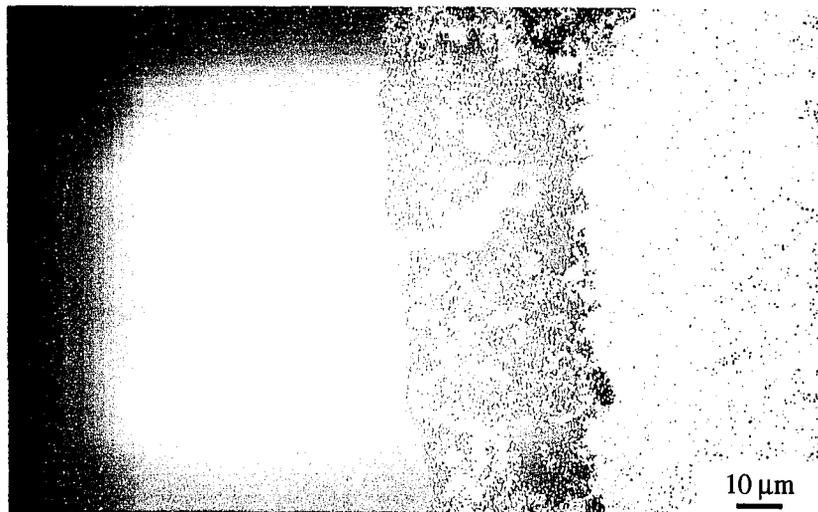


Fig. 19. Concentrations of aluminum and silicon which have diffused into a CP-Ti casting as a result of its contact with an alumina/silica face coat preheated to 800°C.



(a)



(b)

Fig. 20. Microstructure of a CP-Ti casting made in a mold with a yttria/silica face coat, preheated to 800°C. (a) SEM image and (b) a 100% titanium map of the same region.

secondary electron micrograph of the surface of a CP-Ti casting made in a preheated mold (800°C) with a yttria/silica face coat. Figure 20(b) shows the titanium map of the region seen in the 20(a). These figures indicate that the titanium penetrated the face coat. It is likely that the yttrium oxide present in the face coat altered its firing characteristics such that very little sintering occurred. Calvert [14] found that, to produce a sound investment mold for titanium, 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 latter seems excessive especially when one considers the recommendation put forth by Brown and Brown [51], that "the mold should be heated to a temperature which is 60-75% of the temperature at which the metal to be cast will melt."

The thickness of the penetration in Figures 20(a) and 20(b) varies 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 which were between 30 and 50 μm thick. The microhardness, SIMS, and microprobe data which follow exclude this penetrated layer.

Figures 21 and 22 show the effect of mold preheat temperature on the reaction between CP-Ti and Ti-6Al-4V, respectively, and the yttria/silica face coat. The results are similar to those seen in Figures 9 and 10. The higher mold preheat temperature resulted in higher hardnesses up to the point where the alpha case ends, after which there is not a significant difference, and the thickness of the alpha case is greater on the CP-Ti castings (400 μm) than on the Ti-6Al-4V castings (350 μm).

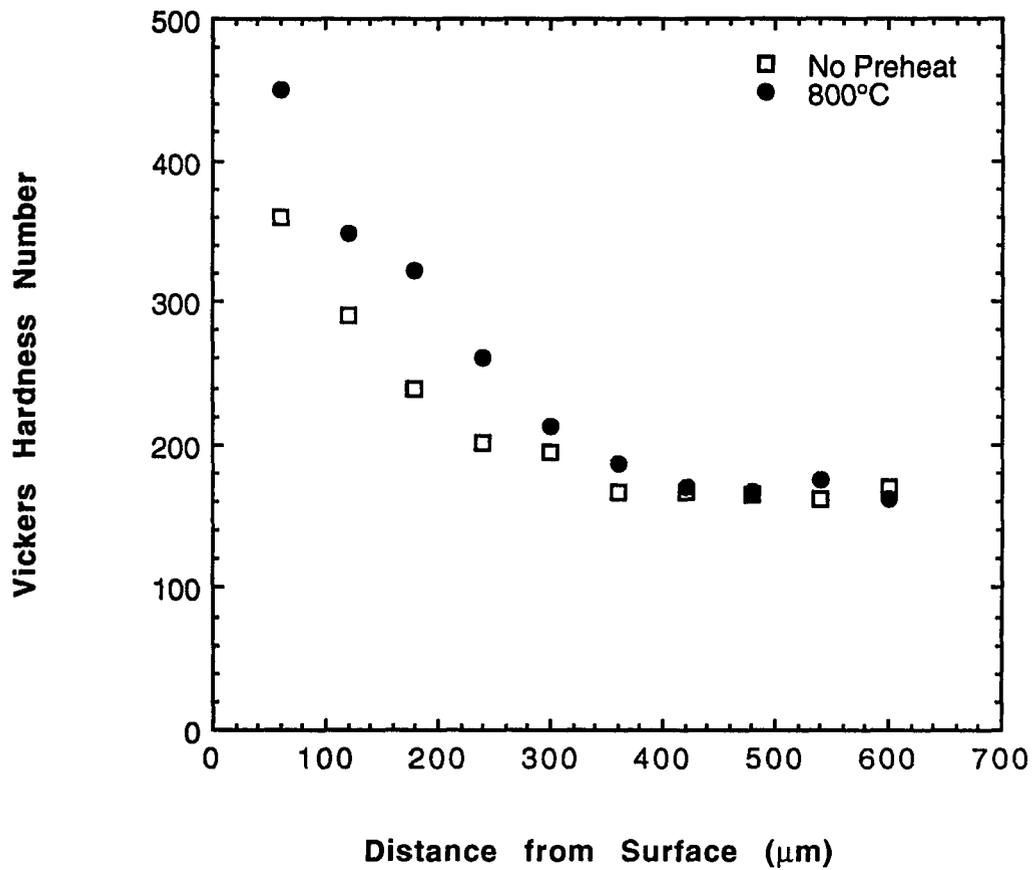


Fig. 21. Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat.

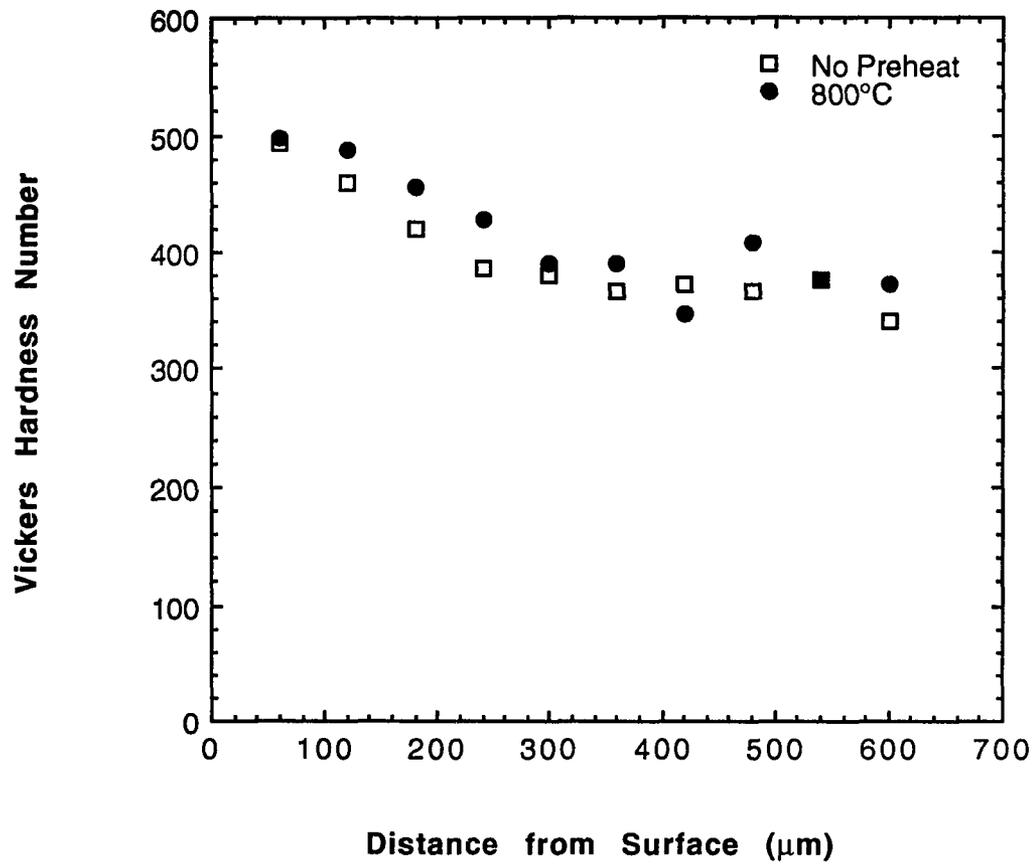


Fig. 22. Microhardness profiles of Ti-6Al-4V castings produced in molds having a yttria/silica face coat.

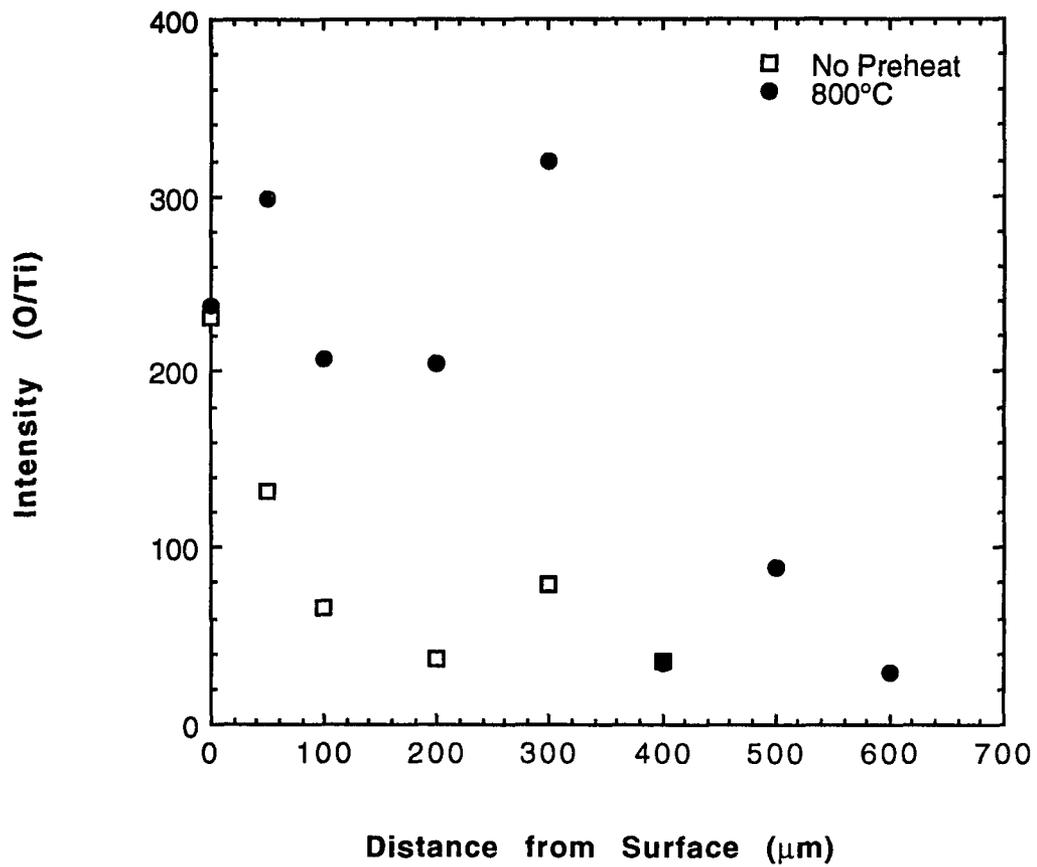


Fig. 23. Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in molds having a yttria/silica face coat.

