

Zr bearing γ -TiAl induction melted

Joaquim Barbosa¹, António Duarte², C. Silva Ribeiro², Filomena Viana², Caetano Monteiro¹

¹ Universidade do Minho, Departamento de Engenharia Mecânica, Guimarães, Portugal
Tel: +351 253 510220, Fax: +351 253 516007, e-mail author 1: kim@eng.uminho.pt

² FEUP, Departamento de Engenharia Metalúrgica e Materiais, Porto
Tel: +351 22 2041786, Fax: +351 22 2041792

Key words: TiAl, induction melting, crucible, heat treating

Abstract

This paper describes the processing results of TiAl alloys melted under argon atmosphere by induction melting, using crucibles made of calcia and stabilized zirconia. Castings were allowed to solidify inside the crucible, in order to simulate the worst situation using this processing. Segregation profiles of residual elements and microhardness of different phases were evaluated, as well as its relation with the “alpha-case” extension.

Two TiAl alloys, with 1 at. % zirconium and zirconium free, were produced and heat treated aiming to replace their as-cast structure by a quasi-lamellar one. The respective zirconium partition amongst microconstituents was evaluated, being demonstrated that zirconium concentrates in the γ -phase and increases the volume fraction of this constituent, showing the γ stabiliser role of zirconium.

1. Introduction

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 were three fold:

- Evaluation of the thermal and chemical stability of some crucible materials on the induction melting of TiAl;
- The relationship between microhardness, the segregation profiles of secondary elements in the as-cast phases and the “alpha-case” extension" (a surface slice with an higher microhardness than the average value in the bulk of the casting);
- Modification of the as-cast structure by heat treatment, in order to achieve a quasi-lamellar structure.

The introduction of residual elements comes from the reduction of oxides from the crucible, which have reacted with the melt. When the alloy is in the molten state there is a strong reaction, which results in a uniform increase in the content of residual elements, due to the stirring effect of the melt, together with high diffusion rates. During solidification the contamination affects mainly the outside region of the specimen, from which results a higher content of contaminant elements near the interface between the crucible and the casting, continually decreasing to a sort of plateau in which the level of contaminants is kept constant (beyond a certain distance from the interface). When an investment casting process is used, oxygen is a common contaminant of these alloys, 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 a higher oxygen content, which some call "alpha-case" [1, 2].

Several γ -TiAl based alloys with small amounts of refractory elements, for increased high temperature properties and grain refiners, have been studied to attain well-balanced room temperature ductility and high temperature strength [3]. Zirconium has been reported to improve the high temperature oxidation resistance of γ -TiAl alloys and, in a similar manner to Mn, increase the ductility of duplex alloys [4,5].

The occurrence of two cascade peritectic reactions during the solidification of these alloys tends to form as-cast segregated microstructures. The peritectic reactions will hardly be complete due to the limited diffusion caused by the solid envelope of the peritectic phase and the remaining liquid enriches in aluminium and solidifies as an interdendritical network. These as-cast structures are responsible for low levels of mechanical properties and have to be modified. Homogenising heat treatments conducted at low temperatures, in the α + γ field, are generally inefficient to eliminate the as-cast microsegregation while the higher temperature treatments, conducted in the α field, are used to attain fully lamellar structure but promote excessive grain growth. Structures with fine mixtures of γ grains and α_2 plates or particles, called "duplex" or "near-gamma", conduct to a reasonable balance of properties while refined lamellar structures are responsible for properties, up to 760 °C, comparable or better than those of nickel based superalloys [3].

2. Experimental technique

A Ti-48Al at% has been used, prepared from pure aluminium and titanium, melted in 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.

Homogenising heat treatments were conducted on two of the γ -TiAl alloys produced: Alloy 1 Ti-47.5/48.2 Al; Alloy 2 Ti-46.0/47.0 Al-1.0/1.2 Zr-0.5/0.9 Fe (at.%).

Castings produced were cylinders. In order to evaluate the structure, samples were collected from the middle of them, by sectioning the cylinders at 50 % of their height. Samples for characterization were prepared using traditional metallographic techniques: surfaces were prepared by mechanical polishing and etched with Kroll solution (2%HF, 4%HNO₃, 94%H₂O).

Phase identification and chemical composition evaluation were performed by quantitative EDS analysis with standards of pure Ti, Al and Zr, using a JEOL JSM 35C scanning electron microscope. A 10keV potential and a 100 second acquisition time were used.

