SOLID STATE REACTIONS OF MECHANICAL ALLOYED Ti-Al AND Ti-Si INTERMETALLICS POWDERS COATED WITH ALUMINIUM

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ABSTRACT: In this paper we propose the use of magnetron sputtering to coat mechanically alloyed powders. $Ti_{80}Al_{20}$ and $Ti_{85}Si_{15}$ powders were coated with Al and studied at room and elevated temperatures. The MA'd powders are formed by Ti solid solutions. During heating there is the formation of Ti_5Si_3 and α_2-Ti_3Al in the core of the $Ti_{80}Al_{20}$ and $Ti_{85}Si_{15}$ powders, respectively. The phase transformations occurring in the coatings can be described as follows: formation of $TiAl_3$ in both systems at relative low temperatures and subsequent formation of α_2-Ti_3Al and γ-TiAl + α_2-Ti_3Al for the Ti-Si and Ti-Al systems at higher temperatures.

1. INTRODUCTION

Ordered structure of intermetallics exhibits attractive elevated temperature properties because long-range ordered superlattice reduce dislocation mobility and diffusion processes [1]. However, this reduced dislocation motion also results in extremely low ambient-temperature properties such as ductility and fracture toughness [2]. Many techniques have been used in the synthesis of intermetallics to improve their mechanical properties, such as Mechanical Alloying (MA) and Physical Vapour Deposition (PVD). These techniques allow the production of intermetallics with compositions and properties impossible to reach with other conventional techniques. In fact, MA process is an effective tool to produce supersaturated solid solutions, phases far from thermodynamic equilibrium, nanocrystalline materials and amorphous alloys [3]. Ti-Al and Ti-Si systems can be seen as model systems with extended solid solutions and amorphous phases, respectively [4]. The good properties of these systems make them suitable for applications in automotive and aerospace industries. Titanium aluminides of γ-TiAl , α_2-Ti_3Al and $TiAl_3$ have low density and high strength and Young modulus at elevated temperatures. Besides, in presence of oxygen, Ti and Al form oxides, improving strength and corrosion resistance of these materials [2,5]. Si appeared to be one of the most attractive candidates raising the creep resistance of these kind of materials since the Ti_5Si_3 phase formed is a strengthening constituent with low specific weight [6]. Ti-Si system is characterized by a large negative heat of mixing and by rather unstable solid solutions, favouring amorphous phase formation. The interdiffusion of Ti-Si multilayers has been studied, in great detail, showing that an amorphous phase with an extended homogeneity range is formed prior the equilibrium intermetallic compounds [7].

Although Mechanical Alloying has long be used for the production of intermetallic powders with good results, the consolidation process of the mixtures is one of the crucial steps to obtain high performance components. In fact, once these intermetallics are formed, the temperature required for a good hot compaction (e.g. HIP) is relatively high, mainly due to the high melting points of these structures. One of the possibilities to overcome this problem is to coat the mechanically alloyed powders with an element (or an alloy) with a low melting point that might react with the powders during the consolidation process. A good choice of the coating could even increase the performance of the final component by the formation of new structures at the interface of the grains. In this work we propose the use of magnetron sputtering to coat mechanically alloyed Ti-Si and Ti-Al powders for subsequent consolidation. Solid state reactions occurring during heating, were studied by means of chemical, structural and thermal analysis of the powders, with and without Al-coating.

