Mechanical and Microstructural Response of an Aluminum Nanocomposite Reinforced with Carbon-Based Particles

José Manuel Mendoza-Duarte*, Ivanovich Estrada-Gueb,*+†, Francisco Carlos Robles-Hernández‡, Caleb Carreño-Gallardo*, Claudia López-Meléndez*, Roberto Martínez-Sánchez*

*Centro de Investigación en Materiales Avanzados – CIMAV, Laboratorio Nacional de Nanotecnología, Miguel de Cervantes, No. 120, C.P. 31136, Chihuahua, Mexico
†Department of Mechanical Engineering Technology, University of Houston, Houston, TX 77204-4020, USA
‡Universidad La Salle Chihuahua, Pról. Lomas de Majalca, No. 11201, CP 31020, Chihuahua, Mexico

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The present work deals with the study of some aluminum (Al) composites reinforced with metallized-graphite (MG) particles prepared by mechanical milling and powder metallurgy routes. Density, morphology evolution and mechanical performance of composites were investigated as a function of MG concentration and milling time. The as-milled powders were characterized by X-ray diffraction and optical/electron microscopy; meanwhile, the mechanical testing was carried out on cylindrical specimens prepared from powders by powder metallurgy. Evidence reveals that high-energy ball milling induce a homogeneous dispersion of graphite nanoparticles in the Al matrix; this is related to an enhancement of hardness and strength response of studied composites. The composite sample with 0.5% MG addition (in weight) reached an increase of 40% on hardness and 50% on strength (compared with pure Al sample); nevertheless an adverse effect was observed with longer milling and/or higher MG concentration.

Keywords: composites, high-energy ball milling, powder metallurgy

1. Introduction

Efforts have been made to development new aluminum (Al) based materials for aerospace and aeronautical applications. Some of the advantages offered on those new Al-base components include: better wear resistance, strength to rupture1-4, modulus5,6, thermal stability7, among others. The aim of a composite material is to get a spectrum of properties that cannot be obtained by any of the constituent alone. The engineering to design a composite aims to achieve properties that are superior to those observed in castings or forged products8,9. Metal matrix composites (MMC’s) are fabricated by different methods such as: powder metallurgy10, spray atomization, co-deposition, plasma spraying, stir casting1-4 and squeeze casting2, where the processing method has a strong influence on the final properties of the composites (e.g. mechanical, tribological, etc.)11,12. Composites manufactured by the casting route6,8,18 are usually challenging due to the different nature of the reinforcement that may have poor wettability and agglomeration problems13. Some reinforcements are highly reactive particularly at high temperature, which induce unwanted reactions between components14. As a result this can affect the strength of final composite.

On the other hand, powder metallurgy reduces segregation, porosity, process temperature, grain size8, recrystallization rate2 and improves homogeneity of final products15. The powder metallurgy products can be consolidated by hot extrusion or sintering10,11. Fiber or particulate graphite is recognized by their high strength and low density16. This makes this type of reinforcements attractive in the manufacturing of MMC’s, particularly Al-matrix composites, due to its low density, high workability and increased properties17.

A major goal of this work is to show that we have been identified a methodology to improve bonding between particles, which in turn, minimize porosity and prevent undesirable chemical reactions8 that is accomplished by mechanical milling (MM) resulting an high homogeneity and grain size refining (100 nm or less)18-20. Experience has shown that milling of Al and graphite is not the right processing method21. In fact, some authors have used copper, silicon, magnesium and nickel-coated graphite as a ways to improve diffusion and bonding with the Al matrix: In the case of nickel (Ni) addition, it serves as a stronger overcoat of the graphite particles, but Ni coating reacts with Al forming brittle NiAl intermetalics at the interface, reducing significantly the toughness of the composites22. On the other hand, copper was used to improve surface wettability and interface bonding between Al and graphite particulate, using a wet cementation process, unfortunately with the following drawbacks: agitating produced an uneven copper-coat on the surface of graphite particulates, great accumulation of particles at the rim of the reaction box due centrifugal force action and unwanted chemical reactions23. Here we show an alternative mechanical method to improve the wettability of Al-graphite couple without the above disadvantages.

*e-mail: ivanovich.estrada@cimav.edu.mx
The mechanical and microstructural characterization of some Al matrix composites reinforced with copper coated graphite is described. Our method is unique in the sense that we discovered a route to cover copper with graphite giving quite promising results along with the fact that it is cost effective, fast and in solid state.

