Shell Materials and Casting Methods for Casting Titanium

Tom Branscomb, Buntrock Industries

Abstract

Casting of Titanium alloys can be done with various primary, intermediate, and backup shell materials. There are also different methods of casting these alloys. Recommendations are given to minimize Alpha Case formation. Two case studies of Yttria and Zirconia prime layers of the shell are presented. Yttria generates far less Alpha Case. The economics of using Yttria is discussed.

Introduction

The main difficulty with casting Titanium alloys is their reactivity with common elements in air like oxygen and nitrogen. Melting and casting of Titanium alloys needs to be done in furnaces with very high vacuum or inert gas to avoid dissolving oxygen and nitrogen in the molten Titanium. Oxygen and Nitrogen are quite soluble in molten Titanium metal. Upon cooling, these elements form oxides and nitrides that affect mechanical properties of the metal and can make it unsuitable for some applications. In addition to atmospheric elements, molten Titanium is reactive with all ceramic oxides. Molten Titanium alloys will reduce or react with ceramic oxides freeing oxygen which dissolves into the Titanium and forms a contaminated surface layer commonly called Alpha Case.

Molten pure Titanium solidifies at 1675^{o}C and has two solid phases. The high temperature Beta phase has a body centered cubic structure. This phase has high strength, but is brittle. The low temperature Alpha phase has a hexagonal close pack structure that is stable below about 880 ^{o}C. The Alpha phase is characterized by good strength and ductility. Each of these phases can be stabilized by the addition of alloying elements. In this manner, it is possible to achieve a good balance between high strength and good ductility over a broad temperature range. When stabilized, the two phases (Alpha and Beta) exist outside the range where they would in pure Titanium. The most common metallurgical Alpha phase stabilizer is Aluminum and the most common Beta phase stabilizer is Vanadium. Unfortunately, both Oxygen and Nitrogen are also Alpha phase stabilizers. A very common Titanium alloy is Ti 6-4, which has a nominal composition of 90% Titanium, 6% Aluminum, and 4% Vanadium. A Titanium alloy for medical parts is Ti 6-7 which includes 6% Aluminum and 7% Niobium. The Niobium improves strength and compatibility of the casting with human bone.

Alpha case is a brittle layer on the surface of a Titanium casting. It is caused mostly by the reaction of the molten Titanium alloy with the ceramic mold. For example, you would not find Alpha case on Titanium metal poured into a water cooled copper mold cast in a good vacuum. See Figure 1, which shows a typical Alpha case layer on a Ti 6-4 casting. The Alpha case layer is Alpha phase Titanium stabilized with mostly oxygen and Aluminum, but could include Nitrogen and Carbon if present at casting. The main body of the casting consists of intentionally stabilized Alpha and Beta phases of Titanium. The Oxygen content in the surface layer is much higher than in the base metal. This layer is hard and brittle compared to the base metal and needs to be removed from many castings, especially those that have critical mechanical property requirements. Alpha case is removed by machining, blasting, and chemically dissolving the surface in strong acids. The removal of the alpha case layer by acid is known as chemical milling.

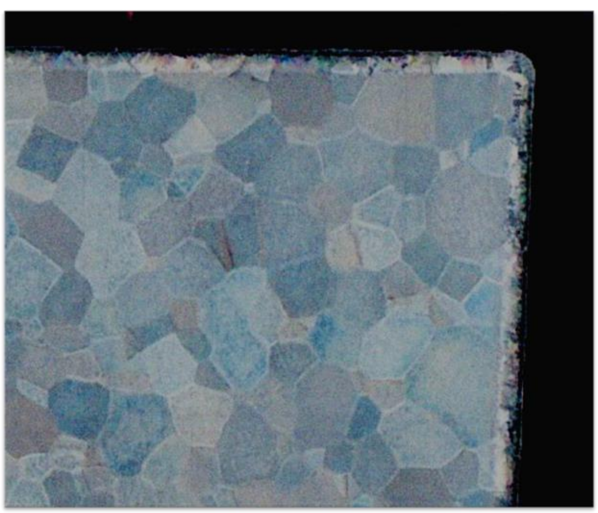


Figure 1. Example of Alpha case layer on Ti 6-4 casting. Layer is 0.025” thick.

