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Mechanical characterisation of γ-TiAl thin films obtained by two different sputtering routes

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Abstract

In this study (TiAl)-based films were magnetron sputtered using two different methods: two targets (Ti + Al) and a γ-TiAl target. In both cases, the as-deposited films had to be heat treated in order to obtain the intermetallic γ-TiAl. The effect of the addition of chromium on the structure and mechanical properties was studied. The films were submitted to ageing treatments and the resulting structures and mechanical properties were also studied. To get more insight into the films, the residual stresses were also evaluated. After heat treatment (HT), the films sputtered from two targets are constituted by a single γ-TiAl phase while in the films produced with one target it is possible to observe the presence of the α_2-Ti_3Al phase. Under annealing, the as-deposited compressive stresses give rise to low tensile stresses. The 18 h HT leads to a pronounced increase in hardness in the films obtained by using two targets. The hardness of the films produced using one target increases gradually with the HT holding time. In all cases, ductility and hardness exhibit inverse trends.

Keywords: Titanium aluminide thin films; Mechanical properties; Residual stress

1. Introduction

Much effort has been put into the study of ordered intermetallic alloys, particularly titanium aluminides. The main research work developed essentially concerns the improvement of mechanical properties [1,2]. This goal has been attained by adding different elements to the chemical composition of the titanium aluminides and by controlling the microstructure, through heat treatments (HTs) at different heating temperatures and cooling rates [3,4].

The sputtering process besides facilitating the production of titanium aluminides with different chemical compositions normally gives rise to metastable structures of a very fine grain size, which should evolve to equilibrium by adequate HTs [5]. Two different methods can be used to produce a γ-TiAl thin film, (1) sputtering from two different targets (one of titanium and the other of aluminium); (2) sputtering from one target itself constituted by bulk γ-TiAl. In the latter, a small quantity of chromium is normally present as a manufacturing aid.

In this research, after the definition of the temperature which is guaranteed to obtain γ-TiAl through HT, the microstructure and mechanical properties (hardness and ductility) of the films were studied as a function of the sputtering route and the ageing time. The influence of the chromium content was also taken into consideration in the structure, microstructure and mechanical characterisation.

As a consequence of this type of study it is possible to envisage sputtering as a screening technique, helpful in microstructural optimisation and acknowledgement of titanium aluminide bulk materials [6]. Nevertheless, on the extrapolation of the films' mechanical properties to bulk materials the effect of residual stresses it should be taken into account.

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2. Experimental details

γ-TiAl based films were deposited onto 304 stainless steel substrates by dc magnetron sputtering using either two targets or only one target. In the former, the titanium target operated at about 840 W and the aluminium one at 500 W in order to achieve an aluminium content close to 48 at.%. In the latter, the γ-TiAl target operated at 1000 W. In both cases the sputtering chamber was evacuated down to 10^{-4} Pa and during deposition argon at a 3×10^{-1} Pa pressure was used.

The films were characterised in their as-deposited state and after isothermal HTs during different holding times in a hydrogenated argon atmosphere. The chemical composition of the films was determined by electron probe microanalysis using a CAMECA SX50 apparatus with an accelerating voltage of 15 keV. X-ray diffraction (XRD) experiments were performed in a Philips X'Pert diffractometer with Co–Kα radiation. Thin foils for transmission electron microscopy (TEM), thinned on both sides by ion milling in an argon atmosphere, were observed in a 300 kV Hitachi microscope with electron diffraction facilities. The hardness tests were carried out on a Fisherscope H100 ultramicrohardness tester equipped with a Vickers indenter, according to the procedure described elsewhere [7]. The tensile tests were performed using tensile samples with special geometry [6,8]. The residual stresses of the films were evaluated using a laser beam apparatus by measuring the curvature induced due to the stresses in the film. The film stresses were calculated based on the Stoney equation [9].

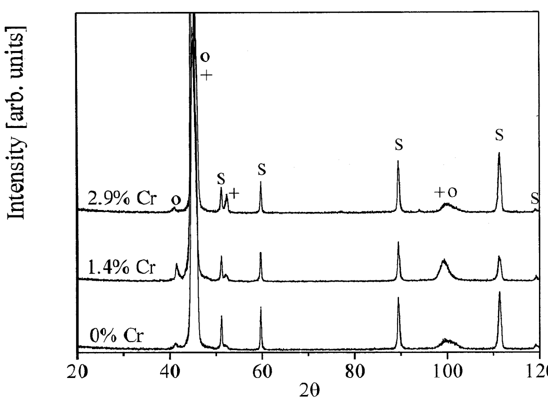


Fig. 1. X-ray diffractograms of as-deposited films via route (1) as a function of Cr content. ○, α-Ti; +, Al; S, substrate.

