J Mater Sci (2007) 42:7684–7689
DOI 10.1007/s10853-007-1663-1

Synthesis of a lightweight Ti–10Al–5Mg (wt.%) alloy by mechanical alloying followed by compaction and sintering

M. Caetano · B. Trindade

Received: 18 January 2007 / Accepted: 5 March 2007 / Published online: 3 June 2007

Abstract A lightweight Ti–10Al–5Mg (wt.%) alloy was synthesized by mechanical alloying followed by cold compaction and sintering. A metastable hcp α-Ti(Al,Mg) solid solution was obtained after 5 h of milling. The *c/a* ratio of the hcp structure was found to increase with milling time. The particle size distribution of the mixture becomes broader and the dp50 value decreases as the milling time increases. The structure of the 900 and 1,100 °C sintered samples consist of an α-Ti(Al) solid solution matrix with α_2-Ti_3Al and MgO precipitates. Values of 11 and 188 GPa were obtained for the Hardness and Young's modulus of 1,100 °C sintered sample, respectively, confirming the strength improvement of the Ti-based alloy.

Introduction

The use of titanium-based alloys is fast expanding from large-sized aerospace components to small components such as hand phone covers. In fact, titanium-based alloys are attractive materials for different structural applications due to their good creep performance, high strength and toughness, as well as excellent corrosion resistance up to 500 °C. However, a major problem with the use of Ti is its high cost [1–2]. One of the ways to overcome this problem is by use a near-net shape process such as powder metallurgy (PM) [3], which normally involves compaction and sintering. In last years, many attempts have been made to optimize the chemical composition of these PM Ti-based materials, in order to obtain better mechanical properties such as higher-specific strength. This can be achieved by reducing density and/or increasing strength. There are some lightweight elements that have been used for this purpose, e.g., magnesium, aluminum, and silicon [4–7]. Titanium and magnesium are immiscible in the solid state and do not form intermetallic phases [8]. On the contrary, aluminum and silicon form intermetallic compounds with titanium [9, 10], which are responsible for the increase of hardness and tensile strength.

In a previous work on the production of a Ti–10Mg–5Al (wt.%) mixture by mechanical alloying and subsequent annealing [6], it was shown that the metastable α-Ti(Al,Mg) solid solution formed during milling decomposes during annealing giving rise to the melting of Mg and subsequent formation of a fine dispersion of MgO particles in the matrix. The Al atoms remained in the hcp-Ti lattice according to the Ti–Al phase diagram. In the present work, a Ti–10Al–5Mg (wt.%) alloy richer in Al was synthesized by mechanical alloying and subsequent compaction followed by sintering with the objective of producing a lightweight Ti-based alloy consisting of a fine dispersion of Ti–Al precipitates in an α-Ti matrix. In fact, according to the Ti–Al phase diagram, the α_2-Ti_3Al intermetallic is formed for Al percentages higher than 6.5% (wt.%) [9]. After milling, the mechanically alloyed sample was isostatically pressed at room temperature (CIP) and sintered at 900 °C and 1,100 °C in vacuum. The structural and mechanical results will be compared with the ones obtained for the Ti–10Mg–5Al (wt.%) alloy.

Experimental details

A Ti–10Al–5Mg (wt.%) mixture, which weighted 24.5 g, was mechanically alloyed in a planetary ball mill from Ti,

M. Caetano · B. Trindade (✉)
ICEMS, Mechanical Department of Coimbra University, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal
e-mail: bruno.trindade@dem.uc.pt

Al, Mg powders with a nominal purity of 99%, 99.5% and 99.6% and an average particle size of 75, 65 and 60 µm, respectively. The ball to powder weight ratio was 20:1 and the rotation speed was 300 rpm. Hardened steel vials and balls sealed under argon atmosphere were used. Small quantities of the powder were withdrawn after 5, 10, and 25 h of milling. Final milling was performed for 50 h.

