In situ Reaction Influence on Hybrid Aluminum / Titan Aluminide and Alumina Composite Hardness

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Aluminum/titan aluminide and alumina (Al/Al_2O_3+$TiAl_3$) hybrid composites were prepared, based on in situ reaction developing during processing, by powder metallurgy route. The reaction was taking place in situ, during milling and sintering, and provides a clean interface between the reinforcing materials and matrix, influencing in a positive way the hybrid composite hardness. Were varied the sintering time and were tested the hardness for each sample obtained. The hardness increases with a mean value of 29.19% as the reaction completes. These results show an improvement in composite hardness obtained in situ by a simple, interface clean method.

Keywords: Al/Al_2O_3+$TiAl_3$ hybrid composite, in situ, hardness, microstructure, chemical reaction

To improve the energy efficiency of structures, the applications of metal–matrix composites (MMCs) have been greatly increased in the automobile, aerospace and electronic industries due to their lighter weight and greater strength and stiffness over conventional metals and alloys [1]. However, due to the incorporation of particulate and fibrous reinforcements, MMCs usually exhibit lower hardness, ductility and toughness, and thus have a lower damage tolerance in comparison with monolithic metals and alloys [2 – 4], which is an obvious drawback to their practical application.

The first requirement for superior performance of a composite material is the homogeneous distribution of the reinforcing phase. In a particulate reinforced composite any agglomeration of the reinforcement particles deteriorates the mechanical properties. Differences in particles size, densities geometries, flow or development of an electrical charge during mixing all contribute to particle agglomeration. A decrease of the reinforcing particles size brings about an increase in the mechanical strength of the composite but the tendency of particles clustering also increases. In powder metallurgy the matrix and the reinforcement mixing process is the critical step towards a homogeneous distribution of the reinforcement particles throughout the matrix [5]. Another critical step for the processing method chosen by us in order to obtain a hybrid composite aluminum based reinforced with titanium aluminide and alumina is sintering time.

Hybrid composite processing consists in combining the thermodynamic and kinetic space with process variables in order to reach the desired duplex structure [6].

The in situ composite concept was studied for other composite as well. L.Lu&all obtained a composite using in melt chemical reaction to obtain Al-Cu4/TiB_2 [7- 9].

Gil-Jae Lee, [10] et all obtained ultrafine $TiAl_3$ powder and also $TiAl_3$ particles with polygonal shape but in their case the shape was close to spherical. They used a higher temperature for obtaining their composites and different reactants.

Z. H. Cai, D.L Zhang [11] studied the reaction between Al and TiO_2 powders at higher sintering temperatures, 1400 – 1650°C, and studied the compounds TiAlx type. They noticed an increase in density resulting in hardness increasing as well.

The main goal was to determine if the reaction is possible at lower temperature, reducing in this way the energy consumption. These types of energy savings are valuable due to the fact that, in the final product, the costs are reduced.

Experimental part

Processing Al/Al_2O_3+$TiAl_3$ hybrid composite by powder metallurgy results in using the diffusion processes in order to start the reaction between the precursor of the reinforcing materials with aluminum powder and thus, to obtain in situ reinforcing particles.

The powders used in obtaining the hybrid composite were aluminum (99.5%) and titanium dioxide (rutile, 99.6%) powders. We milled the powders in order to obtain (3% alumina + 2%titanium aluminide) aluminum based hybrid composite. The temperature during milling increased during the process ensuring in this way the reaction goes on. The ball mill used, RETSCH type, provide high performance in milling, and we could realize an advanced milling in 3 h.

This advanced milling increased significantly the reaction surface between the matrix and precursor of reinforcement material, rutile. The larger surface reaction improves the reaction development in order to reach the desired composite material. Higher milling energy provides a composite structure with powder particles better defined.

After milling, the powders mixture obtained was pressed in a cylindrical dye, using an axial pressing with 100MPa. The dimension of the cylinder sample obtained was h=17 mm and d=8mm. Three sets of samples were obtained and sintered at 640°C for different sintering times as it is shown in table 1.

