Production of Ti-Mg-Si Thin Films by Magnetron Sputtering and their Phase Transformations with Temperature

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Keywords: Light alloys, Ti-Mg-Si, Sputtering, Structural characterisation.

Abstract

In this paper, the development of sputtering technique for the production of new ternary Ti-Mg-Si light alloys is discussed. Structural characterisation of the 'as-deposited' samples and 'heat treated' ternary alloy thin films has been completed. The as-deposited films are structurally metastable, and are consisted of fined-grained solid solutions with enlarged solubility limits. Annealing of the as-deposited ternary samples resulted in the decomposition of the thin film solid solutions to form different Ti-Si intermetallic compounds.

Introduction

Light metals based on aluminium, magnesium, titanium and the intermetallic titanium aluminides are attractive for aerospace systems and advanced automobiles [1]. Density reduction is the most effective parameter in reducing component/vehicle weight in aeroplanes, and dramatically increases efficiency in the reciprocating parts of an automobile engine such as a valve. There are various methods of synthesising and processing these lightweight metals with enhanced physical and mechanical properties such as rapid solidification, vapour deposition and mechanical alloying [2-4]. The literature on the production of Ti-Mg-Si (Ti-rich) lightweight alloys by MA show that is possible to synthesis Ti-Si and Mg-Si intermetallics by annealing at specific temperatures [5]. The goal is to increase the temperature limit of Ti- and Mg-rich alloys by incorporating an alloying element (Si) in order to promote fine dispersions of Mg-Si and Ti-Si intermetallic compounds in a Ti or Mg matrix by annealing. In this work, lightweight Ti-Mg and Ti-Mg-Si sputtered thin films were produced and characterised at room and elevated temperatures.

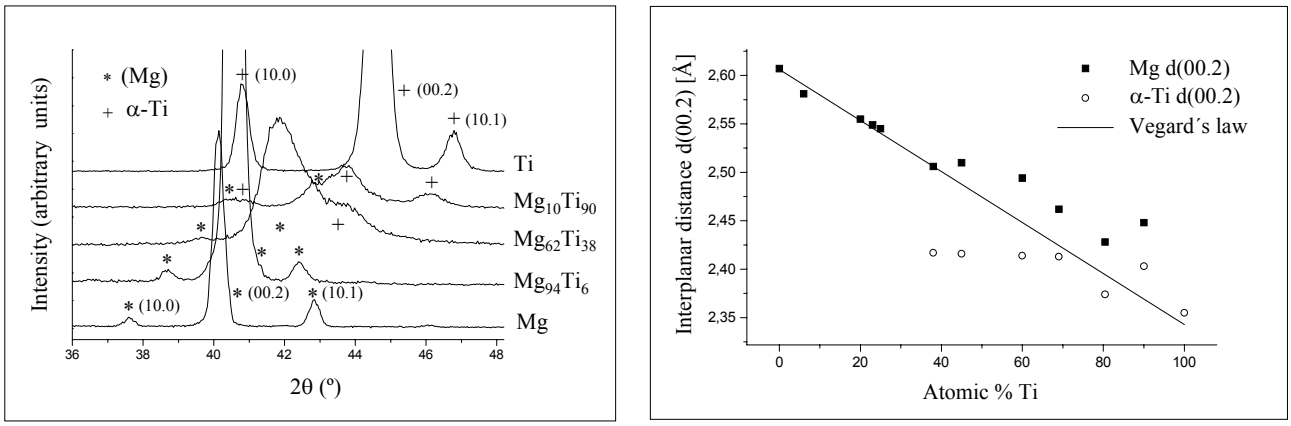
Experimental Details

$TiMg_x$ ($0 \le x \le 100$at.%) and $(TiMg_x)_{91}Si_9$ (x=14 and 82at.%) thin films with ≈ 3μm thickness were co-deposited by d.c. magnetron sputtering. The $TiMg_x$ films were obtained from two elemental targets, titanium and magnesium. The ternary films were sputtered from these two targets, onto which silicon foils were superimposed. Steel and glasses samples were used as substrates. The sputtering parameters used in the depositions were the following: $p_{ultimate} = 10^{-4}$ Pa; $p_{dep.} = 1$Pa; $P_{Mg} = 2.22$ Wcm^{-2}, P_{Ti} and target-substrate distance variable. The substrates were biased (-70V). All the thin films were studied in their as-deposited state. The ternary thin films were isothermal annealed at elevated temperatures in a hydrogenated argon atmosphere (5% H_2). The chemical composition of the films was determined by electron probe microanalysis (EPMA). X-ray diffraction experiments were performed with Co-K_α radiation. Films for TEM analysis were thinned on both sides by ion milling in an argon atmosphere. A 100kV TEM equipment was used.