Figure 23 shows the results of the secondary ion mass spectrometry (SIMS) analyses performed on the CP-Ti castings made in molds with a yttria/silica face coat. In this figure the intensity of the oxygen signal, normalized by the titanium signal, is plotted against distance. The data points corresponding to the mold at RT in Figure 23 are the averages of two SIMS traces. With no preheat the resulting casting had an alpha case 200 μm thick and, when the mold was preheated to 800°C the resulting alpha case was 400 μm thick. These data show, once again, that as the preheat temperature is raised, the amount of oxygen which diffuses into the sample and the thickness of the alpha case increases.

It is of interest again that the high temperature SIMS results compare much better with the microhardness results than do the low temperature results. In the CP-Ti casting produced in the mold preheated to 800°C both SIMS and microhardness indicate an alpha case of 400 μm , but in the casting produced with no preheat an alpha case of 200 μm was observed with SIMS and 360 μm with microhardness.

The microprobe plots shown earlier indicated that other mold constituents besides oxygen had diffused into the titanium (silicon and aluminum, in particular). As mentioned by Saha *et al.* [70] impurities, such as silicon, may contribute to hardening. Figures 24 and 25 show microprobe plots for the CP-Ti castings produced in the molds with a yttria/silica face coat with no preheat and preheated to 800°C, respectively. The plots are similar to those seen earlier, in that as preheat temperature is raised the silicon diffuses further (albeit in smaller amounts). The

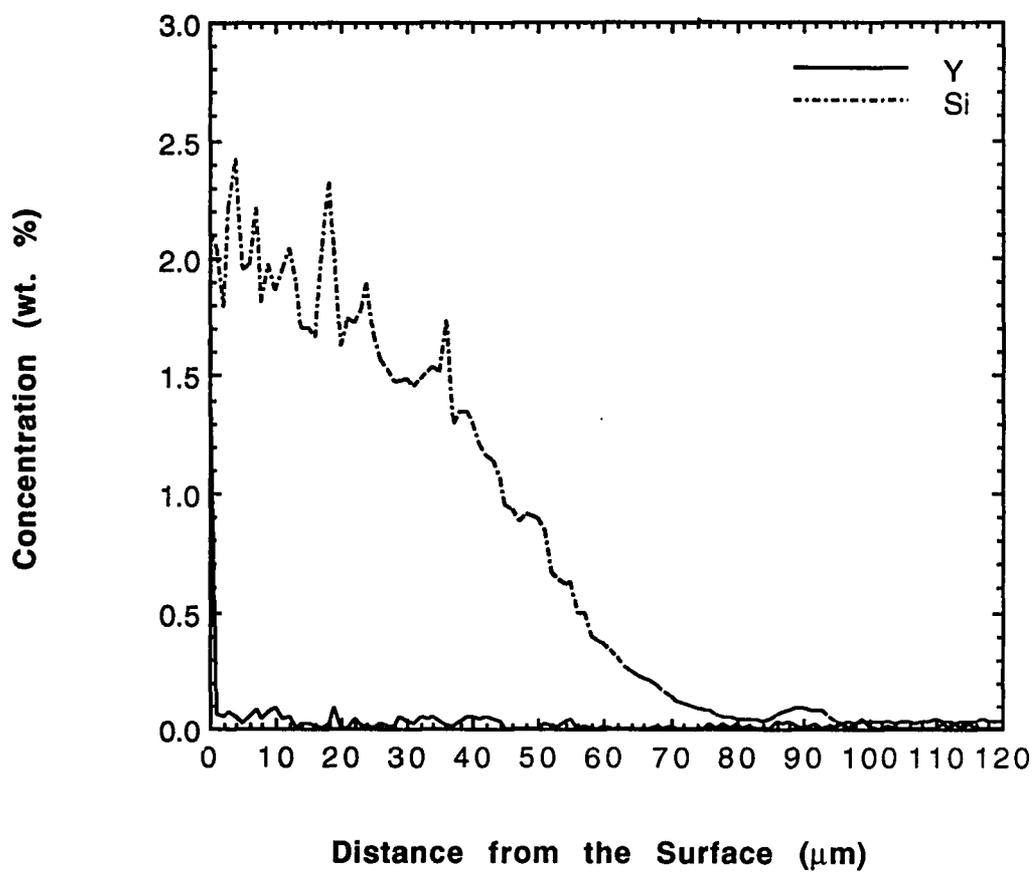


Fig. 24. Concentration of yttrium and silicon which has diffused into a CP-Ti casting as a result of its contact with a yttria/silica face coat with no preheat.

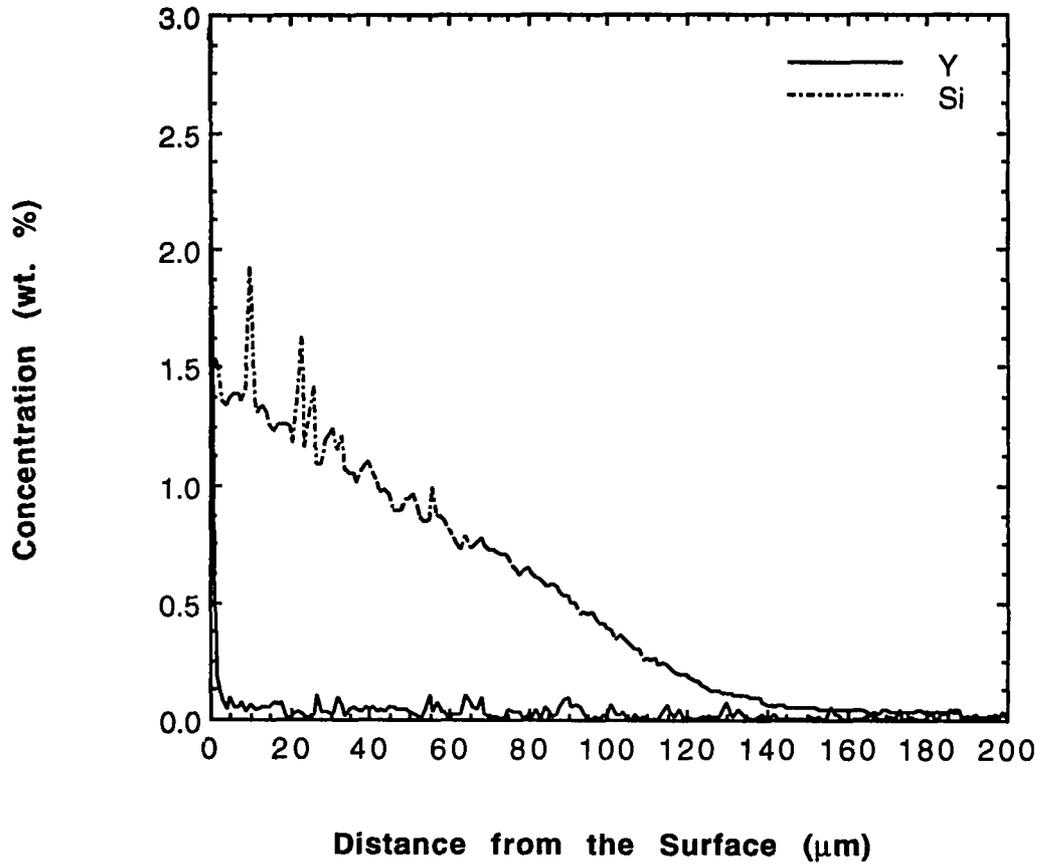


Fig. 25. Concentration of yttrium and silicon which has diffused into a CP-Ti casting as a result of its contact with an yttria/silica face coat preheated to 800°C.

diffusion of silicon, however, does not explain the difference between the microhardness and SIMS data because its diffusion distance is limited to between 70 and 150 μm , depending on the type of face coat and mold preheat temperature. In addition, the diffusion of yttrium is extremely limited, in depth and amount.

There is a possibility that the elevated hardness, as indicated by data from microhardness tests of castings produced in non-preheated molds, may be due to impurities brought into the system via the gas source. As stated by Weber *et al.* [32], "the high degree of sensitivity of Ti to impurities is well known to those who have worked with the material but is difficult to appreciate unless one has had a personal acquaintanceship." Because no precaution, such as flowing the gas over heated titanium chips, was taken to rid the argon of possible impurities its quality could be questioned. For example, to ensure the purity of their helium, Weber *et al.* passed the gas through liquid nitrogen, drierite, and a 1000°C getter furnace. They even used a special getter alloy composed of 65% zirconium and 35% titanium because it had been observed that sponge Ti alone was not enough to remove all oxygen from inert gases [32]. One could also suspect hydrogen resulting from the interaction of titanium with moisture in the mold; although Jaffee and Campbell [7], contrary to others [32], stated that dissolved hydrogen does not affect the hardness.

By comparing data of the titanium-yttria/silica face coat interaction to data of the titanium-alumina/silica face coat interaction, it becomes apparent that no benefit is gained through the incorporation of the more thermodynamically stable yttria within the face coat. In both cases, silica appears to be the culprit.

