MECHANICAL ALLOYING OF Mg-Ti-Si LIGHT ALLOYS AND SUBSEQUENT CONSOLIDATION

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Abstract

This paper presents the results on mechanical alloying and subsequent hot isostatic pressing (HIP'ing) of two ternary $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ milled powders. The produced materials have grain sizes in the nanoscale. The 500ºC consolidated sample with 7at% Si is constituted by Mg + Mg_2Si (35nm) + Ti_5Si_3 (50nm). The structure of the sample richer in silicon HIP'ed at 800ºC was indexed as Mg_2Si (125nm) + Ti_5Si_3 (10nm) + Ti_5Si_4 (7nm). Hardness values of 128 and 526 $HV_{0.05}$ were obtained for these two compacted samples, respectively.

Introduction

Magnesium alloys are expected to be used in the synthesis of light-weight components and to improve their functionality per a unit weight. However, the use of these alloys has been limited, especially in aerospace applications, because of their poor corrosion resistance. Titanium is one if the candidates to be used as an alloying element to magnesium since it is known that it gives rise to a self-healing corrosion layer and low galvanic potential [1]. However, these elements are almost insoluble and 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. These techniques can extend solid solution of both the Mg and Ti hcp phases giving rise to metastable nano-sized or amorphous structures, impossible to be obtained by conventional metallurgical processes. In addition, the incorporation of a third element with a great affinity to Ti and Mg might increase strength by the formation of fine dispersion precipitates of intermetallic phases. This goal can be achieved by silicon, since this element forms with Mg and Ti intermetallic compounds with different mechanical and physical properties.
This paper deals mainly with the compaction of two ternary ball-milled Mg-rich light alloys ($Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$) by HIP'ing. Structural results on the binary Mg-Ti, Mg-Si and Ti-Si systems as a function of milling time are also presented.

Experimental details

Three samples from the binary Ti-Mg, Mg-Si and Ti-Si systems (1:1) and two samples from the Mg-Ti-Si system ($Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$) 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 samples. 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). HIP'ing of the samples was performed by two steps: 450ºC /250Psi /60min + 550ºC /250Psi /120 min and 590ºC /250Psi /60min + 800ºC /250Psi/240min for the samples containing 7 and 30 at.% Si, respectively. The maximal HIP'ing temperatures were selected on the basis of the DSC curves.

Results and Discussion

Binary Systems

Figure 1 shows typical XRD patterns from the as-milled binary samples after different milling times. In the case of the $Mg_{50}Ti_{50}$ sample (fig.1a), there is a significant broadening and decrease of the X-ray diffraction intensities of the Ti phase as a function of milling time, together with a reduction in number of the XRD peaks of the Mg phase. These are no longer resolvable after 35 h of milling, suggesting an incorporation of Mg into the Ti phase (Ti solid solution). Figure 2 illustrates the variation of the "a" and "c" parameters of both Ti- and Mg-phases during milling. The Ti-phase suffers an important increase of both parameters for milling times higher than 20 h. Contrarily, the Mg-phase shows an inverse behaviour, with a decrease of these parameters between 10 and 20 h of milling.

After 35 h, the sample $Mg_{50}Ti_{50}$ is formed by a Ti solid solution with a *c/a* ratio = 1.64 (*a* = 2.960 Å and *c* = 4.846Å). The average crystallites size of this phase, calculated by the Williamson-Hall method [7], is 6 nm. These values 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.

The X-ray analysis of the $Mg_{50}Si_{50}$ reveals the emerging of the Mg_2Si intermetallic phase for 5 h of milling. No significant changes of the XRD patterns were observed for higher milling times. After 20 h of mechanical alloying, the structure of this sample is formed by a fine-grained fcc Mg_2Si phase (13 nm) with a = 6.36(1), dispersed in a Si matrix.

Finally, the $Ti_{62.5}Si_{37.5}$ sample evolves for the formation of Ti_5Si_3 intermetallic during milling. Once this phase is formed, the intensity of the corresponding Bragg peaks decreases and their FWHM's increases as the milling time increases, meaning a grain size refinement of the Ti_5Si_3 phase (1.16 nm after 50 h of MA).

