

Characterization of TiAl Alloys by Secondary Ion Mass Spectrometry

Joaquim Barbosa*, O.M.N.D. Teodoro** , A.M.C. Moutinho** , S. Ribeiro***
and C. Monteiro*

*CITEPE - Centro Interdisciplinar de Tecnologias da Produção e Energia
Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
Tel: + 351 253 510 220, Fax: + 351 253 516 007, email: kim@dem.uminho.pt

** CEFITEC— Centro de Física e Investigação Tecnológica
Departamento de Física da Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa
2829-516 Caparica

***GMM - IMAT (FEUP) – Grupo de Materiais Metálicos do Instituto de Materiais
Departamento de Engenharia Metalúrgica e de Materiais
Faculdade de Engenharia da Universidade do Porto
Rua Roberto Frias, 4200-465 Porto

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Abstract

Titanium aluminides are arising as a valuable alternative to superalloys in applications where the ratio resistance/density is important. Together with excellent mechanical and corrosion properties at high temperatures, such characteristics are very attractive for applications in the aeronautical, aerospace and automotive industries. However, the current high selling price, due to high costs of production and raw materials and the need of very specific equipment, are limitative factors for further applications. With the end of the cold war, and the decrease of traditional markets of TiAl, the strategy to develop other applications, strongly depends on the decrease of production costs. An alternative to the present production routes might be the use of traditional casting techniques, by induction melting of the alloy in a ceramic crucible and pouring into ceramic moulds, made by the investment casting process. However, due to the high reactivity of Ti alloys, the use of traditional ceramic materials cannot be used, as they lead to oxide formation and oxygen pick up both from the crucible and the moulding materials. In this work, the relative oxygen concentration of Ti-48Al castings was measured by SIMS — Secondary Ion Mass Spectrometry. This technique provides a direct measurement of the isotopic composition with high sensitivity. The cylindrical samples were specially prepared to allow the analysis of the area close to the border. Oxygen profiles were acquired for samples obtained by with different mould materials. The comparison of such profiles with hardness profiles, give insight in the significance of the oxygen concentration in the properties of the alloy and in the choice of the most suitable materials for TiAl production

Introduction

During the last decade several intermetallic alloy systems have been identified as potential candidate materials for applications at high temperatures. Among those systems, γ -TiAl was found to be a very promising material, but its currently high cost limits significantly its successful industrial-scale application. Besides, titanium aluminides suffer from quite low ductility at room temperature, and their application is always dependent from the microstructure modification. The best compromise between high temperature properties and room temperature ductility, is achieved

with a two-phase microstructure ($\alpha_2 + \gamma$), for a volume ratio α_2 / γ between 5 and 15%. This is achieved by decreasing the aluminium content of the alloy, and adding small amounts of alloying elements, such as Cr, Mn, V and B, which were found to refine the grain size and stabilize the lamellar structure [1, 2].

On the other hand, γ -TiAl is extremely reactive with almost every known elements, with particular emphasis to oxygen and nitrogen, which dissolves interstitially, leading to a strong hardness increase and alloy embrittlement. The maximum solubility of oxygen in the γ phase is about 250 at.ppm and more than 2,1 at.% in α_2 , and it does not depend on the γ -TiAl alloy composition [3]. According to some researchers [1,3], such difference in the oxygen solubility limits is the most important factor to explain the higher ductility of two-phase γ -TiAl alloys, when compared with single phase γ -TiAl: since the α_2 phase tends to contain more interstitials, namely oxygen, than the γ phase, a scavenging effect in this phase, lowering its interstitials concentration, results in an increase on the dislocation mobility on this phase, and an increase in the alloy ductility. On the other hand, in single phase γ -TiAl, as soon as the oxygen concentration reaches 250 at.ppm, precipitation of titanium oxides starts, until total consumption of oxygen. On two-phase γ -TiAl alloys, the excess of oxygen is absorbed in α_2 , avoiding oxides formation, and enhancing ductility.

