

PRODUCTION AND CONSOLIDATION OF NANOSTRUCTURED MECHANICALLY ALLOYED Ti-Al-Ag INTERMETALLICS

Filipe Neves¹, M.H. Carvalho¹, B. Trindade²

¹INETI – Instituto Nacional de Engenharia e Tecnologia Industrial
Azinhaga dos Lameiros, 1649-038 Lisboa, Portugal

T: 351 21 7165141; F: 351 21 7166568; E: filipe.neves@ineti.pt

²Departamento de Engenharia Mecânica, Universidade de Coimbra,
3030 Coimbra, Portugal

T: 351 239 790700; E: bruno.trindade@dem.uc.pt

Keywords: Mechanical alloying, Nanostructural materials, Intermetallics, Hot Isostatic Pressing, Titanium aluminides.

ABSTRACT

Blended elemental powders of titanium hydride, aluminium and silver, with nominal compositions $\text{TiH}_2-(48-x)\text{Al}x\text{Ag}$ ($x=2$ and 4 at %), were mechanically alloyed (MA) for 50h in a planetary ball mill. The MA powders were consolidated to full density by Hot Isostatic Pressing (HIP) at $900^\circ\text{C}/2\text{h}/150\text{MPa}$, yielding multiphase microstructures. Subsequent heat treatment at 1200°C for 4h resulted in some but not complete homogenization somewhat different for the two alloys.

INTRODUCTION

Titanium aluminides are potential structural materials for application in aerospace systems and advanced automobiles [1,2]. The ordered nature of intermetallics leads to attractive elevated temperature properties such as high strength, increased stiffness and excellent corrosion/oxidation resistance. These attributes are a result of the reduced dislocation motion and low diffusivities. However, this reduced dislocation motion also results in extremely low ambient temperature properties such as ductility and fracture toughness. Therefore, the poor workability they exhibit is a major problem limiting their practical use [2,3]. The common routes adopted to improve the room temperature ductility of intermetallics are the reduction in grain size, the disordering of the lattice to improve dislocation motion and the modification of the crystal structure of the intermetallic phase into a more symmetric one. Non-equilibrium synthesis processes, such as rapid solidification, plasma processing, vapour deposition and mechanical alloying (MA) can achieve this.

MA is a solid-state powder processing technique involving repeated welding, fracturing and rewelding of powder particles in a high-energy ball mill. Originally developed to produce oxide-dispersion strengthened in a nickel-base superalloy for applications in aerospace industry [4], MA has now been shown capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders [5,6]. The application of MA to the processing of titanium aluminide alloys permits simultaneous improvement of workability and mechanical properties through the control of microstructure [7,8]. However, special attention has to be paid to the control of contamination since the main difficulty in the MA of Ti based alloys has been the absorption of O_2 and N_2 from the continuous exposure of fresh metal surfaces to the atmosphere in the milling container [9].

In previous work we used magnetron sputtering [10] and a reactive powder processing technique [11] to produce modified titanium aluminides with different contents of silver [10,11] and chromium [10]. These elements were introduced with the aim of increasing room temperature ductility. The magnetron sputtering was used as a screening technique to obtain useful data prior to production of similar bulk materials [11] by conventional processing techniques, e.g. foundry.

An alternative technique was used in the present study to synthesise these intermetallics. Nanostructured titanium aluminide alloys were produced by mechanical alloying elemental mixtures of titanium hydride, aluminium and silver powders and by subsequent consolidation through hot isostatic pressing. As hydrogen is easily evacuated during heating in vacuum, the use of titanium hydride over titanium powder is advantageous since its brittle particles can be easily crushed on milling, thus avoiding the use of a MA process control agent (PCA) and minimizing contamination of the powder.

EXPERIMENTAL

Elemental titanium hydride (99% purity), aluminium (99.5% purity) and silver (99.99% purity) with particle sizes $<150\mu\text{m}$, $<74\mu\text{m}$ and $<100\mu\text{m}$, respectively, were mixed to give nominal compositions of TiH_2 - 46Al2Ag (alloy 1) and TiH_2 - 44Al4Ag (alloy 2) (at %). 24.5 g of powder were put in a tempered chrome steel vial together with 15 tempered chrome steel balls of 20 mm diameter at a ball-to-powder weight ratio of 20:1. No PCA was added to the charge. The vial was sealed, installed on a Fritsch planetary mono mill “pulverisette 6” and filled with hydrogenated argon gas. The milling process was carried out at 200 rpm and the maximum milling time was 50 hours. The process was interrupted for 5 min each 15 min to cool the vial. Small quantities of powder were withdrawn from the vial after 5h and 26h for X-ray diffraction analysis and powder morphology characterization.

The Mechanically Alloyed powders were cold isostatic pressed at 180 MPa into cylindrical compacts of approximately 10 mm diameter and 16 mm height and about 66% of theoretical density. The compacts were encapsulated in steel cans lined with tantalum foil. The cans were degassed by heating under a 10^{-3} MPa vacuum at $5^\circ\text{C}/\text{min}$ up to 300°C with a 15 min hold at that temperature and then sealed. The compacts were consolidated by Hot Isostatic Pressing (HIP) at 900°C for 2h under a pressure of 150MPa. Heating and cooling rates of $10^\circ\text{C}/\text{min}$ and $40^\circ\text{C}/\text{min}$, respectively, were used. Samples from the HIPed specimens were heat treated at 1200°C for 4 hours under a 10^{-4} MPa vacuum.