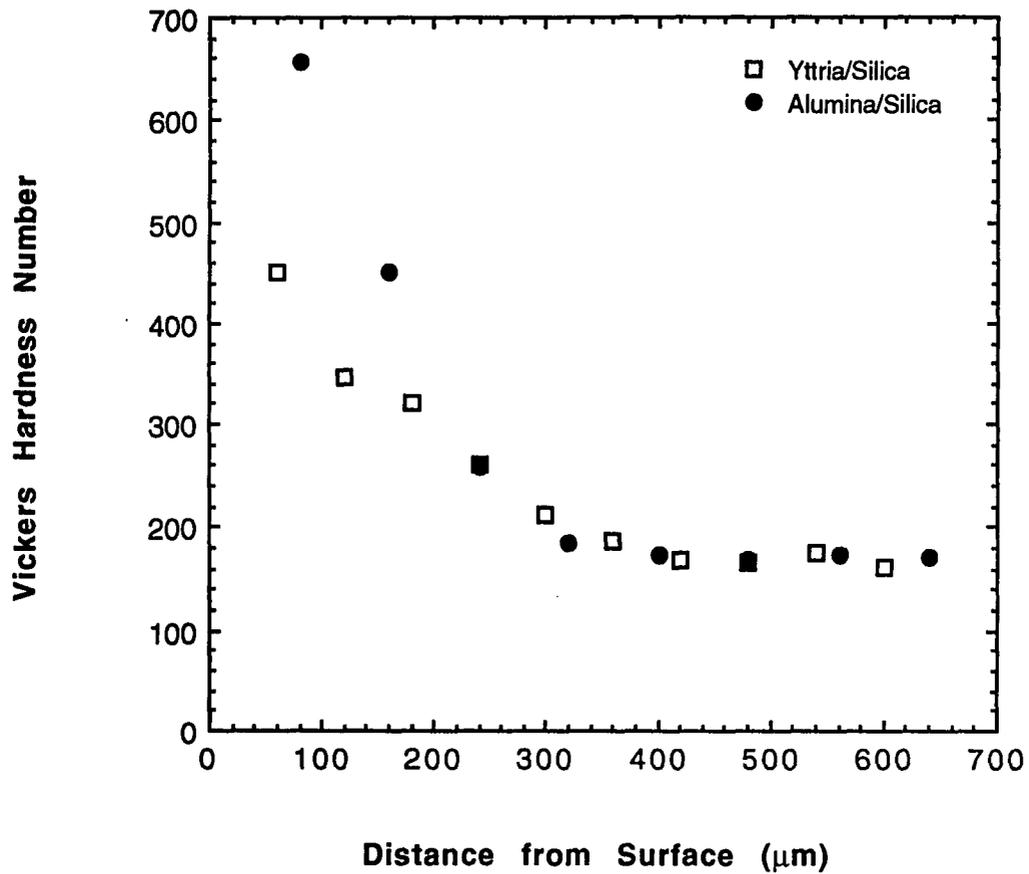


Fig. 26. Microhardness profiles of CP-Ti castings produced in molds preheated to 800°C.

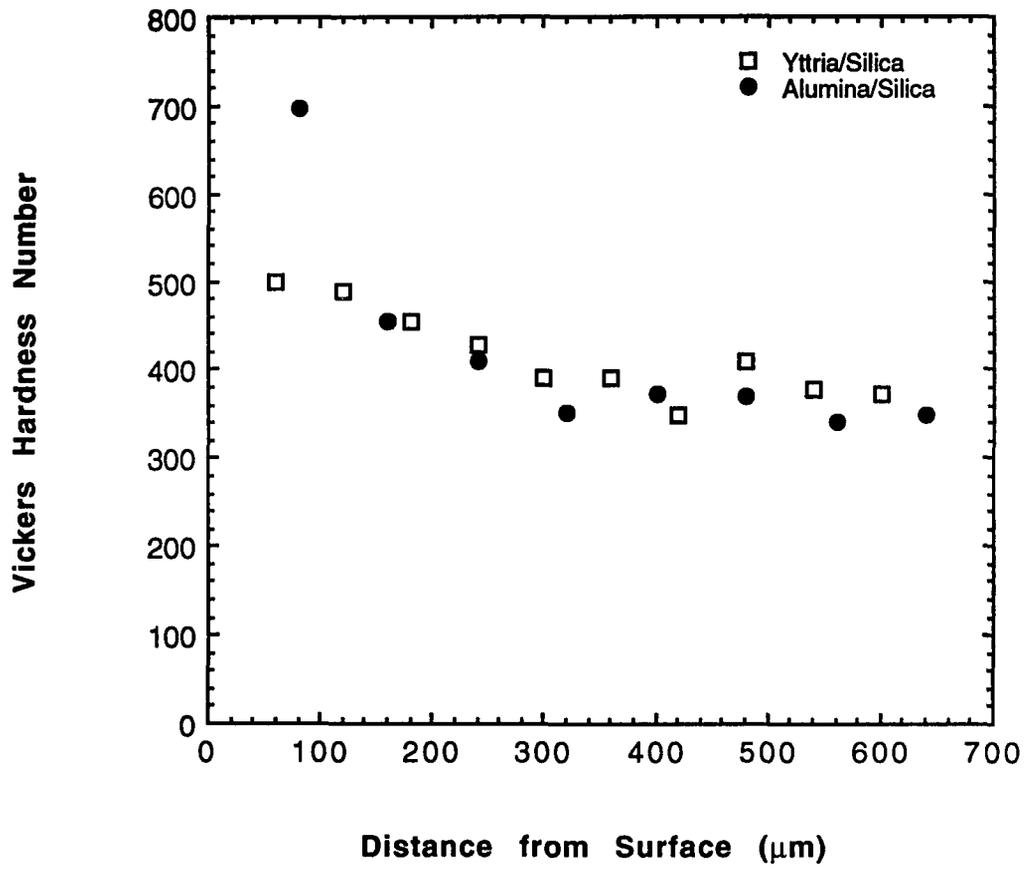


Fig. 27. Microhardness profiles of Ti-6Al-4V castings produced in molds preheated to 800°C.

Figures 26 and 27 show microhardness plots of CP-Ti and Ti-6Al-4V castings made in molds preheated to 800°C. The plots show that the yttria/silica face coat resulted in lower hardness up to the point where the alpha case ends; even so the thickness of the alpha case, and the hardness values thereafter are the same as those resulting from the alumina/silica face coat. These results indicate that the stability of the refractory used in the face coat is undermined by the less stable binder, colloidal silica. This is in agreement with Calvert [14] who indicated that slurries which used silica sols were not acceptable as face coats.

4.1.3 Analysis of Castings Produced in Yttria Crucibles

Figures 28 and 29 show microhardness plots of the CP-Ti and Ti-6Al-4V castings, respectively. As indicated by the plots, yttria appears to be an excellent mold material for titanium as there no indication of an alpha case. Figures 30(a) and 30(b) show optical micrographs of the Ti-6Al-4V castings solidified in the yttria molds. There are no indications of a reaction at the metal/mold interface.

Figure 31 shows oxygen profiles of CP-Ti castings produced in the yttria crucibles. Regardless of the extent of mold preheat, the diffusion depth is 250 μm . Although this diffusion depth is comparable to previous results (Figures 9, 11, 23 and 31), when one compares relative concentration values (proportional to peak height ratios) the effectiveness of yttria is evident. Figure 32 shows SIMS data from CP-Ti castings produced in alumina/silica, yttria/silica, and yttria molds at no preheat. At the surface, the relative amount of oxygen present in the sample produced in the yttria

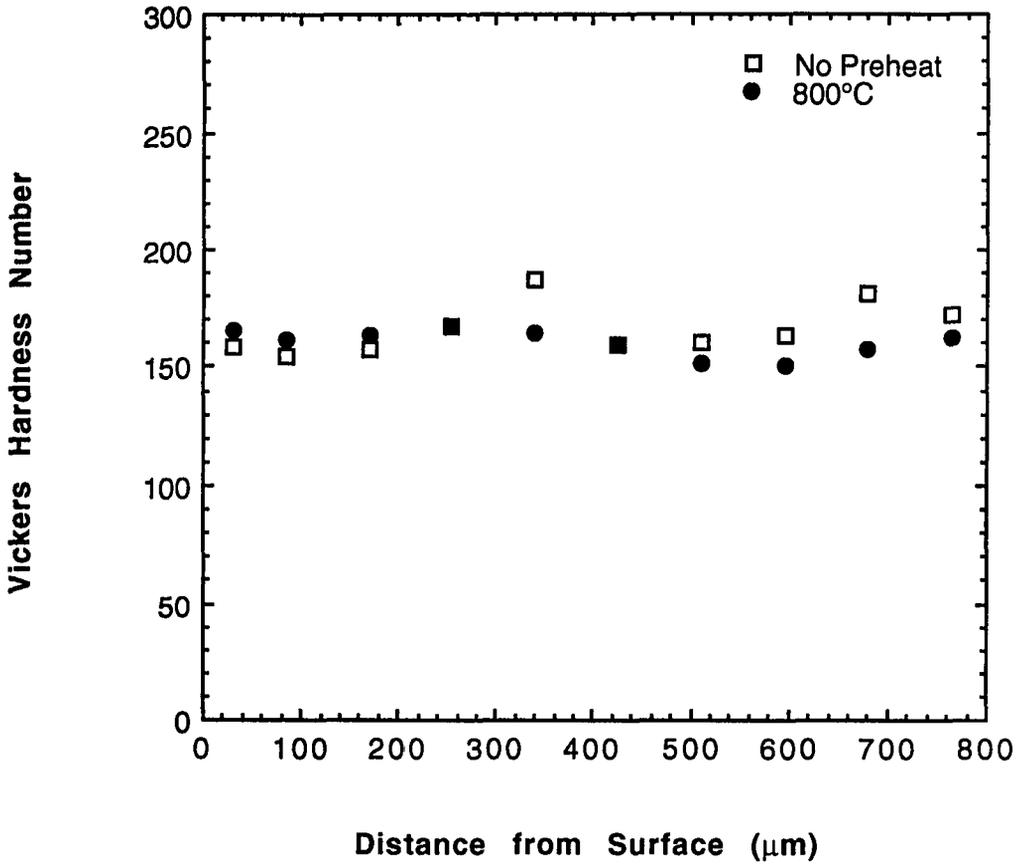


Fig. 28. Microhardness profiles of CP-Ti castings produced in yttria molds.