As TiAl is extremely reactive, its production by foundry processes using traditional crucible and mould materials (usually metal oxides) is a difficult task, because ceramic-alloy interactions are always present, in a certain extent. As a consequence, it is almost impossible to obtain titanium alloys castings free from contaminants. During the last five years, authors have done extensive research work on this field, and a melting and moulding technique, using ceramic materials, was developed, and results published elsewhere [4, 5]. The main purpose of such work was to develop a casting procedure, with which sound γ TiAl components could be produced at competitive prices without, or with controlled residual elements contamination.

Metal-mould interaction

After pouring, and during the cooling and solidification stages, metal-mould interactions might occur. While the metal is in the liquid state, it can dissolve or react with the ceramic mould, into a certain extent. As a consequence, the oxygen and other elements picked up from the mould material, or the reaction products, go into solution with the liquid metal. When solidification starts, the interaction continues, and composition gradients start to develop, from the interface to the inside of the castings. Such gradients lead to diffusion mechanisms, in order to reach the equilibrium situation. As the temperature decreases, diffusion rates become smaller, until they become negligible at low temperatures. As a consequence, chemical composition gradients can be found, at room temperature, from the surface to the inside of castings, leading to significant changes in their mechanical and technological properties, like a surface “hard case”, usually called “*alpha-case*”. As the diffusion rate of oxygen in TiAl is very high, and its presence is known to affect the ductility and hardness of the alloy, its measurement and the knowledge of its variation, are crucial to select proper ceramic materials, for crucible/mould production.

Samples preparation

Ti-48Al was induction melted in multi layered $ZrO_2+Y_2O_3$ crucibles, and cylindrical shaped samples were poured in ZrO_2 , SiO_2 and multi-layered $ZrO_2+Y_2O_3$ moulds (ZrO_2 based, with Y_2O_3 inside contact layer), using the techniques described elsewhere [4, 5, 6]. Microhardness was evaluated on a Shimadzu hardness tester, using a 50g load, for 15 seconds. Overall oxygen content was measured by the IGF technique (Inert Gas Fusion), and SIMS (Secondary Ion Mass Spectrometry) was used to determine the diffusion profile of oxygen.

Cast specimens were cylinders 20 mm in diameter and 85 mm long, and were poured at about 1550°C. Samples for characterization were collected from the middle section of them, by cutting the cylinders at half their height, and prepared using traditional metallographic techniques.

As oxygen measurement was needed at distances from the samples surface less than the beam diameter (50 μm), samples were specially prepared for SIMS characterization by cutting through a plane making a 15° angle with the cylinder axis as described in Figure 1. In this way, analysis could be performed in several points in depth, without the need of long erosion times to reach the bulk.

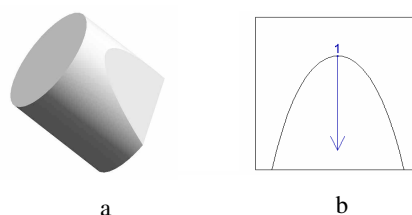


Figure 1 – Sample for SIMS characterization: a) Cut sample b) Beam direction

Experimental procedure

SIMS has been performed in a Multitechnique Surface Analysis System detailed described elsewhere [7]. A 4 keV Ar^+ , 200 nA beam focused in a 50 μm diameter was used. Secondary ions produced by sputtering were mass analyzed by a quadrupole type mass spectrometer. Both positive and negative spectra were taken. Base pressure during analysis was in the order of 10^{-9} mbar.

After cutting, samples were preserved in glycerol until their introduction in vacuum to avoid contamination or reactions with the atmosphere. Then, were carefully washed with solvents and clamped in the stubs to be introduced in the analysis chamber. Surface (or in-depth) profiles were obtained by shifting the sample under analysis along one of the axis of a very accurate XYZ manipulator. Increments of 20 μm were used, starting from the non-polished side (the cylindrical surface). These increments correspond to 5 μm steps in depth, along the cylinder radius. Therefore, the acquired surface profiles could be easily converted in depth profiles.

Experimental results

On previous experiments, several samples melted in crucibles similar to those used on this work, and poured in graphite moulds were found to have a small O and Y contamination – 0,28 wt%O and 0,1 at%Y. For this reason, it is assumed that this corresponds to the initial metal contamination before pouring, used on this work.