The MA powders and the HIP'd and heat-treated materials were characterized through X-ray diffraction (XRD) (Co-K α radiation) and SEM associated with energy dispersive X-ray analysis. Local chemical compositions were determined by electron probe microanalysis (EPMA). Differential thermal analysis (DTA) was carried out on MA'd material. The heating and cooling rates were $10^\circ\text{C}/\text{min}$ and the samples were argon protected during the runs. Thermal stability of the 50h milled powders was evaluated through analysis of material submitted to interrupted DTA's. Hydrogen contents in the MA powders and HIP'd materials were determined using a LECO analyzer.

RESULTS AND DISCUSSION

Mechanically Alloyed Powders

Figures 1 and 2 show the morphology of the mechanically alloyed powder particles after milling for different periods. In the early stages of milling the powders consist mainly of flaky particles and is evident an increase in the particle size (Figure 1(b) vs. 1(a)). This probably derives from a strong cold welding of the elemental crystalline powders at the

beginning of MA. Further milling produces a significant decrease in the particle size with each particle consisting of many very fine particles welded together, Figures 1(d) and 2(c).

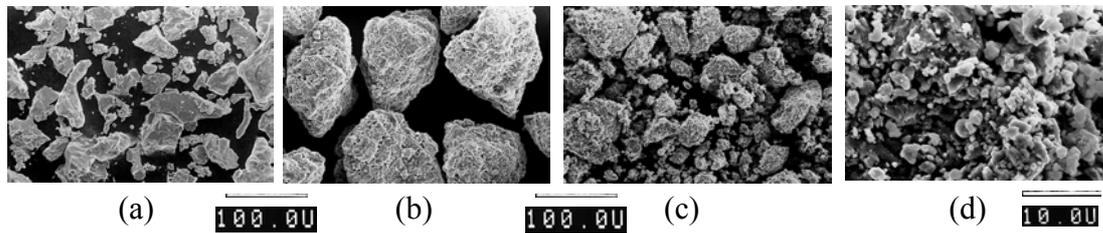


Figure 1 – SEM micrographs of alloy 1 powders milled for: (a) 0h; (b) 5h; (c) 26h; (d, e) 50h.

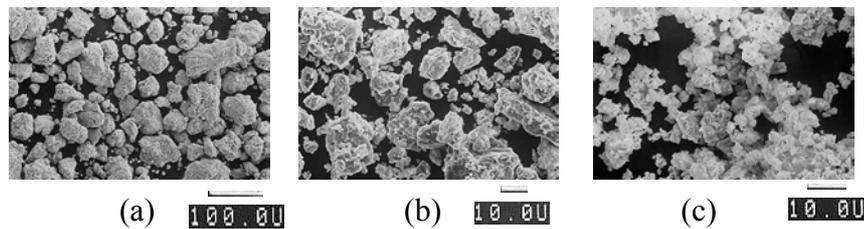


Figure 2 – SEM micrographs of alloy 2 powders milled for: (a) 5h; (b) 26h; (c, d) 50h.

XRD patterns, Figures 3 and 4, show a progressive broadening of the peaks profiles with increased milling time. After 5h of MA, the Al diffraction peaks decrease in relative intensity with respect to the TiH_2 peaks. At this stage, there is already some peak broadening. The slight shift of the original TiH_2 peaks to lower angles can be associated to the solution of Al into this phase. After 50h of milling, the mixtures remain somewhat crystalline although, particularly near $2\theta \approx 45^\circ$ and for 2θ higher than 68° , the diffraction peaks show extensive broadening and very low intensities, in particular for alloy 2 (as indicated by higher FWHM values). The results obtained for the 50h milled samples are consistent with other published work. In fact, some authors [7,8,12] claim that the phases produced by MA of Ti-Al powder mixtures with compositions close to equiatomic proportions consist partially of an amorphous phase or they attained a seemingly complete amorphous state. The coexistence of amorphous and crystalline phases, identified as Ti-rich solid solution or an fcc-like phase suggested to be related to $(\text{Ti},\text{O})\text{N}$ or $(\text{Ti},\text{Al})\text{N}$ compounds, has been reported [7,12,13]. The nature of the obtained phases is, however, strongly dependent on the milling parameters, such as the milling equipment, milling time, intensity of milling among others. In the present work milling times higher than 50h would be required to achieve an almost complete amorphous state.

