Key Engineering Materials Vols. 230-232 (2002) pp. 283-286
online at http://www.scientific.net

Mg-rich Light Alloys Synthesised by Mechanical Alloying

L.Dias[1], C. Coelho[2], B. Trindade[1] and F.H. Froes[3]

[1]ICEMS, Dep. de Engenharia Mecânica, Universidade de Coimbra, 3030 Coimbra, Portugal. Tel: +351 239 790700, Fax: +351 239 790701, e-mail:bruno.trindade@mail.dem.uc.pt
Dept. Eng. Mecânica – Escola Sup. Tecnol. de Abrantes – Instituto Politécnico de Tomar
[3]Institute for Materials and Advanced Processes (IMAP), Department of Metallurgy, Mining and Geological Engineering (M3GE), University of Idaho, Moscow, USA.

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

Abstract

In this work, Mg_xTi_{1-x} (x = 18, 50 and 95 at.%) and $Mg_{88}Ti_4Si_7$ alloys were synthesised by mechanical alloying. Phase transformations occurring in the samples as a function of milling time and during subsequent heating were studied by means of x-ray diffraction, scanning electron microscopy, differential scanning calorimetry and electron probe microanalysis. Concerning the Ti-Mg binary system, super-saturated Ti(Mg) solid solutions with low degree of structural order were obtained after milling. The $Mg_{88}Ti_4Si_7$ mechanical alloyed sample was formed by a Mg_2Si intermetallic phase in a Mg matrix. During heating up to 600ºC, there was the formation of further Mg_2Si at 380ºC, followed by the formation of Ti_5Si_3 at 540ºC. No decomposition of either Mg_2Si or Ti_5Si_3 phases was detected during cooling. The final structure of mechanically alloyed and heat treated $Mg_{88}Ti_4Si_7$ sample consist of a fine precipitation of these two intermetallics in a Mg matrix.

Introduction

The use of magnesium alloys, especially in aerospace applications, has been limited because of their poor corrosion resistance. The incorporation of titanium in these alloys gives rise to a self-healing corrosion layer and reduced galvanic potential [1]. However, according to the Ti-Mg phase diagram, these elements are insoluble and the boiling point of magnesium is lower than the melting point of titanium. Consequently, only far-from-equilibrium processes such as Mechanical Alloying (MA) [2-4] and Physical Vapour Deposition (PVD) [5,6] techniques can be successfully utilised to produce these alloys. Moreover, it is possible to increase the strength of the Ti-Mg binary alloys by alloying with light elements such as silicon in order to allow the formation of intermetallic phases of both Mg-Si and Ti-Si systems, without significantly increasing the density of the alloys. In this work, light-weight Mg-Ti and Mg-Ti-Si alloys rich in Mg were produced by MA and structurally characterised in the as-milled state and after subsequent annealing. The structural influence of Si on the ternary system was studied as a function of the milling time and the annealing temperature.

Experimental Details

Samples with nominal compositions of $Mg_{18}Ti_{82}$, $Mg_{50}Ti_{50}$, $Mg_{95}Ti_5$ and $Mg_{88}Ti_4Si_7$ were synthesised by mechanical alloying from Mg, Si and Ti powders with a nominal purity of 99.6%, 99.5% and 99% and an average particle size of 60, 10 and 75 μm, respectively. Milling was performed in a planetary ball mill using hardened steel vial (250 ml) and balls (15 balls with 20 mm diameter each). A ball-to-powder weight ratio of 20:1 was used. The rotation speed was 500 rpm. In order to avoid contamination milling was performed in an argon atmosphere. The as-mechanically alloyed powders were characterised by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The x-ray diffractograms were obtained using Co K_α radiation. Differential scanning calorimetry (DSC) was used to evaluate the thermal stability of the ternary Mg-Ti-Si sample. The heating rate was 40ºC min^{-1}. Chemical homogeneity of the particles formed during the

milling process was followed as a function of milling time by electron probe microanalysis (EPMA).

Results and Discussion

Binary system Ti-Mg

Fig. 1 shows the x-ray diffractograms of the Ti-Mg powders before and after ball milling.