Shell Materials and Casting Methods

For aerospace quality castings, all alpha case must be removed from the casting in areas defined by the drawing. As mentioned above, this entails metal removal at significant cost. Therefore, it seems reasonable that any processing steps that could be reasonably done to minimize the formation of alpha case should be considered.

To minimize Alpha Case formation, the following is recommended:

1. Minimize gating for faster cooling after casting. Gate to fill, not to feed.
2. Shell burnout should be about 1000 ^{o}C with excess oxygen atmosphere. Cool the shell to room temperature and clean. Minimize foreign material and carbon.
3. Shell pre-heat should be as low as possible at pour. Target 150 - 300 ^{o}C.
4. Use ingot with low oxygen, nitrogen, and carbon levels.
5. Melt the metal in a water cooled copper crucible (consumable arc or induction). See Appendix A for examples of Ti casting furnaces.
6. Use a centrifuge for casting to fill the "cold" mold using small gates.
7. After casting, backfill furnace with Argon, remove shell, fan cool.

The goal of the above list is mainly to minimize the time that the metal - mold interface is at high temperature. The other important factor in producing castings with minimum Alpha Case is the ceramic shell primary dips. They must be the most resistent to reaction with the molten Titanium as possible. Almost all Titanium investment castings are made with either Zirconia or Yttria as the prime slurry flour. Below, the results of two studies performed with our customers are presented.

<u>Case Study 1.</u> Evaluation of Alpha Case formation in Ti 6-4 using Zirconia and Yttria prime slurries.

The wax trees for the test consisted of test pieces that were normally used by the foundry and are not presented here. A "step wedge" was added to the assembly to evaluate Alpha

Case in various thicknesses of metal. The Ti 6-4 pour weight was 30 lbs. The alloy was melted using a traditional consumable electrode arc melting furnace with a water cooled copper crucible. The shells were cast statically.

Three prime slurries were evaluated. Fused Calcium Stabilized Zirconia, Fused Yttria, and a 50:50 blend of the same two materials. The prime slurry binder was a low percent colloidal silica proprietary to Buntrock Industries. Other than the prime slurry, the shells were exactly the same. Three Alumina intermediate dips with alumina stucco and 3 fiber enhanced fused silica backup dips with alumino-silicate stucco and a seal coat. The shells were burned out at 900 C for one hour, cooled to room temperature, cleaned, and prepared for casting. The shells were then pre-heated to 1065 C for 2 hours, and cooled to 450 C for casting. There were no problems with any of the pours. The shells were removed from the castings by normal means. The step wedge was removed and analyzed metallurgically for the extent of Alpha Case contamination. The measured depth of the Alpha Case layer was plotted against the thickness of the step on the wedge. The results are given below in graphical form.