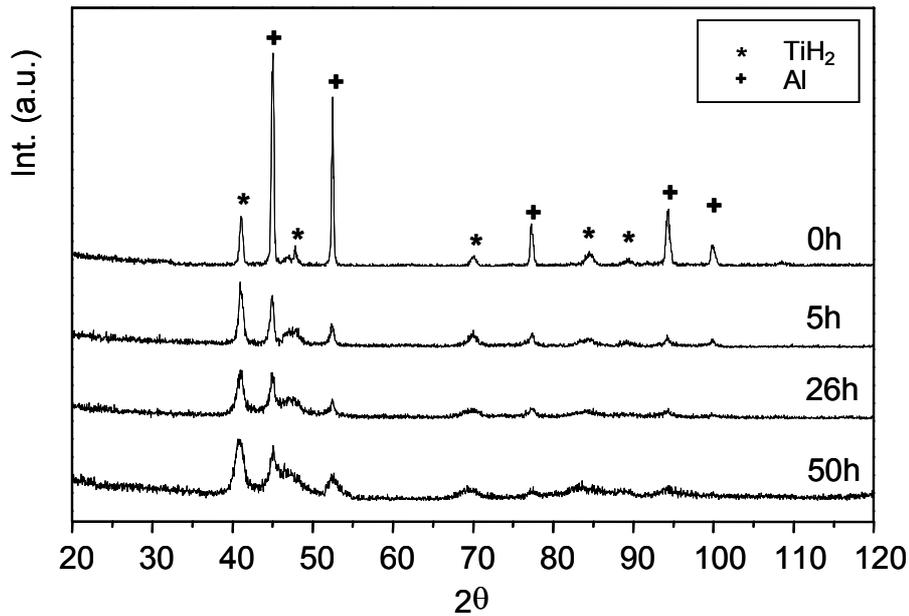


Figure 3 – X-ray diffraction patterns of alloy 1 milled for various times.

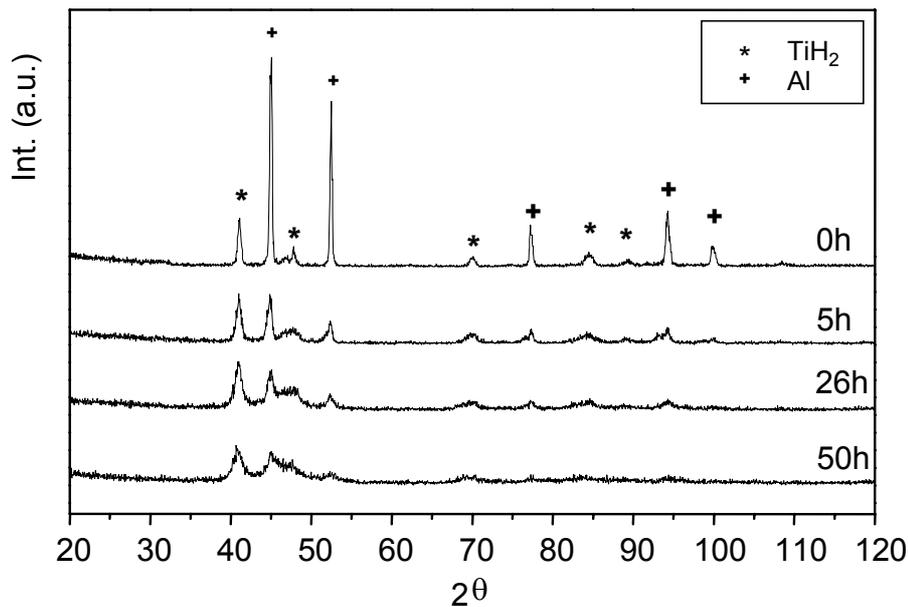


Figure 4 – X-ray diffraction patterns of alloy 2 milled for various times.

SEM-EDS point microanalysis performed on a large number of particles showed that the chemical composition of both alloys varies significantly within the particles as well as from particle to particle. Even after 50h of milling the chemical composition is still not homogeneous as shown, for example, by the SEM/BSE image of Figure 5, corresponding to alloy 1. The large bright areas are Ti-rich while the darker areas have a chemical composition near the starting stoichiometric one.

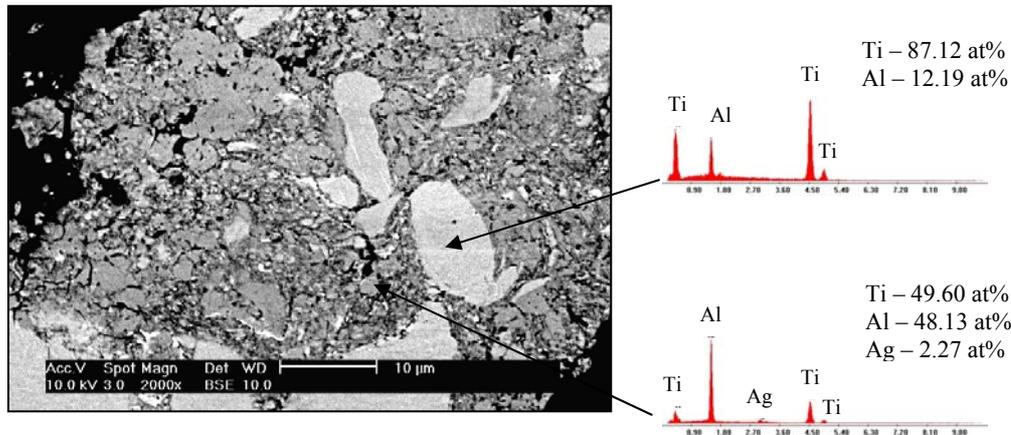


Figure 5 – SEM/BSE image of alloy 1 after 50h of MA and corresponding EDS analysis.

