

PROCESSING OF TITANIUM ALUMINIDES BY CERAMIC CRUCIBLE INDUCTION MELTING

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Key words: TiAl, induction melting, crucible

Abstract: This work describes the processing results of TiAl alloys melted in controlled atmosphere induction furnace, using crucibles made of calcia and zirconia stabilised with yttria, calcia and magnesia, solidified and inside the crucible, in order to simulate the worst situation using this processing. In the results are presented segregation profiles of residual elements and its relation with micro hardness and "alpha-case" extension, in the microconstituents present at room temperature.

1. Introduction

Foundry is one of the technologies available to process titanium alloys. Its use presents some drawbacks from the alloy itself, among which might be emphasised the high reactivity against a large amount of elements (solid, liquid or gaseous) above 500°C, with particular emphasis to oxygen.¹ One of the foundry processes that shows higher potential is induction melting, processing the melt under controlled atmosphere, using suitable ceramic crucibles and investment casting techniques to for the mould production.

The high reactivity of titanium alloys could impair the quality of the castings made using crucible induction melting, due to reactions between the melt and the ceramic materials present both in the crucible and in the mould. These reactions could contaminate the castings, due to the absorption of some residual elements, chemical heterogeneities, inclusions and structural variations.

This paper describes the work done with titanium aluminides, prepared from pure aluminium and titanium melting stock. The main objectives are two:

- Evaluation of some refractory materials behaviour during the melting of TiAl;
- To find a relationship between micro-hardness, the concentration of residual elements in those phases present at room temperature and the extension of "alpha-case" (a surface slice with an higher micro-hardness than the average value found in regions in the bulk of the casting).

The introduction of residual elements comes from the reduction of oxides from the crucible, which have reacted with the melt. The introduction of residual elements occurs during the processing of the alloy. When the alloy is in the molten state there is a strong reaction, which results in an uniform increase of the content of residual elements, due to the stirring effect of the melt, together with high diffusion rates. During solidification there is a smaller contamination, from which results an higher content of contaminant elements near the interface between the crucible and the casting, continually decreasing up to achieving a sort of plateau in which the level of contaminants is kept constant, from a certain distance from the interface. Oxygen is a common contaminant of these alloys, when an investment casting process is used, because mould ceramic oxides are less stable than those resulting from the reaction of melt components with oxygen. This element has a tendency to form an interstitial solid solution with titanium. In practice, there is a superficial layer with an higher oxygen content, which some call "Alpha-case".^{1,2}

2. Experimental technique

A TiAl [Ti-48Al (at%)] has been used, prepared from pure aluminium and titanium, melted into crucibles of different materials. To evaluate the effect of a slower cooling rate upon the residual elements content, the melt was allowed to solidify and cool inside the melting crucible. The results have been evaluated comparing microstructures, micro-hardness shape profile, and chemical composition of phases present at room temperature, using scanning microscopy and microanalysis.

2.1 Process description

Melts have been prepared from pure aluminium and titanium, using an induction furnace with different types of crucible materials. During processing, a controlled atmosphere of commercial pure argon was maintained, because crucibles have been kept inside a tight sealed chamber. It was open only when the sample was at room temperature (see figure 1). As it can be seen, the melting crucible is kept inside an alumina support one, which has a pouring lip. The purpose of this second crucible is two fold: as a coil protection, in case of the primary crucible failure, and to allow a simple and easy way of pouring the melt into moulds, when intended.

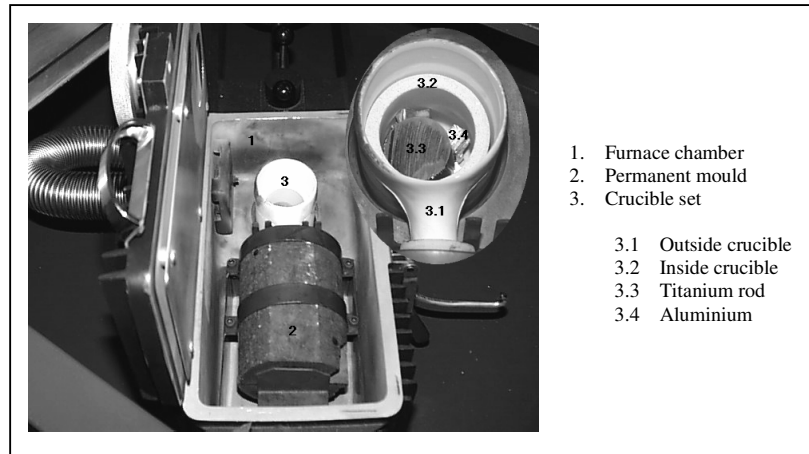


Figure 1 – Ceramic crucible induction furnace

2.2 Crucibles

There is no precise information of practical use of ceramic materials to melt reactive materials. Although there are some insights, protected by patenting, but no public information is released. The selection of refractory materials was made according with thermal chemical concepts, choosing potential materials which oxides have lower free energy of formation than titanium and aluminium oxides. On our work were used calcia and stabilised (with Y_2O_3 , MgO and CaO) zirconia crucibles.