Results and discussion

Binary System Ti-Mg

Figure 1.a shows some representative X-ray diffractograms of the $TiMg_x$ films and their respective atomic chemical composition. Figure 1.b represents the variation of $d_{(00.2)}$ interplanar distances of the Ti and Mg phases of the as-deposited samples as a function of the chemical composition (fig.1.b).



a) b)

Fig. 1 – Structural analysis of the as-deposited $TiMg_x$ binary system: (a) X-ray diffractograms; (b) variation of the $d_{(00.2)}$ interplanar distances of the α-Ti (*hcp*) and Mg (*hcp*) phases as a function of chemical composition.

Concerning the elemental films, equilibrium structures (*hcp*-Mg and -Ti phases) with [00.2] preferred orientations were obtained by magnetron sputtering. This corresponds to the more compact planes (basal planes) of the *hcp* structures. The positions of the diffraction peaks of these phases are very close to those indicated by the ICDD cards. This indicates that the stress level in these films is negligible.

From 0 to 38at.% Ti only the *hcp*-Mg phase can be detected, which means that, Ti is in solid solution in magnesium. The d(00.2) interplanar distances of these samples follow the Vegard's law, indicating that titanium occupies substitutional positions in the *hcp*-Mg phase. This occupancy is not random since some reflection lines of magnesium, e.g. (10.1) plane, do not follow this tendency. From 38 to 90at.% the *hcp* Mg and α-Ti phases co-exist, with a [00.2] texture. As the samples become richer in titanium the number of peaks corresponding to the (Mg) phase decrease and they become broader. The inverse situation occurs for the α-Ti phase. The films with intermediate compositions have diffraction peaks with higher FWHM values. This means that these films present the lowest degree of structural order. The samples which chemical composition lies in this range do not follow the Vegard's law. The appearance of the α-Ti phase might be the responsible for this deviation. While the α-Ti d(00.2) interplanar distance remains constant as a function of chemical composition, the same is not true for the *hcp*-Mg phase. In fact, in spite of this phase does not follow the Vegard´s law for Ti percentages higher than 38at.%, there is a systematic decrease of the Mg d(00.2) interplanar distance as the Ti content in the samples increases. According to these results a solubility of Mg in Ti of about 25at.% may be advanced. Following the same thought a solubility value higher than 38at.% Ti in Mg is achieved. As referred by Simon B. Dodd *et al* [6] the solubility of Ti in Mg or vice-versa reached by other processes such as mechanical alloying is lower than the one reached by synthesis of materials in vapour phase. In fact, the solubility results achieved in the present work are significantly higher than the ones claimed by Simon B. Dodd *et al.* and D. M. J. Wilkes *et al.*, 17,9at.% Mg in *hcp*-Ti and 3,7at.% Ti in *hcp*-Mg, respectively [6, 7], using mechanical alloying. Similar results were obtained by L. Dias *et al.* [8] in a recent work on

the synthesis of Ti-Mg mechanically alloyed materials confirming the higher solubility of Mg in *hcp*-Ti than Ti in *hcp*-Mg. These authors claimed a solubility of 50at.% Mg in *hcp*-Ti and a practically null solubility of Ti in *hcp*-Mg.
Figure 2 shows the microstructure of the Ti-Mg binary films obtained by TEM. These images, together with electron diffraction results, confirm the XRD results concerning to the phases present in the samples and their degree of structural order. As one can see in figures 2.c and 2.d the microstructure of samples with 38 and 69at.% Ti present a second phase (intergranular phase) which doesn't appear in figures 2.a or 2.b. The grain size of the samples varies from about 1μm for 100 at.% Mg to less than 100nm for $Mg_{31}Ti_{69}$.

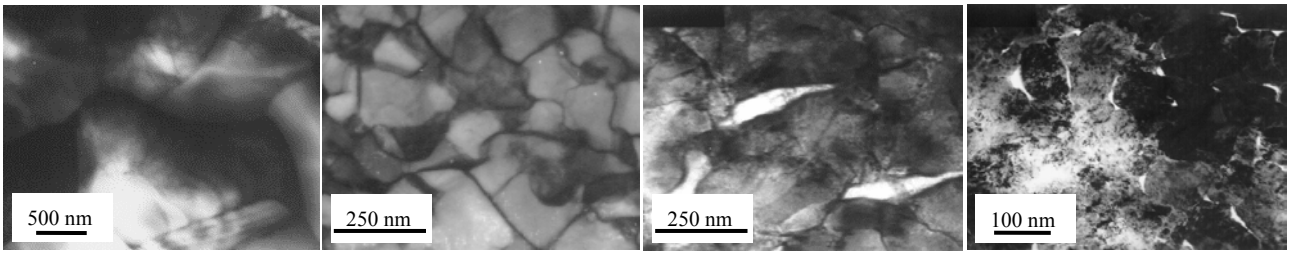


Fig. 2 – TEM images of the as-deposited $TiMg_x$ films (a) Mg ;(b) $Mg_{80}Ti_{20}$; (c) $Mg_{62}Ti_{38}$; (d) $Mg_{31}Ti_{69}$.