2.1 Process description

Melts were prepared from commercially 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 that was open only when the sample was at room temperature (see figure 1). As can be seen, the melting crucible is kept inside an alumina crucible, which has a pouring lip. The purpose of this second crucible is two folds: 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, where necessary.

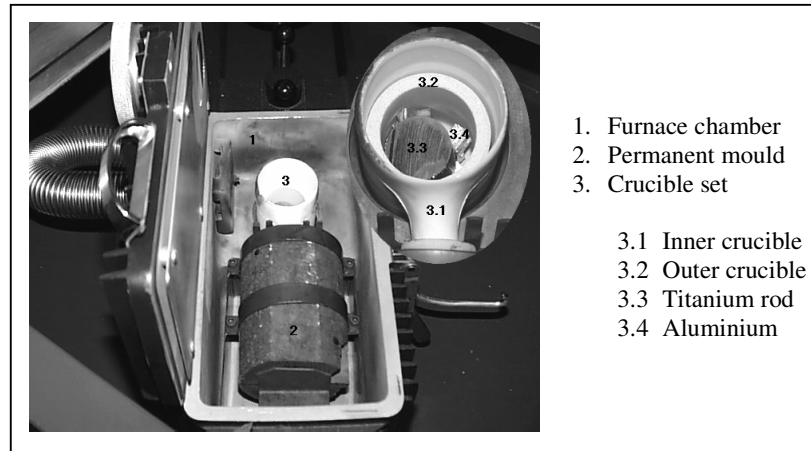


Figure 1 – Ceramic crucible induction

2.2 Crucibles

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 Y_2O_3 , MgO and CaO partially stabilized zirconia crucibles.

2.3. Heat treatment

Homogenising heat treatments were carried out under an argon flux and consisted in pre-heating for 10 minutes at 800 °C, followed by 10 °C/minute heating until a maximum stage temperature and then furnace cooled. The soaking times at maximum temperature are shown in table 1.

Table 1 - Maximum temperature stage conditions.

Temperature, °C	Soaking times, h		
1400	1	6	-
1350	-	6	24
1250	-	6	-

3. Experimental results

Experimental results have been analysed bearing in mind:

- Identification of each phase and microconstituent and the variation of its composition has been made using microanalysis;
- The chemical profile of the as cast samples 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, on the as cast samples;
- Heat treatment was conducted on cast samples from which a 5 mm outside layer was removed.

As shown in figure 2, the as cast microstructure presents two microconstituents: a lamellar one with a strong dendritic pattern, with two phases ($\alpha_2 + \gamma$), and an interdendritic one (γ phase). The 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 towards the inside of them. In all the samples, the lamellar dendritic biphase constituent is richer in titanium and the monophase interdendritic constituent has higher aluminium content, according to the available references [6].

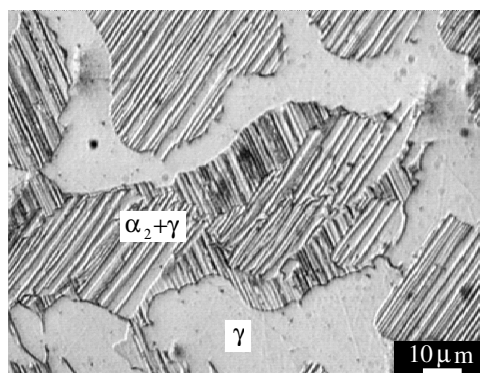


Figure 2 - Microstructure of a casting melted and cooled in a calcia stabilized zirconia crucible

3.1 Zirconia crucibles

The results are summarised in table 2 and figure 3, and all comments are based upon them.

Samples processed in these crucibles have a higher amount of zirconium in the outside part of them. It decreases towards the inside, and after a while it reaches a constant level. The concentration of this element is higher in the interdendritic γ constituent than in the $\alpha_2 + \gamma$,

lamellar dendritic. So, it might be concluded that zirconium is segregated into the interdendritic melt, during solidification, and that it dissolves preferentially there.

Among all tested zirconia crucibles, those stabilized with CaO were the ones that presented lower levels of zirconium absorption. As a global trend, samples processed in the yttria and magnesia stabilized 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 stabilized crucibles (see figure 3 and table 2). This results in a higher volume fraction of γ phase in the as-cast structure, on samples melted in Y_2O_3 stabilized ZrO_2 crucibles.

Table 2 - Microhardness and extension of the “alpha-case” in samples melted and solidified in stabilized zirconia and calcia crucibles.

