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The effect of TiB_2 content on the properties of AA6005/TiB_2 nanocomposites fabricated by mechanical alloying method

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ABSTRACT

An A6005 aluminium alloy composite reinforced with different contents of titanium boride particles (2.5, 5 and 10 wt%) was produced by a mechanical alloying (MA) route. First, the aluminium alloy and titanium boride powders were blended by MA at different milling times, from 1 to 10 h. The samples obtained after MA processing were microstructurally and mechanically characterised by OM, SEM, TEM, LDS, XRD and micro-hardness tests. The optimum size distribution and suitable mechanical properties were obtained with 5 or 10 wt% of titanium boride particles after 8 h of MA, when the steady state is reached. Hot extrusion was employed as a consolidation process. An extruded sample of powders with a 5 wt% reinforcement content that was MA for 8 h was characterised by TEM, FE-SEM and nanoindentation tests. The results show a good distribution of the nano-reinforcement within the aluminium matrix. Nano-indentation test shows an increment in hardness values from 2.6 GPa for the reference extrusion of A6005 powders without MA and reinforcement to 3.3 GPa for the A6005 extrusion with 5 wt% TiB_2 and MA for 8 h.

1. Introduction

The properties, such as thermal stability, high strength and specific modulus, shown by metal matrix composite materials make them interesting for structural elements in aerospace applications and the transport industry [1,2]. Most common particles employed as reinforcements for an aluminium matrix are normally ceramics, including silicon carbide (SiC), alumina (Al_2O_3), titanium carbide (TiC) and titanium boride (TiB_2) [3–7]. Particles are used due to their high versatility regarding the manufacturing process and semi-isotropic properties compared with fibre reinforcements. These composites also present high strength, stiffness, creep and wear resistance, and in addition, good thermal and electrical conductivity. However, ductility is always reduced with reinforcement addition, as well as toughness.

Among all the particles commonly employed as reinforcements, titanium boride is particularly attractive because it combines a high elastic modulus (565 GPa), strength, hardness (25 GPa) and high thermal conductivity (96 W/m·K) [8,9]. Also, it has an elevated melting point (2980 °C) and excellent chemical stability. In addition, it is compatible with all aluminium alloys and does not react with them at low temperatures. For this type of reinforcement, interfacial fragile product formation between the matrix and reinforcement is avoidable [10]. Moreover, in addition to its low cost and optimal specific properties (2.7 g/cm^3), the A6005 aluminium alloy can be a perfect candidate as a matrix due to its high corrosion resistance, excellent response to superficial requirements and good capacity to be extruded and welded.

All of these properties can be improved with matrix and reinforcement grain size reductions [11–13]. Reinforcement agglomeration in nanocomposites is a key issue that needs to be solved in order to benefit the strength and ductility increase associated with the decrease in reinforcement size. It has been reported that the strength of aluminium composites can be improved by ~20% when decreasing the reinforcement size from micrometric to nanometric [14].

Even though the main commercial method to produce alloyed metallic powders has been atomisation, in recent years, coinciding with the development of metal matrix composite materials, new processes based on milling the separated alloy elements are now considered good methods to obtain both alloys that are difficult to process by other methods and composite powders. Of these, one of the most effective and interesting techniques is mechanical alloying (MA) [15–17]. MA has been demonstrated to be the most favourable technique to obtain pre-alloyed powders, due to the possibility of achieving compositions, properties and reinforcement distributions difficult to obtain by other methods, including atomisation. MA also eliminates clustering problems for several nanocomposites [1,18–21]. MA leads to a uniform distribution of the reinforcement, as well as inducing a significant grain size reduction, also beneficial for mechanical properties. Furthermore, the reinforcing phase helps to maintain the submicron grain size obtained from milling by pinning grain boundaries during subsequent processes, such as extrusion. In addition, MA is not performed at high temperature, which avoids problems during manufacturing and reduces costs. It is a simple process but has many

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parameters that must be controlled, including the process control agent, speed, ball-to-powder rate, ball diameters and the operational time [3,16,22–24]. Powders are mixed in a mill through high energy collisions, involving different stages during the process, such as plastic deformation, solid-state welding and fracturing of the particles [25–27]. Powders are welded and fractured many times, and small particle sizes and a homogenous distribution can be obtained until achieving the steady-state equilibrium. In addition, ductile metal powders, such as aluminium, are prone to adhere on the milling media during the milling process. For this reason, to decrease unwanted adhesion, a small amount of process control agent is generally used [28–30].

Although many reports are available regarding the milling of composite powders, microstructural and morphological changes of aluminium reinforced with titanium boride nanoparticles have not been sufficiently studied. The main aim of this research is to evaluate the effect of different nanometric TiB_2 particle contents and the optimum milling time to produce very fine grained compounds by MA. This goal can be achieved through composite material characterisation, by studying the mechanical, microstructural and morphological changes and comparing the effect of reinforcement nanoparticles and MA in the extruded product.