2. EXPERIMENTAL DETAILS

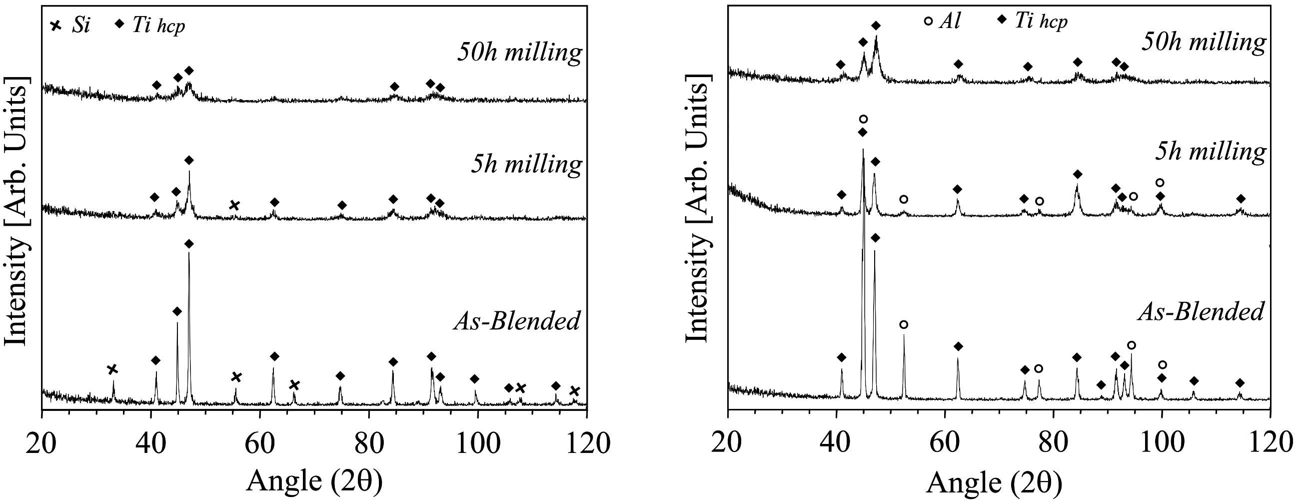
Samples with nominal atomic compositions of $Ti_{80}Al_{20}$ and $Ti_{85}Si_{15}$ were synthesised by mechanical alloying from Ti, Al and Si powders with a nominal purity of 99.5%, 99.5% and 99% and a maximum particle size of 100, 75 and 45 μm, respectively. Milling was performed in a planetary ball mill using hardened steel vial and 15 balls with 20 mm diameter each. The milling procedure was interrupted each 15 min, for 10 min, to cool down the system. A ball-to-powder weight ratio of 20:1 was chosen and the milling intensity was adjusted to 200 rpm. In order to avoid contamination, milling was performed in a hydrogenated argon atmosphere (5% H_2) and was interrupted after selected times to take out small amounts of powder for analysis.

$Ti_{80}Al_{20}$ and $Ti_{85}Si_{15}$ powders milled for 50 hours were coated with Al during 90 minutes by d.c. magnetron sputtering, with a specific discharge power of $2{,}62\mathrm{x}10^{-2}$ W/mm^2. The deposition was performed in a pure argon atmosphere ($5\mathrm{x}10^{-3}$ Pa) after the evacuation of the chamber down to an ultimate pressure of 10^{-6} Pa. During sputtering, the MA'ed powders were continually shacked by vibration and translation movements, in order to produce a continuous coating on each powder.

The milled powders with and without Al-coating were characterised by the following techniques: X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) with EDS analysis and electron probe microanalysis (EPMA). For SEM analysis, the powders were embedded in a thermosetting polymer, grinded, and polished with diamond down to 3 μm. In order to obtain relative high density of the green compacts, some samples were cold compacted with a pressure of 190 Pa.

3. RESULTS AND DISCUSSION

The structural results of the mixtures with milling time are presented in figure 1a) and 1b).