$Mg_{18}Ti_{82}$

The x-ray diffractograms of this mixture recorded after different milling periods indicates incorporation of magnesium in the α-Ti phase. After 5h of milling the Mg peaks are no longer visible. At the same time, the Ti peaks are shifted to higher diffraction angles confirming the formation of a Ti(Mg) solid solution. Further increase in ball milling duration resulted in a significant broadening of the Ti x-ray reflections and a decrease in their intensities. The c/a ratio and the grain size (calculated from the Scherrer formula) of the Ti(Mg) solid solution milled for 10h are equal to 1.59 (a = 2.962 Å and c = 4.704 Å) and 24 nm, respectively.

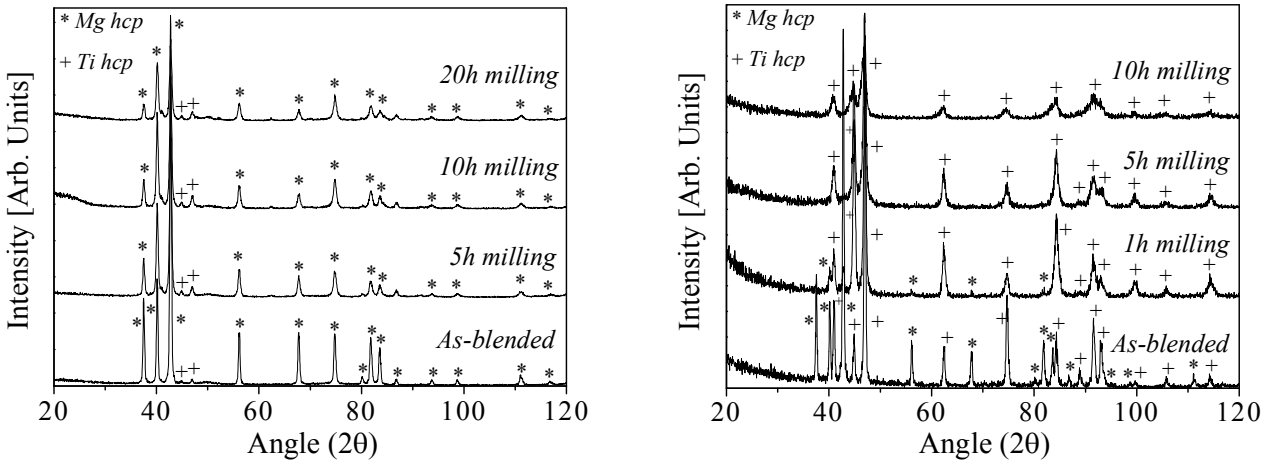

Fig. 1 - X-ray diffractograms of the Ti-Mg powders as a function of milling time. (a) $Mg_{18}Ti_{82}$, (b) $Mg_{50}Ti_{50}$ and (c) $Mg_{95}Ti_5$.

$Mg_{50}Ti_{50}$

A broadening of the Ti and Mg x-ray reflections and a decrease in their intensities occur with milling time. The Mg peaks are no longer resolvable after 35 h of milling. In addition, a shift in the Ti peaks towards higher d values can be observed for this milling time, indicating that a Ti solid solution was formed with a c/a ratio = 1.64(a = 2.960 Å and c = 4.846Å) and a grain size of 6 nm. The values of lattice parameters a and c obtained in the present work are lower than what should be expected from Vegard´s law. Similar results were obtained by Ward-Close *et al.* [6] who investigated vapour deposited Ti-Mg alloys.

$Mg_{95}Ti_5$

The x-ray analysis shows the coexistence of Mg and Ti phases even for 20h of milling. Moreover the positions of the Mg and Ti peaks remain constant during the milling process. This means that no solubility of magnesium in titanium was achieved in this work.

Ternary system $Mg_{88}Ti_4Si_7$

Figure 2 illustrate the structural evolution of the $Mg_{88}Ti_4Si_7$ mixture with milling time.

The diffraction peaks of magnesium (major phase) gradually broaden with milling up to 25h. There are traces of the Mg_2Si from the beginning of the milling process. For 25h of milling, it is very difficult to confirm the non existence of titanium or silicon as elemental phases due to their low percentages in the sample, together with both broadening and intensity decrease of their peaks as a function of milling time. However, the positions of the magnesium peaks are not shifted to different angles when compared to the corresponding ones of the as-blended mixture. This might mean that titanium and the remaining silicon are not in solution in the Mg phase, otherwise a contraction of the lattice should be expected. The average grain sizes of magnesium and Mg_2Si phases after milling, calculated by the Scherrer formula, are of approximately 20 nm.