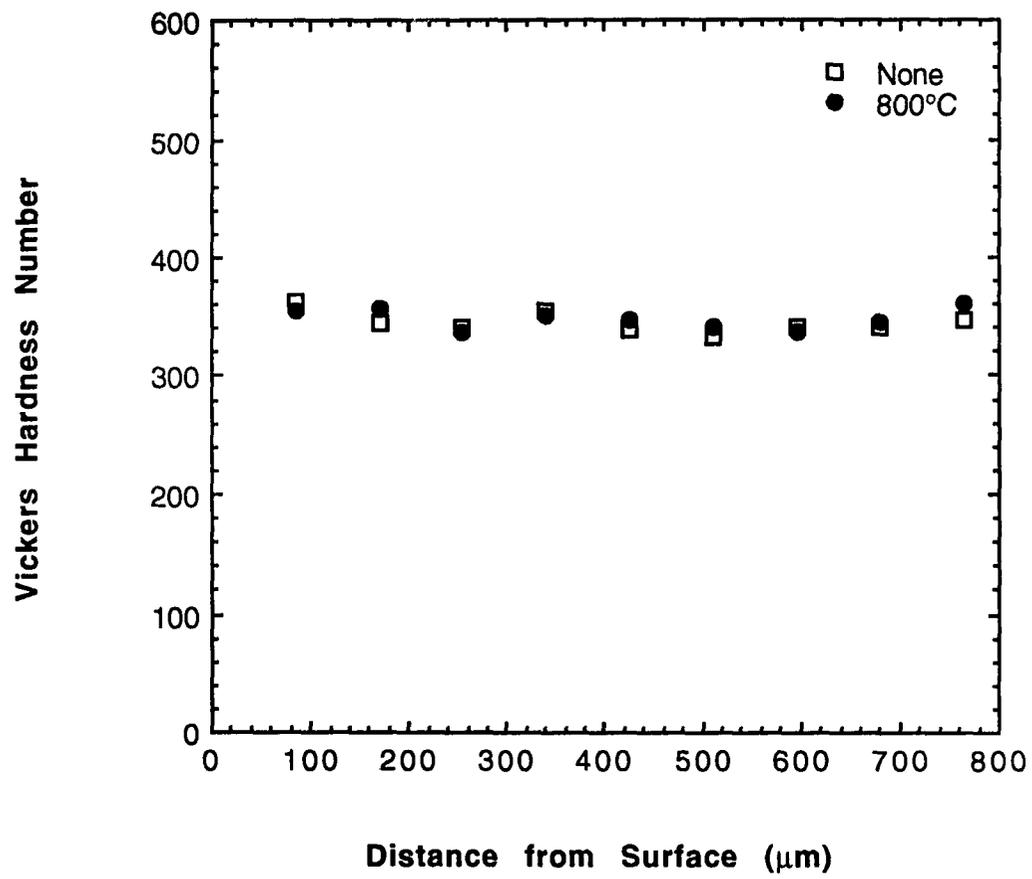
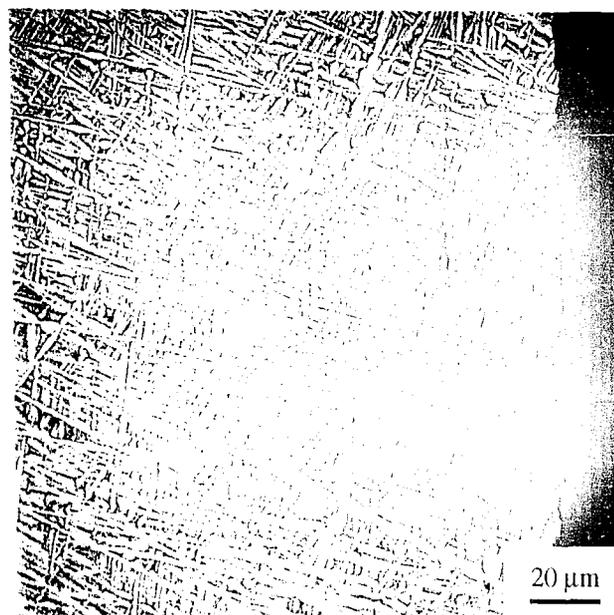
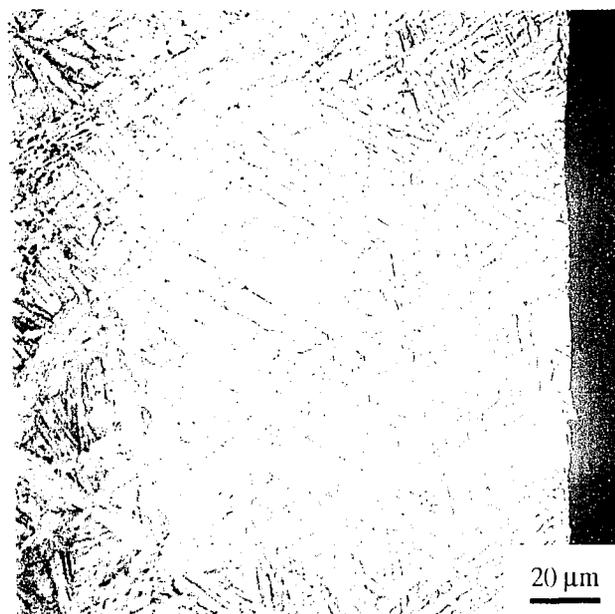


Fig. 29. Microhardness profiles of Ti-6Al-4V castings produced in yttria molds.



(a)



(b)

Fig. 30. Micrograph of Ti-6Al-4V castings produced in yttria molds (a) with no preheat and (b) preheated to 800°C. Etched with Kroll's reagent.

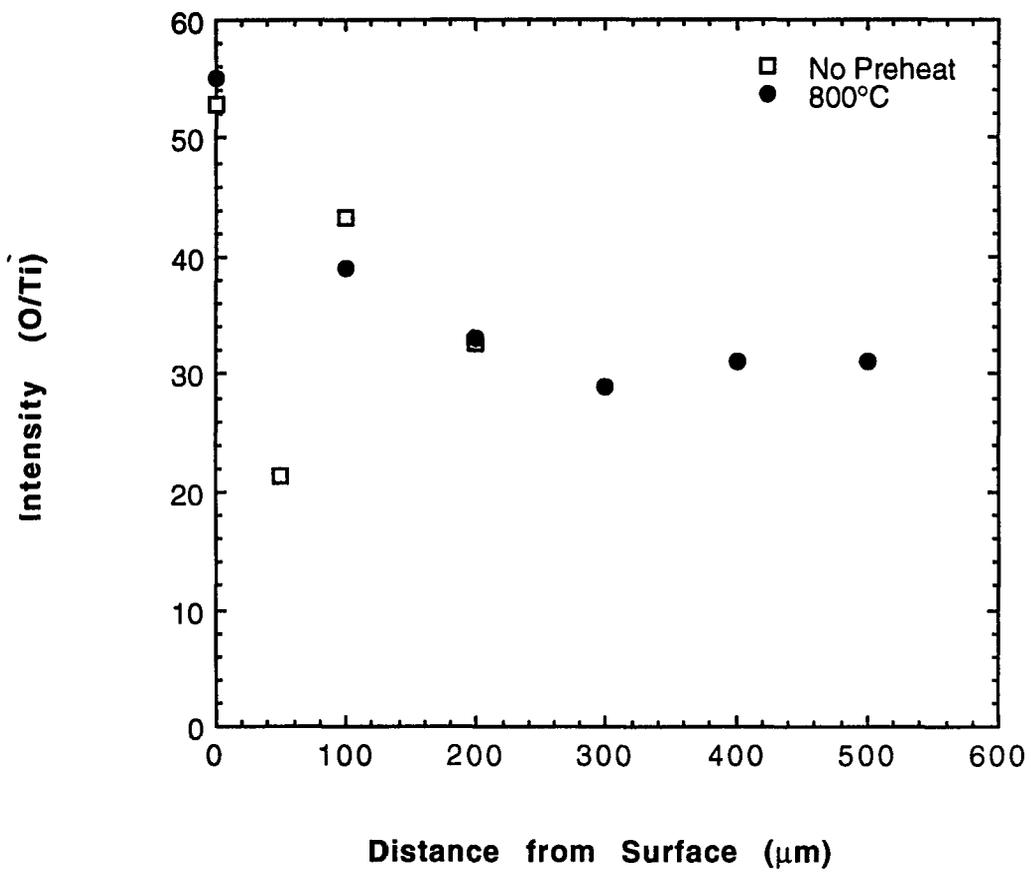


Fig. 31. Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in yttria molds.

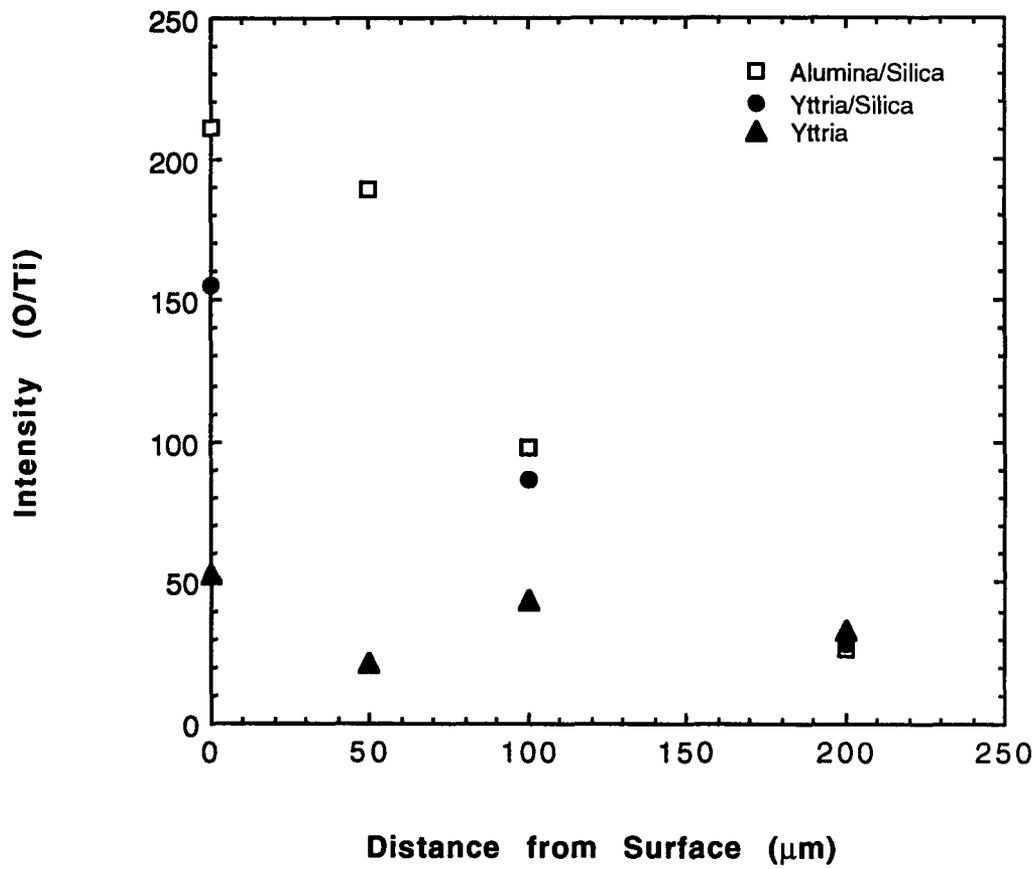


Fig. 32. Oxygen profiles, as determined by SIMS, of CP-Ti castings produced in alumina/silica, yttria/silica, and yttria molds with no preheat.

