

Process Development of γ -TiAl Based Alloys and their Consolidation

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Abstract. The present paper describes part of the work that is being carried out to investigate the formation of Ti-Al-Ag nanostructured intermetallic compounds using Mechanical Alloying (MA). Mixtures of elemental powders with nominal compositions $52TiH_2$ -(48-x)AlxAg (x=0, 2 and 4 at. %) were milled for 25h at 500rpm in a planetary ball mill. The MA led to the formation of a TiH₂ (Al) solid solution coexisting with L1₂-TiAl₃ phase. In all cases, Hot Isostatic Pressing (HIP) at 900°C/150MPa/2h and the subsequent heat-treatment at 1200°C/4h resulted mainly in γ -TiAl phase formation. When compared with similar alloys produced in previous work by MA at 200rpm for 50h and consolidated in the same conditions more homogeneous microstructures were obtained. Addition of Ag led to a formation of Ag-rich phases preferential located at the grain boundaries.

Introduction

 γ -TiAl based alloys possess many attractive properties for high temperature structural applications, including excellent oxidation and corrosion resistance, relatively light material weight and superior strength at medium-high temperatures [1,2]. Some of the current research is aimed at improving their poor ductility through various approaches, including the use of new methods of production or through alloying. Consequently, the use of MA as a synthesis process to prepare fine-structured titanium aluminide intermetallics has received increasing attention in the last few years [3,4].

In previous work, $52TiH_2-46Al-2Ag$ and $52TiH_2-44Al-4Ag$ (at. %) alloys were produced by MA at 200rpm for 50h [5]. The MA powders were consolidated by HIP at 900°C/150MPa/2h and the subsequent heat-treatment was carried out at 1200°C/4h. It was found that the predominant phases after heat-treatment were γ -TiAl and α_2 -Ti₃Al for 52TiH₂-46Al-2Ag and 52TiH₂-44Al-4Ag, respectively, with Ti still present. It was concluded that to obtain more homogeneous structures, the milling process should be more intensive and/or the subsequent consolidation/heat-treatment should be modified. In the present work only the MA parameters were modified; their influence as well that of the added silver on the formation of nanostructured intermetallics is evaluated.

Experimental

Blends of elemental powders of TiH₂ (99.00% purity and <150 μ m), Al (99.50% purity and <74 μ m) and Ag (99.99% purity and <100 μ m) with nominal compositions of 52TiH₂-48Al, 52TiH₂-46Al-2Ag and 52TiH₂-44Al-4Ag (at. %) were prepared as starting materials. The mixtures were mechanically alloyed in a planetary ball mill for 25h in a hydrogenated argon atmosphere using a tempered chrome steel vial (250ml) and balls (15 balls with 20mm diameter each). The ball-to-powder weight ratio was 20:1 and the powders were milled under a speed of 500rpm. No process control agent was added to the charge. The process was interrupted for 15 min each 15 min to cool the vial. Differential thermal analysis (DTA) was carried out on the obtained powders. The mechanically alloyed powders were cold isostatic pressed (CIP) at 300MPa into cylindrical compacts of approximately 12 mm diameter and 35 mm height and about 75% of theoretical density. The compacts were encapsulated in steel cans lined with tantalum foil. The cans were degassed by heating under a 10⁻³Pa vacuum at 5°C/min up to 300°C with a 15 min hold at that temperature and then sealed. Consolidation was achieved through HIP at 900°C/150MPa/2h. Subsequent heat-

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treatment (HT) was conducted at 1200°C for 4h under a 10^{-4} Pa vacuum. The as-mechanically alloyed powders and the consolidated compacts were characterized by X-ray diffraction (XRD) (Cu-K_{α} radiation) and Scanning Electron Microscopy (SEM) associated with Energy Dispersive Spectrometry (EDS).

Results and Discussion

Mechanical Alloyed Powders. Fig. 1 shows the XRD patterns for the 52TiH_2 -48Al alloy, in the asblended state and after milling. After MA, the XRD peaks from Al disappeared and the peaks from TiH₂ became wider and less intense than in the as-blended powder. It is also observed that the peaks of this phase are slightly shifted to higher angles after 25h of milling. This can be partly explained by the dissolution of Al in TiH₂, i.e. formation of TiH₂(Al) solid solution, which is consistent with the decrease of the lattice parameter *a* of cubic TiH₂ as shown in Table 1.