2. Material and Methods

Preparation method is divided into two parts: a) synthesis of the reinforcement copper coated graphite (metallized graphite, MG), and b) Formulation of Al-MG composites. Raw materials are: graphite (99.9% purity and -850 +200 μm, in size), copper (99.5% -100 μm) and aluminum (99.5% -45 μm) in powder form.

2.1. MG preparation

A weighted mixture of graphite and metallic copper with the ideal composition tested before of 15 at. % Cu was processed in a high-energy SPEX 8000M mill. The milling media was hardened steel vial and balls. The balls to powder ratio was 5 to 1 (in weight). Milling was accomplished after a period of 4h, under an inert argon atmosphere.

2.2. Composite preparation

The Al-MG composites were prepared by milling mixtures of Al powder and MG particles with the following concentrations: 0, 0.5 and 1.0 (in weight %). This second process was carried out in a ZOZ-CM01 Simoloyer device for times between 1 to 8 h. Methanol was added to as a control agent (0.8 wt. %).

2.3. Characterizations and Testing

Scanning electron microscopy (SEM) characterization was conducted on a JEOL-JSM 7201F SEM/EDS. X-ray diffraction (XRD) analyses were carried out using a PAN analytical X’pert PRO diffractometer using a CuKα (λ = 1.5405 Å). The density of the sintered specimens was calculated according to Archimedes’ method. Cold-consolidated samples were obtained by room temperature pressing (950 MPa) in a cylindrical die followed by sintering at 823K for 3h under an inert Ar atmosphere. Hardness tests were performed following the ASTM E18 standard using a Wilson Rockwell hardness meter (model C503 R) using HRF scale (1/16” ball indenter and 60 kgf of load) and compression tests were done in an Instron universal machine (model 4468); both test were achieved at room temperature (20°C). Using the experimental strain stress plot by triplicate, the mechanical behavior of samples was determined as the strength at the elastic limit.

3. Results and Discussion

3.1. Morphological analysis

The initial particles (Figure 1a) present a spheroidal morphology characteristic of atomized metal powders. The particles milled for 4h (Figure 1b) are large due to a particle-particle weld process, forming big agglomerates. With further milling, the fracture of agglomerates (due hardening by cold working) reduces the particle size of the sample (Figure 1c). The Figure 2 shows the internal characteristics of the particles (cross section), finding a typical convoluted lamellar morphology at short milling times (Figs. 2a and 2c), after 8h of milling a more homogeneous structure with absence of coarser layers is evident (Figures 2b and 2d). As a general result, the composite particles become more homogeneous and isotropic with the milling process. Once the powders are homogeneous in size, further milling can refine the layered structure as Figures 2b and 2d show. On the other hand, the Al-0.5%MG composite does not form large particles even after 4h of milling (Figure 1e), with 8h of milling is noticeable that particles get a flat morphology (Figure 1f). We attribute those changes to a modification of the weld and fracture equilibrium induced by the presence of the MG particles. The small particles (white arrows) are identified as the reinforcement phase composed by copper and carbon (Figure 2c and 2d). MG particles were homogeneously distributed by trapping them between the ductile lamellae and surrounding by the Al matrix during the milling process (further milling means higher homogeneity), as was reported elsewhere. Also, the lamellar microstructure, homogeneity and MG distribution in the Al-1.0%MG composite was improved after 8h of milling. Figure 3a shows a close-up of a single MG particle, where is possible to observe that this “single” particle is in fact composed by a group of nanometric agglomerates. Through energy dispersive spectroscopy (EDS) elemental analyses we could identify the presence of carbon and copper on the matrix (Figures 3a and 3b). Figure 3c exhibits a transmission electron microscopy (TEM) micrograph of a particle showing its chemical composition of copper and carbon. Apparently, this thin layer of carbon is enough to maintain the copper particles insoluble during the sintering process; otherwise they would be easily dissolved due to the high solubility of copper in aluminum particularly at high temperature.

3.2. X-Ray diffraction

Figure 4a shows the XRD pattern of the Al-0.5%MG composites in powder form, processed at different milling times. The presence of the MG particles is not detected by XRD due to their low concentration. The intensity of the Al reflections decreases with milling time, milling of ductile Al particles induces significant microstructural changes such as severe plastic deformation accompanied by strain
**Figure 1.** SEM-SE micrographs of sample powders: Al and Al-0.5%MG composite at different milling times: a) 0h, b-e) 4h, c-f) 8h and d) 2h.