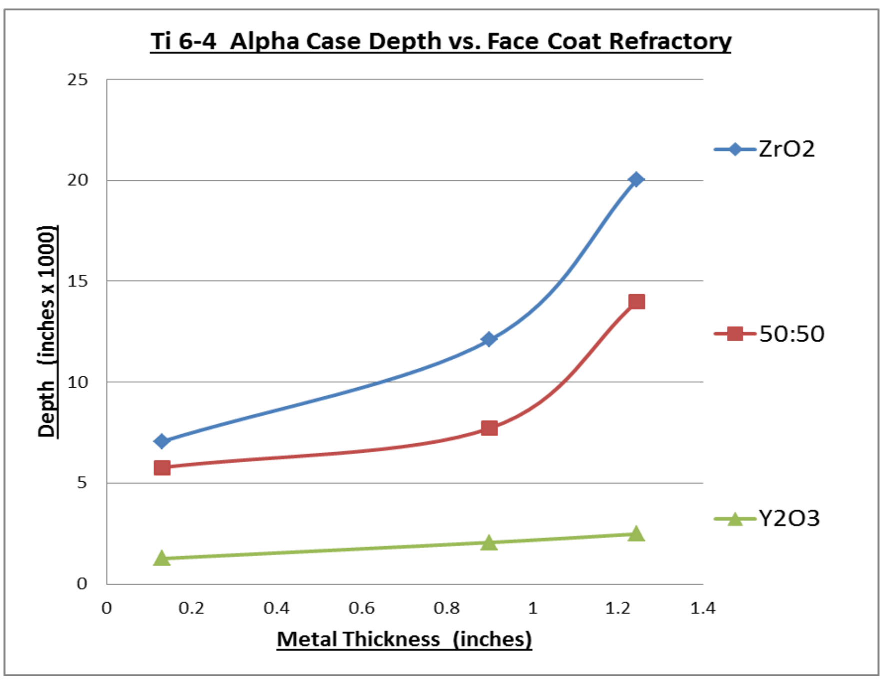


Figure 2. Alpha Case Measurements for Case Study 1.

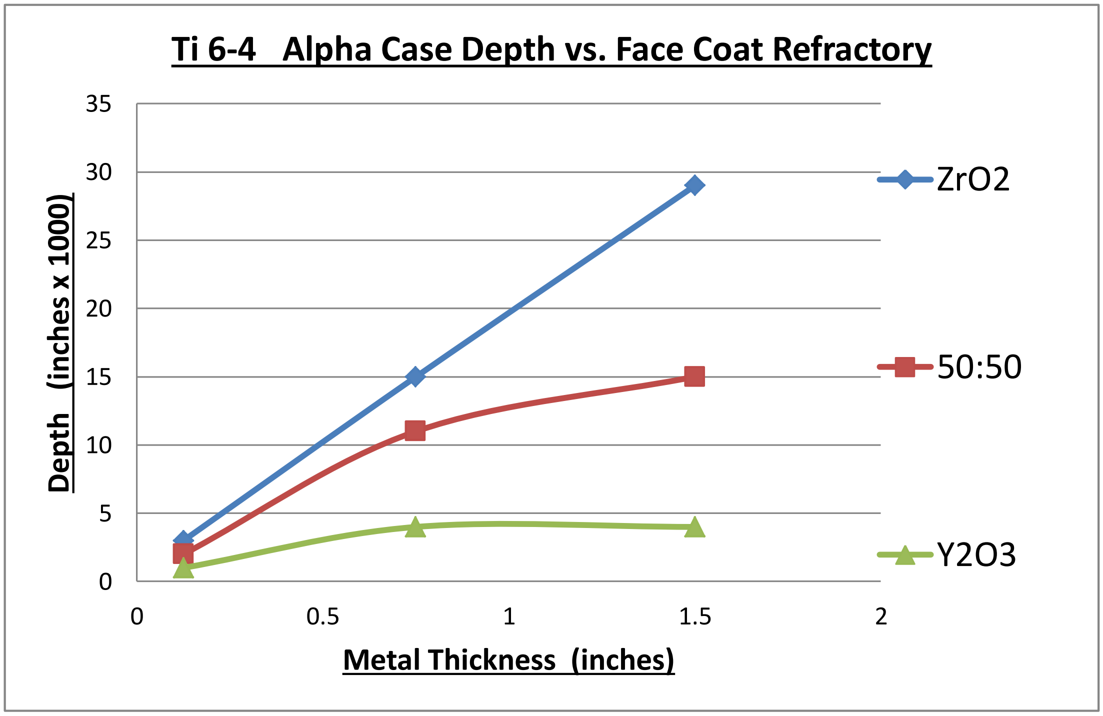
Clearly, fused Yttria produces less Alpha case in Ti 6-4 alloy compared to Zirconia . As the thickness of the metal increases, so does the depth of Alpha case contamination. This is likely due to the extra time that it takes to cool the thicker metal sections allowing more time for diffusion of oxygen into the metal.