3. Experimental results

Experimental results have been analysed considering:

- Identification of each phase and microconstituent to which a quantitative chemical analyses variation has been made using microanalysis;
- Chemical profile has been elaborated, from the outside to the inside of the samples, in each of the microconstituents;
- The microhardness profile has been made, from the outside to the inside in each of the microconstituents.

As presented in figure 2, the as cast microstructure presents two microconstituents: one with a strong dendritic pattern, with two phases ($\alpha_2 + \gamma$), and a γ interdendritic phase. The previous dendritic constituent is present in a higher quantity in all the samples. The amount of interdendritic γ is lower in the outside part of the samples and increases to the inside of them, following the decrease of cooling rate. In all the samples, the lamellar dendritic biphasic constituent is richer in titanium and the monophasic interdendritic constituent has a higher aluminium content, according to the available references.³

3.1 Zirconia crucibles

The results are summarised in table 1 and all comments are based upon it.

Samples processed in these crucibles have a higher amount of zirconium in the outside part of them. It decreases to the inside, and after a while it reaches a constant level. This concentration is higher in the interdendritic

γ constituent than in the α_2 , lamellar dendritic. So, it might be concluded that zirconium is segregated to the interdendrit melt, during solidification, and that it dissolves preferentially there.

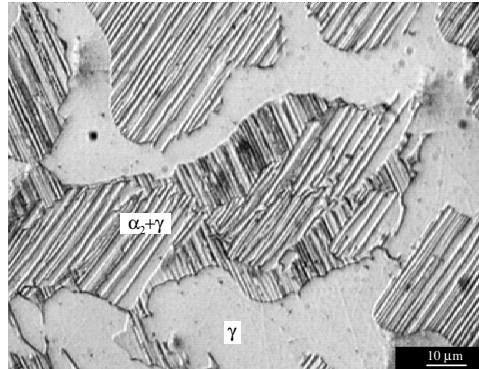


Figure 2 - Microstructure of a casting melted and cooled in a calcia stabilised zirconia crucible

Among all tested zirconia crucibles, those stabilised with CaO were the ones that presented lower levels of zirconium absorption, both for the outside and the inside mean level. Samples processed in the yttria and magnesia stabilised zirconia crucibles present about the same level of zirconium absorption and profile in the dendritic constituent. Although, there is a higher absorption of zirconium in the γ interdendritic constituent, when the melt was processed in yttria stabilised crucibles (see figure 3 and table 1).

Table 1 - Microhardness and extension of the “Alpha-case” in samples melted and solidified in stabilised zirconia and calcia crucibles, and in a sample poured in a graphite mould.

Crucible	Vickers hardness on "alpha-case" (max)		Vickers hardness on bulk		Zr content on bulk (at%)		“Alpha-case” thickness (μm)
	$\alpha_2 + \gamma$	γ	$\alpha_2 + \gamma$	γ	$\alpha_2 + \gamma$	γ	
ZrO ₂ /MgO	644	594	549	473	0,93	3,36	400
ZrO ₂ /Y ₂ O ₃	580	412	473	313	0,57	4,96	600
ZrO ₂ /CaO	473	321	351	257	0,27	0,88	300
CaO	341	303	313	280	-	-	200

In what is concerned with microhardness, as mentioned by other references, there is a decrease from the outside to the inside of the samples. This hardness profile has about the same shape in both microconstituents but dendritic α_2 is always harder than γ , for all the samples. The outside layer, which is harder than the average, and named “Alpha –case”, have an extension between 300 to 600 μm (Table 1). The microhardness profile has two different behaviours: near the surface there is a quick decrease with the increase of distance to the interface sample / refractory. The inner part of the sample has about a constant hardness value as shown in figure 3. This last behaviour suggests that there is a constant level of contaminant, resulting from the time where the metal was in the molten state. The outside profile suggests that it resulted from the reaction during the cooling of the sample in the solid state.