Sintering was realized in vacuum with heating and cooling rate of 3°C/min. For all samples the density was measured with standard Archimedes method and XRD diffraction was carried out on the polished surface of the samples using a X'Pert PRO MDP system with Cu α radiation and SEM microscopy using a electron microscope HITACI S 2600N.

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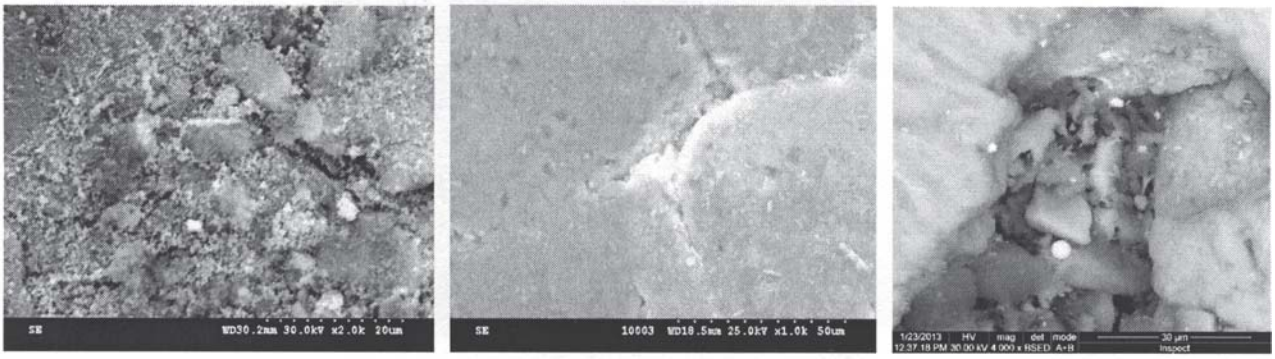
Table 1
SINTERING PROCESS VARIABLES

Sample	Sintering time, min	Sintering temperature °C
A	20	
B	40	640
C	60	



a b c

Fig. 1. SEM images obtained after sintering the samples for different periods of time at 640°C: a. Sample A sintered for 20 min; b. Sample B sintered for 40 min; c. Sample C sintered for 60 min

Results and discussions

The microstructures of the samples obtained are shown in figure 1. For this paper one representative microstructure for each group of samples denoted as in table 1 was chosen.

The microstructures reveal the fact that the main phase is aluminum and the compounds formed during milling are based on titanium and aluminum. The micro-structure of sample A (representative for the first sintered parts) reveals pores distributed in $TiAl_3$ phase. For sample B we can observe the alumina particles having light grey color and small needle shape, white color titanium aluminide particles. In figure 1 C the microstructure of the sample reveals also light grey alumina particles and white needle shape titanium aluminide particles. For this last sample was obtained the diffraction pattern shown in figure 2.

The XRD analyses confirmed that the titanium aluminide and alumina compounds were formed during sintering for 60 min at 640°C in the amount of 3% respectively 2%.

The necessary framework was provided by milling the powders in a high power planetary ball mill with alumina balls and containers preventing contamination processes that could appear during ordinary milling in steel containers and steel balls.

The maximum energy evolved during milling determines an increase of the temperature in container and also the grain boundaries increase considerably during milling influencing thus in a positive way the diffusion process.

The reaction control is very important in order to obtain the desired composition. In melt reaction can be difficult to control but the use of milling followed by pressing and