Alloy	a [Å] of TiH ₂		a [Å] of TiAl₃
	0h MA	25h MA	25h MA
0 Ag	4.4508	4.4366	3.9806
2 Ag	4.4563	4.4292	3.9689
4 Ag	4.4579	4.4449	3.9776

Moreover, $L1_2$ -TiAl₃ phase was detected and some degree of amorphization of the powder mixtures became also evident after the milling process. The lattice parameters *a* of the L1₂-TiAl₃ determined for the three alloys after MA, given in Table 1, are in good agreement with literature data [3,6].

For the alloys with Ag added the XRD profiles do not show any structural differences. The XRD patterns are somewhat different from those previously obtained. In the case of 52TiH₂-46Al-2Ag and 52TiH₂-44Al-4Ag alloys milled at 200rpm, reported in [5], the major Al and TiH₂ peaks could still be clearly identified after 26h of milling. Even with 50h of MA, the product of milling was a mixture of Al and TiH₂, although extensive broadening and very low intensities were observed.



Fig. 2. Peak deconvolution of the XRD pattern (52TiH₂-48Al) showing an amorphous component in the final stage of milling.

Table 2. Crystallite size and internal strain of $TiH_2(Al)$ and $L1_2$ - $TiAl_3$ after MA for 25h (calculated using the (111) and (200) reflections).

Alloy -	Cryst. Size [nm]		Internal strain [%]	
	$TiH_2(Al)$	TiAl ₃	TiH2(Al)	TiAl ₃
0 Ag	7	10	1.02	3.13
2Ag	8	7	1.86	4.44
4Ag	25	7	3.80	4.35

Thus, the larger amount of energy transmitted to the powders in the milling conditions used in the present work had a significant influence on the evolution of the mechanically alloyed powder mixtures. The slightly more complex XRD patterns from $2\theta=30^{\circ}$ to $2\theta=50^{\circ}$ can be explained by the overlap of peaks from the coexisting phases in the final stage of milling. By applying a peak fitting procedure the halo of the amorphous phase can be distinguished from the diffraction peaks of the solid solution and L1₂-TiAl₃ phases (Fig. 2). The results for the crystallite size and for the internal strain, calculated by the Williamson and Hall method [7], are reported in Table 2 and indicate that for all cases the observed broadening of the diffraction peaks is associated to a reduction in the crystallite size and an accumulation of mechanical strain. Additionally, the results also show a systematic decrease in the crystallite size of TiH₂(Al) with the decrease of Ag content, particularly for the alloys with 0 and 2at.% Ag. In the case of the L1₂-TiAl₃ phase a slight decrease in the crystallite size was measured with the Ag addition.

Fig. 3(a) shows the DTA curves of the mechanically alloyed powder mixtures. All the three DTA curves have a similar trend, characterized by one endothermic and two exothermic peaks, indicating phase reactions. To understand the nature of these reactions, small samples of the mechanically alloyed powder mixtures were heated to temperatures corresponding to the characteristic points shown in the DTA curves (Fig. 3(a)). The samples were immediately cooled after reaching this temperature and were analyzed using XRD. Fig. 3(b) shows the corresponding XRD patterns for 52TiH₂-48Al alloy. It should be pointed out that no phase transformations were detected during cooling from the maximal temperature achieved in all DTA runs.



Fig. 3. (a) DTA curves of the mechanically alloyed mixtures and (b) XRD patterns of the 52TiH₂-48Al samples heated to the temperatures shown in the respective DTA curve.

During heating at 545°C, the peaks from TiH₂(Al) decrease significantly suggesting that the endothermic peak, in the temperature range 290°C to 600°C, corresponds to the TiH₂ decomposition. After heating at 610°C, the peaks from the TiH₂ completely disappeared. At this temperature, a new phase, TiN, was detected together with L1₂-TiAl₃. Nevertheless, the peaks shape indicates that some amount of amorphous phase is still retained after thermal treatment at 610°C. As can be seen, a crystallographic change was observed in the 610°C - 715°C interval, Fig. 3(b-715°C). The peaks were mainly from the L1₂-TiAl₃ phase below 610°C, however, peaks from a TiAl phase appeared above 715°C. The stronger peak from Ti₃Al phase was also indexed at this temperature. The exothermic peak, with an onset at 610°C and maximum at 650°C, is then related to the formation of TiAl. The XRD pattern of the sample heated to 840°C shows the formation of the final stable L1₀-TiAl compound. The tetragonal superstructure of the equilibrium TiAl intermetallic compound is characterized by the superlattice peaks in the low-angle part of the XRD pattern, as well as by the good definition splitting of the (200) reflection. The XRD pattern also shows the presence of some additional reflections which were indexed to oxides and nitrides, namely, Ti₅Al₃O₂ and TiN.