The hydrogen content measured in the powder mixtures after MA was 1.3582 wt% and 1.2672 wt% for alloy 1 and alloy 2, respectively. Taking into account the hydrogen content of the TiH_2 powder (2.1192 wt%) and the weight percentage of TiH_2 in the original mixtures, no relevant hydrogen changes are detected.

Thermal Stability of MA Powders

Figures 6(a) and 7(a) show the DTA curves of alloy 1 and alloy 2 powders, respectively, MA'd for 50h. Figures 6(b) and 7(b) show XRD patterns of these powders heated to the temperatures corresponding to the arrows marked in the DTA curves. A very broad endothermic peak in the temperature range 340°C to 700°C, and two small exothermic peaks overlapping the endothermic peak around 460°C and 580°C are observed when the powders were heated up to 1200°C. Related with these transformations changes are detected in the XRD patterns. After heating up to 460°C the $2\theta \approx 41^\circ$ to $2\theta \approx 45^\circ$ diffraction peaks became already better defined in comparison with those of the as-milled materials. With the increasing of temperature, the intensity of the isolated diffraction peaks of TiH_2 ($2\theta \approx 47^\circ$ and $2\theta \approx 70^\circ$) decrease gradually until they completely disappear above 580°C. The decrease of the TiH_2 peaks results from the decomposition of TiH_2 into Ti and H_2 and is associated with the broad endothermic DTA peak, which for both alloys starts at around 350°C and has a maximum at 590°C. After heating at 750°C for 2h, crystallization is evident and TiAl and Ti_3Al , together with unreacted Ti, are the main phases present in the system. Four phases, TiAl , Ti_3Al , Ti_2Al and Ti were detected upon heating at 1200°C for 2h. Vestiges of Al_2O_3 were also detected. Although precautions were taken to avoid contamination from nitrogen/oxygen during milling, which was conducted in hydrogenated Ar atmosphere, contamination from these elements was almost inevitable due to the opening of the vial for sampling purposes

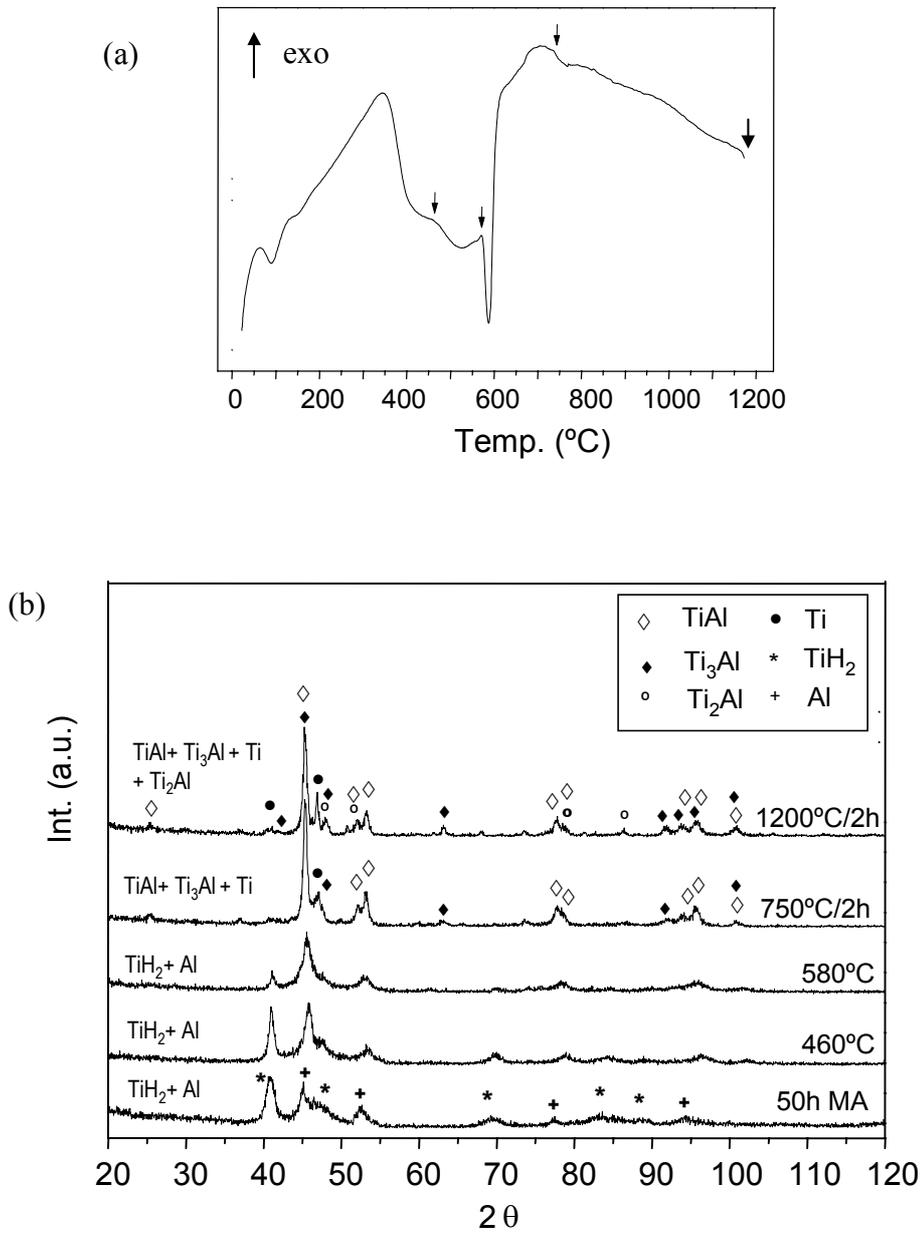


Figure 6 – (a) DTA heating curve of the alloy 1 MA'd powder for 50h and (b) XRD spectra of the powder heated to the temperatures marked in the DTA curve.