Ternary Systems

Figure 3 shows the XRD patterns obtained from samples $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ after different milling times. In both samples, the line reflections of magnesium (major phase) gradually broaden with milling time, meaning a decrease of the structural order of this phase during the milling process. In the case of sample with 7at.% Si, there is the formation of the intermetallic Mg_2Si from the beginning of the process (traces of this phase can be already detected in the X-ray diffractogram obtained after 1h of milling). The

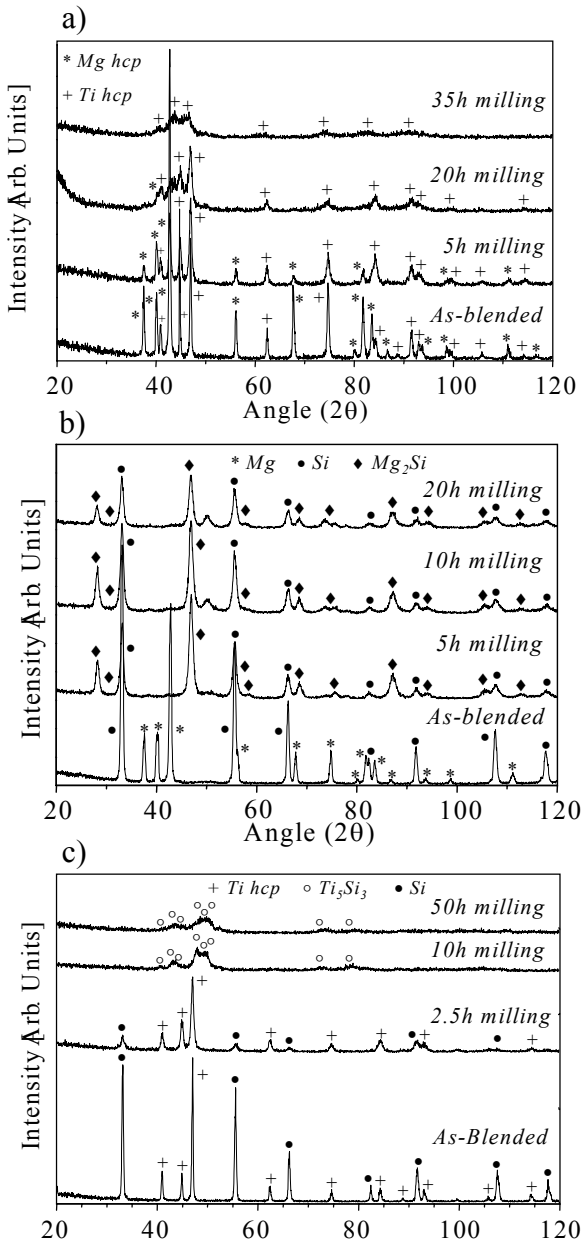

Figure 1 - Structural evolution of the (a) $Mg_{50}Ti_{50}$, (b) $Mg_{50}Si_{50}$ (c) $Ti_{62.5}Si_{37.5}$ mixtures with milling time.

existence of this intermetallic is clearly detected in both samples - $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ - milled for 25 and 10h, respectively. The final structure of the sample with the lower silicon content is formed a dispersion of Mg_2Si in a Mg matrix. The positions of the magnesium reflections are not shifted to different angles when compared to the corresponding ones of the as-blended mixture. This might mean that titanium and the eventual remaining silicon are not in solution in the Mg phase; otherwise a contraction (or dilation depending on the occupancy of the Si atoms in the *hcp* lattice) should be expected. The average grain sizes of magnesium and Mg_2Si phases after milling are of approximately 20 nm.

Concerning the $Mg_{60}Ti_{10}Si_{30}$ sample, there is the formation of Ti_5Si_3 from 10 to 20h of milling, consuming the whole remaining silicon. The intensity of the Mg_2Si phase line reflections increases as a function of milling time meaning that the Ti_5Si_3 phase is formed by a 5Ti + 3Si -> Ti_5Si_3 reaction instead of 3(Mg_2Si) + 5Ti -> Ti_5Si_3 + 6Mg. In fact, no vestiges of the *hcp* Mg phase are detected after 10h of milling.

Both mixtures were compacted into a disk with 10mm diameter and 1mm thickness ($\sigma = 2x10^3$ MPa) and its hardness measured with a load of 100g. Average hardness values of 170 and 440 HV were obtained for the $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ samples, respectively.