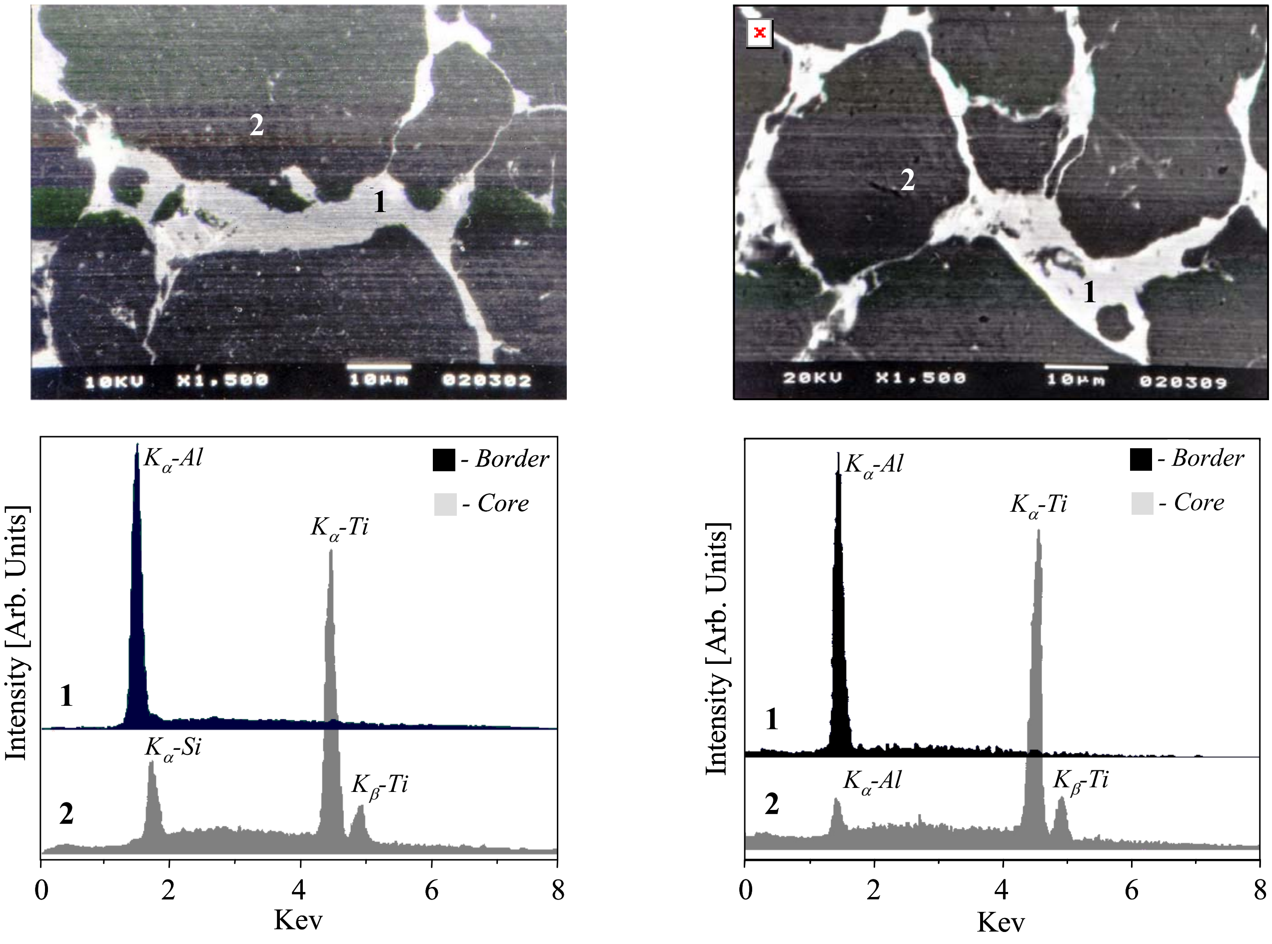


(a) (b)

Figure 1- XRD patterns of the a) $Ti_{85}Si_{15}$ and b) $Ti_{80}Al_{20}$ mixtures (Co K_{α} radiation), as a function of milling time.

Both systems show a decrease of the intensity of XRD peaks during the milling process, this decrease being less pronounced for the α-Ti phase. Furthermore, the peaks of this phase are shifted to slightly higher angles, corresponding to the formation of a α-Ti solid solution with Al or Si in substitutional positions in the hcp lattice. It should be pointed out that the atomic radii of Al and Si are lower than the one of titanium. For 50 hours milling, the structure of the mixtures $Ti_{85}Si_{15}$ and $Ti_{80}Al_{20}$ is formed by a single Ti phase with grain sizes of 18 and 13 nm, respectively. Even after a prolonged milling amorphization is not reached.

