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# Structure and properties of sputtered TiAl–M (M = Ag, Cr) thin films

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#### Abstract

The aim of this work was to study the influence of two additional elements — silver and chromium — on the structure and mechanical properties of TiAl–M (M=Ag, Cr) thin films synthesised by sputtering. The films were studied in the as-deposited condition (metastable state) and after successive annealings performed in order to obtain the stable ( $\gamma$ -TiAl)-based intermetallic phase. The experimental techniques used in this work for chemical and structural characterisation were electron probe microanalysis, transmission electron microscopy/electron diffraction, X-ray diffraction and differential scanning calorimetry. The mechanical analysis consisted of the determination of hardness and ductility. To do this, a new tensile test procedure able to evaluate the ductility of thin films was developed. The results showed that, contrary to the as-deposited state, the addition of silver or chromium does not lead to a significant improvement in the mechanical properties, hardness and ductility of the heat-treated films ( $\gamma$ -TiAl structure). However, they did contribute to a better understanding of the role of silver and chromium on the structure of these titanium aluminides. © 1999 Elsevier Science S.A. All rights reserved.

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#### 1. Introduction

Titanium aluminides are attractive materials for aerospace structural applications owing to their high specific strength and creep resistance at high temperatures (700-950°C) which is associated with good fatigue resistance [1,2]. However, these materials, like intermetallic compounds in general, have only been used as high temperature structural materials due to their room temperature brittleness [3]. To overcome this deficiency, many studies have been carried out in order to improve the intermetallics' ductility and oxidation resistance through chemical composition modification (shifting of stoichiometry and addition of alloying elements) and the use of new production techniques [3,4]. The microstructure of the  $\gamma$ -TiAl alloys depends on both its chemical composition and microstructure. Among the most common microstructures of these alloys, the duplex one presents the best ductility (2.6% for the Ti-48Al alloy [1]). Some authors claim that this property can be further improved by introducing 1-3 at% of alloying elements such as V, Cr, Mo or Mn [5,6]. Additionally, some authors justify the

ductility improvement due to these elements by claiming substitution for Al, which reduces the covalent character of the Ti bonding. These alloving elements reduce the stability of the  $\alpha_2$ -Ti<sub>3</sub>Al phase favouring the presence of  $\gamma$ -TiAl and are responsible for the presence of small amounts of  $\beta_2$ . Moreover they induce a decrease in the grain size [1,6], contributing for the ductility increase. It seems that the influence of a third element on the  $\gamma$ -TiAl structure depends on its content and its position in the lattice. In previous studies, Huang and Hall [7] verified that for a  $Ti_{(50-y)}Al_{(49+y)}X_1$  alloy, the third element site at  $1300^{\circ}$ C strongly depends on the value of y. In this study the addition elements were divided into two groups, one including Co, Cr, Ni and Mo and the other including Mn, Nb and V. In the Ti-rich samples the first group elements occupy the Al sites, while the second group elements occupy both Ti and Al sites. In the Ti-deficient samples, the first group elements substitute for Ti and Al and those of the second group substitute for Ti.

The aim of the present work is to study the influence of two metallic elements with different electronic configurations (silver and chromium) on the structure and mechanical properties (hardness and ductility) of TiAl produced by magnetron sputtering. The investigation of a third element effect in the TiAl structure on an atomic scale may provide a better understanding of the relation-

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ship between the chemical composition and mechanical properties for these types of materials.

In addition, a new tensile test procedure was developed to evaluate the ductility of these films. This work is part of a more extensive project whose purpose is to develop and to study the properties of (TiAl)-based intermetallics produced by sputtering. The idea is to obtain useful data concerning the synthesis of titanium aluminide materials with better ductility and to consequently make it easier to process these materials by conventional techniques such as foundry and hot isostatic pressing (HIP).