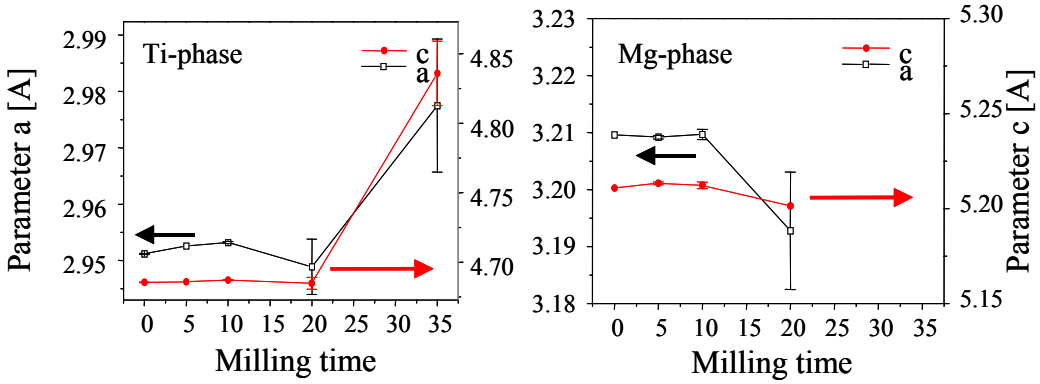

Figure 2 - Evolution of parameters a and c of the Ti and Mg phase of the $Mg_{50}Ti_{50}$ sample for different milling times.

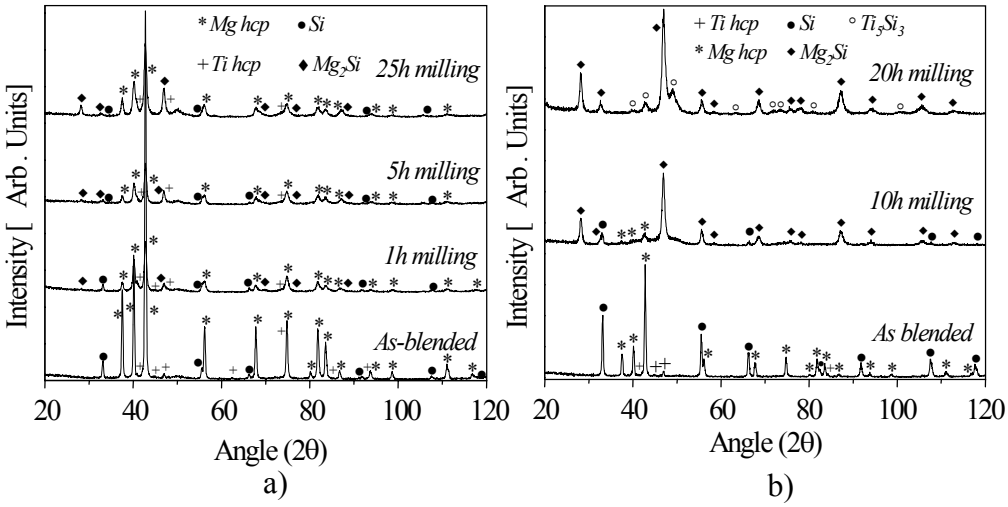

Figure 3- Structural evolution of the (a) $Mg_{88}Ti_4Si_7$ and (b) $Mg_{60}Ti_{10}Si_{30}$ mixtures with milling time.

EPMA measurements in different particles of the consolidated samples (fig. 4) revealed that they are chemically homogenous and no significant changes of the overall chemical composition occurred during the milling process.

