Characterisation of Modified Sputtered (TiAl)-Based Intermetallic Materials Doped with Silver and Chromium

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ABSTRACT

TiAl-M (M = Ag, Cr) thin films were synthesised by sputtering and heat-treated in order to obtain the γ -TiAl phase. The results showed that the addition of silver or chromium does not lead to a significant improvement of the mechanical properties of the γ -TiAl structure. However, structural results obtained from similar materials produced by foundry confirm that sputtering might be used as a screening technique, in order to give helpful information for the future production of better performance bulk (titanium aluminide)-based materials.

INTRODUCTION

Different methodologies have been followed with a view to attempting to increase the ductility of the ordered phase γ -TiAl: (i) the use of the composition Ti-48Al, as a way of obtaining a two-phase structure formed by γ -TiAl together with a small amount of α_2 -Ti₃Al [1,2] (ii) microstructural refinement by heat treatment [3], (iii) the addition of alloying elements in order to reduce the covalent degree of Ti-Al bonding [4-6] and finally (iv) the use of new processing techniques, such as mechanical alloying [7], rapid quenching [8] and sputtering followed by posterior annealing, to obtain the ordered γ -phase with controlled grain size [9-11].

The aim of this study is to use magnetron sputtering as a screening technique, to produce modified titanium aluminides with different contents of silver and chromium, which could be produced later as bulk materials using other techniques.

EXPERIMENTAL DETAILS

Ti-xAl ($0 \le x \le 100$ at.%) and TiAl-xM (M=Ag, Cr and $0 \le x \le 10$ at.%) thin films (table I) with $\approx 3\mu$ m thickness were co-deposited by d.c. magnetron sputtering onto metallic substrates. The Ti-xAl films were obtained from a single target with foils of the other metal superimposed (titanium target with aluminium foils or *vice-versa*). The TiAl-M films were sputtered from two elemental targets – aluminium and titanium – onto which silver and chromium foils of differing sizes were placed. The samples were studied in their as-deposited state and after isothermal annealing at high temperatures and holding times in a hydrogenated argon atmosphere (5% H₂). The chemical composition of the films was determined by electron probe microanalysis (EPMA). X-ray diffraction experiments were performed with Co-K α radiation. Differential scanning calorimetry (DSC) measurements were carried out in a dynamic N₂ atmosphere with 5% of H₂. Films for TEM analysis were thinned on both sides by ion milling in an argon atmosphere. A 300kV TEM equipment was used. The

hardness tests were carried out with loads of 70 and 300mN in an ultramicroindentation device with a Vickers indenter. A correction method [12] was applied during the calculation procedure.

Denie wyćie u	0/ T:	0/ 11	Designation	% Ti	% Al	% Ag	% Cr
Designation	% 11	% Al	TiAl	52.3	47.7		
Ti	100	-	TiAl-0.5Ag	51.2	48.3	0.5	
Ti-18Al	81.8	18.2	TiAl-1 1Ασ	49 1	49.8	11	
Ti-27Al	73.4	26.6	Ti Al-1 64g	50.2	48.2	1.1	
Ti-51Al	49.5	50.5	$T_{iAl} = 2.4 \alpha$	40.0	40.2	2.2	
Ti-58Al	42.0	58.0	TIAI-2.5Ag	49.9	47.0	2.5	
Ti-64Al	36.5	63.5	<i>TtAl-2.9Ag</i>	49.7	47.4	2.9	
Ti-74Al	25.6	74.4	TiAl-3.7Ag	47.5	48.9	3.7	
Ti_8941	10.9	89.1	TiAl-0.6Cr	50.0	49.4		0.6
$T_i = 0.1 Al$	6.2	02.7	TiAl-1.4Cr	51.0	47.6		1.4
11-94Al	0.5	95.7 100	TiAl-2.9Cr	49.0	48.1		2.9
Al	-	100	TiAl-4.6Cr	48.4	47.0	—	4.6
(a)					(b)		

Table I – Chemical composition (at.%) of the (a) Ti-xAl and (b) TiAl-xM (M=Ag, Cr) thin films

The ductility of the films was evaluated using a tensile sample with a geometry developed for this purpose [13]. The deformation gradient in the sample was determined measuring it in fifteen regions along the sample (each one 5mm long). The deformation was measured using a travelling microscope, with a accuracy of 1 μ m. After tensile test the films present cracks where the strain imposed exceeds their ductility, as seen in figure 1. Optical microscopy was used to define the boundary of the region where cracks appear. The strain attained is this region characterises the ductility of the film.



Figure 1 - Example of observations, by optical microscopy, after deformation, showing the development of cracks. Three different regions of a TiAl-Ag sample, annealed during 1 h, are shown: (a) 1%, (b) 2% and (c) 5% of deformation.

RESULTS

Before studying the Ag and Cr element influence on the γ -TiAl phase, differently composed Ti-xAl ($0 \le x \le 100$ at.%) thin films were produced. After chemical and morphological characterisation, the films were analysed by XRD as a way of evaluating their degree of structural order. The obtained results are summarised in figure 2.