Case Study 2. Evaluation of Alpha Case formation in Ti 6-4 using Zirconia and Yttria prime slurries. This was a different customer than in Case Study 1. Step wedges were atached to test molds. The dipping sequence used for “standard” shells dipped at the customers shop was: Three Zirconia primes using variuos commercial colloidal silica binders and Zirconia stucco, followed by 3 fused silica dips with Alumino-Silicate stucco and a seal coat. All backups were the same. A total of eight shells were made cast and evaluated.

Two waxes like those standard waxes above were invested at the Buntrock Industries Technology Lab with the following sequence. Two different primes: One using Fused Yttria flour and one using 50% Yttria and 50% Calcium Stabilized Zirconia. The binder in both cases was the same proprietary collidal silica used in Case study 1. Only one prime was applied to each wax and Fused Alumina stucco was used. The remainder of the shell was like that in Case Study 1. Three intermediates with Alumina stucco and three backups of fiber enhanced fused silica using Mulgrain 47 stucco. A seal coat was last. The shells were dewaxed at the Buntrock Lab, inspected and then shipped to the customer for firing and casting.

All shells were fired to 1093 C and cast with a shell temperature of 371 C. Alpha case was measured by the customer on three sections of the step wedge. The results are presented below. Values plotted for the standard shells are the average of the eight shells.

Figure 3. Alpha Case Results for Case Study 2.



Case Study 2 results are essentially a repeat of Study 1. Yttria is much better than Zirconia at preventing the formation of Alpha Case in Ti 6-4. It is fully expected that if a cooler shell and a centrifuge was used at casting that all the castings would have had less Alpha Case.

Yttrium Oxide is expensive comparred to other ceramics used to make shells for casting Titanium. Clearly, there is a benefit in terms of lower Alpha Case, if Yttria is used for the prime layer of the shell. The question becomes, is Yttria worth the extra cost. One potential savings is the cost of the metal that is removed from the casting by Chemical Milling. Let's compare the cost of 0.025" of metal per square foot of casting surface to the added cost of using Yttria versus Zirconia for the prime slurry.

Volume of metal removed = 12x12x 0.025 = 3.6 in^3

Weight of metal removed = 3.6 in^3 x 0.16 lb/in^3 = 0.576 lbs.

Cost of metal removed = 0.576 lbs. x $10/lb. = $5.76 per sq.ft.

Compare this metal savings to the extra cost of using Yttria to replace Zirconia in the prime slurry per sq. ft of surface.

Assumptions:

1. Cost of Yttria is $50 /lb. and cost of Zirconia is $5/lb.
2. One coating only and the coating thickness is 0.006".
3. Density of coating is 80% of theoretical density of the oxide.

Volume of coating = 12x12x0.006 = 0.864 in^3

Weight of Yttria coating = 0.864 in^3 x 0.181 lb/in^3 x 0.8 = 0.125 lbs.

Weitht of Zirconia coating = 0.864 in^3 x 0.205 lb/in^3 x 0.8 = 0.142 lbs.

Cost of Yttria coating per sq. ft. = 0.125 lbs. x $50/lb = $6.25

Cost of Zirconia coating per sq. ft. = 0.142 x $5 = $0.71

Differential Cost of using Yttria over Zirconia for one coat = $5.54 per sq.ft.

Thus it is estimated that in just metal cost alone, all the extra cost of using Yttria is re-couped. If the lower cost of chemical milling a smaller amount of metal off the casting is factored in, there may be a cost savings for using Yttria, even at today's prices.

