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Thermal Behaviour of Nanostructured Intermetallics Synthesized by Mechanical Alloying and Coated with Metallic Elements

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Abstract. Ti₅₂Al₄₈ and Ti_{62.5}Si_{37.5} alloys were synthesised by mechanical alloying (MA) from blended powders of titanium, aluminium and silicon, and then coated with Al and Ti by magnetron sputtering. The phase transformations occurred during milling were followed by X-ray diffraction (XRD) analysis. Scanning calorimetry (DSC) was used to study the thermal behaviour of the powders, with and without metallic coating, up to 1000°C. After 50h milling the Ti₅₂Al₄₈ alloy was formed mainly by Ti(Al) + Ti₃Al. The Ti₅Si₃ intermetallic was present in the final structure of the milled Ti_{62.5}Si_{37.5} alloy. During heating, γ -TiAl + Ti₃Al and Ti₅Si₃ are formed in powders core for the Ti-Al and Ti-Si systems, respectively. Al-coating showed a higher ability to react with the powders to form intermetallics than Ti-coating. In the first case, the Ti₃Al, γ -TiAl and TiAl₃ phases were detected at the powders surface. Ti-coating was stable up to high temperatures. No reaction of this element with the powders was observed.

Introduction

Ordered structure of intermetallics exhibits attractive elevated temperature properties, however, these materials show low room-temperature properties such as ductility and fracture toughness [1]. The industrial applications of intermetallics are restricted to solutions where the components need a good performance at elevated temperatures and simultaneously, the performance required at roomtemperature not be high. This is the case of the Ti-Al and Ti-Si intermetallics which are used in automotive and aerospace industries, where high temperature strength, low density and good corrosion resistance are essential requirements. Many synthesis techniques, such as Mechanical Alloying (MA) and Physical Vapour Deposition (PVD), have been used in production of intermetallics with improved mechanical properties. These techniques allow synthesis of supersaturated solid solutions, phases far from equilibrium and nanocrystalline materials [2,3]. In the present research we used MA and magnetron sputtering to produce Ti₅₂Al₄₈ and Ti_{62.5}Si_{37.5} nanostructured intermetallics powders coated with a ductile material. The goal is to study the phase transformation occurring in the milled powders/coating interfaces during heating in order to optimise the process for future powders consolidation. It is expected that a new phase (ductile) be formed at the surface that might improve the final product (after compaction) in terms of the mechanical properties as referred above.

Experimental Details

Samples with atomic compositions of $Ti_{52}Al_{48}$ and $Ti_{62,5}Si_{37,5}$ were synthesised by mechanical alloying from Ti, Al and Si powders with nominal purities of 99.5%, 99.5% and 99% and maximum particle sizes of 100, 75 and 45 mm, 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,

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milling was performed in an inert atmosphere of argon with 5% of hydrogen and was interrupted after selected times to take out small amounts of powder for analysis.

The Ti₅₂Al₄₈ and Ti_{62.5}Si_{37.5} mixtures milled for 50 hours were coated with two different metallic elements (Al and Ti) by d.c. magnetron sputtering, with a specific discharge power of 2.62×10^{-2} W/mm², during 3h. The depositions were performed in a pure argon atmosphere (5×10^{-3} Pa) after the evacuation of the chamber down to an ultimate pressure of 10^{-6} Pa. The powders were continually shacked by vibration and translation movements during the depositions, in order obtain homogeneous coatings. The samples were embedded in a thermosetting polymer, or alternatively, were cold compacted with a pressure of 190 Kgf/mm². After these procedures, the samples were grinded and polished with diamond down to 3 μ m. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used for the powders analysis. The XRD diffraction patterns were obtained with Co K_a radiation. The DSC runs were performed in a hydrogenated argon flux, with a heating rate of 40°C/min.

Results and Discussion

Characterization of the Mechanically Alloyed Powders. The XRD patterns of the mixtures as a function of milling time are presented in Figure 1.



Fig. 1. XRD patterns of the a) Ti₅₂Al₄₈ and b) Ti_{62.5}Si_{37.5} mixtures as a function of milling time.

In both systems the diffraction peaks become less intense with increasing milling time as a result of a grain size refinement and internal strain induced by plastic deformation [4]. For 10h of milling the structure of the $Ti_{52}Al_{48}$ and $Ti_{62.5}Al_{37.5}$ mixtures is formed by $Ti(Al) + Ti_3Al +$ vestiges of Al and $Ti_5Si_3 +$ vestiges of Ti, respectively. Extended milling times doesn't lead to any further structural changes.

To study the thermal stability of mechanically alloyed (MA'ed) powders, DSC runs were made up to 1000°C. The powders were structurally characterized by XRD at room temperature after each run (figures 2a) and 2b)). On same figures inserts of the respective DSC curves are displayed.

Phase transformations of both systems occurred during heating. Concerning the $Ti_{52}Al_{48}$ system (fig. 2a), one broad exothermic peak with a maximum intensity at 560°C is detected on the corresponding DSC curve. This peak is assigned to the formation of the γ -TiAl intermetallic phase from the Ti(Al) solid solution, which is confirmed by XRD analysis. In the XRD pattern corresponding to the heating up to 1000°C some diffraction peaks were detected that could not be ascribed to a Ti-Al phase. These peaks can be the result of a partial oxidation of the sample, as they seem to be identified to Ti-based oxides.



Fig. 2. XRD patterns of the a) $Ti_{52}Al_{48}$ and b) $Ti_{62.5}Si_{37.5}$ samples.