mold is four times less than the amount found in the sample produced in the alumina/silica mold, and three times less than the amount found in the sample produced in the yttria/silica mold. The differences between the intensity values decreases with distance, but they are evident for 200 μm . A comparison of those data obtained from molds preheated to 800°C shows a similar trend, only it is amplified.

The microprobe data shown in Figure 33 show that only a small amount of yttrium diffused into the CP-Ti castings made in yttria molds. With no preheat, yttrium diffused to a depth of 1 μm , and with a preheat of 800°C it diffused to a depth of only 2 μm .

By comparing microhardness data of the castings produced in the yttria crucibles with data from the castings produced in molds with a yttria/silica face coat, it becomes apparent that the beneficial thermodynamic properties of yttria are not realized when combined with a silica binder (Figures 34 and 35). Both figures indicate that if a silica free yttria face coat were developed then the alpha case would be reduced significantly or even eliminated. It must be remembered, however, that the castings produced were quite small and cooled quickly. Feagin [12,13], however, reported encouraging results when he cast Ti-6Al-4V in molds, with a near 100% yttria face coat, which were larger (10 cm) and found an alpha case of less than 3 μm .

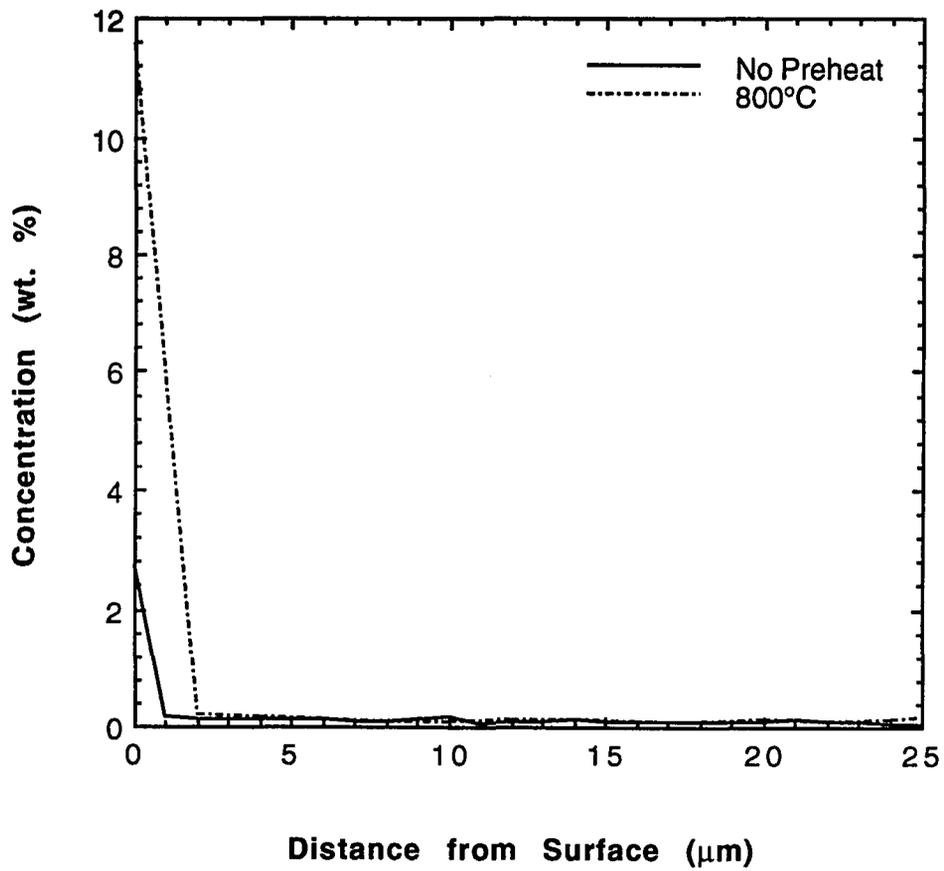


Fig. 33. Concentration of yttrium which has diffused into a CP-Ti casting as a result of its contact with a yttria mold.

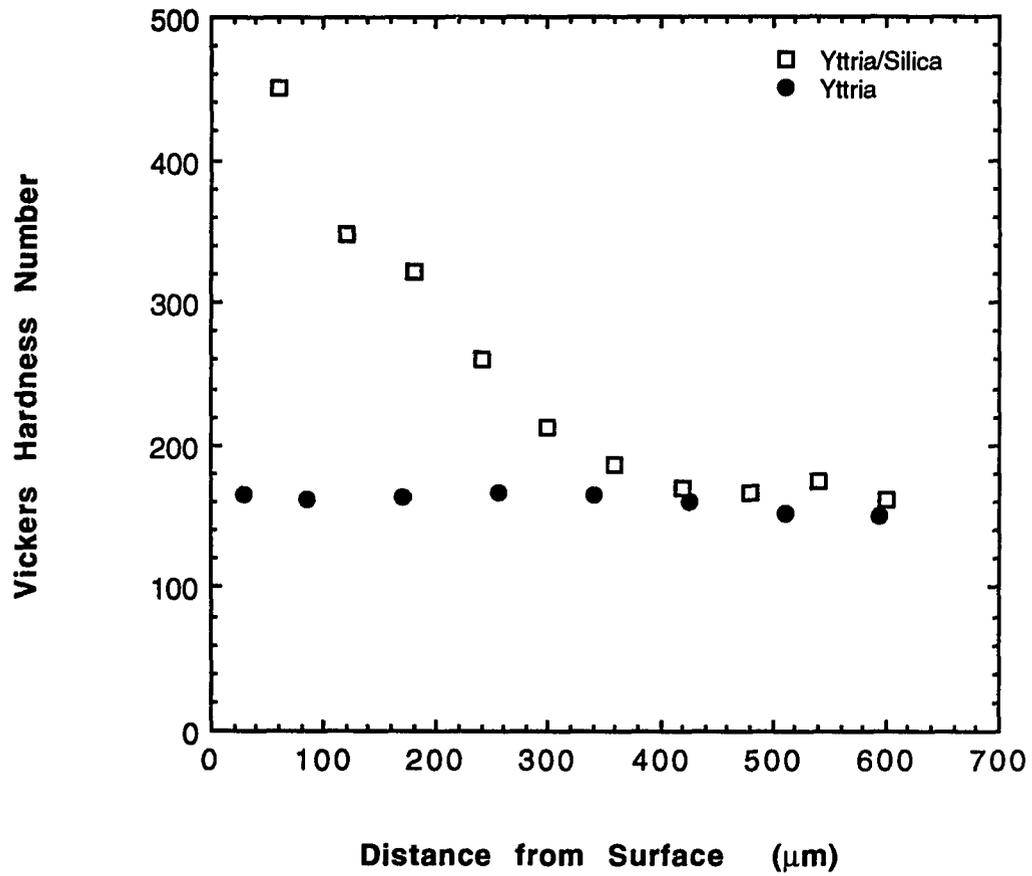


Fig. 34. Microhardness profiles from CP-Ti castings produced in either a yttria crucible or a mold having a yttria/silica face coat; molds were preheated to 800°C.

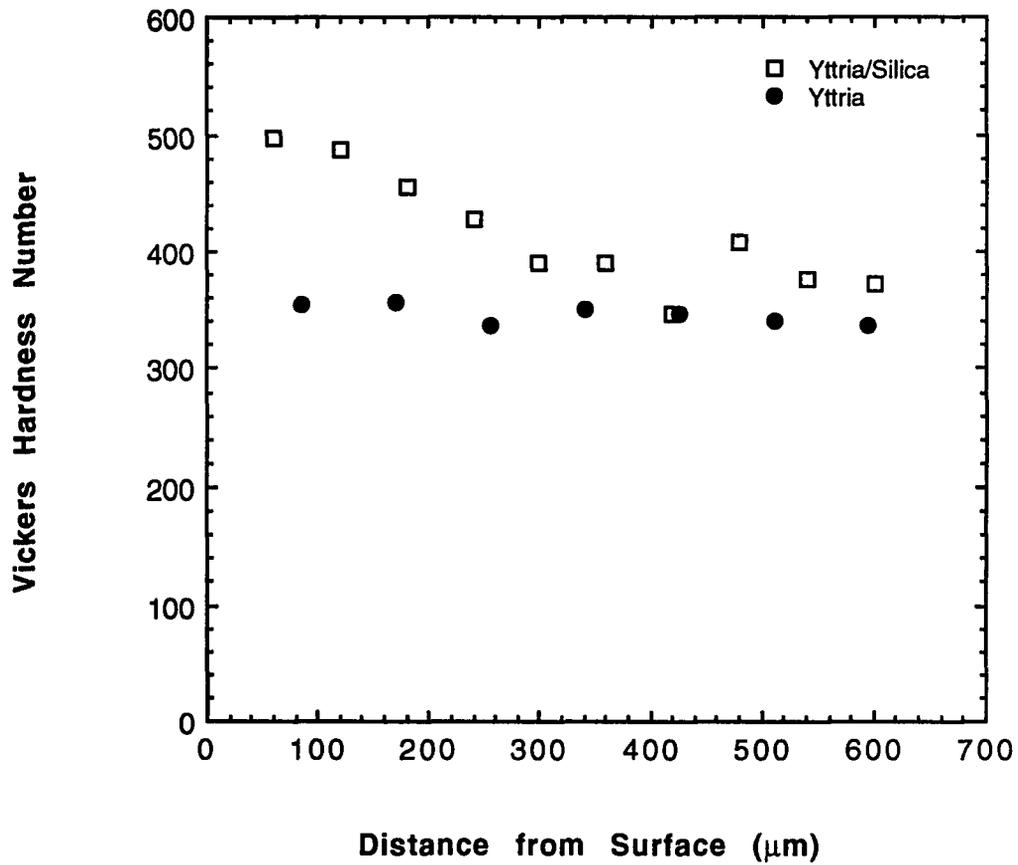


Fig. 35. Microhardness profiles from Ti-6Al-4V castings produced in either a ytria crucible or a mold having a ytria/silica face coat; molds were preheated to 800°C.