The phase constituents of the samples were analyzed by means of X-ray diffraction (XRD) using an X'pert Philips equipment with Co-K_α radiation. A Philips XL30 FEG scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) from EDAX was used for surface analysis. Electron probe microanalysis (EPMA)—Camebax SX50 from CAMECA—was also used for chemical analysis. Particle size distributions were determined by laser scattering (Coulter LS 130 equipment) from a powder suspension in water under mechanical agitation after a 60-s sonication. Sample density was measured by He picnometry (Micromeritics Accupy 1330). Ten runs were performed and the average value calculated. Porosity of the samples was evaluated by mercury porosimetry (Micromeritics 9320).

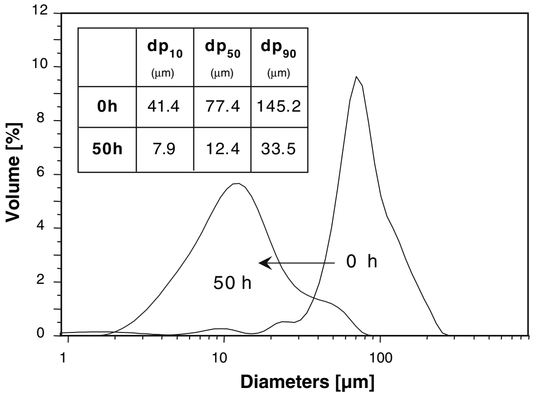
The thermal behavior of the mechanically alloyed (MA'ed) samples was evaluated by differential scanning analysis (DSC) and thermogravimetry (TG) up to 900 °C in a PL-STA equipment from Polymer Technologies, applying an heating rate of 0.25 C/s.

The 50 h MA'ed mixtures were encapsulated in latex tubes (ϕ_i = 8 mm) and were isostatically pressed at room temperature (CIP) under a pressure of 330 MPa. The CIP'ed cylindrical samples were subsequently sintered at two different temperatures, 900 and 1,100 °C, for 12 h, in vacuum atmosphere. The indentation Young's modulus and the hardness of the annealed samples were obtained by indentation on flat polished surfaces using a Vickers diamond indenter and a 200 mN load, according to method described elsewhere [11].

Results and discussion

Mechanical alloying

Elemental powders of Ti, Al and Mg (Fig. 1) were mixed in order to obtain the Ti–10Al–5Mg (wt.%) composition and were mechanically alloyed for 50 h. The particle size distributions of the as-blended and 50 h milled mixtures are shown in Fig. 2. The as-blended mixture is characterized by a relatively large distribution of particle size with a dp50 value of 77.4 µm. Milling gave rise to a much large distribution centered at lower values (dp50 = 12.4 mm). This is typical of ductile–brittle mixtures in which after milling for a certain period of time, smaller particles are able to withstand deformation without fracturing and tend to be welded into larger pieces, with an overall tendency to drive both very fine and very large particles [12]. Figure 3 shows the structural evolution of the mixture as a function of milling time. The XRD patterns reveal the formation of an α-Ti(Al,Mg) solid solution for very short periods of milling (5 h). With increasing time the XRD peaks become less intense and broader, meaning a decrease of the structural range order (decrease of the crystallite size). The grain size of the α-Ti(Al,Mg) phase milled for 50 h was calculated by the Williamson-Hall method [13]. The value obtained (38 nm) is typical of nanostructured materials.

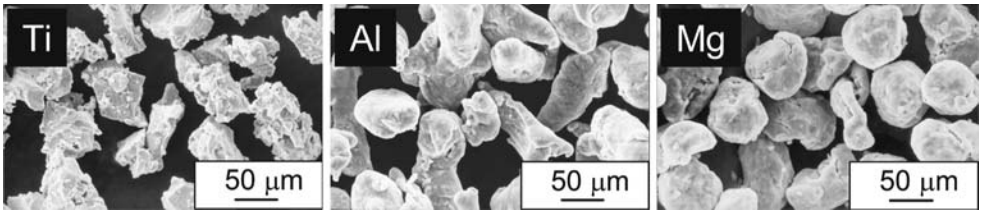


	dp$_{10}$ (µm)	dp$_{50}$ (µm)	dp$_{90}$ (µm)
0h	41.4	77.4	145.2
50h	7.9	12.4	33.5

Fig. 2 Particle size distributions and dp values of the as-blended and 50 h milled mixtures