Similar conclusions were derived from the 52TiH₂-46Al-2Ag and 52TiH₂-44Al-4Ag alloys XRD pattern.

Consolidated MA Powders. XRD patterns of the 52TiH₂-48Al, 52TiH₂-46Al-2Ag and 52TiH₂-44Al-4Ag alloys after HIP at 900°C/150MPa/2h, followed by heat treatment at 1200°C for 4h, are shown in Fig. 4, while SEM/BSE photomicrographs are shown in Fig. 5. All the alloys consist essentially of γ -TiAl (L1₀ structure), however, peaks from nitrides and oxides were also detected.



These phases are present as a result of contamination from the milling media and the atmosphere. The absence of α_2 -Ti₃Al phase may be partially a consequence of the formation of those Ti nitrides and oxides, with a resulting decrease of the available amount of Ti in the Ti-Al matrix. Comparison with the results in [5] shows that the different phases produced as a result of the same consolidation procedure can be explained mainly on the basis of varied compositional homogenization degrees of attained with the different milling procedures. On the other hand, the higher speed of milling used in the present work may be responsible by the degree of contamination that it was reached.

The lattice parameters of γ -TiAl phase tend to vary slightly with the composition. The *a* and *c* parameters varied from 3.9914Å and 4.0674Å, respectively, for the 52TiH₂-48Al alloy to 3.9908Å and 4.0646Å for the 52TiH₂-46Al-2Ag alloy, respectively. Consequently, small or negligible decreases in the unit cell volume ca^2 and in the c/a ratio were measured, from 64.7983Å³ to 64.7112Å³ and from 1.0190 to 1.0187, respectively. However, for the 52TiH₂-44Al-4Ag alloy an increase in the ca^2 to 64.8497Å³ was measured, mainly due to a slight increase in the *a* parameter to 3.9945Å. As the *c* parameter shows a negligible decrease to 4.0642Å, a slight decrease in c/a to 1.0174 was again measured. General arguments have been proposed in previous studies, reported in [1] and [8], suggesting that additions of an element, which decreases the c/a ratio or ca^2 will result in ductility is still lacking at present, as the ductility of γ -TiAl alloys is also strongly dependent on the microstructure, on the Al concentration and on the amount of impurities. Therefore, as Ag addition caused very small variations in both the c/a and ca^2 it is not viable to suggest any potential positive or negative contribution of Ag in the ductility of γ -TiAl alloys.



Fig. 5. SEM photomicrographs of the alloys after HT (a) 52TiH₂-48Al, (b) 52TiH₂-46Al-2Ag and (c) 52TiH₂-44Al-4Ag.

Although apparently full densification was achieved in the three alloys after HIP, as determined by optical metallographic examination, for the 52TiH₂-46Al-2Ag alloy a swollen structure was formed after the HT. In fact, a significant amount of porosity was observed in this alloy after the HT. It is believed that gases not expelled during the degassing procedure caused the volume change.

SEM observation of the microstructures (Fig. 5) reveals a generally coarse structure, particularly for the $52TiH_2$ -44Al-4Ag alloy, and that an Ag-rich phase occurs in some locations, much more abundant at the grain boundaries (Fig. 5 (b-c)). Some nano-precipitates were also observed in all alloys. Further observations and analysis are presently being done in order to study the nature of these nano-precipitates, the formation of the Ag-rich phase and the influence of the presence of some impurities on the evolution of the final structure.

Conclusions

Mechanical alloying for 25h, under a speed of 500rpm, of elemental powder mixtures with nominal compositions of 52TiH_2 –(48-x)AlxAg (x=0, 2 and 4 at. %) produced TiH₂(Al) solid solution, L1₂-TiAl₃ phase and an amorphous phase, as compared with a somewhat crystalline mixture of Al and TiH₂ obtained when using lower-energy milling conditions, i.e., 200rpm for 50h. However, the higher milling speed used caused a higher degree of contamination. Differential thermal analysis showed that a TiAl phase could be formed at temperatures as low as 705°C-720°C.

In the as consolidated and heat-treated condition, HIP at 900°C/150MPa/2h followed by HT at 1200°C for 4h, the present materials showed a more homogeneous microstructure, consisting mainly of γ -TiAl phase for the three compositions. However, the addition of Ag led to the formation of Ag-rich phases, which tended to precipitate at the grain boundaries. The Ag additions caused small or negligible variations in the c/a ratio and in the unit cell volume ca^2 of the γ -TiAl phase.

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