Ternary System Ti-Mg-Si
Figure 3 shows the X-ray results of the two ternary samples ($Ti_{77}Mg_{14}Si_9$ and $Mg_{82}Ti_9Si_9$) in the as-deposited state and after heat treatment at different temperatures. These temperatures were selected on the basis of DSC runs performed in this study.

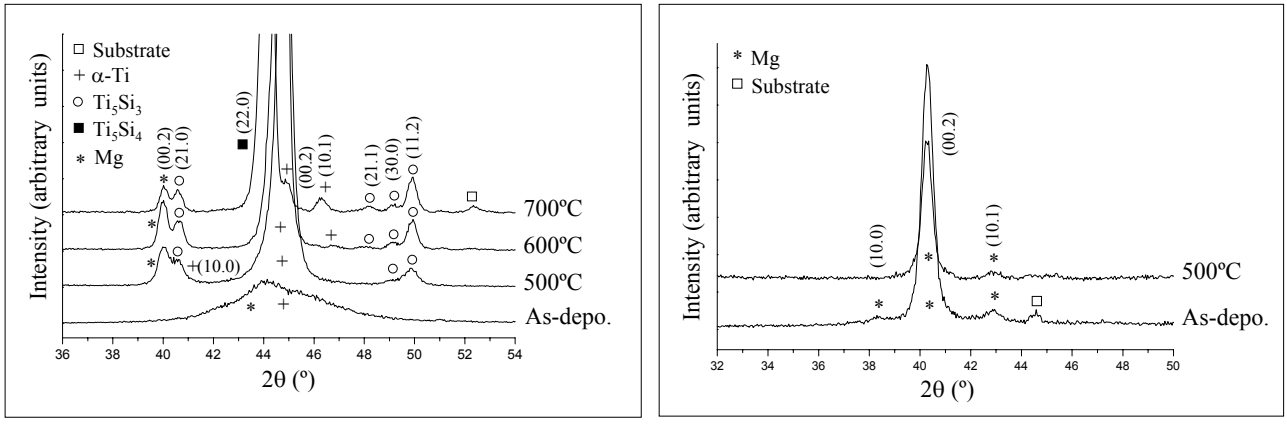


Fig. 3 – Structural evolution of the (a) $Ti_{77}Mg_{14}Si_9$ and (b) $Mg_{82}Ti_9Si_9$ samples as a function of temperature.

The $Ti_{77}Mg_{14}Si_9$ as-deposited sample is formed by a two phase (α-Ti + Mg) structure with a low degree of structural order (fig. 3.a). Comparing this sample with the binary $TiMg_x$ sample with a approximate value of Ti/Mg, it can be noticed that introduction of silicon in the films, decreases the degree of structural order leading to amorphization. In the case of the sample rich in magnesium, $Mg_{82}Ti_9Si_9$, a *hcp*-Mg phase is easily detectable (fig. 3.b). No vestiges of x-ray diffraction peaks of the Si or Ti phases could be observed which means that these elements are in solid solution in the

hcp-Mg phase. Heat treatment of both films leads to an increase of their structural order, i.e. a grain growth occurs with temperature. For the Ti-rich sample, the phases α-Ti, (Mg) and Ti_5Si_3 co-exist after 1 hr annealing at 500 and 600ºC. At 700ºC, together with these phases another phase is formed, likely the intermetallic Ti_5Si_4 with a [22.0] texture. However, this texture gives rise only to two parallel diffraction peaks and turns the indexation difficult with a certain degree of incertitude. Longer isothermal annealings at 700ºC are required to confirm the presence of this phase.
The heat treatment of the Mg rich sample at 500ºC didn't give rise to any structural change. Unfortunately, heat treatments at higher temperatures were not possible to be performed in this sample due to the poor adhesion of the film to the steel substrate.

Conclusions

The elemental films have a *hcp* structure with *d* values very closed to those indicated by the ICDD cards. All the as-deposited binary films are crystalline with a [00.2] preferred orientation. Super-saturated (α-Ti) and (Mg) solid solutions were obtained for these films (25at.% of Mg in Ti and more than 38at.% Ti in Mg). From 38 to 90at.% Mg the *hcp* Mg and α-Ti phases co-exist. Films with the intermediate compositions have the lowest degree of structural order (smallest grain size). The as-deposit ternary Ti-Mg-Si films present metastable solid solutions (α-Ti + Mg and Mg for the Ti- and Mg-rich films, respectively). Also, it should be mentioned that a small (9at.%) addition of silicon to the Ti-rich alloy ($Ti_{77}Mg_{14}Si_9$) results in the film amorphisation. During annealing of the this film there was the formation of Ti_5Si_3 and the increasing of the structural order of the (Mg) and (α-Ti) phases at 500ºC, followed by the formation of a Ti_5Si_4 phase at 700ºC. Annealing of the ternary Mg-rich film up to 500ºC didn't give rise to phase transformations.

Acknowledments

Support by FCT through project POCTI 35448/CTM/2000 is gratefully appreciated.

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