Figure 2 shows SEM pictures and EDS results obtained from green compacts of MA'd powders coated with aluminium. As it can be seen in both samples, there is a well-defined coating around the powders. The maximum thickness of the coatings, measured by SEM analysis from individual powders (before compaction) was 3 µm. The EDS analysis confirms SEM observations. A signal of Al is detected in the border whilst Ti + Si and Ti +Al signals were detected in the core of the $Ti_{85}Si_{15}$ and $Ti_{80}Al_{20}$ samples, respectively. Similar to the XRD analysis, no significant iron contamination from the vial and balls was observed by EDS, even for 50 hours of milling. Moreover, the chemical composition of the powders, measured by EPMA, remains constant during mechanical alloying, meaning that no preferential cold welding between powder particles and vial/balls occurred with milling time.



(a) (b)

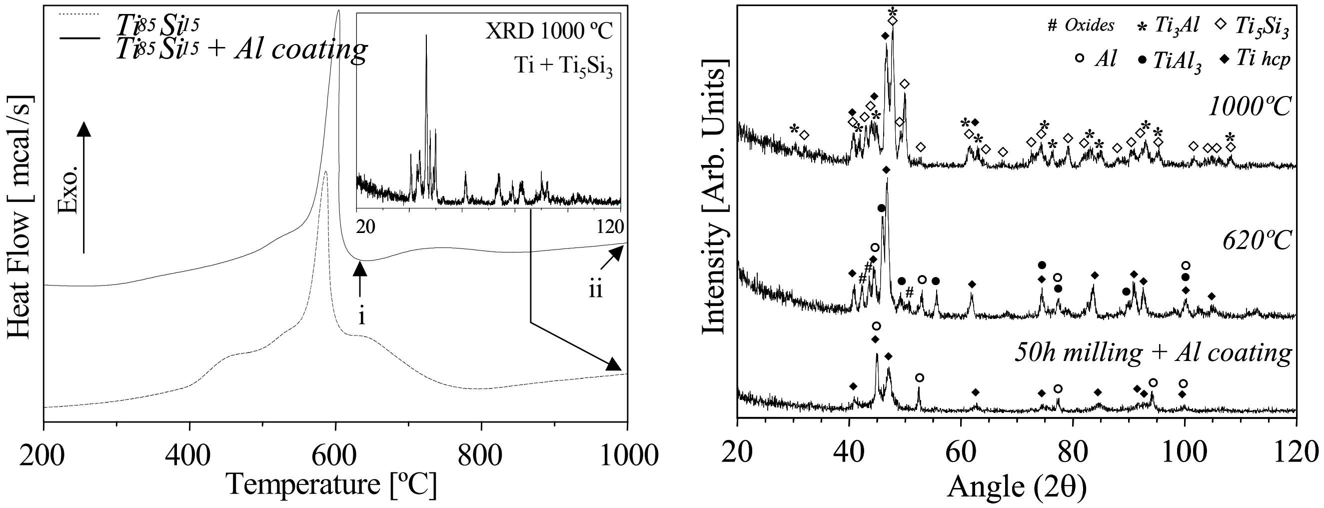
Figure 2 – Back scattering SEM images and EDS analysis of cross-section cold compacted samples a) $Ti_{85}Si_{15}$, b)$Ti_{80}Al_{20}$

To study the thermal stability of MA powders, DSC runs were made up to 1000ºC. The powders were structurally characterised at room temperature after each run.

Ti-Si System

Figure 3a) shows DSC curves of 50 hours $Ti_{85}Si_{15}$ milled powders with and without Al coating. On same figure an insert of the XRD pattern of the uncoated sample heated up to 1000ºC is displayed. Both DSC curves have a similar trend, characterized by a narrow exothermic peak at about 580ºC, corresponding to the formation of Ti_5Si_3 phase.

Figure 3b) represents the XRD patterns of the Al-coated $Ti_{85}Si_{15}$ powders heated up to 620 and 1000ºC (see arrows i and ii on figure 3a). Ti_5Si_3 is the only silicide produced during heating, as a result of the partial decomposition of the solid solution Ti(Si). The formation of this intermetallic corresponds to a Gibbs energy of –579,5 kJ/mol, against -129,7 and –133,9 kJ/mol for the TiSi and $TiSi_2$ phases, respectively [8]. Although Ti_5Si_3 has only been detected by XRD at 1000ºC, this phase is known to exist at 620 ºC, according to the DSC curve. However, the reason why it was not detected by XRD after 620ºC, is because it is formed mainly in the core of each powder. At 1000ºC, the Ti_5Si_3 diffraction peaks are well-defined because Al of the coating diffuses from the surface into the core of the powder (fig. 4), the coating powder interface becoming less sharp.