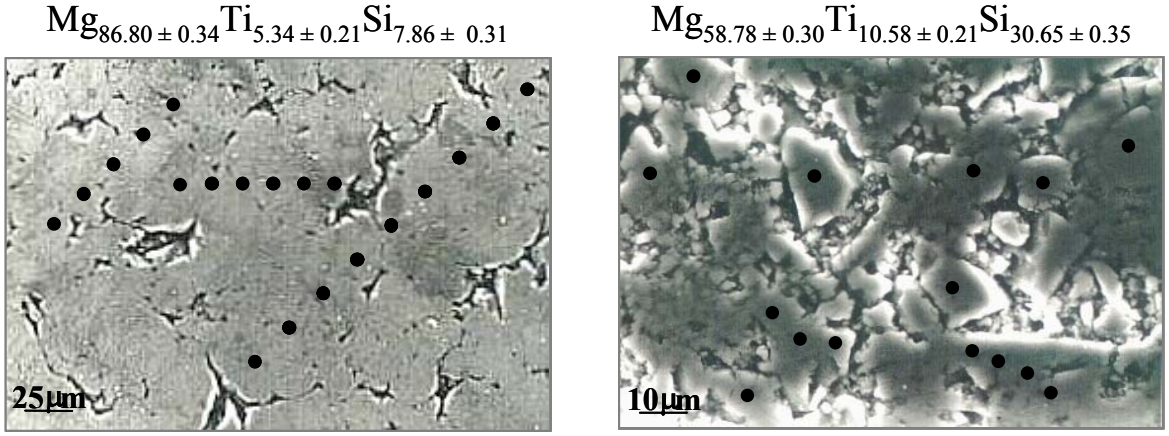

Figure 4 - SEM images of the (a) $Mg_{88}Ti_4Si_7$ and (b) $Mg_{60}Ti_{10}Si_{30}$ samples after room temperature. Dots represent points where the chemical composition was measured.

Figure 5 shows DSC curves of the two samples as well as the room temperature structural characterisation performed by XRD after each run. In the first case (sample with 7at.%Si) 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 the second case (sample with 30 at.%Si) two DSC runs were performed up to 700ºC on the mixtures milled for 10 and 20h. The objective was to determine the influence of initial structure on the temperature and type of phase

transformations occurring during heating. The DSC curve of the former sample recorded up to 600ºC show 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 XRD patterns 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 height (grain size increasing). 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 emerge 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* [8] 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 for the $Mg_{88}Ti_4Si_7$ sample indicates that the $_2Mg + Si$ -> 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.

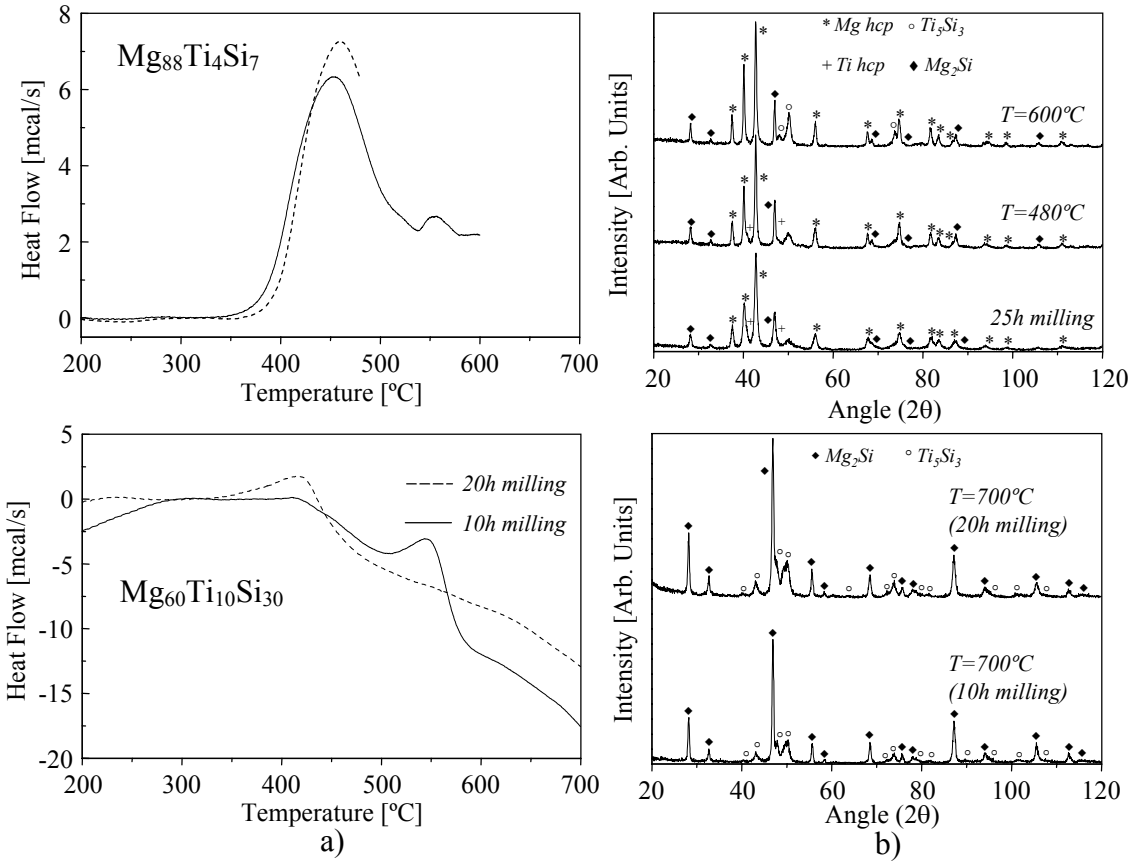

Figure 5 - (a) DSC curves and (b) x-ray diffractograms of the $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ mixtures obtained at room temperature after DSC