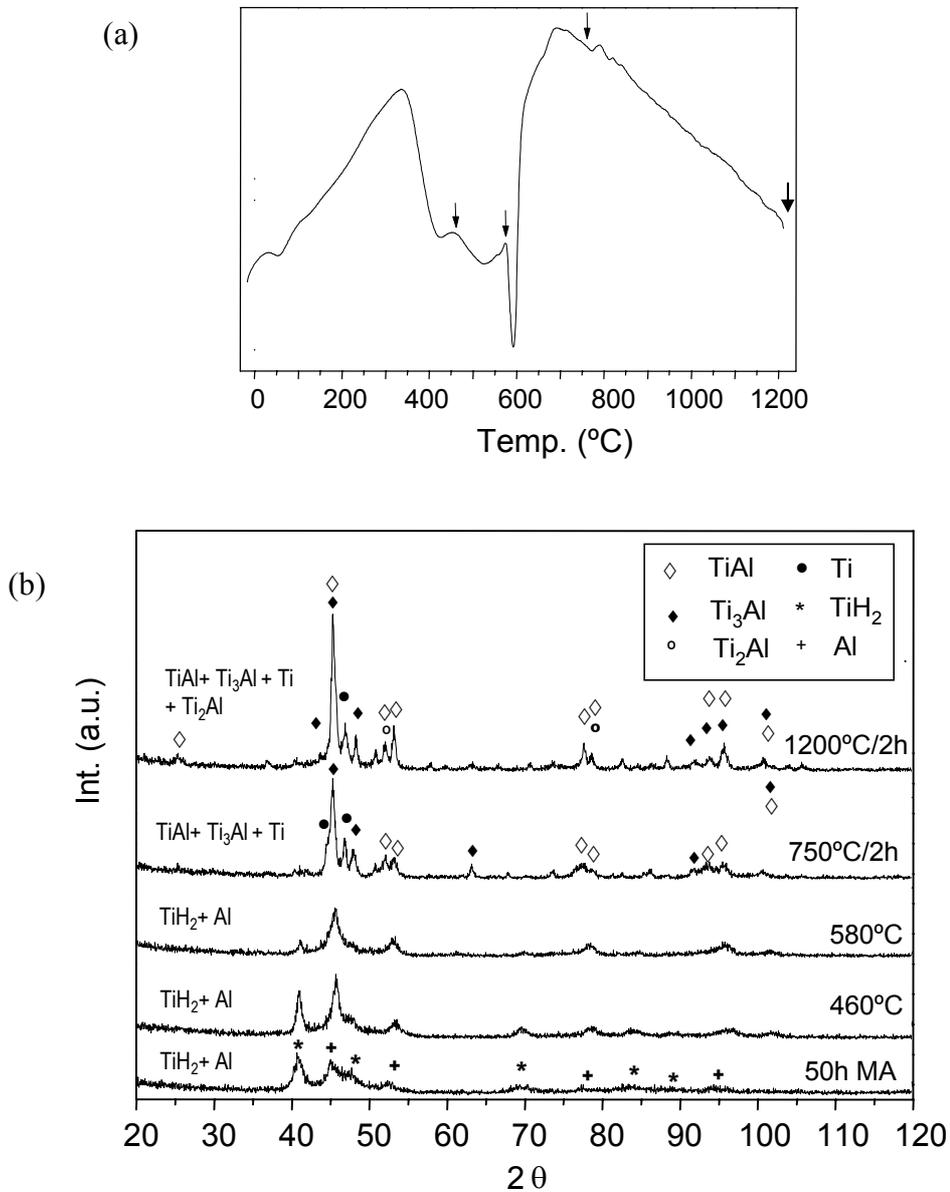


Figure 7 – (a) DTA heating curve of the alloy 2 MA'd powder for 50h and (b) XRD pattern of the powder heated to the temperatures marked in the DTA curve.

Consolidation and heat treatment

The HIP temperature and time are critical parameters for achieving full density and conditioning the final grain size. The previously reported results show that at 750°C TiAl and Ti_3Al are already formed; however unreacted Ti is present after 2h both at 750°C and 1200°C. An intermediate temperature was therefore chosen for HIP. The consolidation of the MA'd powder mixtures was carried out at 900°C/2h/150MPa and led to fully dense materials, i.e., full density is achieved at a relative low temperature when compared with the non-mechanically alloyed powders [7].