(a)

(b)

Figure 3– a) DSC curves of $Ti_{85}Si_{15}$ mixtures with and without coating, heated with a rate of 40 ºC/min b) XRD patterns of $Ti_{85}Si_{15}$ coated, obtained at room temperature after each run.

Concerning the reactions occurring at the coating interface, $TiAl_3$ and α_2-Ti_3Al are detected by XRD analysis after DSC runs up to 620 and 1000ºC, respectively (fig. 3b). Similar results were obtained by others authors [3,9], who claims that reaction products strongly depend on the chemical composition of the mixture [3]. However, these phases are not detected on the corresponding DSC curve because the volume of the coating is relatively low and its exothermic heat flows are relatively weak, when compared with exothermic heat flow of Ti_5Si_3 [10]. $TiAl_3$ is the first intermetallic to be formed in regions where the Al/Ti atomic ratio is higher than unity (close to the interface). Aluminium of the coating is all consumed in the formation of Ti aluminates before melting.

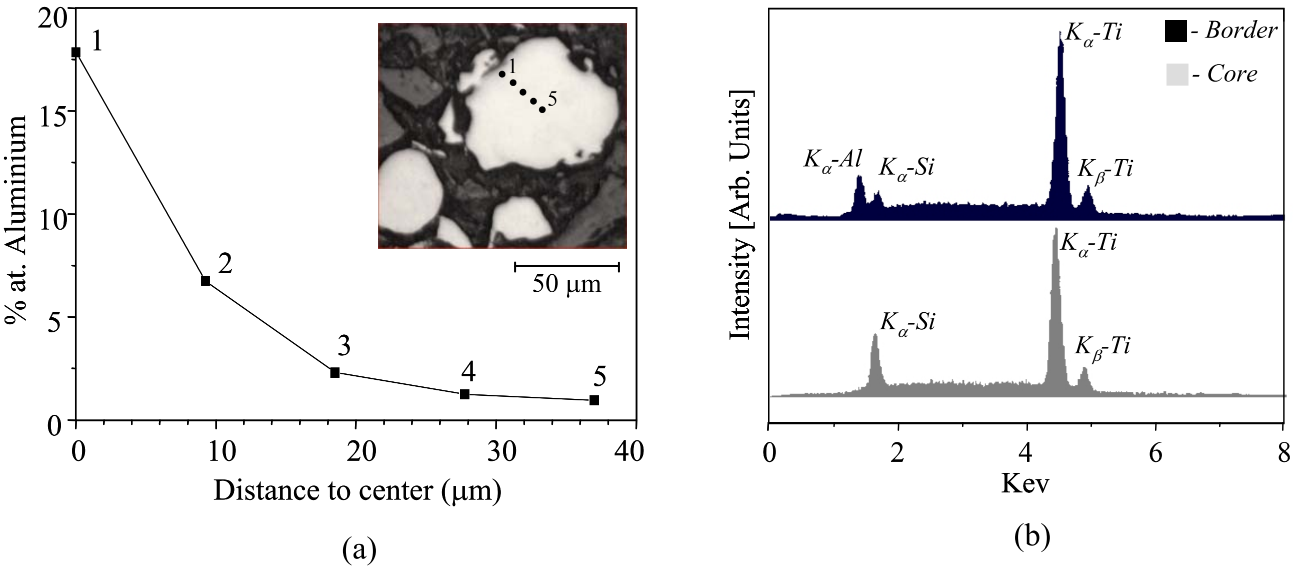


Figure 4 – Analysis of $Ti_{85}Si_{15}$ coated powders cross-section heated up to 1000ºC, embedded in thermosetting polymer. a) EPMA analysis , b) EDS analysis

Ti-Al System

Figure 5 shows DSC curves and XRD patterns of MA'd Ti-Al powders.