Crucible	Vickers hardness on "alpha-case" (max)		Vickers hardness on bulk		Zr content on bulk (at. %)		“Alpha-case” extension (μm)
	$\alpha_2 + \gamma$	γ	$\alpha_2 + \gamma$	γ	$\alpha_2 + \gamma$	γ	
	ZrO₂/MgO	644	594	549	473	0,77	
ZrO₂/Y₂O₃	580	412	473	313	0,62	4,96	600
ZrO₂/CaO	473	321	351	257	0,27	0,88	300
CaO	341	303	313	280	-	-	200
ZrO₂/Y₂O₃ (coated)	-	-	297	288	-	-	-

In what concerns the microhardness values, as mentioned in other references [1, 2], there is a decrease from the outside towards the inside of the samples. This hardness profile has about the same shape in both microconstituents but dendritic $\alpha_2 + \gamma$ is always harder than γ , for all the samples. The outside layer, which is harder than the average, and named “alpha –case”, has an extension between 300 and 600 μm (Table 2). The microhardness profile has two different types of behaviour: near the surface there is a rapid decrease of microhardness with the increase in distance from the sample / refractory interface. The inner part of the sample has a near constant hardness value as shown in figure 3. This last behaviour suggests that there is a constant level of contamination, resulting from the period when 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 towards 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. Taking into account the reduction of ZrO_2 , the only remaining factor 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 [7].