The lattice parameters *a* and *c* of the α-Ti solid solution were calculated as a function of milling time (Fig. 4). As can be seen, there is an increase of *c* and a decrease of *a* up to 25 h milling. In spite of Mg being, in equilibrium, insoluble in the α-Ti phase, its incorporation in the hcp-Ti lattice has been referred in different works using mechanical alloying [14–16] and PVD [4, 17] as synthesis techniques. However, the increase of the *c*/*a* ratio must be attributed mainly to the incorporation of Al in the hcp

Fig. 1 Elemental powders of Ti, Al and Mg used in this work



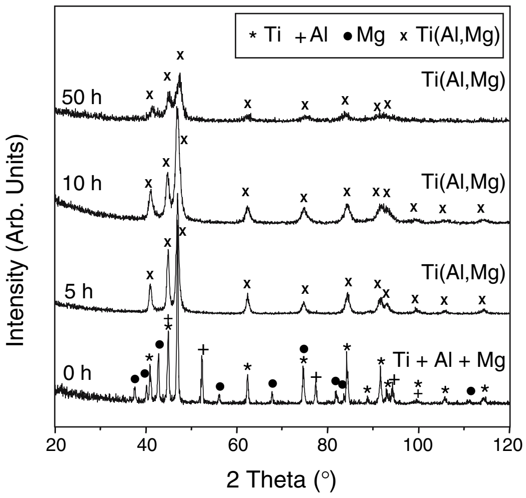


Fig. 3 Structural evolution of the mixture as a function of milling time

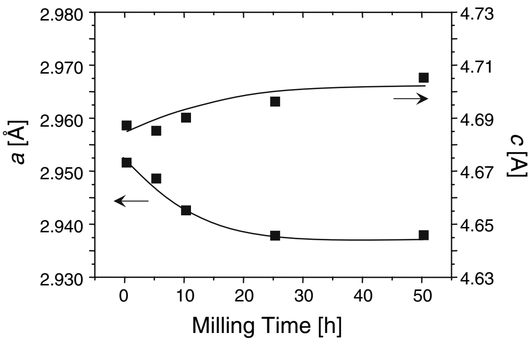


Fig. 4 Lattice parameters *a* and *c* of the α-Ti solid solution as a function of milling time

lattice of Ti and not to Mg. In fact, in a previous work on the mechanical alloying of a Ti–18Mg (at.%) mixture [14] it was shown that the incorporation of Mg in the hexagonal lattice of Ti leads to an increase of both *a* and *c* parameters. Therefore, the presence of Al in solid solution might increase the covalent degree of the Ti–Al bonding leading to a distortion of the hcp α-Ti lattice.

After 50 h milling, the volume of the hcp-Ti unit cell is not so different from the one of the Ti starting powder (35.38 Å^3 against 35.20 Å^3, respectively). This is in accordance with the atomic radius of the solute metallic elements and their percentages in the mixture. Contrarily to magnesium, the aluminum atom is smaller than the titanium atom (r_{at} Ti = 1.47Å, r_{at} Al = 1.43Å, r_{at} Mg = 1.60Å), the atomic radii difference being higher for the Ti–Mg pair than for the Ti–Al one. However, the alloy contains more Al than Mg (10 and 5 wt.%, respectively), which counterbalance the former effect.

Thermal behavior

The DSC and TG curves of the 50 h milled mixture are shown in Fig. 5a. The XRD patterns obtained at room temperature before and after heating cycle are presented in Fig. 5b.

The DSC curve shows a relatively large exothermic peak in the range 500–600 °C followed by an endothermic peak close to 650 °C. To the first peak corresponds a weight gain (TG curve) whilst a weight lost occurs in the temperature range of the endothermic peak. In order to identify the exothermic peak, an additional DSC cycle was performed up to 600 °C in a 50 h MA'ed sample. However, no structural transformations were detected by XRD after this cycle meaning that this DSC peak cannot be ascribed to a phase transformation. It is likely that this peak might correspond to an incorporation of oxygen with partial oxidation of the Ti-based solid solution. Nevertheless, this hypothesis could not be confirmed by XRD analysis. The endothermic DSC corresponds to the melting of Mg.