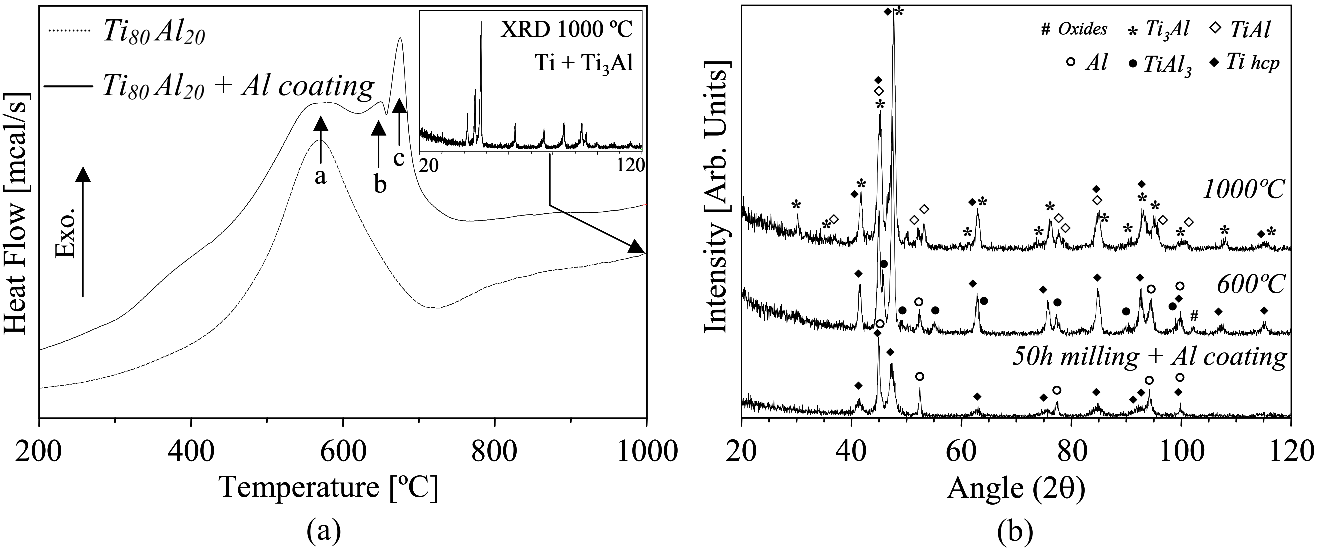
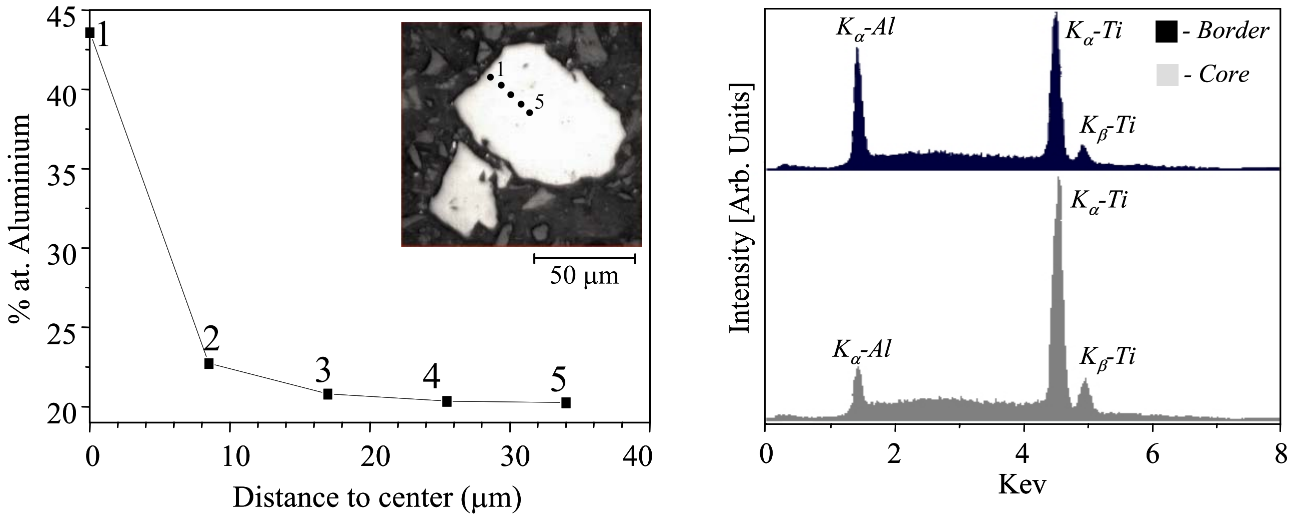