Conclusions

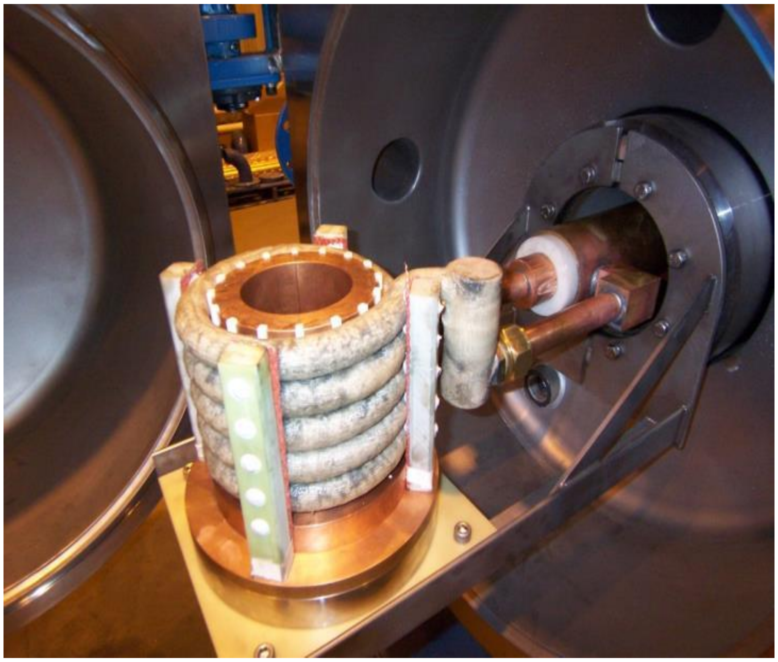
To make Titanium castings with minimum Alpha Case,

1. Use Yttria as a face coat because it results in castings with less Alpha Case
2. Use low ceramic shell temperatures at time of casting
3. Use minimal gating
4. Use a centrifuge to cast the metal into the cool shell
5. Cool shell quickly after casting
6. Although Yttria is expensive as a ceramic material, the potential cost savings in pouring fewer pounds of metal and reducing the cost of chemical milling may more than off set the purchase price of the Yttria.

Apendix A. Examples of Titanium Casting Furnaces

Courtesy of Retech Systems, LLC Ukiah, California

Cold Hearth Induction Melting Furnace

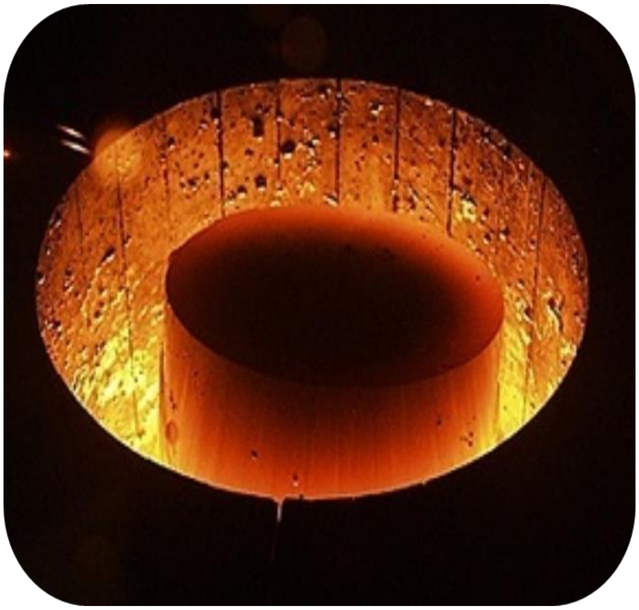


Benefits:

Allows for metal superheat

Improved metal temperature control

Accurate metal weight poured



Capacity: 200 Kg of Titanium

Centrifuge Capability

Electric Arc Consumable Electrode Cold Hearth Titanium Casting Furnace

Standard Furnace Designs up to:
Shell Dimensions 1.7 meters diameter x 1.7 meters tall
Pour Weight: 1000 Kg