Figure 2 – XRD analysis of the Ti-xAl ($0 \le x \le 100$ at.%) films. (a) typical X-ray diffractograms; (b) mean grain size as a function of the aluminium content in the films.

As can be observed, looking firstly at the Ti-rich side, the structure of the films goes from α -Ti (hcp) to Al (fcc), involving a two-phase domain, α -Ti + (Al), for atomic percentages of aluminium between 58 and 59.5 (figure 2a). If the phases obtained are compared with those foreseen in the Ti-Al phase diagram, it can be verified that the produced films are metastable and present structures with enlarged solubility domains. Moreover, it is possible to introduce more aluminium in the hcp titanium phase, than titanium in the aluminium fcc phase, such as happens, to a lesser extent, in equilibrium.

The degree of the structural order of the films was analysed using XRD and TEM / ED. The results show that the introduction of the substitutional element seems to favour the process of grain germination, a structure of smaller grain size is obtained for films with composition within the range 50 to 60 at.% (figure 2b).

After studying the Ti-Al system, special attention was given to the Ti-48Al alloy, hereafter TiAl, and to the influence of silver and chromium on its structure. For this two targets (Ti + Al) were used, with foils of element Ag (Cr) superimposed on the Al (Ti) target. The XRD and TEM / ED analysis of the TiAl alloy (figure 3) reveal the existence of a fine-grained structure (some dozens of nanometers), which is constituted by two phases, α -Ti + (Al) observed from deconvolution of the (00.1) and (111) peaks, respectively. This two-phase structure differs from that obtained in films deposited with a single target (α -Ti solid solution).

The influence of deposition geometry on the structure of the films is an important point to bear in mind. In the case of the co-deposition process, the continuous rotation of the substrate is responsible for the separation of these two phases. During one rotation, a layer with thickness of ≈ 3.3 nm is formed, with a composition varying from 0 to 100 at. % of one of the elements Ti or Al, whether the substrate is in a region of exclusive influence of either the Al or the Ti target, respectively. However, and as will be seen, the films will tend towards equilibrium with the temperature increase, independent of the deposition conditions, i.e. the initial structure.



Figure 3 – Structural analysis of the as-deposited TiAl sample. (a) X-ray diffractogram; (b) TEM images (bright and dark fields).

The addition of silver or chromium does not induce structural changes in the as-deposited films. None of the systems present other phases besides α -Ti and (Al). Moreover, silver or chromium does not significantly influence the lattice parameters of these phases.

In order to evaluate the structural stability of these films as a function of the temperature, DSC runs up to 700°C were carried out. Figure 4a shows the DSC curves of three different materials: TiAl, TiAl-5Ag and TiAl-5Cr. The room temperature structural results obtained from the TiAl alloy, after this thermal cycle, are shown in figure 4b. In each DSC curve, two exothermal peaks in the range of temperatures between 450 and 700°C are detected (figure 4a). Silver favours the transformation of the initial structure, while chromium has a opposite effect. By XRD, one might conclude that the first peak is as a result of the α -Ti + (Al) transformation into a disordered TiAl solid solution (fcc structure), while the second peak corresponds to the formation of the ordered γ -TiAl structure (figure 4b).

Based on the DSC results, the samples from the TiAl-Ag system were annealed at 600°C for 1, 3 and 6h. After heat treatment the samples were analysed by XRD and TEM / ED.



Figure 4 - (a) DSC curves of the TiAl samples with and without the additional element M. (b) structure of the TiAl sample after the DSC run.

The obtained results show that annealing induces microstructural changes in the films. The definition of the γ -TiAl phase increases, with the increase of either the heat treatment duration or the silver content. This element impedes the formation of the α_2 -Ti₃Al phase and induces the precipitation of a silver solid solution (figure 5). The *c/a* ratio of the γ -TiAl phase slightly increases with the silver content, mainly due to the increase in parameter *c*.



Figure 5 – Structural analysis of the samples with high silver content. (a) TEM image; (b) X-ray diffractograms (overall view and deconvolution of the Ag (111) and γ -TiAl (111) peaks).

As far as element Cr is concerned, the presence of any rich phase in this element was not detected after 700°C annealing. Thus, one might suppose that this element is in solution in the γ -TiAl phase. Contrary to the TiAl-Ag system, chromium induces a slight decrease of the relationship c/a of the ordered phase.

Hardness and tensile properties of the TiAl-M films were determined in their as-deposited state and after heat treatment at 600°C / 1h. (figure 6). Unfortunately, it was not possible to evaluate these properties at higher temperatures in order to study the influence of this element on the γ -TiAl phase of the Ti-Al-Cr system. The stainless steel used in this work suffers a precipitation process of chromium carbide along the grain boundaries, due to the decomposition of austenite at elevated temperatures, which would affect the measured values of the mechanical properties.



Figure 6 – Hardness (a) and ductility (b) of the TiAl-M (M = Ag, Cr) films with and without heat treatment as a function of the M content.