A variety of intermetallic phases was formed, as indicated in XRD patterns of Figure 8. For alloy 1, the predominant phase is the TiAl intermetallic but several other phases are also present, namely Ti, Ti₂Al, TiAl₂ and Ti₃Al. For alloy 2, the major phase seems to be Ti but, again, all the other phases were formed, namely, TiAl, Ti₃Al, Ti₂Al and TiAl₂. Some Al₂O₃ was also found in both alloys. These variety of phases produced on consolidating the mechanically alloyed powders can be associated to the not complete compositional homogenization after milling. According to T. Itsukaichi *et al* [12], the response of the MA powder to the consolidation process is related to the existence of a substantial amount of amorphous phases in the MA powders, i.e., the higher the amorphization level of milled powders the higher the homogenization of the final compacted product. In this way, the compositional and structural heterogeneity of the MA alloys produced in the present work may be responsible for the significant amounts of different phases formed through HIP on alloy 1 and alloy 2 MA'd powders.

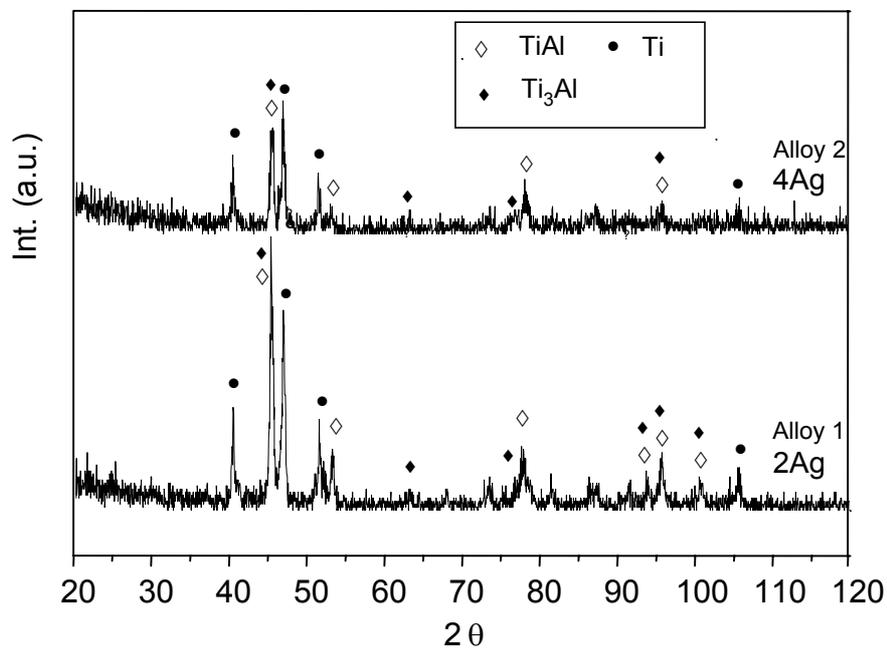


Figure 8 – X-ray diffraction patterns of alloy 1 and alloy 2 HIP'd at 900°C/2h/150MPa.

Figure 9 shows SEM images taken from the consolidated materials. The non-homogeneity of the structure is visible on these images. The background in the regions marked with 1 in Figures 9(a) and 9(d) show a composition of almost pure Ti, Table1. The regions denser with bright particles (micro and nano), marked with 2, show areas with compositions in Ti varying from 49 to 54 at%. This result is consistent with the presence of several aluminide phases seen in the XRD spectra (Figure 8). High magnification SEM pictures (Figures 9(c) and 9(f)) revealed nano-precipitates that at this point could not be identified. By SEM-EDS microanalysis, the chemical composition of some micro-particles was determined to be either TiAl phase or Ti₃Al phase.