4.2 Contact Experiments

4.2.1 Microhardness Analysis of Ti-6Al-4V Buttons Produced in Yttria Crucibles

In order to simulate larger castings, two Ti-6Al-4V buttons were made using the procedure described in Chapter 3. They were held above the liquidus for 15 and 30 s. Microhardness tests indicated no variation of hardness with distance from the metal/mold interface. The average hardness of the 15 and 30 s samples was 354 and 390 VHN, respectively. From these data it may be ascertained that as melt time increases, the amount of diffused oxygen increases. Furthermore, these data elude to the effect casting size would have on the thickness of the alpha case.

4.2.2 SIMS and Image Analysis of Ti-6Al-4V Buttons Produced in Yttria Crucibles

SIMS analyses confirmed that with an increase in melt time, there is an increase in oxygen pickup. Unlike the microhardness tests, however, SIMS indicated the presence of an oxygen concentration gradient in both samples, as can be seen in Figure 36. As expected the oxygen content is higher in sample held above the liquidus for 30 s.

Present in both samples were yttria precipitates at the prior β grain boundaries. Figures 37(a) and 37(b) show secondary electron micrographs taken of the surface of a Ti-6Al-4V button melted in a yttria crucible. Figure 37(a) shows that the precipitates decorate the grain boundaries; Figure 37(b) shows the blocky nature of some of the precipitates. It was confirmed through the use of an energy-dispersive

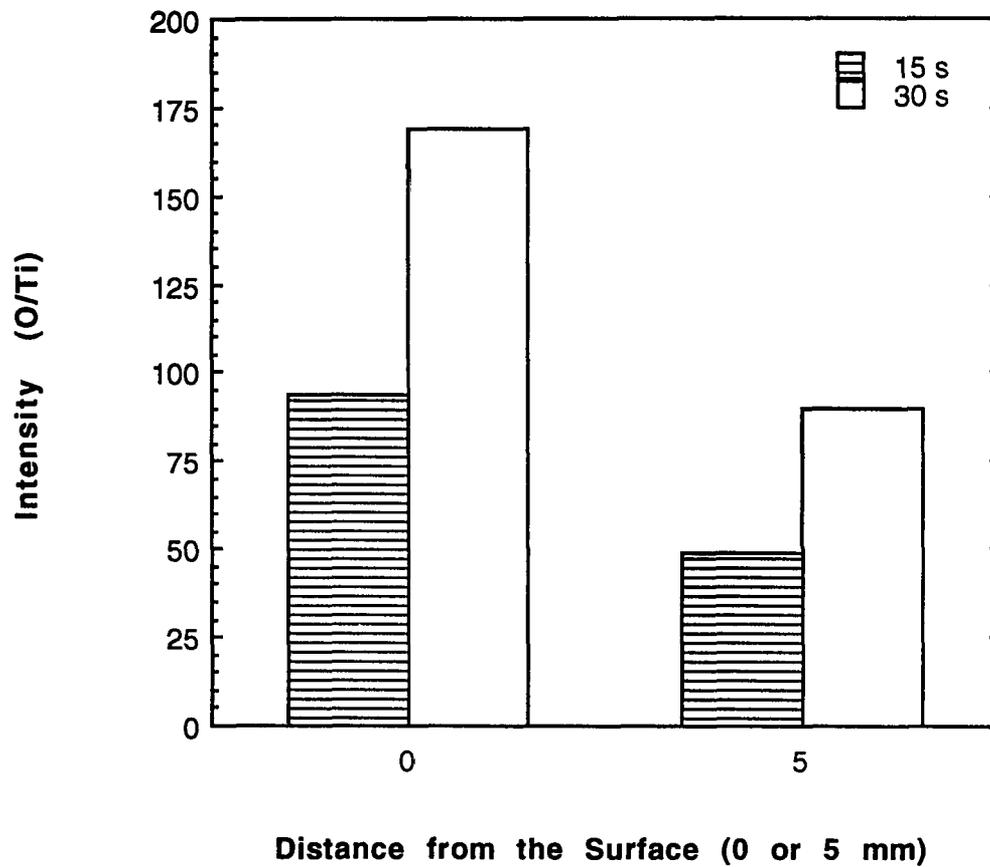
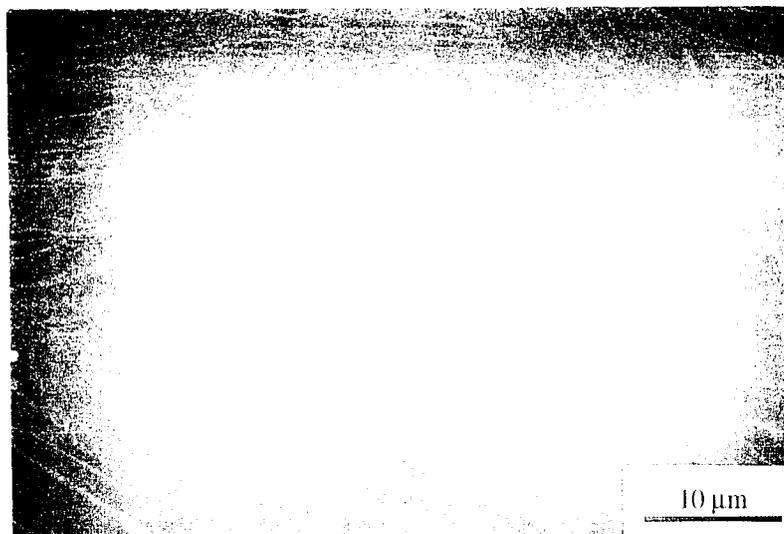


Fig. 36. The oxygen concentration gradient, as determined by SIMS, in Ti-6Al-4V buttons melted and held above the liquidus for 15 s and 30 s in yttria crucibles.



(a)



(b)

Fig. 37. Secondary electron micrographs taken of the surface of a Ti-6Al-4V button made in a yttria crucible: (a) distribution of precipitates at grain boundaries and (b) blocky appearance of a large precipitate.

spectrometer that these precipitates are yttrium rich. Others who have used yttria as a crucible material for titanium have also indicated the presence of these precipitates [36-40,43,44]. The precipitates were evenly dispersed across the samples and in higher concentrations on samples kept liquid for longer periods of time. Using image analysis techniques, it was determined that the area fraction of these precipitates for the 15 s sample is 2.28%, and for the 30 s sample is 4.31%.

Helferich and Zanis [36] found that titanium melts made in yttria crucibles picked up oxygen (determined by chemical analysis) without an increase in hardness. They suggested that the oxygen is concentrated in the "yttrium-rich" precipitates. Although the results presented in this work indicate that there was an increase in the hardness, it should be noted that the time of contact with yttria was short, especially when compared to the 5 min. melt time of Helferich and Zanis.

By adding increasing amounts of yttrium to titanium, Alexander *et al.* [38] found that the bulk hardness of titanium decreased; they attributed this to the yttrium scavenging oxygen from the melt. Holcombe and Serandos [37] used electron probe microanalysis techniques to confirm that the "yttrium-rich" precipitates were essentially yttria. One of the reasons they put forth to explain the existence of the precipitates is that the yttrium in solution getters the oxygen.

It is likely that, because the solid solubility of Y in Ti is small [81], that the excess Y getters oxygen during cooling. Another mechanism, suggested by Holcombe and Serandos, could be that the entrapped or dissolved gaseous elements could also react to form precipitates. This is likely because Y has a considerable

vapor pressure at 2000 K (>4.2 Pa [82]) and YO and TiO are gaseous above the melting point of titanium.

Regardless of the mechanism, if yttrium does act as an oxygen getter in titanium, it suggests that yttrium might be used as a way to provide low temperature ductility for intermetallics such as titanium aluminides by reducing the oxygen content, which has been reported to severely reduce its ductility [83-86].

Chapter 5

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, and suggest a way for industry to reduce or eliminate it. The major conclusions of this research are the following.

- (1) Silica, used as a binder for investment shell mold, drives the Ti/mold reaction regardless which refractory is used.
- (2) The use of refractories, such as yttria, as face coat materials represents an unnecessary expense when combined with a silica binder.
- (3) Using yttria as a face coat material could be an excellent way to reduce the alpha case, if a silica free binder is developed.
- (4) A silica free face coat based on yttria will not eliminate the alpha case if the castings are large.
- (5) Ti-6Al-4V castings had a thinner alpha case than those produced from CP-Ti.
- (6) It is possible that by altering the composition of the alloys used to produce titanium castings the alpha case could be substantially reduced.