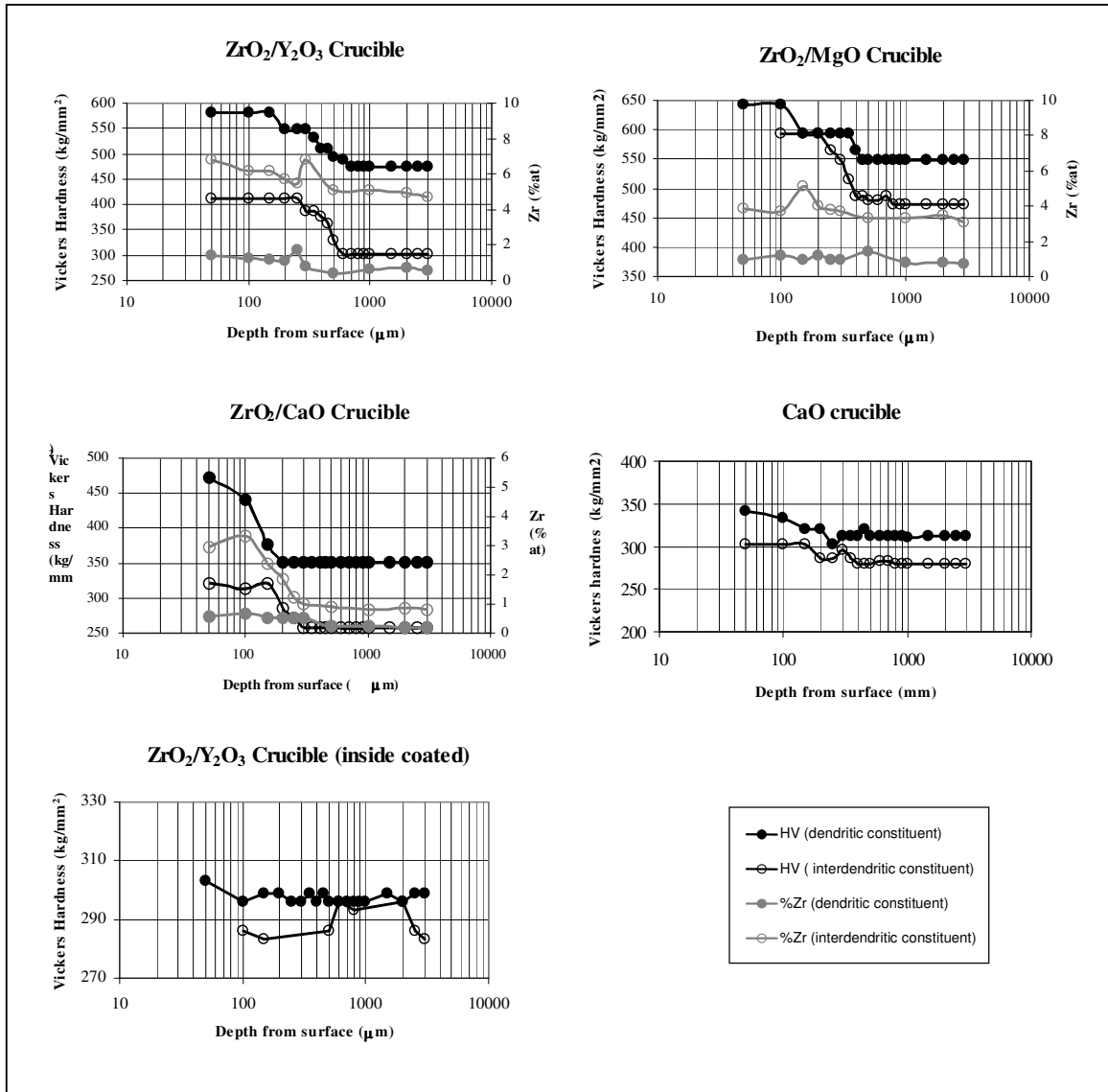


Fig. 3 -Microhardness and Zr (at.%) profiles in samples melted and cooled in stabilized zirconia and calcia crucibles.

3.2 CaO crucibles

The CaO crucibles produced better results than ZrO_2 crucibles. As can be seen in table 2 and figure 3, samples present lower microhardness values, both in the base metal and in the “alpha-case” in both microconstituents. The “alpha-case” extension - about $200\ \mu\text{m}$ - is also lower than in samples produced in ZrO_2 based crucibles.

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

The slight hardness variation that is seen in the outer part of samples is not fully understood. Calcia is a more stable oxide than alumina or titania so there is a very small probability that the reduction of calcia might occur in this kind of melt. The introduction of oxygen seems very unlikely, because, in this situation, the overall microhardness in the interior of the sample should be higher. According to some authors [8], the only factor, which might increase hardness, could be a smaller grain size.

3.3 Coated zirconia crucibles

Some yttria stabilized zirconia crucibles were coated inside with a refractory material chemically more stable with TiAl than zirconia. The coating was applied as a normal painting and allowed to dry for 24 hours before use.

Samples melted on these crucibles do not present any contamination with Zr or any other residual element, what confirms the high stability of the refractory material that was used (see table 2 and figure 3). Microhardness value is almost constant throughout the sample (around 290 HV), and alpha-case was not detected (see table 2 and figure 3).

3.4 Heat Treatment

As-cast structure characterization

The as-cast microstructures, as can be seen in figure 4, present dark lamellar dendrites ($\alpha_2+\gamma$) and a white interdendritic phase (γ); the interdendritic γ -phase has higher Al and Zr contents than the lamellar dendrites, as already presented, Fe distributes equally in both regions.

Comparing the structures of the two alloys it can be seen that Alloy 2 (Zr bearing) has higher volume fraction of interdendritic phase and smaller dendritic arm spacing. Alloy 2 has a lower Al content than Alloy 1, 46.0 - 47.0 against 47.5 - 48.2 respectively which accordingly to the Ti-Al phase diagram implies a progressively smaller fraction of γ phase. The higher volume fraction of γ -phase must then be the result of the Zr segregation to this phase.

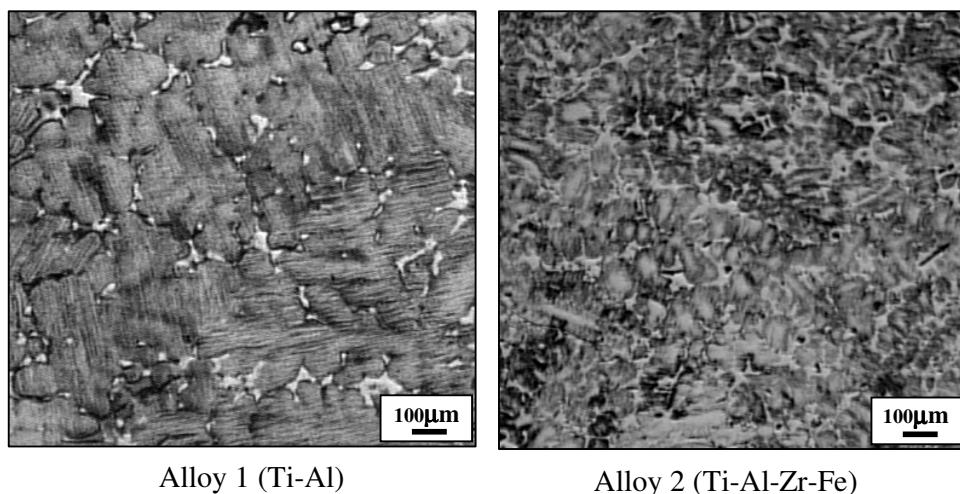


Figure 4 - Microstructure of the as-cast samples used for the heat treatment.