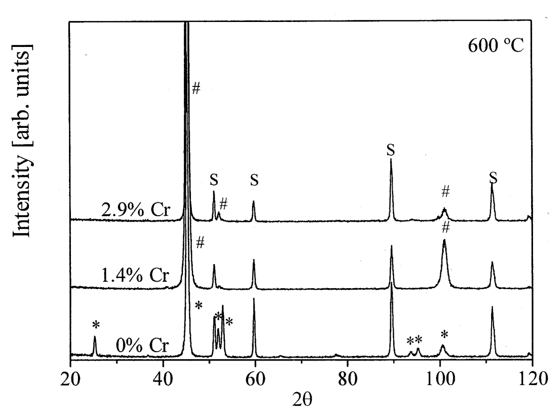


Fig. 2. X-ray diffractograms of films heat treated at 600 °C/1 h as a function of Cr content. *, γ-TiAl; #, disordered TiAl; S, substrate.

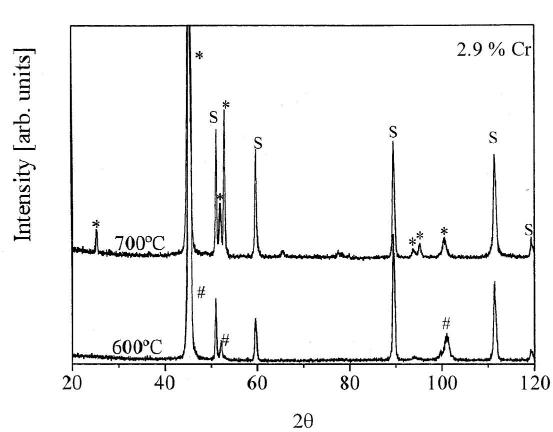


Fig. 3. X-ray diffractograms of a 2.9 at.% Cr film produced via route (1) heat treated at 600 and 700 °C/1 h. *, γ-TiAl; #, disordered TiAl; S, substrate.

3. Results and discussion

3.1. Microstructure

In order to compare the behaviour of thin films deposited from routes (1) and (2), first it was necessary to study the probable effect of the presence of low quantities of chromium in sputtered films deposited using two targets (route 1). Thus, films without chromium and with 1.4 and 2.9 at.% Cr were deposited from two targets, putting small Cr foils upon the titanium target. The X-ray diffractograms of the as-deposited films produced according to route (1) did not reveal any structural difference with and without chromium (Fig. 1). In all cases, the microstructure of the as-deposited films obtained from two targets is only formed by the titanium and aluminium rich phases, as confirmed by TEM analysis [10]. However, the presence of chromium influences the structure after 1 h HT at 600 °C. In Fig. 2 it can be seen that contrary to the binary films, those with chromium did not evolve to the intermetallic structure during 1 h at 600 °C. Thus, the films were annealed at 700 °C, after which the γ-TiAl phase is obtained (Fig. 3). These results agree with the differential scanning calorimetry (DSC) tests according

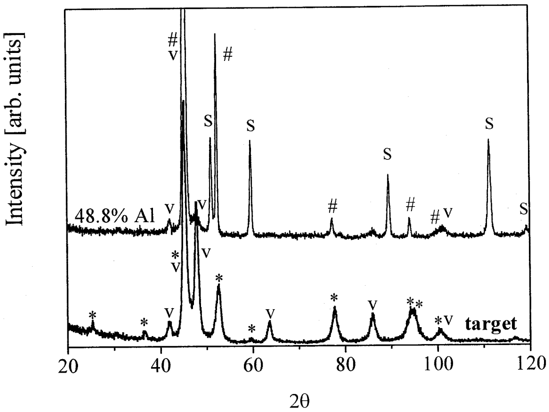


Fig. 4. X-ray diffractograms of as-deposited films via route (2). *, γ-TiAl; v, α_2-Ti_3Al; #, disordered TiAl; S, substrate.