## 2. Experimental

Ti–Al–M (M=Ag, Cr) thin films with  $3 \mu m$  thicknesses were co-deposited by DC magnetron sputtering onto 304 austenitic stainless steel (AISI) substrates as described elsewhere [8]. The choice of this steel was made taking into account the following aspects: the 304 steel is ductile, it does not suffer structural transformation in the temperature range of this study, and its linear expansion coefficient is similar to that of the  $\gamma$ -TiAl phase. The samples were studied in the as-deposited state and after isothermal annealing at different temperatures  $(T_{\text{max}} = 600^{\circ}\text{C})$  and holding times  $(t_{\text{max}} = 9 \text{ h})$  in a hydrogenated argon atmosphere (5% H<sub>2</sub>). The chemical composition of the films was determined by electron probe microanalysis (EPMA) using Cameca SX50 equipment. X-ray diffraction (XRD) experiments were performed at room and high temperature in a hot stage Philips X'Pert diffractometer with Co-Ka radiation allowing observing in situ the structural evolution with temperature of the TiAl–M films. Differential scanning calorimetry (DSC) measurements were made in a Polimer Science STA1500 equipment under a dynamic N<sub>2</sub> atmosphere containing 5% of H<sub>2</sub>. Films for TEM analysis were supported between two-nickel grids and thinned on both sides to electron transparency by ion milling in an argon atmosphere. The microstructural analysis was performed using a 300 kV Hitachi equipment. The hardness tests were performed with loads of 70 and 300 mN in a ultramicroindentation device (Fisherscope H100) with a Vickers indenter. A correction method [9] was applied in the calculation procedure. Moreover, the hardness results were also corrected for thermal drift of the equipment. The ductility of the films was evaluated by means of a new tensile testing according to a procedure specially developed for this purpose [8].

#### 3. Results and discussion

#### 3.1. Structure

Thin films of TiAl–M (M=Ag, Cr) with 0 < at%Ag < 10.5 and 0 < at%Cr < 4.6 were deposited by



Fig. 1. Characterisation of the Ti–Al as-deposited film. (a) X-ray diffractogram (F, film; S, substrate); (b) TEM micrograph; (c) ED micrograph. Values in italic correspond to the Al phase.

magnetron sputtering onto stainless steel substrates. The films obtained were characterised by XRD and TEM (Fig. 1). Whatever the system (TiAl with or without addition of a third element), the microstructure of the as-deposited samples is formed by two phases, one rich in titanium ( $\alpha$ - and/or  $\alpha'$ -Ti) and another rich in aluminium. The  $\alpha'$ -Ti phase is the common martensitic structure of Ti–6Al–4V alloys quenched from the above  $\beta$ -transus and has a c/a ratio close to that of the  $\alpha$  phase [10].

The position of the diffraction peaks of the Ti-rich structure is shifted to angles higher than those of the ICDD cards for pure  $\alpha$ -titanium [11]; the opposite situation being observed in the case of the aluminium structure [11]. This might be an indication of a partial intersolubility between titanium and aluminium. It should be noted that the titanium atomic radius is higher than that of aluminium (being 0.147 and 0.143 nm, respectively). For the compositions studied here, the c/aratio of the  $\alpha$ -Ti structure and the lattice parameter a of the aluminium phase are not significantly influenced by the presence of silver or chromium. No other phase related to the presence of silver or chromium in the structure was detected. According to the Ti-Al phase diagram, the Ti-Al film should lie in a TiAl+Ti<sub>3</sub>Al twophase domain instead of forming a metastable structure of two terminal solid solutions (titanium- and aluminium-rich). The reason why metastable structures are



Fig. 2. – DSC curves of the TiAl, TiAl–Ag<sub>5</sub> and TiAl–Cr<sub>5</sub> films.

obtained by sputtering is due to the process of deposition. The very high cooling rates of this production technique do not give the adatoms time to organise themselves into stable structures, which gives rise to metastable structures with higher solubility domains than those indicated in the literature and/or with reduced structural order (nanocrystalline or amorphous).