Figure 5 – a) DSC curves of $Ti_{80}Al_{20}$ mixtures with and without coating, heated with a rate of 40 ºC/min b) XRD patterns of $Ti_{80}Al_{20}$ coated, obtained at room temperature after each run.

DSC measurements performed on the uncoated MA´d powders reveals an exothermic peak at about 560ºC, correspondent to the formation of α_2-Ti_3Al. The coated powders have a more complex evolution during heating, with overlapping of exothermic peaks in the range 400-700ºC. First exothermic peak (arrow a – fig. 5a) corresponds to the appearing of Ti_3Al in the core of the powders. The reactions that take place in the Al-coating are similar to the ones observed in the coating of $Ti_{85}Si_{15}$ powders, i.e. formation of $TiAl_3$ (arrow b – fig. 5a) and its transformation into Ti_3Al at higher temperatures (arrow c – fig. 5a). However, since γ-TiAl was detected after heating up to 1000ºC, the third exothermic peak must be ascribed also to the formation of γ-TiAl from α_2-$TiAl_3$. To make it possible to occur in terms of chemical composition, this reaction needs to evolve titanium, (i. e. Ti + $TiAl_3 \rightarrow \gamma$-TiAl + α_2-Ti_3Al). In fact, this phase exists during all the MA'ing process as well as during heating (Fig. 5b).

Basis on these results is possible to conclude that the α_2-Ti_3Al phase, occurring in the interior of the powders, is formed at lower temperatures than the α_2-Ti_3Al in the coating. The Ti/Al atomic ratio (80/20) of the powders requires a slight diffusion to form α_2-Ti_3Al. Contrarily, the Al amount in the coating is higher than Ti amount, which allows the formation of an Al-rich phase, i.e. $TiAl_3$, and afterwards this phase transforms into α_2-Ti_3Al. These results agree with others studies [3,11], in which it is refereed that α_2-Ti_3Al, γ-TiAl and $TiAl_3$ are possible to form during heating, according to the relative amount of elements in the mixture.

Similar to the results obtained from the Ti-Si system for Ti_5Si_3 phase, the α_2-Ti_3Al phase was not detected in the XRD pattern obtained after 600ºC. This phase was only observed at higher temperatures (fig. 5b). The explanation for this fact is exactly the same as the one referred above for the previous system and concerns the decrease of the coating thickness during heating, by the diffusion of Al into the powder (Fig. 6). The endothermic peak detected at 660ºC in the DSC curve of the coated Ti-Al system (between arrow a and arrow b – fig 5a) corresponds to the melting of Al, meaning that a certain amount of this element might exists, as an elemental phase, in the coating,



(a) (b)

Figure 6 – Analysis of $Ti_{80}Al_{20}$ coated powders cross-section heated up to 1000ºC, embedded in thermosetting polymer. a) EPMA analysis , b) EDS analysis