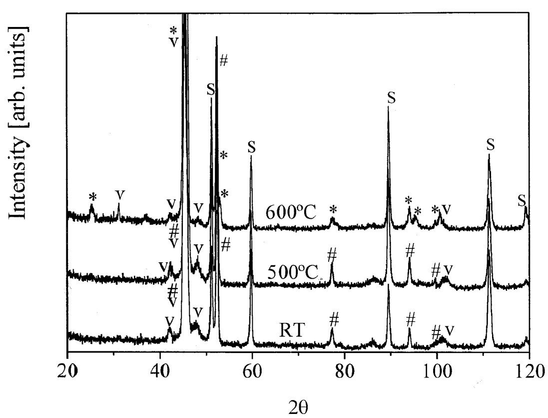


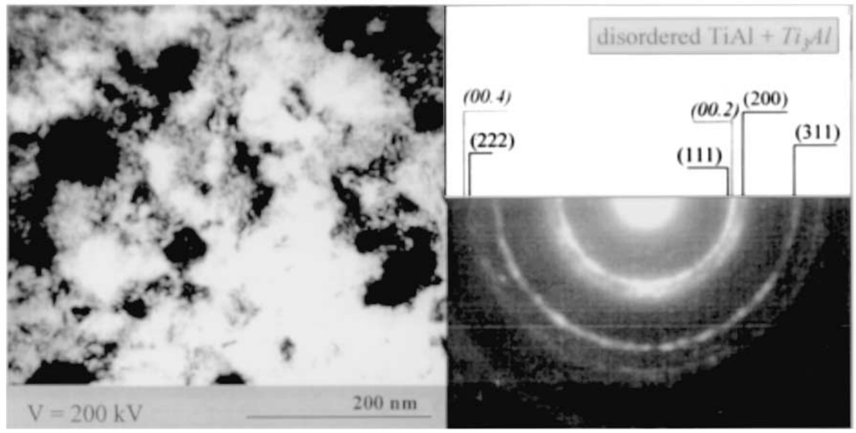
Fig. 5. X-ray diffractograms of films produced via route (2) as a function of the annealing temperature. RT, room temperature. *, γ-TiAl; v, α_2-Ti_3Al; #, disordered TiAl; S, substrate.

to which the chromium retards the transformation α-Ti + (Al) → disordered TiAl → γ-TiAl, with the DSC curves showing the corresponding exothermic peaks shifted to higher temperatures [10].

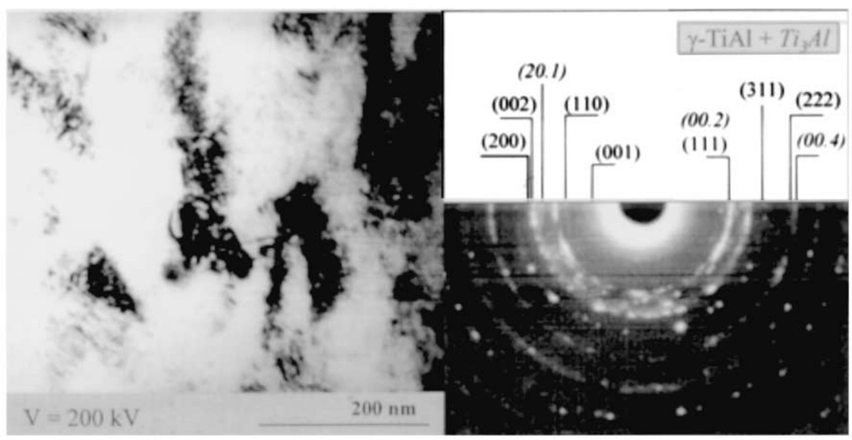
In spite of the ordered structure of the TiAl target, the films obtained from it have an Al face centered cubic (fcc)-type structure indexed as disordered TiAl (Fig. 4). Although the aluminium contents are close to those of the films produced via route (1), the presence of the α_2-Ti_3Al intermetallic phase is notorious in these films. Once again, the as-deposited films must be heat treated to promote the formation of the γ-TiAl equilibrium phase, but in this case the transformation consisted of a single step, disordered TiAl → ordered γ-TiAl. Through the increase of the HT temperature to 600 °C it was possible to observe the X-ray superlattice peaks of the γ-phase, namely the (001) at $2\theta \approx 25°$, indicative of the ordered structure (Fig. 5). It should be noted that for similar chemical compositions (1.4 at.% Cr) the films produced using two targets had to be heat treated at 700 °C to obtain the γ-phase. Fig. 6 shows a distinct morphology between the as-deposited state and post HT performed in order to attain the equilibrium phase (600 °C, 1 h). The films present two domains in bright field images at high magnifications, a dominant phase (white) surrounded by a very fine dispersed phase (dark). The diffraction patterns indicate in white zones the presence of disordered TiAl or γ-TiAl, respectively, after sputtering or HT, and in dark zones TiAl (disordered or ordered) and α_2-Ti_3Al. Thus the fine phase observed in a bright field image possibly corresponds to α_2-Ti_3Al or to a very fine lamellar structure constituted by TiAl and α_2-Ti_3Al, as in bulk titanium aluminides (Fig. 7). The difference between Fig. 6a and b lies in the extent and size of the TiAl phase. The heat treated thin films shows a larger fraction of TiAl crystals.