After the initial characterisation, the samples were annealed at different maximum temperatures and holding times. Three films (TiAl, TiAl–Ag<sub>5</sub> and TiAl–Cr<sub>5</sub>) were submitted to DSC runs up to 900°C with a heating rate of 30°C min<sup>-1</sup>. The DSC curves of these samples (Fig. 2) show two exothermic peaks in the range 450–700°C attributed to the decomposition of the as-deposited metastable structure. In opposition to chromium, the addition of silver favours this transformation; the DSC peaks being shifted to lower temperatures when compared to those of the Ti–Al sample. XRD analysis performed on this sample at temperatures of 450 and  $550^{\circ}$ C (Fig. 3) show that the as-deposited structure



Fig. 3. In situ X-ray diffractograms of the TiAl film at 450 and 550°C. \*,  $\gamma$ -TiAl; +, Al; X,  $\alpha$ -Ti; S, substrate.

evolves towards the formation of disordered TiAl (Al fcc-type structure) and then later shifts towards the formation of a  $\gamma$ -TiAl (ordered structure). The X-ray diffractograms obtained from samples with silver and chromium annealed at  $600^{\circ}$ C/1 h confirms that silver favours the formation of the ordered structure, while chromium retards it (Fig. 4). In fact, the sample with silver presents well-defined peaks of  $\gamma$ -TiAl, which is not the case of the sample containing chromium submitted to the same thermal cycle. This sample has a disordered TiAl structure, corresponding to an intermediate stage between the as-deposited structure and the ordered  $\gamma$ -TiAl one. The X-ray diffractogram of the sample with silver shows a shoulder on the left side of the most intense diffraction peak of the  $\gamma$ -TiAl phase, indexed as a (111) plane of silver. In order to determine the morphology and the site occupation of the (Ag) phase in the microstructure of the Ti-Al-Ag heat treated films, a sample with a high silver content was produced and analysed by TEM/ED.

Fig. 5 shows TEM/ED micrographs of some Ti–Al– Ag films annealed at 600°C for 9 h. As can be seen, the structure of these films after heat treatment is a function of the chemical composition. In the case of the Ti–Al binary system, a final equilibrium structure of  $\gamma$ -TiAl+ $\alpha_2$ -Ti<sub>3</sub>Al is achieved, with a very fine grain size. In spite of it not being possible to distinguish these two phases in the microstructure, all the microdiffraction patterns obtained correspond to the  $\gamma$ -TiAl phase (Fig. 6). This is not a surprising result since according to the Ti–Al phase diagram,  $\gamma$ -TiAl should exist as the major phase at room temperature. The introduction of



Fig. 4. X-ray diffractograms at room temperature of TiAl–Ag<sub>5</sub> and TiAl–Cr<sub>5</sub> films after 600°C annealing for 1 h. \*,  $\gamma$ -TiAl; +, Al; X,  $\alpha$ -Ti; S, substrate.



Fig. 5. Microstructure of: (a) TiAl; (b) TiAl–Ag<sub>3</sub> and (c) TiAl–Ag<sub>10</sub> films after annealing at  $600^{\circ}$ C/9 h. Values in italic correspond to the Ti<sub>3</sub>Al phase.



Fig. 6. – ED patterns of the  $\gamma$ -TiAl structure. (a) B=[011] and (b) B=[110].

silver hinders the formation of the  $Ti_3Al$  phase and the films are constituted only by a  $\gamma$ -TiAl phase with well-defined grains. The TEM micrograph of the most silver rich sample reveals broadening of the grain boundaries and intergranular precipitation not detectable in the

other samples. Although the silver diffraction rings are superimposed with those of the  $\gamma$ -TiAl phase, it seems that for high silver contents this element segregates during the formation of  $\gamma$ -TiAl, precipitating as a solid solution (Ag). This result is in accordance with the X-ray analysis, in which a silver phase could be detected. Finally, it should be noted that, like in the XRD analysis, no ED diffraction rings related to the existence of silver compounds with Ti, Al or both were observed.