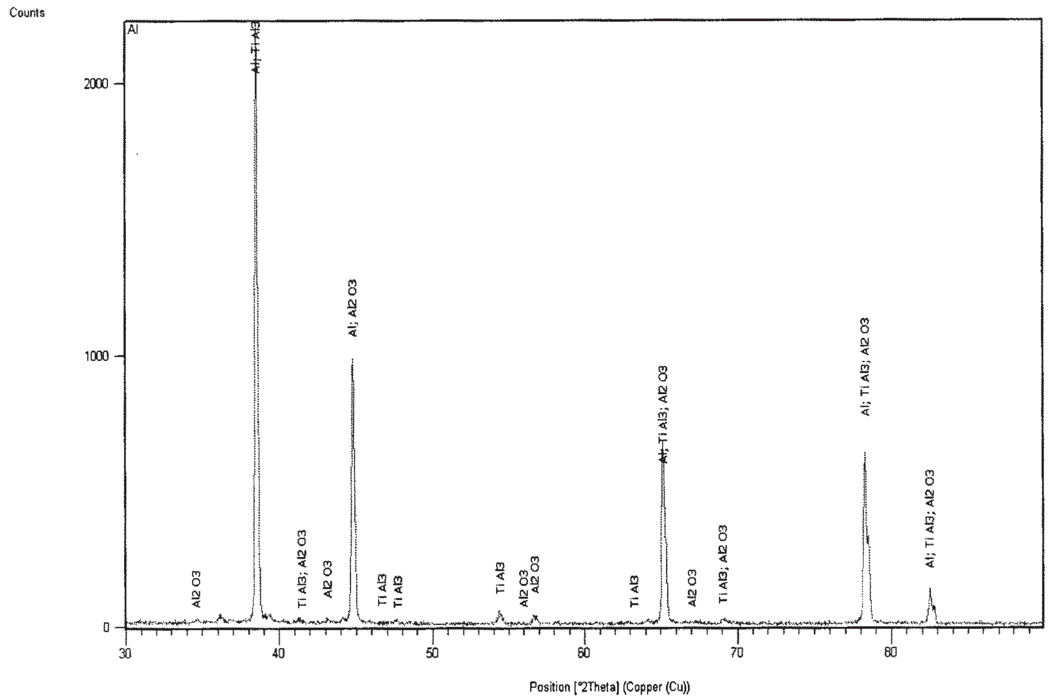


Fig. 2. Diffraction pattern for sample C: (complete reacted; the compounds titanium aluminide and alumina are observed in the sample)

sintering for this specific composite is the most controllable way to obtain the desired composition.

The sintering time was varied in order to study the effect of sintering on the chemical reaction developing in situ in order to see how hardness values are modifying for this type of hybrid composite.

The temperature and time for sintering have an interchangeable role in ensuring the desired densification degree for a sintered part but the intensity of these two factors is different. The sintered time is proportional with the ratio between the mean value for particles radius (usually for calculus the particles are suppose to be spherical) and the diffusion coefficient. The diffusion coefficient is exponential increasing with temperature and thus is the link between these two variables. The sintering time was chosen as listed in the above table and their impact on microstructure and hardness for hybrid aluminum/titanium aluminide and alumina in situ composite was studied.

From the thermodynamic point of view at 600°C the reaction is:

$$3TiO_2 + 13Al = 2Al_2O_3 + 3TiAl_3 \quad (1)$$

and Gibbs free energy has a value of -819.895kJ/mol which is sufficient for the reaction to go in the desired direction. In the titanium – aluminum system the phases titanium aluminide has Gibbs free energy, at the same temperature 600°C, has a value of -29,07kJ/mol indicating stability in the system. The reaction taking place in the composite material during sintering has self propagating character and auto ignition character developing by diffusion and adsorption: $TiO_{2gs} + Al_s$ (diffusion) $\rightarrow TiO_2 . Al$ (adsorption) $\rightarrow Me_2O_3 + Ti$ (intermediary reaction)$\rightarrow Al . Me_2O_3$ (diffusion) $\rightarrow Al_2O_3 + TiAl_3 + Al$ (final reaction) [12].

The reaction starts during milling the powders. The reaction efficiency is improved by the major increase of the grain boundaries due to milling. After this the reaction is controlled due to the sintering temperature and time. Usually the metallic cathions and oxygen diffusion through the reacted layers of the materials rates slowly than the reducer diffusion, adsorption, and effective chemical reaction and desorption of the reaction products. The final reaction products of the reaction between rutile and aluminum are alumina and titanium aluminide dispersed in the bulk aluminum.