On Figure 2 microhardness variation profiles on $\alpha_2+\gamma$ and γ microconstituents, and oxygen concentration profiles (intensity of O signal, normalized against Al signal) from the surface to the inside of samples poured in different moulds, are presented. From Figure 2, a correlation between oxygen concentration and microhardness can be established, which agrees with different references for commercially pure Ti [8,9]: for every sample, hardness variation and oxygen concentration profiles show the same development from the surface to the inside of casting. Both profiles reveal two distinct regimes: in the first regime, starting from the casting wall, profiles exhibits a gradual decrease as a function of distance from surface, which represents diffusion of

the ceramic constituents that occur after solidification starts; after a certain distance from the casting surface, the second regime starts, being characterized by constant values both of oxygen concentration and microhardness. However, this correlation is valid, only for the lamellar $\alpha_2+\gamma$ microconstituent hardness, because on the γ constituent hardness is almost constant all over the samples. Besides, for each mould material, the distance from the castings surface, at which $\alpha_2+\gamma$ hardness and oxygen concentration become invariant (*alpha-case* extension) is basically the same. These facts confirm Menand references [3], suggesting that oxygen dissolves preferentially on α_2 phase, and reveal a direct relation between the two parameters.

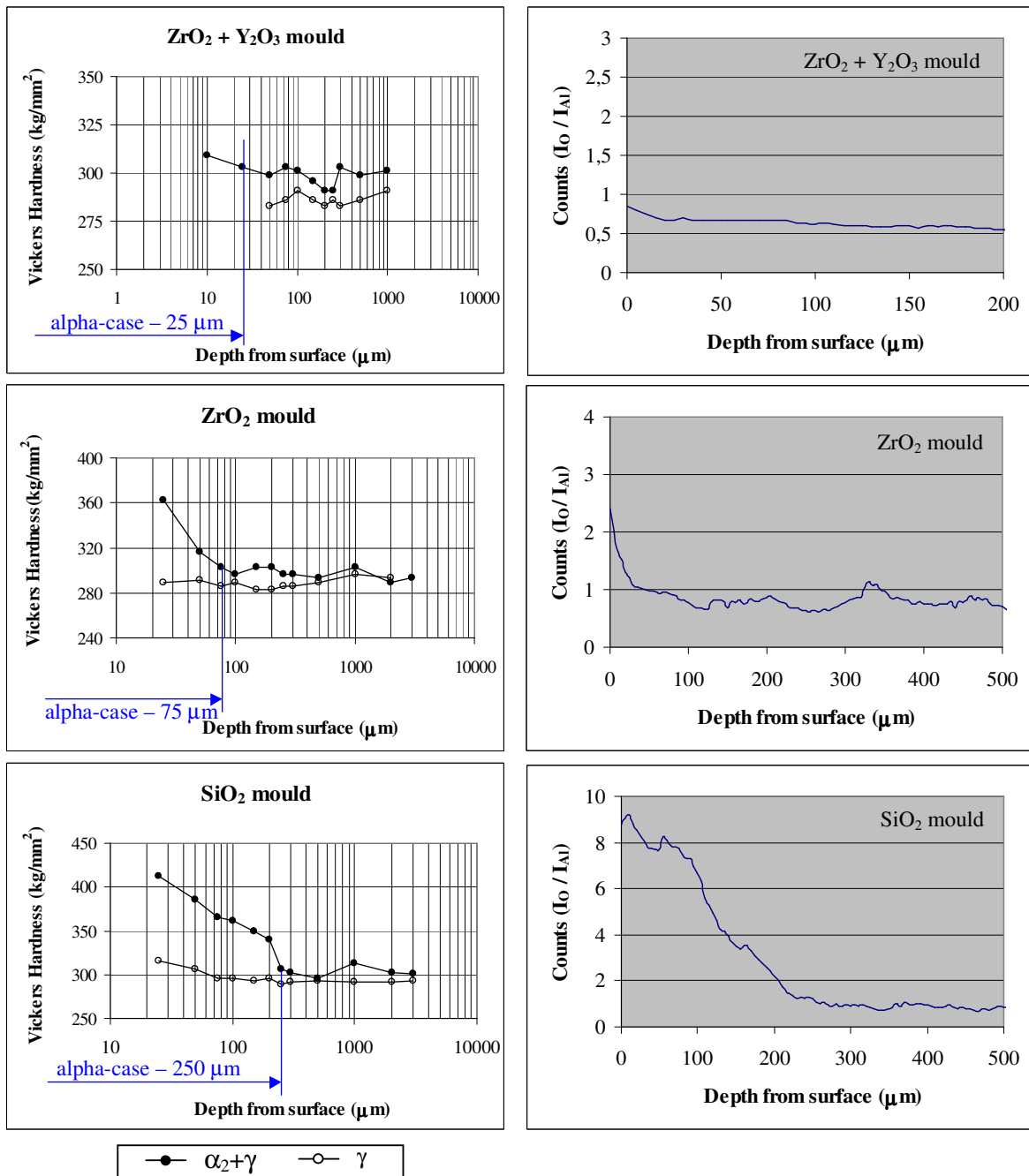


Figure 2 – Microhardness and oxygen concentration profiles, from the surface to the inside of samples, poured in multi layer ZrO₂ + Y₂O₃, ZrO₂ and SiO₂ moulds.

On the other hand, Figure 2 shows that high O concentrations always correspond to high hardness levels, and for the mould materials used, they are maximum on samples obtain in SiO₂ moulds, and minimum on those produced in Y₂O₃ ones, which is in accordance with those materials respective thermodynamic stability. Concerning the average oxygen content of samples, measured by IGF, it is of the same magnitude as the initial oxygen level (0,28 wt%) for every sample, suggesting that contamination only occurs on a very thin layer on the castings surface.