**Figure 2.** Cross section optical images of Al milled samples a) 1h and b) 8h. SEM-BSE micrographs of Al-1.0%MG composites milled c) 1h and d) 8h, white bright dots are the MG particles embedded in the metal matrix.
hardening and grain refining. The change in lattice parameter is measured by the distortion and shift of characteristics Al peaks. Variations in the Al (111) reflection are observed in Figure 4 along with the grain size determination as a function of milling time and MG addition. The absence of shift suggests a limited presence of dissolved Cu into the Al matrix by milling. In the SEM micrographs (Figures 3a and 3b) the MG particles remain distributed within the Al matrix and they do not dissolve. In Figure 4b are given the results of grain size based on the reflection (111) for Al. This calculations were conducted using the Williamson-Hall method. It is observed a clear reduction of the grain size even for short milling times (1h). After this sharp reduction in grain size, it stays almost constant up to 8h of milling; final grain sizes are about 35 nm for further milled samples. The presence of MG particles does not affect the grain size evolution due these possible causes: There is a critical concentration of particles of second phase that allow a grain size reduction, in our study 0.5 and 1.0% (in weight) apparently is not enough to induce further grain refining. If we reach a minimum critical size, any addition of particles or further milling, induce an opposite behavior (grain growth).

3.3. Density

This parameter is measured as a general approach to assess the soundness of the mechanical performance of specimens. Figure 5 shows the effect of milling time on density of the composite samples. It is of interest that denser products are associated with lower milling
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Figure 4. a) XRD patterns of Al+0.5%MG composite after milling time with a close up on aluminum (111) main diffraction peak and b) composites grain measures calculated from Al (111) plane.

Figure 5. Density variation of sintered samples as a function of the milling time and MG addition.

Figure 6. Mechanical response of composites: a) Hardness and b) strength as a function of milling time.

These samples have a broad particle size distribution, which allows them to become denser due to a high interstitial occupancy by the smaller particles in the vacant spaces. Contrary, samples with 4h of milling present an important decrease in density caused essentially by poor packing of particles due their increased hardness by severe deformation27, this behavior has been previously reported28. In addition, the presence of MG particles also affects the densification, because the modification of particle size distribution due increased small particles generation. The densification in the studied samples reach values above 95% with respect to the theoretical. The exceptions are samples Al-4h, Al-8h and Al-0.50%MG-8h. Although a stable state was reached with the composites after 8h of milling, this does not necessarily mean that densification level increases too. On the contrary, it is evident that the
density is negatively affected when the powder particles are severely deformed by further milling resulting in an increase of work hardening. Because, the particles with high levels of plastic deformation do not compact efficiently (due their reduced ductility), the samples reach low-density values due high porosity derived from poor compaction of powder particles as mentioned above.

3.4. Mechanical Testing

Sintered samples prepared from mixed powders (Al-0h, Al-0.5%MG-0h and Al-1.0%MG-0h) present lower hardness when are compared with their milled counterparts. In Figures 6a and 6b can be observed that both: milling time and MG additions have a direct influence on the mechanical properties of composites. For instance the hardness increased exponentially from 0 HRB in the raw samples to 28 (Al), 46 (Al-0.5%MG) and 36 (Al-1.0%MG) after just 1h of milling, as the first part of the plot shows (Figure 6a). With 2h of milling, we reach the optimum processing time, where the mechanical properties are maximized for Al (52) and Al-1.0%MG (64) composite. Meanwhile the composite prepared with the composition Al-0.5%MG with 4h of milling reaches a value of 73 HRB (the highest hardness value of studied samples). The Figure 6b presents a graph of the strength of the composites as a function of milling time. In the figure can be noticed that the mechanical performance of the prepared composites is related with hardness and strength, show a similar behavior (dotted lines): values ranging from a minimum at 0h (un-milled samples), passing for an optimum (2 or 4h) showing a fall of the properties with 8h of milling. This pattern can be attributed to grain size reduction, increase of porosity, poor bonding between particles, etc. For this study, the highest strength in Al sample is 15 MPa and 17 MPa in the Al-0.50%MG milled for 4h having a hardness of 73 HRB and an elastic limit of 20.6 MPa. Further possessing and higher MG concentration cause a reduction of 43% on hardness and 50% on strength with respect to the AI-0.5%MG. For Al (52 HRB/14.9 MPa) and Al-1wt%MG (64 HRB/17.1 MPa) best mechanical properties were found in the samples milled for 2h.

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6. References

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