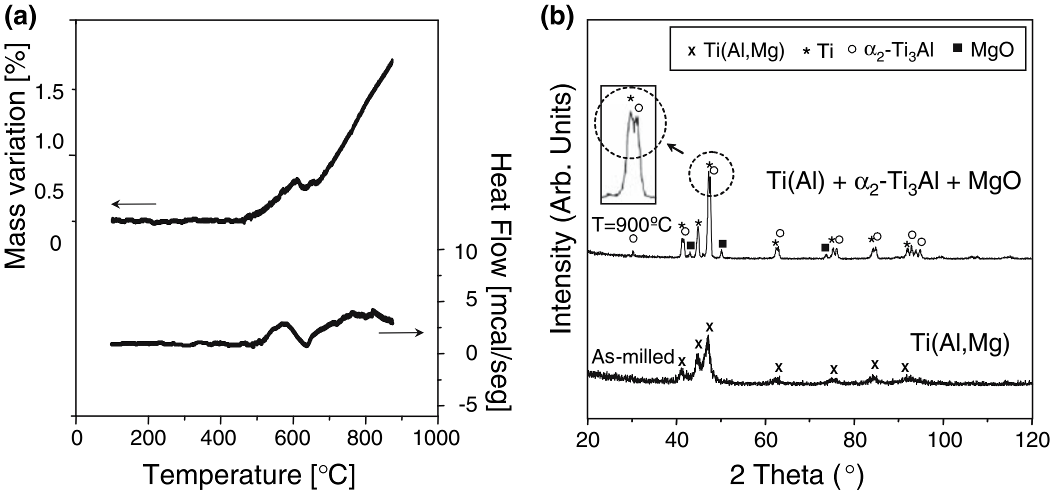


Fig. 5 (**a**) DSC and TG curves up to 900 °C and (**b**) XRD patterns of the as-milled and 900 °C heated mixtures

This means that during annealing, and as expected, Mg went out of the hcp-Ti(Al,Mg) metastable solid solution since at the equilibrium state its solubility in the α-Ti phase is almost zero.

For T = 900 °C, peaks of the α_2-Ti_3Al aluminide can be observed in the corresponding XRD pattern. The structure of the Ti–10Al–5Mg (wt.%) heated sample consists mainly of hcp-Ti phase with MgO and α_2-Ti_3Al as secondary phases. This indicates that Mg reacted with oxygen to form a Mg oxide. Concerning Al, it reacted with titanium to form the α_2-Ti_3Al intermetallic. This phase transformation occurred at high temperatures (after Mg melting) and it was not perceptible in the DSC curve. It is likely that the hcp-Ti phase might contain some Al atoms even after heating up to 900 °C. In fact, as mentioned before, up to 6 wt.% of Al can be dissolved in titanium at room temperature, the domain of solubility increasing with increasing temperature. Energy-dispersive X-ray spectroscopy analysis performed in the annealed powders confirms this hypothesis showing some regions with 13.7 wt.% (22 at.%) Al and others poor in this element with 5.9 wt.% (10 at.%) Al and 0.2 wt.% (0.4 at.%) Mg (Fig. 6). The former ones correspond to the α-Ti_3Al intermetallic and the last ones to the α-Ti(Al) solid solution. Few MgO particles could also be detected by SEM.

As already mentioned, the density of the 900 °C heat-treated sample was calculated by pycnometry. A 4.09 g/cm^3 density average value was obtained, which is 10% lower than the density of titanium (4.54 g/cm^3).

Compaction

The mechanical alloyed mixtures were isostatically pressed at room temperature (CIP) and subsequently sintered at different temperatures (900 and 1,100 °C). Figure 7 shows some SEM images of the compacts sintered at these temperatures. As can be seen, 900 °C sintering was insufficient to obtain a dense sample, in which a great amount of pores is observed (Fig. 7a). On the contrary, the sample sintered at 1,100 °C (Fig. 7b and c) shows a relatively low porosity. The detected pores have micrometer size (<30 μm). A value of 4.8% of open pores was determined by mercury porosimetry for this sample. This corresponds to a sample density of 4.1 g/cm^3 (average value obtained by pycnometry), which is 10% lower than the density of titanium (4.54 g/cm^3). Small precipitates (<2 μm) with different