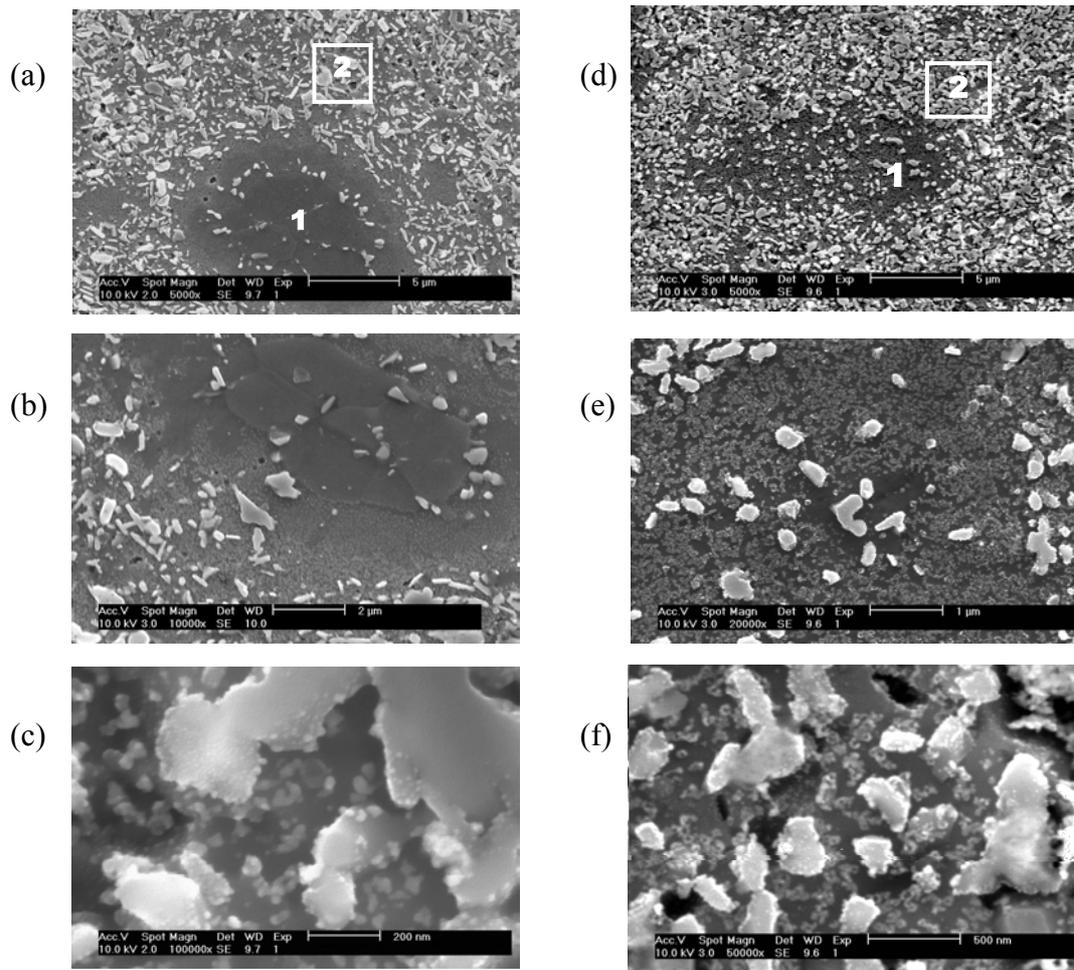


Figure 9 – SEM images of HIP'd material: (a, b, c) alloy 1; (d, e, f) alloy 2.

Table 1 – Chemical composition (at%)

	Alloy 1				Alloy 2		
	Ti	Al	Ag		Ti	Al	Ag
2	54.32	43.6	2.08		51.23	44.78	3.99
	48.60	49.53	1.87		49.87	46.31	3.82
	52.31	45.85	1.85		49.79	46.38	3.83
	50.29	47.05	2.66		50.84	44.63	4.54
	49.16	48.92	1.92		53.13	41.59	5.29
1	99.31	0.68	0		99.74	0.26	0

Following HIP, the hydrogen content was found to be 0.15833 wt% and 0.19344 wt% for alloy 1 and alloy 2, respectively. Although this values could have been lowered by a more drastic degassing step, hydrogen content is expected to decrease to acceptable levels with appropriate vacuum thermal treatment. The nitrogen content was kept at the same level as the ones present in the MA'd powder mixtures, 1.3678 wt% for alloy 1 and 1.3490 wt% for alloy 2, similar with other reported values [7,13].

When comparing HIP'd alloys 1 and 2 after subsequent heat treatment the XRD patterns shown in Figure 10 indicate that TiAl phase predominates in alloy 1 and Ti₃Al phase in

alloy 2, as suggested by the results obtained by XRD of the HIP material shown in Figure 8. However, besides the TiAl and Ti₃Al phases unreacted Ti is still present. On the other hand, high magnifications SEM images, Figure 11, show micro and nano-particles/precipitates present in both alloys after heat treatment. The nature of these particles and precipitates has yet to be characterized by SEM/EDS analysis and by TEM.

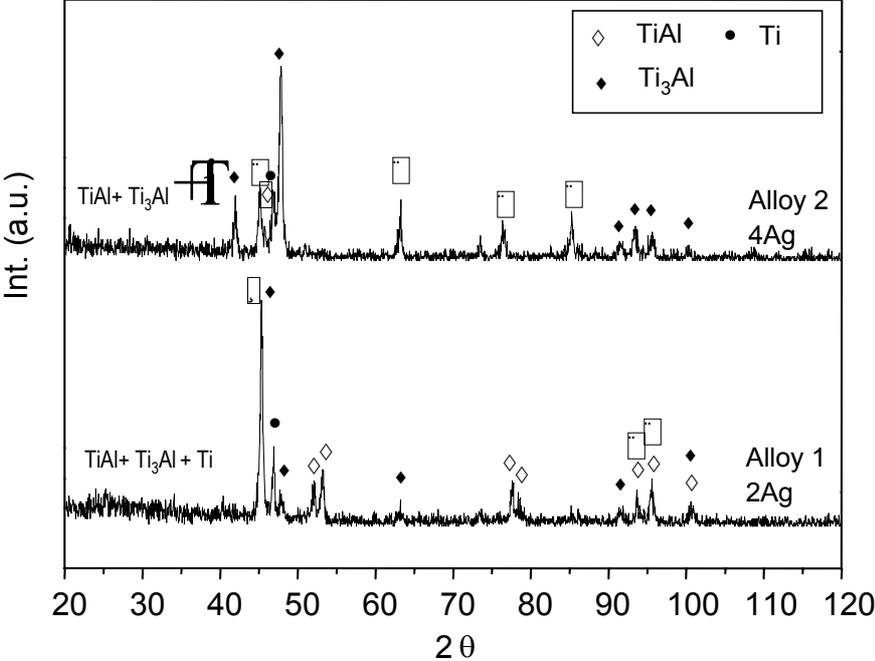


Figure 10 – X-ray diffraction patterns of alloy 1 and alloy 2 after heat treatment at 1200°C/4h.