In order to study the effect of ageing treatments at the transformation temperatures (600–700 °C), in both cases (route (1) and (2)), the films were annealed during long holding times ($t = 1$–162 h). The TEM images of Fig. 8 show an increase of the films' grain size as the ageing time increases, in spite of being far from the bulk materials grains of the order of 100 μm. For long holding times it is possible to observe a bimodal distribution of grain size. In TEM images large grains are surrounded by small grains. The original grains are partially converted. Two processes may be responsible for this behaviour, abnormal grain growth by grain boundary diffusion or dynamic recrystallisation, due to the deformation of the thin films structure by the intrinsic stresses usually present in thin films after deposition. Table 1 summarises the residual stress values obtained according to the description in the experimental details. First, it should be noted that for all cases the as-deposited films are in a compressive stress state. In fact, compressive stresses are often observed for sputtered films [9]. The growing films tend to expand relative to the substrate due to the incorporation of the discharge gas, usually argon. However, both the film and the substrate must have the same length. Therefore, the substrate bends convexly outward according to the sequence of events leading to compressive stresses in films. Nevertheless, compared with ceramic sputtered films [11], the films under study have low residual stresses. Secondly, the route used to deposit titanium aluminides does not affect the residual stresses in the as-deposited state.

As far as the heat treated films are concerned two situations must be taken into consideration, since the starting point structures are different and, consequently, under annealing the sequence of transformations is not the same. In the case of the films produced using two targets the specific volume of the α-Ti + (Al) as-deposited structure is considerably higher than the specific volume of the γ-TiAl structure obtained after HT leading to tension stresses. Indeed, the shrinking of the volume generates tensile stress [12]. The stress evo-



(a)



(b)

Fig. 6. TEM images and ED patterns of films produced via route (2). (a) As-deposited. (b) Heat treated at 600 °C/1 h.

lution is characterised by an irreversible change in compressive stresses to lower tension stresses. In the case of the films produced using one target, although there is a decrease of the specific volume, this decrease is not so pronounced and the tension stresses are lower than in the films deposited using two targets. Long ageing treatments did not lead to significant variations of the stress values. The tension stresses are constant with the increase of ageing time, thus the strain of thin films is also constant.

3.2. Mechanical properties

After the HT, which is necessary to produce the intermetallic structure, a higher hardness is observed for the binary films compared with the as-deposited ones. The increase in hardness with the formation of the γ-TiAl phase was expected, as one of the mechanical characteristics of the intermetallic ordered structures is its high hardness [13]. The ductility of the as-deposited binary films decreases, as a result of the formation of the ordered γ-TiAl phase under annealing [7].

In Fig. 9 it is possible to observe the influence of the ageing time on the hardness of the films produced according to the two routes adopted in this study. For the films obtained using two targets, the most relevant feature is a pronounced increase in hardness after annealing during 18 h. The high hardness achieved could

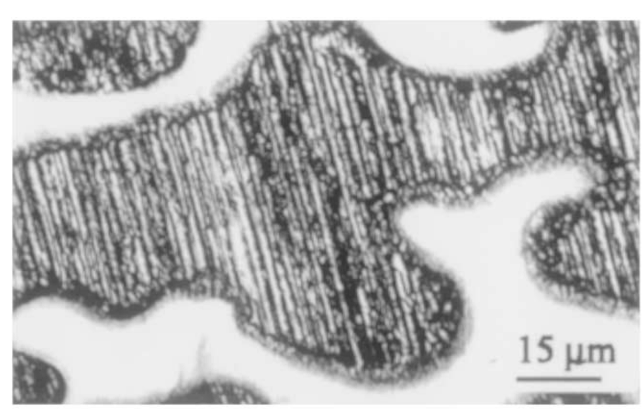


Fig. 7. Scanning electron microscope image of a bulk material. White zones ≡ γ-TiAl, dark zones ≡ $\alpha_2 + \gamma$ lamellae.