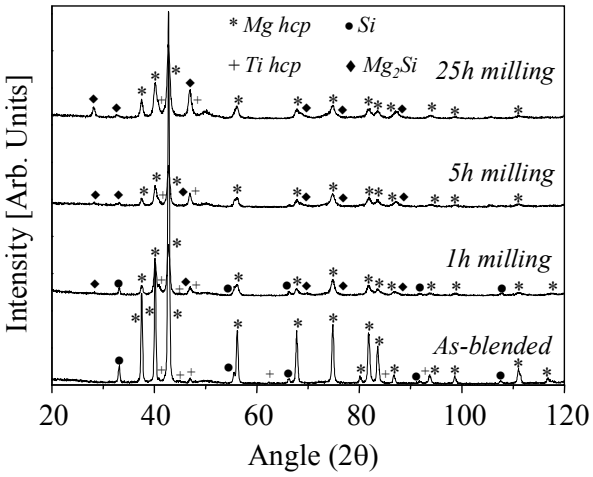

Figure 2 - Structural evolution of the $Mg_{88}Ti_4Si_7$ mixture with milling time.

The mixture was compacted into a disk with 10mm diameter and 1mm thickness (F = 20 tones) and its hardness measured with a load of 100g. An average hardness of 170 HV was obtained, which is consistent with a dispersion of intermetallic phases in a soft magnesium matrix. EPMA measurements in different particles of the consolidated sample revealed that the sample is chemically homogenous and no changes in the chemical composition occurred during either the milling process or the heat treatment.

Two DSC runs were performed on the powders mechanically alloyed for 25h (Fig. 3(a)). Firstly a maximal temperature of 600ºC was chosen. On the basis of the curve obtained, and in order to determine the phase transformations that occurred during heating, a second run to 480ºC was performed. In both cases, the samples were cooled to ambient temperature and subsequently characterised by XRD (Fig.3(b)). The DSC curve recorded up to 600ºC shows two exothermic peaks, one at about 450ºC and the other close to 550ºC. The x-ray analysis performed after the DSC runs shows very little changes between the x-ray diffractograms of the sample before and after annealing at 480ºC. The only thing to notice is the increase in peak intensities of the Mg_2Si phase and a decrease of its full width at half maximum (grain size increasing). This means that the milling process was not completed after 25h and that further Mg_2Si was formed during heat treatment. Silicon was no longer detected after 5h of milling, meaning that part of it should be in solid solution either in magnesium or in titanium, or even in both elements. The comparison of the diffractograms obtained after 480ºC and 600ºC reveals the appearance of some fairy peaks, corresponding to the titanium silicide Ti_5Si_3 phase. The formation of this phase must correspond to the second DSC exothermal peak. Since the intensity of the Mg_2Si diffraction peaks is not altered by the emergence of the Ti_5Si_3 phase, it can be suggested that this phase is formed by the remaining Si and not by a Mg_2Si -> Ti_5Si_3 phase transformation. This result is in accordance with the work of Senkov et al [7] on the synthesis of a low-density Ti-Mg-Si (Ti-rich) sample by mechanical alloying. These authors refer the formation of the Mg_2Si phase after heating to 450ºC and appearance of the Ti_5Si_3 phase after heating to 570ºC. In fact, analysis of the DSC curve obtained in the present work, indicates

that the $_2$Mg + Si -> Mg_2Si reaction was not complete when the intermetallic Ti_5Si_3 started to form. Thus, the final structure of mechanically alloyed and heat treated $Mg_{88}Ti_4Si_7$ mixture up to 600ºC consist of a fine precipitation of these two intermetallics in a magnesium matrix. No phase transformations were detected during cooling from the maximal temperature achieved in either DCS run.