Concerning the $Mg_{60}Ti_{10}Si_{30}$ mixture, the DSC curve recorded from the sample milled for 10h shows one exothermal peak at 550ºC corresponding to the formation of Ti_5Si_3. It should be pointed out that the same isothermal peak was detected during heating of the $Mg_{88}Ti_4Si_7$ ball milled mixture. The 700ºC heat-treated $Mg_{60}Ti_{10}Si_{30}$ sample milled for 10h is formed by a two-phase structure of Mg_2Si + Ti_5Si_3. The same structure was obtained for the sample milled for 20h, after similar heat treatment. This means that the structure after annealing was independent on the milling time, for the periods of mechanical alloying used in this work (10 and 20h). The DSC curve recorded from the $Mg_{60}Ti_{10}Si_{30}$ sample milled for 20h does not show any "strong" peak that could be ascribed to a phase decomposition of the initial structure (Mg_2Si + Ti_5Si_3). This is in accordance to the XRD results obtained before and after sample annealing. In fact, the only difference observed concerns the definition of the intermetallic phases reflection lines, mainly intensity and FWHM. Heat treatment of this sample only induced a grain growth of the phases formed during milling and no phase transformations occurred at elevated temperatures. Based on these results, the mechanical alloyed $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ powders were HIP'ed at 550 and 800ºC, respectively. Figure 6 shows the XRD patterns obtained after compaction. Analysis of these patterns reveals phase transformations during HIP'ing. In fact, the compacted sample with 7at% Si is composed by two intermetallics, Mg_2Si (35nm) +Ti_5Si_3 (50nm), dispersed in a Mg phase, while the sample richer in silicon is mainly formed by a mixture of Mg_2Si (125nm) + Ti_5Si_3 (10nm).

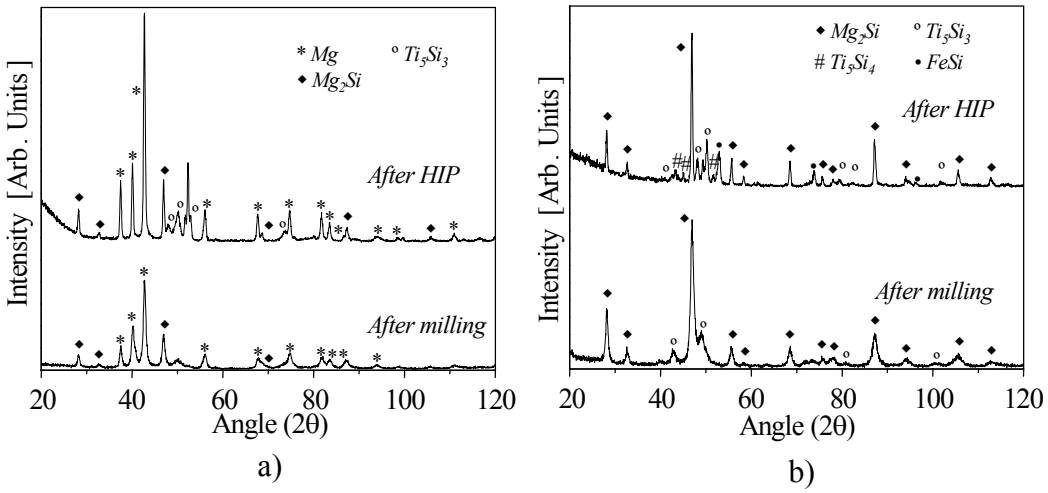

Figure 6 - XRD patterns obtained from samples (a) $Mg_{88}Ti_4Si_7$ and (b) $Mg_{60}Ti_{10}Si_{30}$ after HIP'ing.