APPENDIX

MICROHARDNESS PROFILES

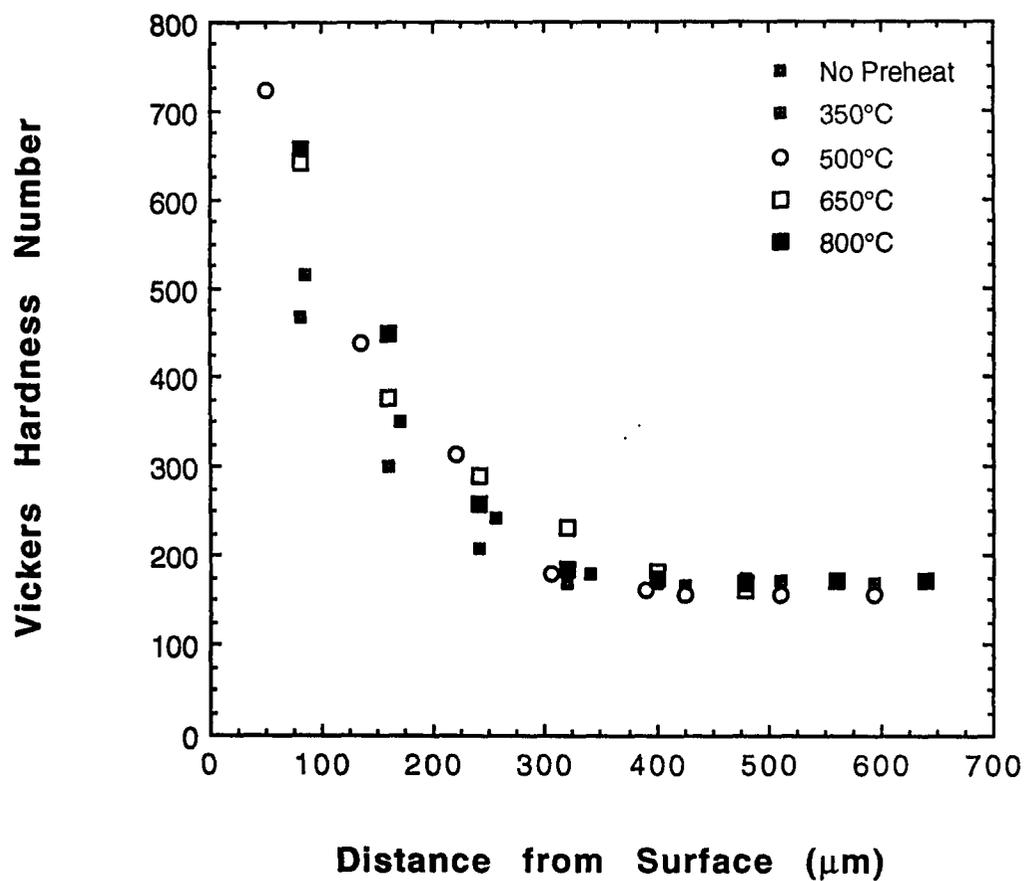


Figure A1. Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat.

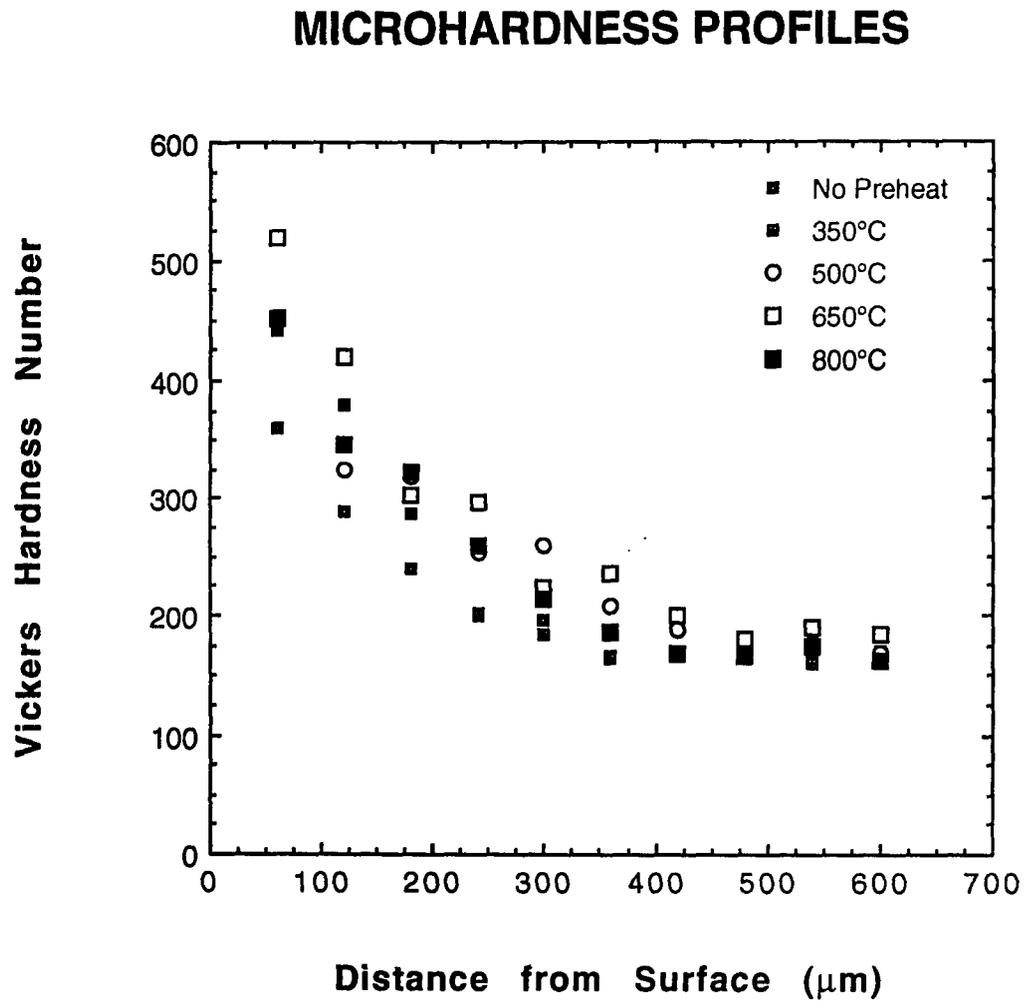


Figure A2. Microhardness profiles of Ti-6Al-4V castings produced in molds having an alumina/silica face coat.

MICROHARDNESS PROFILES

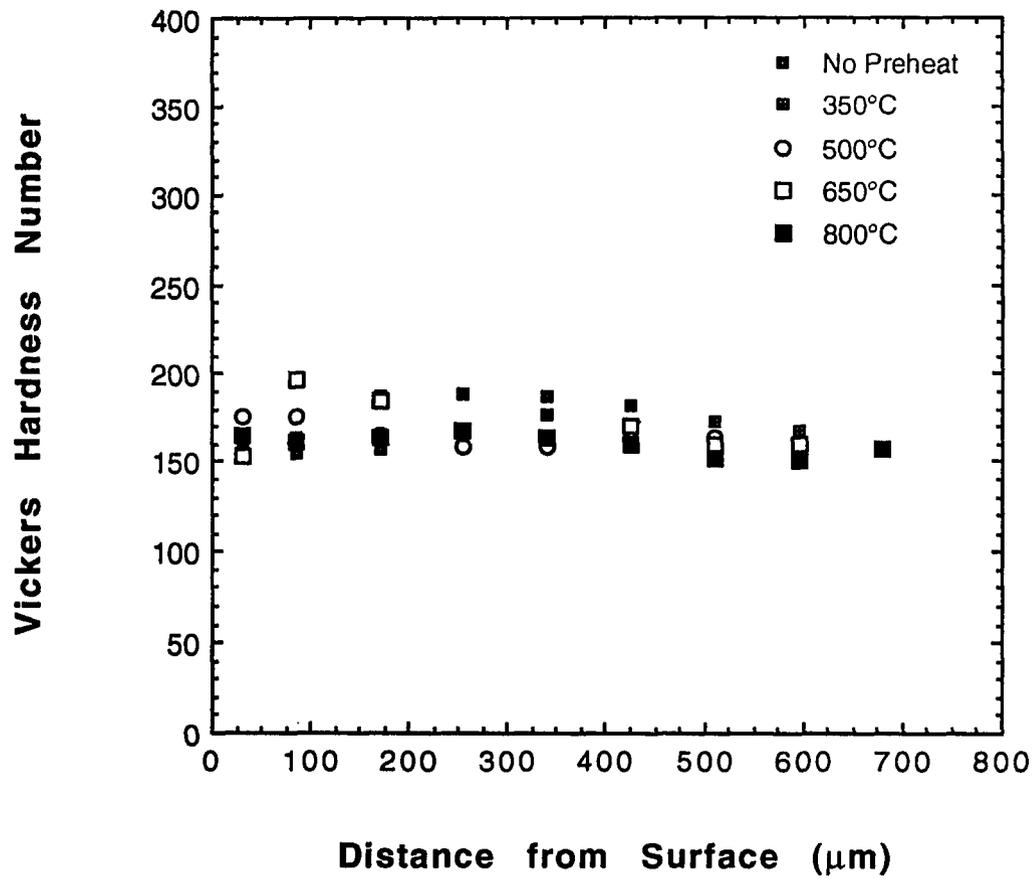


Figure A3. Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat.

MICROHARDNESS PROFILES

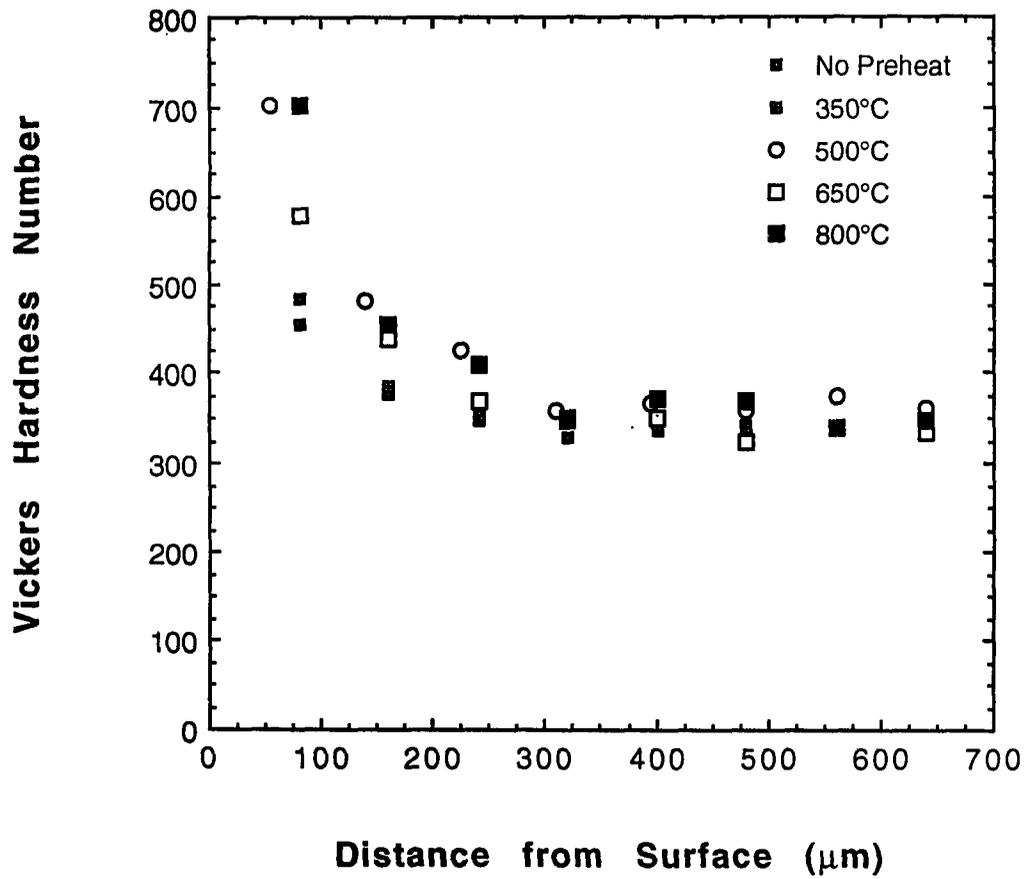


Figure A4. Microhardness profiles of Ti-6Al-4V castings produced in molds having a yttria/silica face coat.