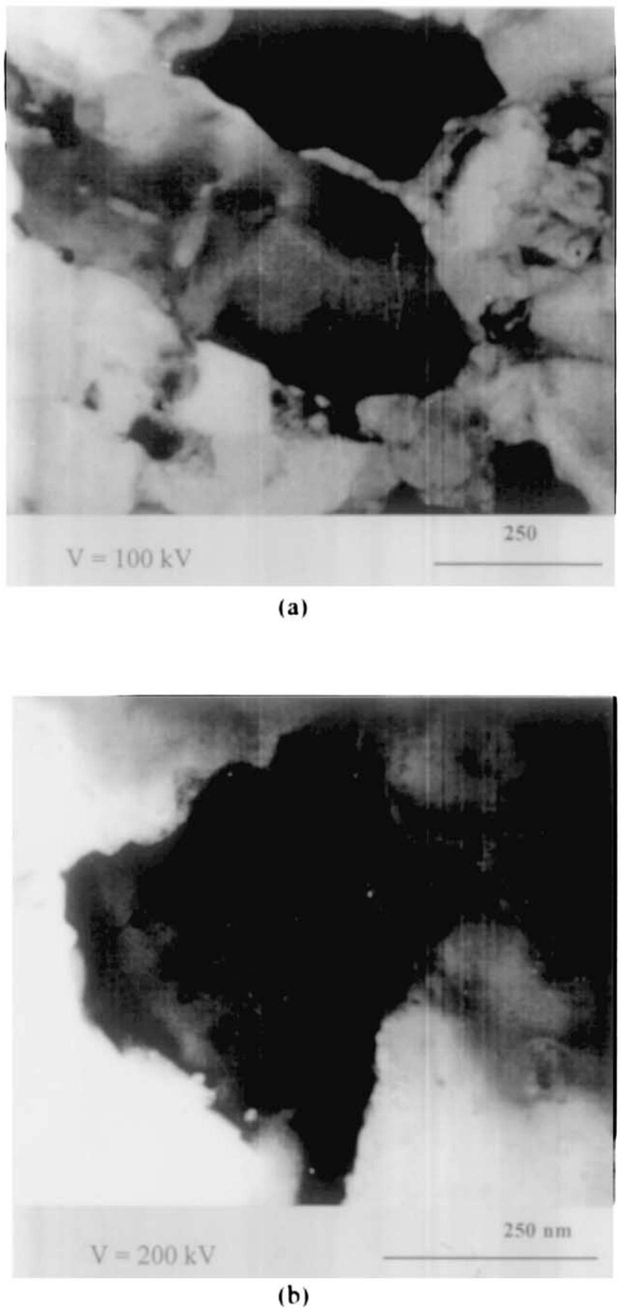


Fig. 8. TEM images of films heat treated at 600 °C during 162 h. (a) Two targets. (b) One target.

result from a fine precipitation of material that might remain after 1 h HT. During the longest ageing treatment (162 h) the crystallites became larger and consequently a progressive slight decrease in hardness is observed. As far as the films sputtered from one target are concerned the ordering process led to a slight increase in hardness after 1 h HT. By increasing the holding time there is a slight gradual increase in hardness, which can be related to the role of chromium in grain boundaries. This element makes diffusion more difficult and consequently the growth of the new phase is similar to that observed in the ageing of films obtained by using two targets. It is interesting to note that the use of a single target always gives rise to a higher hardness than if two targets operated simultaneously. A higher percentage of the α_2-Ti_3Al phase (as indicated by the XRD results) than in the films deposited from two targets associated to the presence of chromium could explain this fact. Chromium is responsible for a gradual increase in the hardness of the heat treated films. The hardness and ductility results of the films sputtered from two targets as a function of the chromium content are summarised in Fig. 10. In the as-deposited state a maximum hardness is obtained for 1.4 at.% of Cr, close to the chromium content of the films deposited from one target, probably due to the solid solution effect or to a precipitation of a very fine soft Cr-rich phase for higher contents (not detectable by XRD), as already observed for films doped with silver [7]. For low chromium contents it is likely that this element is in solution contributing to a hardening effect. Moreover, the ductility of the intermetallic films slightly decreases with the increase in the chromium content.

The ductility results obtained for the two types of films are plotted in Fig. 11 as a function of the HT holding time. For the films produced using two targets, the ductility curve agrees with the relationship between hardness/ductility. In fact, the increase in hardness after

Table 1
Stress values of the as-deposited films and after HT

Stress (GPa)	Two targets		One target
	TiAl	TiAl+Cr	
As-deposited	−1.0	−0.9	−0.9
HT 15 min.	0.5	–	0.3
HT 1 h	0.6	–	0.3
HT 18 h	0.5	–	0
HT 162 h	0[a]		

[a] Considering 1 h HT as reference.