As regards hardness, the as-deposited films with Ag and Cr undergo similar behaviour, i.e., there is a structural hardening up to M content close to 1.5at.%, followed by a softening for those of a higher silver or chromium content. The hardness of the binary Ti-Al film (9.2GPa) is significantly higher than for pure bulk titanium or aluminium (≈ 0.5 GPa). The existence of a fine-grained structure together with stresses, resulting from the sputtering process, are possible explanations for this hardening effect.

The shape of the hardness curves of the as-deposited films might be a result of two different factors: (i) limited solubility of silver and chromium in the α -Ti and (Al) phases and the precipitation of M-rich phases, with a low degree of structural order undetectable by X-ray diffraction or (ii) a decrease in the covalent character of the Ti-Al bonding resulting from the introduction of silver and chromium, whose effect superimposes the distortion on the crystalline lattice, due to the presence of these elements in substitutional sites.

The hardness of the heat-treated Ti-Ag-Al system is almost independent of the silver content. In the case of the films with chromium, the curve obtained for the annealed samples is parallel to the one corresponding to the as-deposited state, shifted to higher values. In this case, the heat treatment temperature (600°C) did not initiate the formation of the γ -TiAl ordered phase – only an f.c.c. disordered phase was formed.

With regard to the tensile tests, the results showed that the Ti-Al-Ag as-deposited samples have higher elongations than those which were annealed. The initial structure formed by two solid

solutions instead of the intermetallic compounds might explain these results. The ductility of the γ -TiAl phase slightly increases through the addition of small amounts of silver (\approx 1at.%). However, the obtained values are relatively low, as a result of a high level of tensile stresses brought on by the formation of the γ -TiAl phase from α -Ti + (Al) [13]. The production of titanium aluminides of good ductility will necessarily involve the use of a γ -TiAl target, in place of two elemental targets, in order to obtain an as-deposited structure as close as possible to equilibrium.

Finally, it should be pointed out that the main objective of using the sputtering technique for the production of titanium aluminides was not the synthesis of structural thin films but to give information which will be necessary for other elaboration techniques in the future development of new materials of better performance than those presently available. With this aim in mind, TiAl-Ag alloys of identical chemical compositions to those studied in this work were produced by foundry. The obtained structural results are in agreement with those obtained in this study, i.e. the γ -TiAl phase has limited silver solubility, a solid solution (Ag) is formed for higher silver content. However, it is evident that the mean grain size of the γ -TiAl phase obtained by foundry, followed by hot working and annealing at 1350°C is, in any of the cases, higher than the annealed sputtered samples during high holding times at 600°C.

CONCLUSIONS

This work is a first approach towards the future development of modified titanium aluminides of high ductility. The methodology used revealed to be useful in the study of the influence of silver and chromium on the γ -TiAl phase. The geometry of the tensile sample seems to be suitable for the evaluation of the ductility of the films. However, the obtained values are lower than expected, which could be a result of an important level of stress in the films. We think that in the future this work will have to involve the use of a γ -TiAl target in place of the two elemental targets used, in order to obtain a structure which is as close as possible to equilibrium.

References

- [1] S. C. Huang and J. C. Chesnutt, *Intermetallics Compounds*, ed. Westbrook and Fleischer, John Wiley & Sons, W. Sussex, England vol. II (1994) 77.
- [2] F. H. Froes, Proc. Internat. Workshop on Ordered Intermetallics, Hangzhou, China (1992).
- [3] Y.M. Kim, Intermetallics 6 (1998) 623.
- [4] T. Kawabata, T. Tamura and O. Izumi, *Metallurgical Transactions A*, vol. 24A (1993) 141.
- [5] R. D. Reviere, X. F. Chen, B. F. Olivier, C. R. Brooks and J. R. Dunlap, *Mat. Science and Eng.*, A172 (1993) 95.
- [6] Y. G. Li and M. H. Loretto, Acta Metall. Mater. 6 (1994) 2009.
- [7] F. H. Froes, Proc. of the 7th National Meeting of the Portuguese Materials Society, Aveiro, Portugal, vol. I (1995) 5.
- [8] D. Vujic, Z. Li and S. H. Whang, Metallurgical Transactions A, 19A (1988) 2445.
- [9] F. Sanchete, Synthese et Caracterisation de Depots Al-Cr-(N) et Al-Ti-(N) Obtenus par Pulver. Cathodique Magnetron en Cond. React., Tese de Doutoramento, Inst. Poly. de Lorraine (1996).
- [10] T. Suzuki, H. Umehara and R. Hayashi, J. Mat. Res., vol. 9 (4) (1996) 1028.
- [11] R. Banerjee, S. Swaminathan, R. Wheeler and H. L. Fraser, Mat. Res. Soc. Symp. Proc., vol. 400 (1995) 215.
- [12] A. Cavaleiro, C. Louro, C.M.A. Brett and J.V. Fernandes, Vacuum, 52 (1999) 157.
- [13] M.T. Vieira, A.S. Ramos, B. Trindade, J.V. Fernandes and M.F. Vieira, Accepted for publication in Thin Solid Films.