Vestiges of Ti_5Si_4 (7nm) were also observed in the XRD patterns of this last sample. In the first case, the structural results obtained after HIP'ing agree to what we expected from the DSC runs. However, in the case of the sample with 30at.% Si the emerging of the Ti_5Si_4 phase during HIP'ing is quite surprising and it was not observed after thermal cycles (DSC) up to 700ºC. This means that this phase is formed at high temperature either from the Ti_5Si_3 phase or the decomposition of the Mg_2Si. Taking into account that (i) values of parameters "a" and "c" of the Ti_5Si_3 phase, obtained after mechanical alloying and DSC runs, are different from the equilibrium ones of the ICDD card [9] (in particular parameter "c" which is lower that the one of equilibrium) and (ii) the values obtained for this phase after HIP'ing are equal to those in the ICCD card, it is likely that the formation of Ti_5Si_4 occurs from Ti_5Si_3. This means that the composition of this phase obtained during milling

and/or subsequent thermal cycle might not be stoichiometric, the Ti_5Si_3 being rich is Si (poor in Ti). Pressure and temperature of the consolidation process might be responsible for the evolution of this phase towards equilibrium.
Contamination by iron was observed in some regions of both HIP'ed samples, in particular in the centre of the compacts (fig. 7). This segregation might result from the material used to encapsulate the samples (iron) and/or from the milling process itself. However, it should be pointed out that no important signal of iron was detected by EPMA after the different periods of milling time, meaning that contamination may arise preferential from the consolidation process. Hardness values of 128 and 526 $HV_{0.05}$ were obtained for the two HIP'ed samples, respectively, corresponding to the formation of intermetallic phases with a nanometric size.

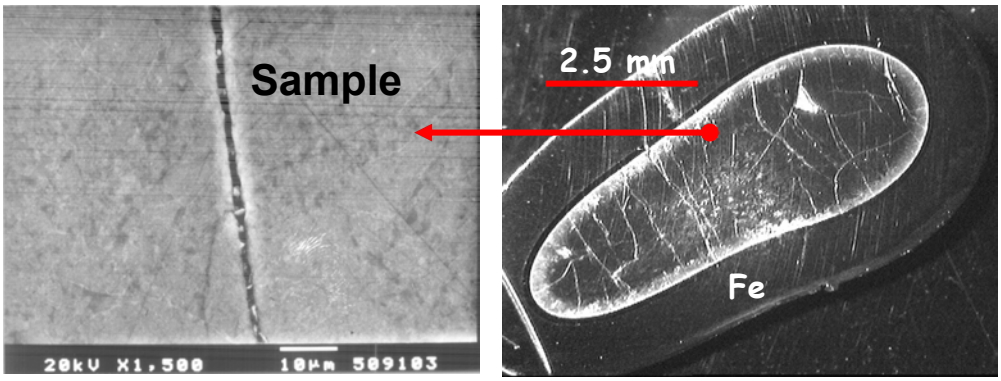

Figure 7 - SEM and optical images of the HIP'ed sample $Mg_{60}Ti_{10}Si_{30}$, where contamination by iron can be seen in the centre of the compacts.

Conclusions
This work shows that mechanical alloying and subsequent HIP'ing allow the formation intermetallic dispersed nanophases from elemental metallic pure powders. The results can be summarised as follows:
Super-saturated Ti(Mg) solid solutions with low degrees of structural order were obtained by mechanical alloying of Ti and Mg. Mechanical alloying of Ti and Si gives rise to the intermetallic Ti_5Si_3 with a low degree of structural order (tendency for amorphisation). Mg_2Si is formed during mechanical alloying of Mg + Si elemental powders. This phase is also formed during milling of both ternary $Mg_{88}Ti_4Si_7$ and $Mg_{60}Ti_{10}Si_{30}$ mixtures. Moreover, for the last mixture, another intermetallic rich in titanium (Ti_5Si_3) appears after 20h of milling. The HIP'ed materials have grain sizes in the nanoscale. The 500ºC consolidated sample with 7at% Si is constituted by Mg + Mg_2Si (35nm) + Ti_5Si_3 (50nm). The structure of the sample richer in silicon HIP'ed at 800ºC was indexed as Mg_2Si (125nm) + Ti_5Si_3 (10nm) + Ti_5Si_4 (7nm). Hardness values of 128 and 526 $HV_{0.05}$ were obtained for these two compacted samples, respectively.

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