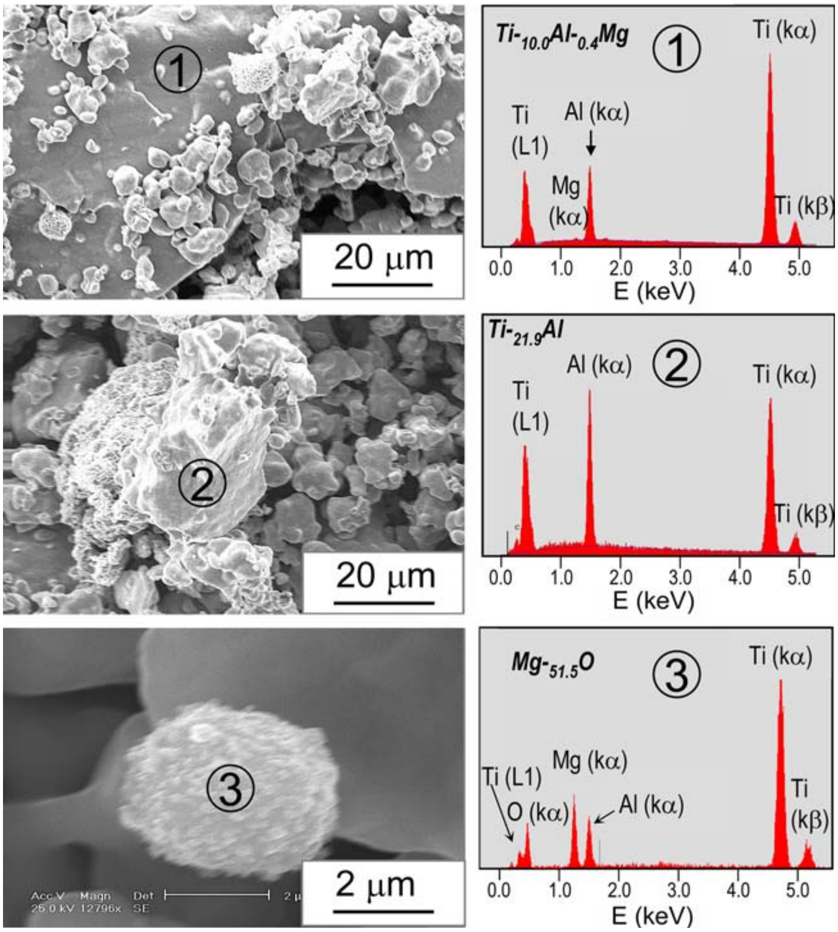
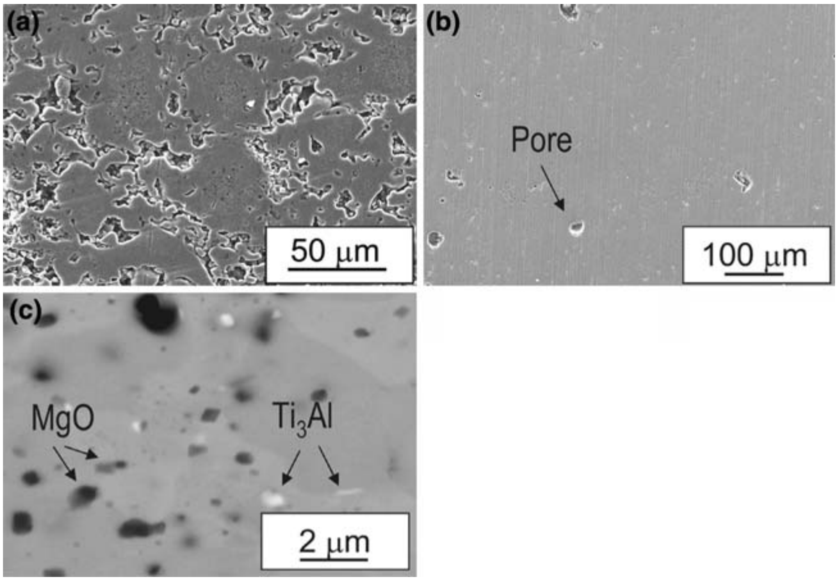