#### 3.2. Hardness and ductility

Hardness and tensile properties of the Ti–Al–M films were determined before and after heat treatment at 600°C/1 h. These results are presented in Figs. 7 and 8. Concerning the hardness, the as-deposited films with Ag and Cr have similar behaviour, that is, there is a structural hardening up to M contents close to 1.5 at%, followed by a softening for higher silver or chromium contents. The hardness of the binary Ti–Al film (9.2 GPa) is significantly higher than pure titanium and aluminium hardness values (~0.5 GPa). The existence of two structures ( $\alpha/\alpha' + Al$ ) with reduced grain size and



Fig. 7. Hardness of as-deposited and heat-treated Ti–Al–M films as function of the metal M content.



Fig. 8. Ductility of as-deposited (M = Ag) and heat-treated (M = Ag, Cr) Ti-Al-M films as a function of the metal M content.

the existence of film stresses as a result of the sputtering process are possible explanations of this hardening effect. The shape of the hardness curves of the as-deposited films might be the result of two different factors:

- 1. limited solubility of silver and chromium in the  $\alpha$ -Ti and (Al) phases and precipitation of M-rich phases with a low degree of structural order not detectable by XRD; or
- 2. a decrease in the covalent character of the Ti–Al bonding resulting from the introduction of silver and chromium, whose effect superimposes a distortion on the crystalline lattice due to the presence of these elements in substitutional sites.

While in the case of the as-deposited state, the systems with Ag and Cr have similar behaviour, this is not true for the annealed state. In fact, the relationship between hardness and the metal M content obtained from the annealed Ti-Al-Ag films is almost horizontal, that is, not silver content dependent. In the case of the Cr films, the curve obtained for the annealed samples is parallel to the one corresponding to the as-deposited state, but shifted to higher values. These results agree well with the XRD and TEM structural analysis. The formation of the  $\gamma$ -TiAl intermetallic compound occurs yielding a hardness increase typical of ordered structures [12]. As stated above, the  $\alpha_2$ -Ti<sub>3</sub>Al phase vanishes with the introduction of silver in the Ti-Al system and a silverrich phase appears for films with high silver contents. However, in the case of the Ti-Al-Cr system the heat treatment temperature (600°C) did not initiate the formation of the  $\gamma$ -TiAl ordered phase — only a fcc disordered phase was formed.

With regard to the tensile tests, the results showed that it is possible to increase the ductility of the  $\gamma$ -TiAl phase only slightly through the addition of small amounts of silver (~1 at%). In addition, the tests performed with Ti–Al–Ag as-deposited samples lead to higher elongations than the annealed ones. The initial structure formed by two solid solutions instead of the intermetallic compounds ( $\gamma$ -TiAl and  $\alpha_2$ -Ti<sub>3</sub>Al) might explain these results.

## 4. Conclusions

The methodology used for the synthesis and characterisation of these Ti–Al thin films, with and without addition elements, allowed the following to be concluded:

- 1. The as-deposited films form a metastable structure of  $\alpha$ - or  $\alpha'$ -(Ti)+(Al) with silver and chromium in solid solution. These elements give rise to an improvement in hardness and ductility of the as-deposited films for concentrations in the range of 1–1.5 at%.
- 2. By means of annealing it is possible to modify the structure of the as-deposited films in order to obtain

the  $\gamma$ -TiAl phase and to control its grain size. The structure of the heat-treated Ti-Al films without a third element is formed by an equilibrium structure of  $\gamma$ -TiAl +  $\alpha_2$ -Ti<sub>3</sub>Al. The addition of silver impedes the formation of the Ti<sub>3</sub>Al phase, giving rise to a new phase indexed as Ag. In contrast to the as-deposited films, the elements silver and chromium do not lead to a significant improvement of the mechanical properties of the Ti–Al films.

3. It is hoped that it will soon be possible to compare these results with the results of a parallel study on the synthesis of materials with the same composition by different production techniques, that is, foundry and HIP.

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