Heat treatment structure characterization

Alloy 1

The microstructures of Alloy 1 (Ti - 47.5/48.2 Al) after heat treating at 1250, 1350 and 1400°C show that the volume fraction of the γ -phase increased slightly and, in some regions, thickening of α_2 lamellae has occurred, as is shown in figure 5. Analysis by EDS showed that as the heat treatment temperature is raised, the Al concentration of γ -phase and lamellar regions (which at the treatment temperature are α -phase) increases (see table 3).

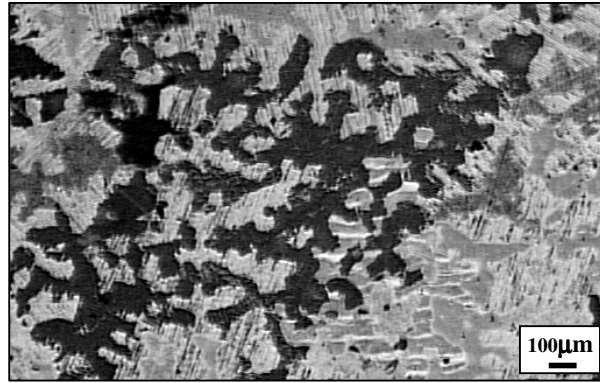


Figure 5 - Microstructure of Alloy 1 after heat treating at 1350°C for 6h.

In previous work with Ti-47Al and Ti-50Al alloys, heat treating at the same temperatures resulted in similar observations. However, for the Ti-47Al alloy, after 1h at 1400°C (in the α field) the alloy exhibited a fully lamellar structure [9]. The present results indicate that all the treatments were performed in the $\alpha+\gamma$ field for Alloy 1, even at 1400°C. To attain a fully lamellar structure it is necessary to raise the heat treating temperature.

Table 3 - Al content of the constituents of Alloy 1 after heat treatment

Constituent	1250 °C	1350 °C
Lamellar regions	45.55 at.%	47.93 at.%
γ -phase	47.91 at.%	49.33 at.%

Alloy 2

The microstructures of Alloy 2 after heat treating at 1250°C did not cause any appreciable changes in the structure, see figure 6. A quasi lamellar structure with small particles of γ -phase is attained by heat treating at 1350 and 1400°C, grain growth and the decrease of the volume fraction of γ -phase are the more relevant effects of these treatments as can be seen in figure 7.

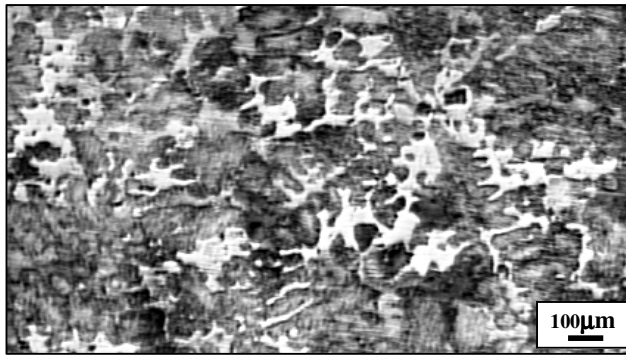


Figure 6 - Microstructure of Alloy 2 after heat treating at 1250°C for 6h.

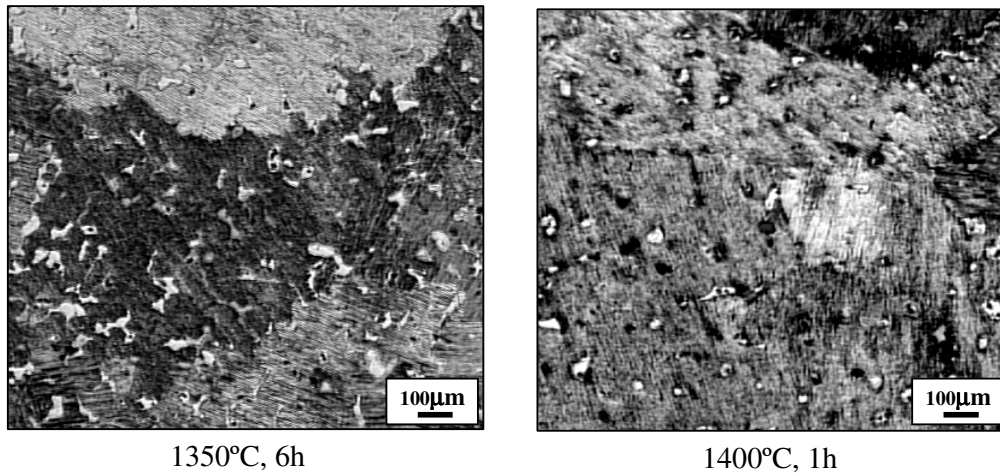


Figure 7 - Microstructure of Alloy 2 after heat treating at 1350°C for 6 hours and 1400°C for 1 hour.