2. Experimental materials and methods

2.1. Experimental procedure

A6005 aluminium powders were used as the matrix with an average initial particle size before MA of 30.9 μm. The nominal composition is shown in Table 1. These data were provided by the manufacturer, Ecka Granules Co. Titanium boride powders were employed as reinforcements with a size between 30 and 50 nm (American Elements Co.). MA was carried out by mixing aluminium powders with different volume fractions of titanium boride nanoparticles (2.5, 5 and 10 wt%) with a horizontal attritor mill (Simoloyer CM01), in AIMEN Technological Centre. The ball-to-powder weight ratio was 10:1 and the 100Cr6 steel ball diameter was 5 mm. In addition to A6005 powders and reinforcement particles, 3 wt% of methanol was added as the process control agent (PCA) due to its volatility and low toxicity. The total charge of the powders together with the PCA was 200 g, and the capacity of the processing chamber was 2 l. An argon atmosphere was employed to avoid oxidation of the aluminium powders during milling. To avoid powder overheating, the mill worked in a cyclical operation mode and stops of 3 min every 15 min were performed (three cycles). Each cycle was 5 min long (4 min at 500 rpm and 1 min at 300 rpm). These parameters were selected based in previous studies [31] and trials made by AIMEN, changing the operation modes (continuous, cyclic or continuous-cyclic). This method avoids sticking and agglomerations of the reinforcement. A small amount of milled powders (less than 5 g) was collected every 60 min for testing up to 10 h of milling, except for samples with 10 wt% reinforcement, which were tested only up to 8 h. Knowing the hardness values obtained at 7 and 8 h for these samples, it would not be convenient to increase the hardness values further to carry out a posterior extrusion.

X-ray diffraction (XRD) was used to determine any structural changes and crystal size evolution in each sample. A Panalytical diffractometer was employed using monochromatic $K_{\alpha}Cu$ (1.54056 Å) as the radiation source with 45 kV and 40 mA. Diffraction patterns were recorded in an angular interval of 5–90°, with the step of $\Delta 2\theta = 0.05°$ and time per step of 1 s. Laser diffraction spectroscopy (LDS) was used to analyse the particle size distribution, by employing a Mastersizer 2000. Samples were cold-mounted in conductive resin and polished with 3 and 1 μm diamond pastes for microstructural observation and micro-hardness measurements. The microstructure was revealed by attack with Keller's reagent and studied with a LEICA/DMR optical microscope, a Hitachi S3400N scanning electron microscope and a Philips Nova NanoSEM FEI 230. The nanoparticle dispersion within the matrix was studied using a Philips Tecnai 20–200 kV transmission electron microscope (TEM). For TEM powder preparation, a suspension in acetone was prepared and held for 5 min in ultrasound. Finally, a drop of the suspension was deposited on a copper grid and allowed to dry. Hardness was measured with a Shimadzu HMV-2 micro-hardness indenter, applying a load of 10 g ($HV_{0.01}$) for 15 s over the particle transversal section, ensuring that the load was sufficient to obtain indents much smaller than the powder particles. To obtain high precision hardness values, 16 measurements were performed for each sample and with Grubbs test outliers were discarded from the population.

Table 1
Chemical composition of A6005 aluminium alloy powders (weight percent).

Al	Si	Mg	Fe	Cu	Mn	Cr	Zn	Ti
Bal.	0.88	0.57	0.18	0.11	0.13	0.01	0.11	0.10

Hot extrusion was chosen as the consolidation process. A6005 powders reinforced with 5 wt% titanium boride and mechanically alloyed for 8 h were selected for extrusion and characterisation. The powders were cold compacted previously at 300 MPa in a cylindrical die and then were preheated for 30 min at 500 °C both to eliminate the process control agent and to favour the diffusion processes between powders. Hot extrusion was carried out in CENIM-CSIC, employing a horizontal extruder at 500 °C with a load of 1364 MPa and a ram speed of 2 mm/s. The die shape was rectangular with a die angle of 90°. The extruded bar had a rectangular section of 40 × 3 mm.

The extruded sample was characterised by XRD, SEM, FE-SEM and TEM. Nano-indentation tests were carried out to observe the effect of MA and reinforcement addition on the mechanical properties. FE-SEM sample was prepared by employing an extruded section of 10 × 10 mm. This sample was polished up to 1 μm with diamond paste, and subsequently, an ionic polishing with argon was performed. The TEM sample preparation was carried out by preparing a thin sheet from the extruded sample with a thickness of 50 μm polished up to 1 μm with diamond paste. It was subsequently cut with an ultrasonic cutter to obtain a thin sample with a diameter of 3 mm. Then, this sample was introduced to an ionic slimmer to obtain a thickness inferior to 20 nm. Nano-indentation tests were conducted using a MTS Nano indenter XP equipped with a Berkovich diamond indenter tip, employing a continuous stiffness measurement module. The same sample employed for FE-SEM characterisation was used. The depth of the nano-indentations was 500 nm. Several indentations on randomly selected sites were performed in order to obtain similar repeatable load-displacement and hardness curves from the experiment.

2.2. Base materials characterisation

The titanium boride nanoparticle size, morphology and composition were analysed before milling. Most nanoparticles were nearly spherical with a size between 20 and 60 nm (Fig. 1(a)), determined by conducting a total of 50 measurements over different FE-SEM micrographs. The main problem was the presence of agglomerates from 1 to 5 μm. for this reason, in order to improve composite properties, it was necessary to eliminate these clusters through MA processing. Neck formation between particles was noticed at higher magnification by TEM, as shown in Fig. 1(b). These necks may have formed during the manufacturing processing by atomic diffusion between powder surfaces during particles growth. The nano-reinforcement composition was analysed by XRD, showing two main phases, one of titanium monoboride (TiB, ICDD 00-006-0641) and other one of titanium diboride (TiB_2, ICDD 00-035-0741), seen in Fig. 1(c). The TiB characteristic peaks are much more intense than the TiB_2 peaks, meaning that TiB is the majority phase. This has been confirmed through electron diffraction analysis performed over a particle cluster, where all the diffraction rings corresponded with titanium boride crystals (Fig. 1(d)).