Fig. 6 SEM images and EDS spectra of the different particles heated up to 900 °C

Fig. 7 SEM images of the compacts sintered at (**a**) 900 °C and (**b**) and (**c**) 1,100 °C



grey tones could be observed all over the sintered samples (Fig. 7c). The bright precipitates correspond to a Ti-rich phase (probably α_2-Ti_3Al) and the dark ones to a magnesium- and oxygen-rich phase (probably MgO). In fact, the X-ray diffraction pattern of the 1,100 °C sintered sample (Fig. 8) consists mainly of a submicrometer α-Ti(Al) phase as matrix and α_2-Ti_3Al and MgO precipitates as minor phases.

The hardness and Young's modulus of the 1,100 °C sintered sample were obtained from the indentation curves. The measured values (H = 11 ± 1 GPa, E = 188 ± 23 GPa) are much higher than the ones obtained in a previous work for a mechanically alloyed and annealed Ti–5Al–10Mg mixture (H = 5 GPa, E = 70 GPa [6]). This can be explained by the final structure of the two alloys, the one corresponding to the present work being formed by α-Ti(Al) + α_2-Ti_3Al + MgO and the other (Ti–5Al–10Mg) being formed only by α-Ti(Al) + MgO. The hardness of the α_2-Ti_3Al phase reported in the literature for conventional microstructures obtained by foundry is in the range 1.8–3.5 GPa [18], which is much lower than the value obtained for the alloy synthesized in the present work. The α_2-Ti_3Al phase was formed from the α-Ti(Al) solid solution during heating and therefore its crystallite size is lower than the one of the α_2-Ti_3Al phase obtained conventional synthesis techniques (e.g., foundry). In fact, both α_2-Ti_3Al and MgO precipitates of this sample under investigation have sub-micrometer size. This gives rise to a strengthening effect and impedes grain growth of the α-Ti(Al) phase, leading to a significant increase of hardness and other mechanical properties such as the elastic modulus.

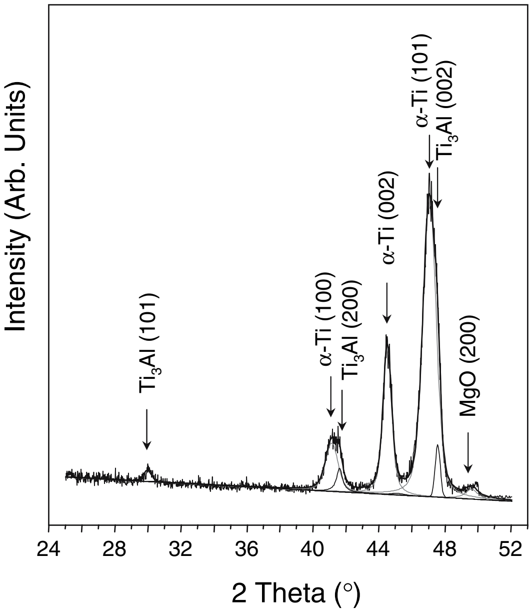


Fig. 8 XRD pattern of the 1,100 °C sintered sample

Conclusions

A lightweight Ti–10Al–5Mg (wt.%) alloy was produced by mechanical alloying and subsequent annealing. During milling the elements Al and Mg substitute for titanium in the α-Ti lattice. A metastable α-Ti(Al, Mg) solid solution was obtained after 50 h of milling. During heating up to 900 °C, Ti reacted with Al to form an intermetallic phase (α_2-Ti_3Al), whilst Mg reacted with oxygen, giving rise to MgO. Therefore, the structure of the 900 and 1,100 °C sintered samples consist of an α-Ti(Al) solid solution as main phase and α_2-Ti_3Al + MgO precipitates as secondary phases. Values of 11 and 188 GPa were obtained for the Hardness and Young's modulus of 1,100 °C sintered sample, respectively, which confirms the strength improvement of the Ti-based alloy by the α_2-Ti_3Al + MgO reinforcements.

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