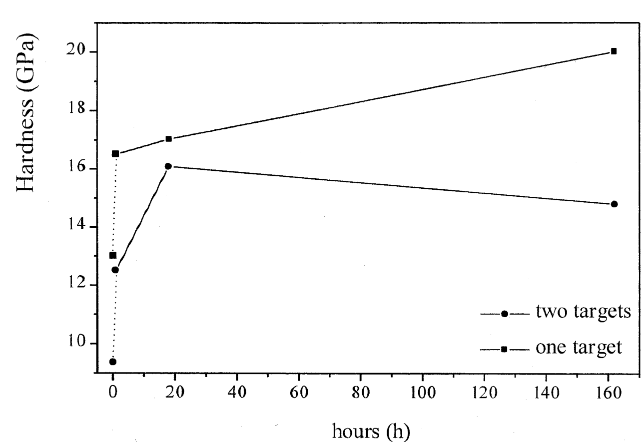


Fig. 9. Hardness as a function of the HT holding time.

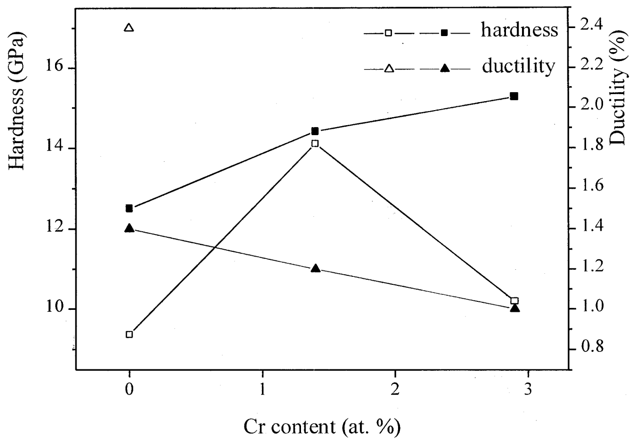


Fig. 10. Hardness and ductility of films produced using two targets as a function of the Cr content. Open symbols ≡ as-deposited, solid symbols ≡ heat treated.

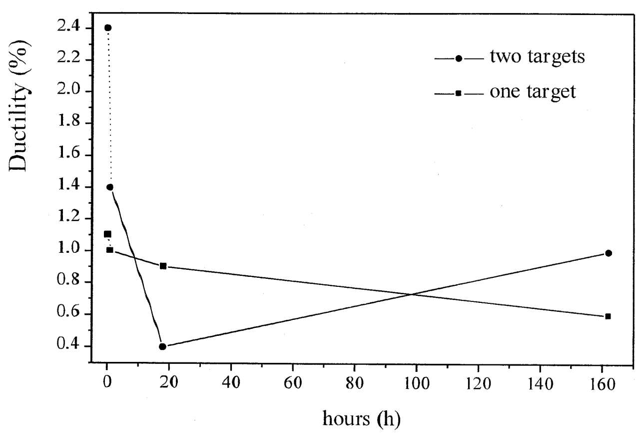


Fig. 11. Ductility as a function of the HT holding time.

annealing, especially during 18 h, is responsible for the low ductility values obtained. Besides, the high ductility of the as-deposited films should be related to the existence of the α-Ti + (Al) two solid solution structure. In the case of the films obtained via route (2) the initial structure is indexed as disordered TiAl and the ductility is already quite low in the as-deposited state. The ordering process and the consequent increase in hardness explain the decrease in ductility observed after 1 h HT. Once again, ductility and hardness have an inverse trend as a function of the HT holding time.

4. Conclusions

Titanium aluminides thin films are successfully produced by two different magnetron sputtering routes after proper annealing. In order to get additional information regarding bulk materials the use of a γ-TiAl target seems more promising because for similar chemical compositions the films have a γ-TiAl + α_2-Ti_3Al two phase structure with γ-grains and $\gamma + \alpha_2$ lamellae, as in bulk titanium aluminides. The films produced using two targets present only traces of the α_2-phase and are constituted by a single phase (γ-TiAl).

This study focuses on the mechanical properties of the TiAl thin films, namely on the hardness and ductility. It is concluded that the techniques used are adequate for the mechanical characterisation of thin films.

In the future it would be interesting to increase the HT holding time to try to homogenise the grain size, as after 162 h annealing only some selective grain growth is observed.

Acknowledgements

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