Conclusions

1. SIMS characterization allows to conclude that diffusion depth of oxygen strongly depends on the moulding material. Although, as the metal alloy and solidification time is the same for every sample, the difference in diffusion depth appears to be a consequence of different dissolution rates of the mould material, being maximum for SiO₂, and minimum for Y₂O₃;
2. Hardness of $\alpha_2+\gamma$ constituent mostly depends on α_2 oxygen concentration;
3. “Alpha-case” extension is a good indicator to identify contamination of γ TiAl alloys with oxygen, and corresponds to the diffusion depth of oxygen;
4. Among every moulding materials studied on this work, only multi-layered ZrO₂ + Y₂O₃ moulds appear to be a good solution to produce γ TiAl castings, as ZrO₂ and SiO₂ moulds lead to severe metal contamination with residual elements and oxide formation at the castings surface;
5. The developed technique, using multi-layered ZrO₂ + Y₂O₃ ceramic moulds, appears to be a good alternative to actual processing routes of γ TiAl castings.

References

- [1] Y.W. Kim, D.M. Dimiduk: *JOM*. (August 1991), p. 40.
- [2] T.K. Roy, R Balasubramaniam, A. Ghosh: *Metallurgical and Materials Transactions A*. Vol. 27A, (December 1996), p. 2993.
- [3] A. Menand, A. Huguet, A. Nerac-Partaix: *Acta Materiallica*. Vol. 44, nr 12 (1996), p. 4729.
- [4] J. Barbosa: *PhD thesis*, University of Minho, Portugal, 2002.
- [5] J. Barbosa, S. Ribeiro, C. Monteiro: *Materials Week 2001 Congress*, Munich, Germany.
- [6] J. Barbosa, S. Ribeiro: *International Journal of Cast Metals Research*, nr12, 2000, p.293.
- [7] O.M.N.D.Teodoro, J.A.M.C. Silva and A.M.C. Moutinho, *Vacuum* 46, (1995) p. 1205
- [8] R.L.Saha *et al* : *Metallurgical Transactions B*. Vol. 21B, (June 1990), p.559.
- [9] R.L.Saha *et al* : *AFS Transactions*. (1990), p.253.