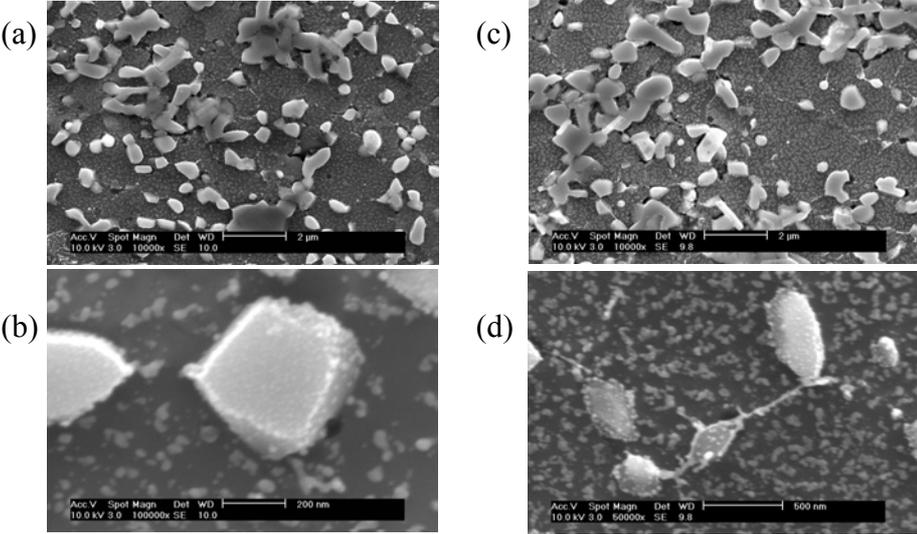


Figure 11- SEM images of alloy 1 (a, b) and alloy 2 (c, d) after heat treatment at 1200°C/4h.

CONCLUSIONS

Ti(H₂)-46Al-2Ag and Ti(H₂)-44Al-4Ag (at%) alloys have been produced by mechanical alloying of elemental powders in a planetary ball mill for 50h. As expected the use of titanium hydride showed to be very efficient during the milling process because of reduced sticking of the milled powders to the inner wall of the vial and balls.

After 50h of milling, the mixtures remain somewhat crystalline although extensive broadening and very low intensities of the diffraction peaks were observed.

First consolidation experiments of these milled alloys by HIP at 900°C led to full density and a multiphase microstructure. Subsequent heat treatment resulted in the formation of a more homogeneous microstructure but still with Ti present; the Ti(H₂)-46Al-2Ag (at%) alloy consisting mainly of TiAl phase while for Ti(H₂)-44Al-4Ag (at%) alloy the predominant phase was Ti₃Al. No Ag-based phases were detected during milling or after consolidation followed by heat treatment.

These results indicate that for homogeneous structures to be obtained mechanical alloying has to be more intensive and/or the subsequent consolidation/heat-treatment need to be modified.

REFERENCES

- [1] Toshimitsu Tetsui, *Adv. Eng. Mat.*, 3, No. 5, 2001, pp. 307-310.
- [2] Y.K. Kim, *JOM*, Vol. 46, No. 7, 1994, pp. 30.
- [3] G. Sauthoff, *Intermetallics*, VCH, Publishers, N.Y., 1995, pp. 5-30.
- [4] J.S. Benjamin *Met. Trans.*, Vol. 1, 1970, pp. 2943-2951.
- [5] C. Suryanarayana, *Progr. Mat. Sci.*, Vol. 46, 2001, pp. 1-184.
- [6] L. Lü and M.O. Lai, *Mechanical Alloying*, Kluwer Academic Publishers, USA, 1998, 84-101.
- [7] L. Lu, M.O. Lai, F.H. Froes, *JOM*, Vol. 54, No. 2, 2002, pp. 62-64.
- [8] Jung-Ho Ahn and Kang-Yull Lee, *JIM*, Vol. 36, No. 2, 1995, pp. 297-304.
- [9] P.S. Goodwin, T.M.T. Hinder, A. Wisbey and C.M. Ward-Close, *Mat. Sci. Forum*, Vols. 269-272, 1998, pp. 53-62.
- [10] C. Coelho, A.S. Ramos, B. Trindade, M.T. Vieira, J.V. Fernandes and M. Vieira, *Key Eng. Mat.*, Vol. 188, 2000, pp. 37-44.
- [11] F. Neves, T. Marcelo, M.H. Carvalho, *Materiais 2001*
- [12] T. Itsukaichi, K. Masuyama, M. Umamoto, I. Okane and J.G. Cabañas-Moreno, *J. Mater. Res.*, Vol. 8, No. 8, 1993, pp. 1817-1828.
- [13] F.S. Biancaniello, F.W. Gayle, C. Suryanarayana and F.H. Froes, *Mat. Sci. Forum*, Vols. 225-227, 1996, pp. 483-488.