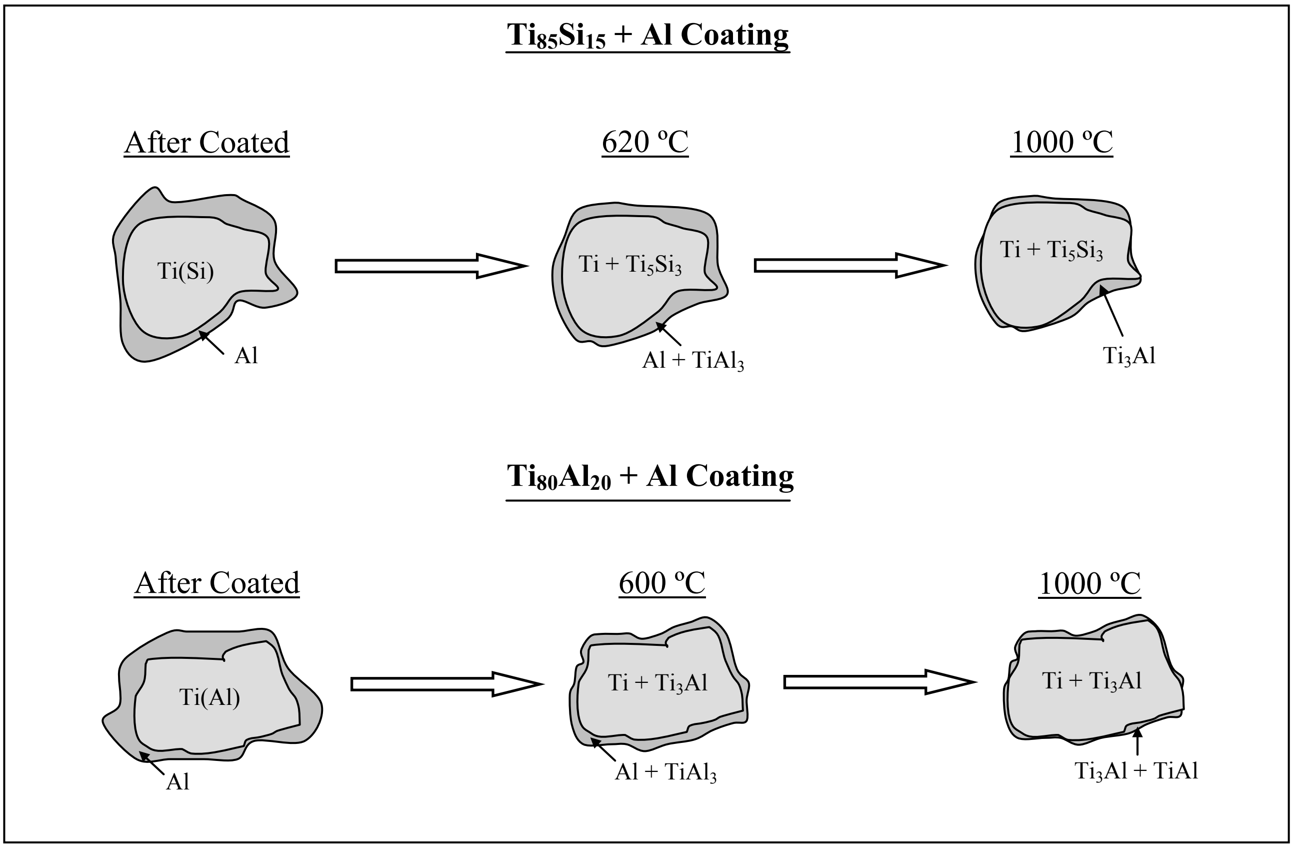
4. CONCLUSIONS

This work shows that the use of magnetron sputtering to coat mechanically alloyed powders is a promising process for a good subsequent compactation. In fact, during heating, there is a diffusion of the coating element into the core of the powders, at relative low temperatures, giving raise to new structural phases.

From results and discussion is possible to conclude the following: for 50 hours milling, the mixtures $Ti_{85}Si_{15}$ and $Ti_{80}Al_{20}$ are formed by nanostructured single solid solutions of Ti(Si) and Ti(Al), respectively. After sputtering, MA´d powders shows a well-defined coating with a sharp interface. During heating there is a short-range diffusion of aluminium into the powders. The structural transformations occurring during heating in the core of the MA´d with or without Al-coating, are exactly the same, i. e. Ti_5Si_3 and α_2-Ti_3Al for the Ti-Si and Ti-Al systems.

The phase transformations in the coatings are completely distinguished from the ones occurring in the powders core. $TiAl_3$ was observed in both systems for relative low temperatures. For higher temperatures, this phase evolutes to α_2-Ti_3Al in Ti-Si system, and to γ-TiAl + α_2-Ti_3Al in Ti-Al system.

The transformations studied are schematically described as follows:



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