$Al/(TiAl_3+Al_2O_3)$ hybrid composite (sample C) is fully reacted and has more homogeneous reinforcement materials distribution in aluminum matrix in comparison with sample A and sample B, due to the exothermic reaction detected during milling and sintering. The sintering time had a significant influence on the reaction development during composite obtaining. After the experiments we observed that only after 60 min of sintering at 640°C the composite was fully reacted and we obtained the best reinforcement materials distribution.

The theoretical density of the samples was calculated using equation (2):

$$\rho = \%Al * 2.71 + \%Al_2O_3 * 3.95 + \%TiAl_3 * 4.1 \ [g/cm^3] \quad (2)$$

The value obtained was ρ_{th}=2.7685g/cm^3. The relative density calculated as the ratio between the measured by classical Archimedes method density and theoretical density is shown in figure 3.

Were measured the HB hardness using a classical method for the samples and drew graphs for the results obtained. These graphs are shown in figure 4.

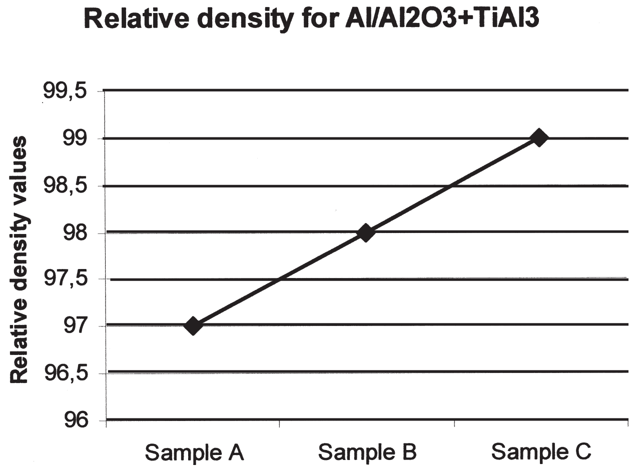


Fig. 3. Variation of relative density for samples A, B and C

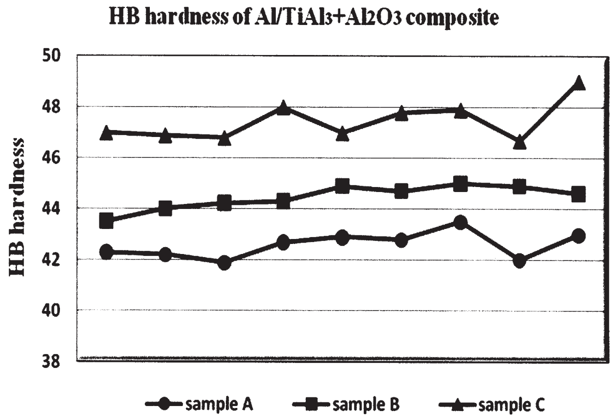


Fig. 4. Average values for HB hardness for samples A, B, C $Al/Al_{32}O_3$ + $TiAl_3$ hybrid composite

The sintering time has a high influence on the reaction (1). The first set of sample denoted with A – hybrid composite $Al/(TiAl_3+Al_2O_3)$ is not fully reacted. Thus, a small amount of alumina particles is formed and the hardness is obviously increased in comparison with simple aluminum but with increasing the sintering time we obtained better results. The complete sintering process proved to be after 60 min and the final $Al/(TiAl_3+Al_2O_3)$ composite denoted with C has the best structure. This final composite also presents the highest HB hardness values proving the fact that the alumina particles present in the final composite highly influence the HB hardness value.

Conclusions

The best hardness values were obtained for the sample C, the fully reacted composite. But the hardness value was highly improved, in comparison with simple Al hardness from the first composite, sintered for 20 min. The hardness value increased with 26.6% for sample A and with 32% for sample C.

A hybrid composite, aluminum / titanium aluminide +alumina, using a simple and efficient in situ method, by powder metallurgy technique was obtained. Variation of sintering time for this composite was realized in order to obtain a significant improvement for hardness values and it was observed, after experiments that the best hardness value, 49.9HB was obtained for sample C, hybrid composite aluminum based reinforced with $TiAl_3$ and Al_2O_3 sintered for 60 min at 640°C.

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