MICROHARDNESS PROFILES

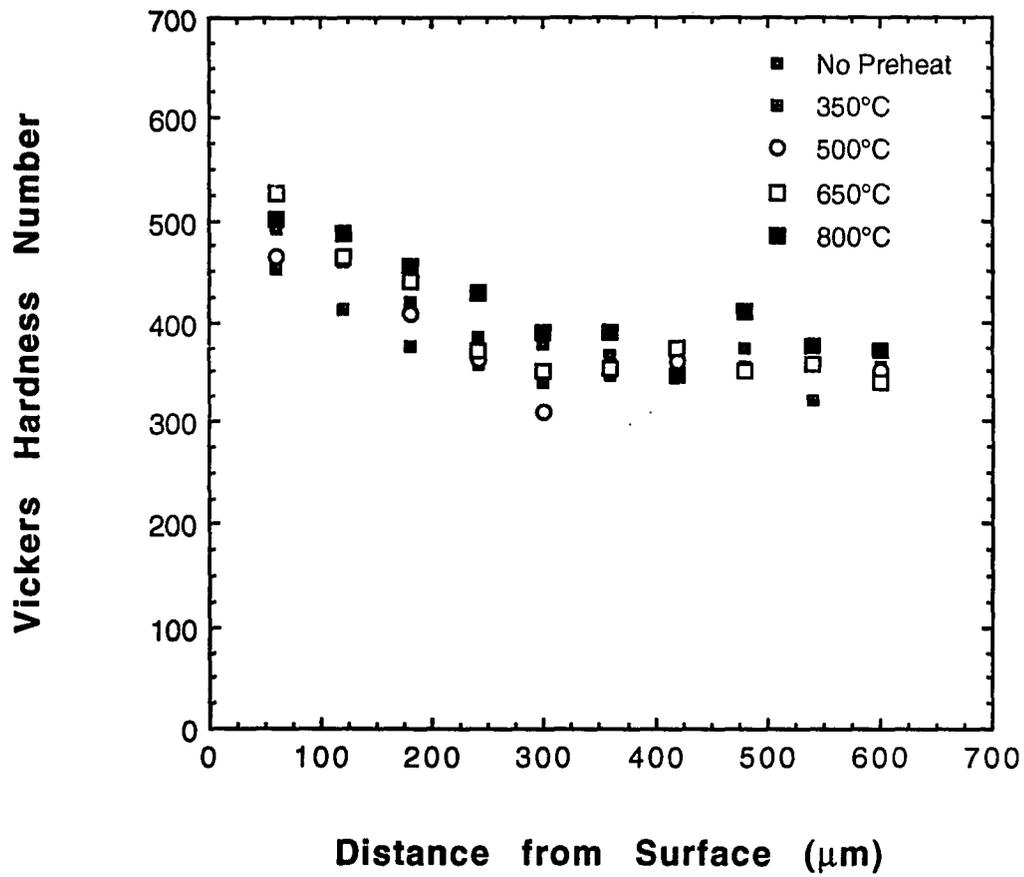


Figure A5. Microhardness profiles of CP-Ti castings produced in yttria molds.

MICROHARDNESS PROFILES

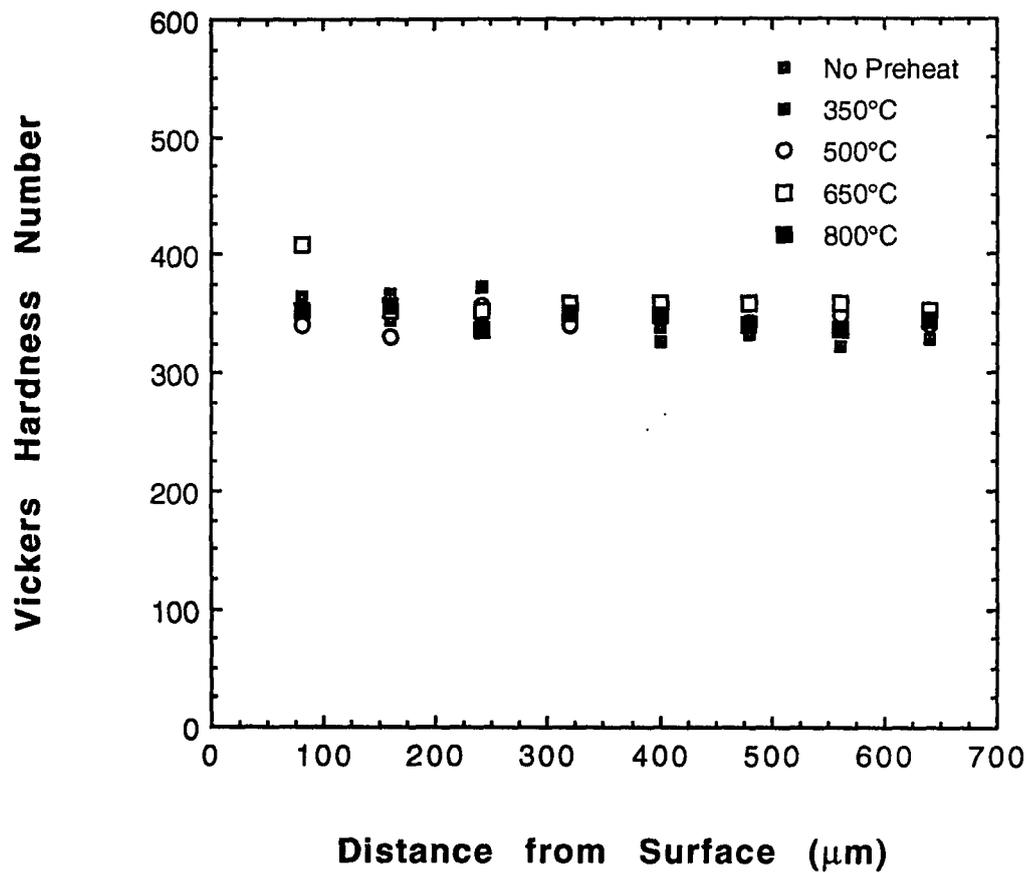


Figure A6. Microhardness profiles of Ti-6Al-4V castings produced in yttria molds.

MICROHARDNESS PROFILES

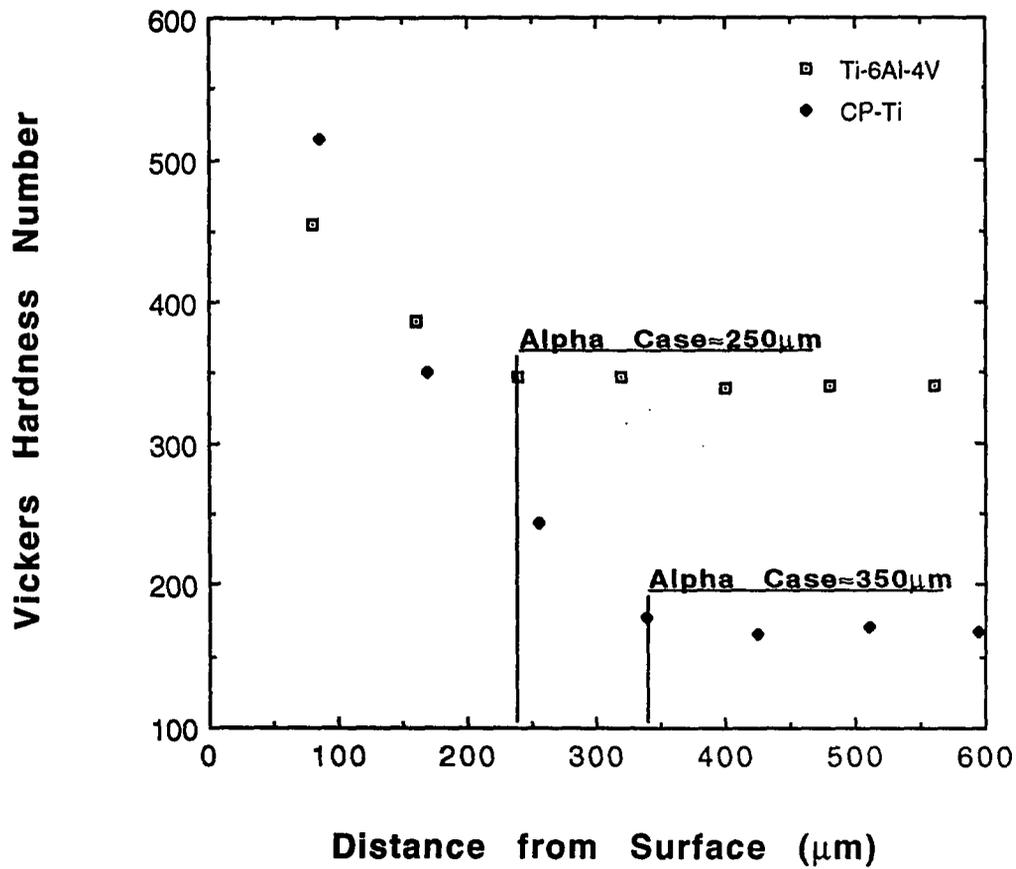


Figure A7. Microhardness profiles of castings (CP-Ti and Ti-6Al-4V) produced in molds, preheated to 350°C, having an alumina/silica face coat.

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