Analysis by EDS showed that the Al and Zr concentrations of γ -phase and lamellar regions increase with heat treatment temperature, the values presented in table 4 demonstrate that raising the temperature from 1250 to 1400°C increase the Zr concentration in γ -phase from 1.71 to 2.48 at. %.

Table 4 - Al and Zr contents of Alloy 2 constituents after heat treatment.

Constituent	1250 °C	1350 °C	1400 °C
Lamellar regions	43.47 at.% Al	44.44 at.% Al	46.86 at.% Al
	1.02 at.% Zr	1.06 at.% Zr	1.15 at.% Zr
γ-phase	49.34 at.% Al	53.19 at.% Al	53.91 at.% Al
	1.71 at.% Zr	1.72 at.% Zr	2.48 at.% Zr

Alloy 2 has an Al content of 46-47 at. % and so a fully lamellar structure was expected after heat treatment at 1400°C [9]. The presence of γ -phase indicates that for this alloy 1400°C is still in the $\alpha+\gamma$ field. The present result leads to the conclusion that the Zr segregation to γ -phase plays an important role in the stabilisation of this phase. This statement is reinforced by the presence of a higher volume fraction of γ -phase in the as-cast structure of the Zr bearing alloy.

Conclusions

- In all samples melted in zirconium based crucibles, there is evidence of contamination with Zr. In those processed in calcia and coated zirconia crucibles there is no evidence of contamination.
- The dissolution of Zr occurs preferentially into interdendritic γ . This results in a higher volume fraction of γ phase in the as-cast structure.
- Samples melted and cooled in CaO and ZrO₂ based crucibles present an outside layer harder than the bulk, called “alpha-case”. Microhardness decreases from the outside to the inside of samples, with a profile that tallies some references.
- Only samples melted in coated ZrO₂ crucibles do not present “alpha-case”.
- Microhardness profiles do not match with Zr segregation profiles, although they follow the same trend. This fact leads to the conclusion that zirconium is not the only or the most important element to affect hardness, and that the possible presence of oxygen must play a very important role in hardness variation.
- Heat treating the Ti-Al alloy at a temperature range from 1250 to 1400°C failed to achieve a quasi lamellar structure; the dendritic aspects of the as-cast structure remain visible.
- The zirconium segregation to γ -phase affects the alloy behaviour during heat treating by delaying γ dissolution.
- Heat treating the Ti-Al-Zr-Fe alloy at 1350°C for 6 hours and at 1400°C for 1 hour is able to replace the as-cast structure by a quasi lamellar one.

Bibliographic References

- [1] T.S. Piwonka, *42Th Annual Technical Meeting of the Investment Casting Institute*, publ. Investment Casting Institute, USA, 1994.
- [2] J. Schädlich-Stubenrauch, G. Dieckhues, P.Sahm, *27th Dedicated Conference on New and Alternative Materials for the Transportation Industries*, Aachen, Germany, November 1994.
- [3] Y.W. Kim, D. Dimiduk, *Structural Intermetallics 1997*, Ed M. Nathal et al., TMS, 1997, p.531-543.
- [4] D.L. Anton, D.B. Snow, M. Nanzy, M. Staubli, *Structural Intermetallics*, Ed R. Dariola et al., Publ. TMS, 1993, p. 265-274.
- [5] S.C. Huang, *Structural Intermetallics*, Ed R. Dariola et al., Publ. TMS, 1993, p. 299-305.
- [6] D. Larsen, C. Govern, *Gamma Titanium Aluminides*, Ed Y-W Kim, R. Wagner, M. Yamaguchi, Publ. TMS, 1995, p.405-414.
- [7] R.L. Saha, et al., *Bulletin Mater. Science*, Vol. 12, n°5, December 1989, p.481-493.
- [8] *Materials Properties Handbook - Titanium Alloys*, Section VI - “Titanium Aluminides”, ASM, June 1994.
- [9] A. Duarte, F. Viana, H.M.C.M. Santos, *Materials Research*, Vol.2, n° 3, 1999, p. 191-195.