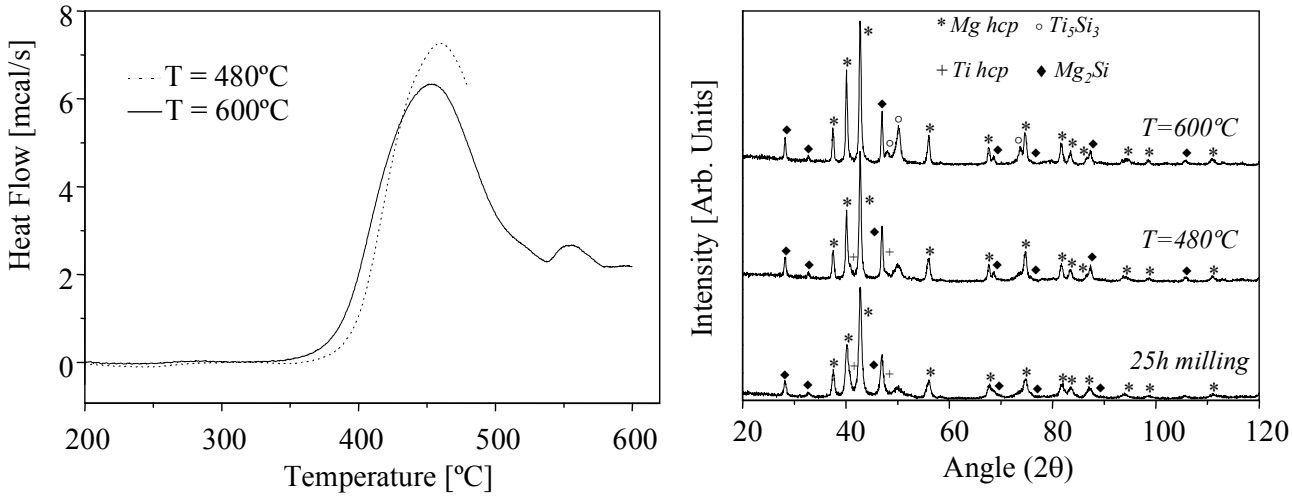

Fig. 3 – (a) DSC curves and (b) x-ray diffractograms of the $Mg_{88}Ti_4Si_7$ mixture obtained at room temperature after each DSC run.

Conclusions

Super-saturated Ti(Mg) solid solutions with low degrees of structural order were obtained by mechanical alloying. The structure of the ternary $Mg_{88}Ti_4Si_7$ ball milled mixture was formed by a Mg_2Si intermetallic phase in a Mg matrix. During heating up to 600ºC, there was the formation of further Mg_2Si at 380ºC, followed by the formation of Ti_5Si_3 at 540ºC. No decomposition of either the Mg_2Si or Ti_5Si_3 intermetallic phases was detected during cooling. The final structure of mechanically alloyed and heat treated $Mg_{88}Ti_4Si_7$ sample consist of a fine precipitation of these two intermetallics in a magnesium matrix.

References

[1] S.B. Dodd, S. Morris and M. Wardclose, Synthesis of Lightweight Metals III, 1999, pp. 117-184, F.H Froes, Ed. Warrendale: Minerals Metals & Materials Soc.
[2] M. Hida, K. Asai, Y. Takemoto and A. Sakakibara, Materials Science Forum, 1997, Vol. 235, pp. 53-58, Ed. Zurich-Uetikon, Transtec Publications Lda.
[3] E. Zhou, C. Suryanarayana and F.H Froes, Materials Letters, 23 (1995) 27-31.
[4] D.M.J. Wilkes, P.S. Goodwin, C.M. Ward-Close, K. Bagnall and J. Steeds, Materials Letters, 27 (1996) 47-52.
[5] K.E. Bagnall, P.G. Partridge, J.W. Steeds, S.B. Dodd and R.W. Gardiner, Proceedings of the First International Magnesium Conference, 1997, pp. 299-312, Lorimer G.W., Ed. London: Inst. Materials.
[6] C.M. Wardclose G. Lu and P.G. Partridge, Materials Science and Engineering A, 1994, Iss 1-2, pp 247-255.
[7] O.N. Senkov, M. Cavusoglu and F.H. Froes, Synthesis of Lightweight Metals III, 1999, pp. 59-66, Froes F.H., Ed. Warrendale: Minerals Metals & Materials Soc.