The DSC curve of the $Ti_{62.5}Si_{37.5}$ mixture does not reveal any significant change in heat flux, this fact being confirmed by XRD. In fact, Ti_5Si_3 is the unique phase detected in XRD patterns after heating up to 1000°C, which is already present after 50h milling. However, it is likely that remaining Ti existing after milling react with some silicon (not detected in the XRD pattern of the milled sample) to form further Ti_5Si_3 phase. This could explain the exothermic DSC peak detected at 560°C. The formation of Ti_5Si_3 intermetallic corresponds to a Gibbs energy of -579,5 Kj/mol, against -129,7 and -133,9 Kj/mol for the TiSi and TiSi₂ phases, respectively [5], confirming that once formed, the Ti_5Si_3 phase does not transform in any other titanium silicide. The heat release observed in the DSC curve close to 450° C (fig. 2b) is not ascribed to phase transformations. Some authors detected similar phenomenon and attribute it to structural and stress relaxation of the asmilled phases [6,7]. The main phases detected in both systems, during thermal behaviour, are in agreement with respective phase diagrams.



Fig. 3. DSC curves of the a) Ti₅₂Al₄₈ and b) Ti_{62.5}Si_{37.5} samples with and without coating

Characterization of $Ti_{52}Al_{48}$ and $Ti_{62.5}Si_{37.5}$ powders coated with metallic elements. In order to study the chemical reactions between the coatings and the powders during heating, DSC (fig. 3) and XRD (figs. 4 and 5) measurements were performed on powders coated with Al and Ti. Comparing the results obtained from the powders with and without coating, it was possible to determine the structural transformations induced by the coatings in the powders surfaces.

XRD patterns of the Ti-Al and Ti-Si coated powders (figs. 4 and 5, respectively) confirm the presence of Al and Ti in their surface.

Ti₅₂Al₄₈ coated with Al - Ti₃Al, γ-TiAl and TiAl₃ phases (fig. 4a) coexist in the Ti₅₂Al₄₈/Al sample

after heating up to 550°C. Taking into account the results obtained for the same system without Al coating, one may say that the TiAl₃ phase is formed from the reaction between Al of the coating and the Ti(Al) solid solution of the powders, leading to a new interface. This reaction does not give rise to a well-defined DSC exothermic peak, because the phase quantities engaged in the phase transformation is relatively low (interface with a few μ m size). After 1000°C, TiAl₃ is replaced by γ -TiAl as result of the reaction between TiAl₃ (surface) and Ti₃Al (adjacent to the surface). This reaction gives rise to a sharp DSC exothermic peak close to 620°C (fig.3a – dashed curve).



Fig. 4. XRD patterns of Ti₅₂Al₄₈ sample at room temperature after each run a) Al-coating b) Ti-coating

 $Ti_{52}Al_{48}$ coated with Ti - Ti₃Al + γ -TiAl + Ti phases are detected in the XRD pattern of the Ti₅₂Al₄₈/Ti sample heated at 570°C (fig. 4b). Since the Ti₃Al and γ -TiAl phases concern to the powders core transformations, such as explained before, one may consider that the Ti _{hcp} coating remain unaltered up to this temperature, i.e. it doesn't react with the powders. The exothermic peak occurring in the DSC curve at 470°C might be ascribed to the γ -TiAl formation for the same reasons stated for Al-coating. However, there is no apparent reason for justifying its lower temperature compared to the one observed for the same system without Ti coating. Therefore, it is likely that this peak might be also ascribed to a grain growth of the Ti phase and/or structural relaxation of the as-milled structures. After 1000°C, all but the Ti _{hcp} phase referred before persist. Ti reacts with oxygen to give rise titanium oxides.



Fig. 5. XRD patterns of Ti_{62.5}Si_{37.5} sample at room temperature after each run a) Al-coating b) Ti-coating

 $Ti_{62.5}Si_{37.5}$ coated with Al - No structural transformations take place in this system up to 550°C. However, the TiAl₃ phase is detected after 1000°C (fig.5a). It is obvious that this phase occurs at the interface, replacing the original Al-coating layer. This means that some free Ti should exist in this range of temperature, since it is improbably that Ti arises from the decomposition of the stable Ti₅Si₃ phase. This reaction gives rise to an exothermic peak at 640°C (fig.3b – dashed line).

 $Ti_{62.5}Si_{37.5}$ coated with Ti - In this case, such as happen to $Ti_{52}Al_{48}$ system, the Ti coating layer does not react to form intermetallics. Once again, after 1000°C, instead of Ti _{hcp} coating, some Ti oxides are present in the structure of this system. The DSC peak detected at 400°C (fig. 3b) is not ascribed to any phase transformation and is probably due to grain growth of the Ti phase and/or structural relaxation of the as-milled structures.

Conclusions

This work shows that the use of magnetron sputtering to coat mechanically alloyed powders is a promising process to obtain a metallic layer suitable for subsequent compaction. By comparing the DSC curves and XRD patterns obtained from the powders, with and without coating, it is possible to understand the influence of the metallic layer on the phases transformations occurring during heating up to 1000°C. The structure of the Ti-Al and Ti-Si as-milled systems is formed by Ti(Al) + Ti₃Al + Al (vestiges) and Ti₅Si₃ + Ti (vestiges), respectively. Heating of these systems leads to phase transformations in the core of the powders as well as in the coatings / powders interfaces. Ti₃Al + γ -TiAl and Ti₅Si₃ are formed in the uncoated Ti₅₂Al₄₈ and Ti_{62.5}Si_{37.5} powders. Contrarily to the systems coated with aluminium, no phase transformations occurred at the interface of the heat-treated systems coated with titanium. For Ti-Al system, TiAl₃ phase is formed from the reaction between Al coating and the Ti(Al) solid solution. After 1000°C, the TiAl₃ phase is replaced by γ -TiAl.

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