In our samples there is not a direct relationship between the amount of zirconium in the microstructure and microhardness. Although they present the same type of profile, that is, both decrease from the outside to the inside of the sample, and both profiles became constant after a certain distance from the outside. If figure 3 is taken in consideration, it can be noticed that both profiles do not overlap.

One possible justification, is that zirconium is not the only, or the most important element to affect hardness. Assuming the reduction of ZrO₂, the only factor remaining is the possible presence of oxygen, as this element has a much higher diffusion coefficient in pure titanium. Some authors, in similar works also refer the presence of oxygen, when melting commercial pure titanium.⁴

3.1.2 CaO crucibles

The CaO crucibles produced the best results. As it can be seen in table 1, samples presented the lowest microhardness, both in the base metal and in the “alpha-case”. It was also the shortest “alpha-case” of all the produced samples - 200 μm .

Those samples do not present a calcium concentration higher than the detection level of 0.1%, free or as an alloy solution. This may confirm a high stability of this refractory and a low solubility of calcium in this kind of alloy.

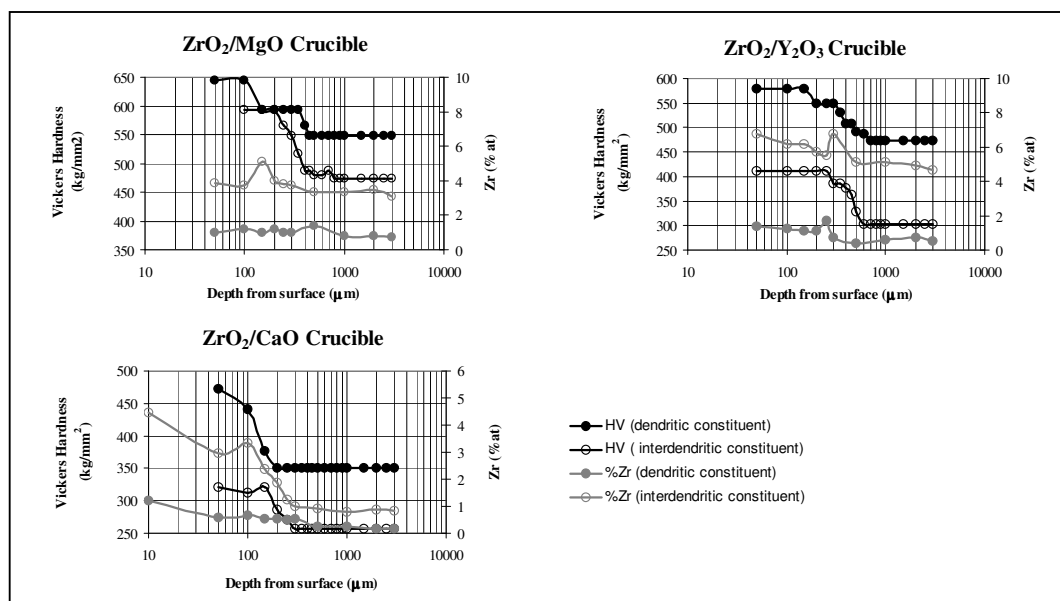


Fig. 3 – Microhardness and Zr(%at) profiles in samples melted and cooled in zirconia stabilised crucibles

Conclusions

1. In all samples melted into zirconium based crucibles, there is evidence of contamination with this residual element. In those processed into calcia crucibles, there is no evidence of contamination. (see table 1);
2. Samples that cooled inside zirconia crucibles presented a decreasing contamination profile, from the outside to the inside of castings. It is thought that it might result from the solid state cooling. The level of contamination in the centre is a result of reaction between melt and crucible material.
3. The dissolution of residual elements occurs preferentially into interdendritic γ , because the concentration into lamellar dendritic α_2 is much smaller.
4. Microhardness decreases from the outside to the inside of castings, with a profile that agrees with some references. The microhardness is higher in an external layer, called "alpha-case", as a result of contamination with some residual elements. Zirconium is a potential candidate, but because hardness and contamination profiles do not match, and considering that it comes from a reaction of melt elements with the refractory oxide, then oxygen might also be present.⁴
5. Calcia crucibles produced the thinnest "Alpha-case" (see table 1) extension. The level of residual element contamination was also the smallest.
6. Only those alloys processed into calcia or calcia stabilised crucibles presented microhardness values, which agrees with references, considering the chemical compositions of our alloys. This might suggest that these crucibles might be used to process TiAl alloys, although some external contamination could occur.

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