

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

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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 rupture<sup>1-4</sup>, modulus<sup>5,6</sup>, thermal stability<sup>7</sup>, 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 products<sup>8,9</sup>. Metal matrix composites (MMC's) are fabricated by different methods such as: powder metallurgy<sup>10</sup>, spray atomization, co-deposition, plasma spraying, stir casting<sup>1-4</sup> and squeeze casting<sup>5</sup>, where the processing method has a strong influence on the final properties of the composites (e.g. mechanical, tribological, etc.)<sup>11,12</sup>. Composites manufactured by the casting route<sup>5,6,8</sup> are usually challenging due to the different nature of the reinforcement that may have poor wettability and agglomeration problems<sup>13</sup>. Some reinforcements are highly reactive particularly at high temperature, which induce unwanted reactions between components<sup>14</sup>. As a result this can affect the strength of final composite.

On the other hand, powder metallurgy reduces segregation, porosity, process temperature, grain size<sup>6</sup>, recrystallization rate<sup>5</sup> and improves homogeneity of final products<sup>15</sup>. The powder metallurgy products can be consolidated by hot extrusion or

sintering<sup>10,11</sup>. Fiber or particulate graphite is recognized by their high strength and low density<sup>16</sup>. 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 properties<sup>17</sup>.

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 reactions<sup>8</sup> that is accomplished by mechanical milling (MM) resulting an high homogeneity and grain size refining (100 nm or less)<sup>18-20</sup>. Experience has shown that milling of Al and graphite is not the right processing method<sup>21</sup>. 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 intermetallics at the interface, reducing significantly the toughness of the composites<sup>22</sup>. 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 reactions<sup>23</sup>. Here we show an alternative mechanical method to improve the wettability of Al-graphite couple without the above disadvantages.

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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  $\mu\text{m}$ , in size), copper (99.5% -100  $\mu\text{m}$ ) and aluminum (99.5% -45  $\mu\text{m}$ ) 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<sup>24</sup> 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 CuK $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ). 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

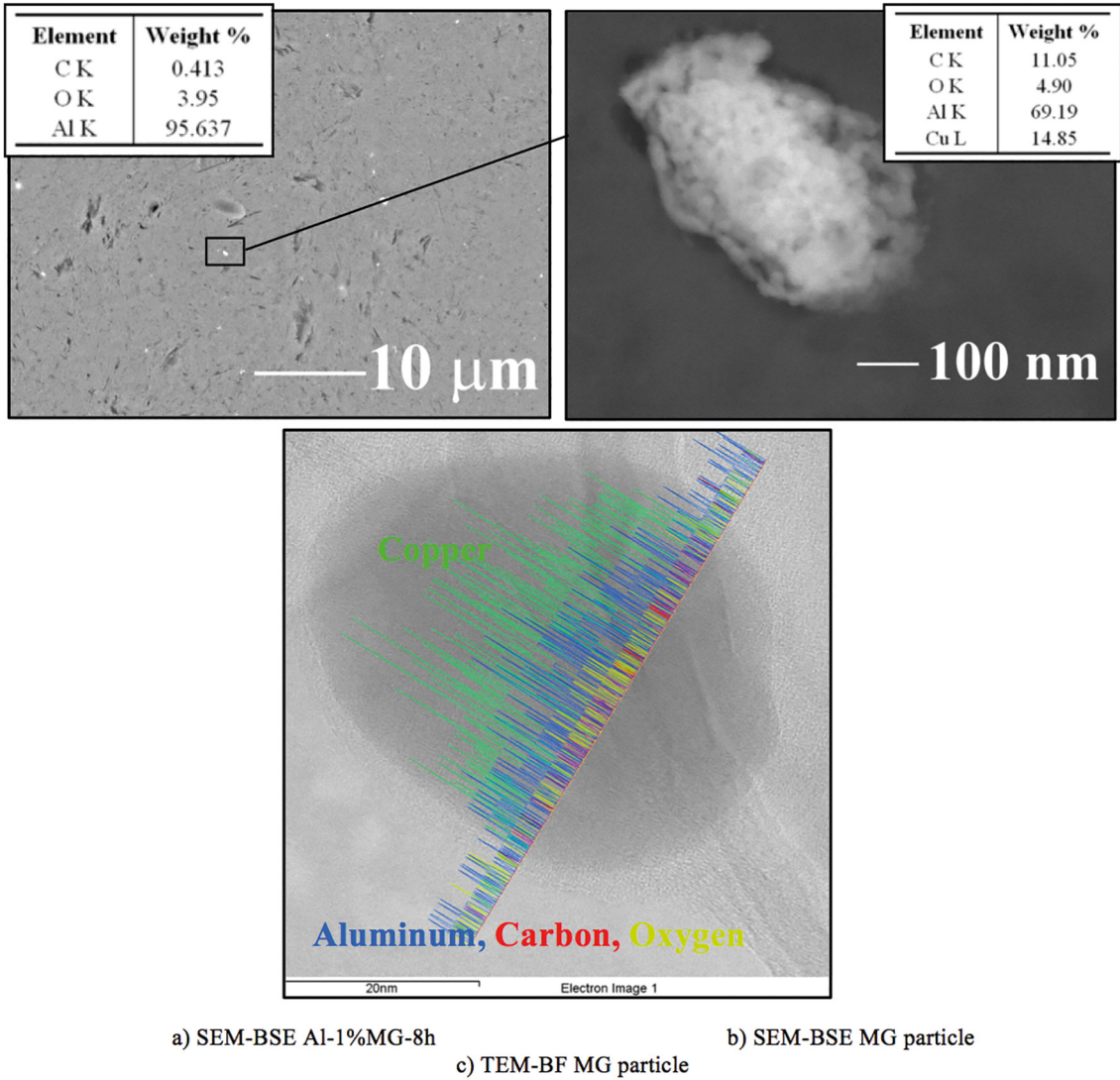
### 3.1. Morphological analysis

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<sup>16</sup>. 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<sup>25</sup>.

### 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 3.** a) SEM-BSE micrograph of Al-1%MG-8h composite after sintering process, the tabulated data shows the general composition of composite, b) SEM-BSE image of MG particle with its elemental composition and c) TEM-BF micrograph of a single MG particle showing the chemical distribution of components.

hardening and grain refining. The change in lattice parameter is measured by the distortion and shift of characteristic 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<sup>26</sup>. 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

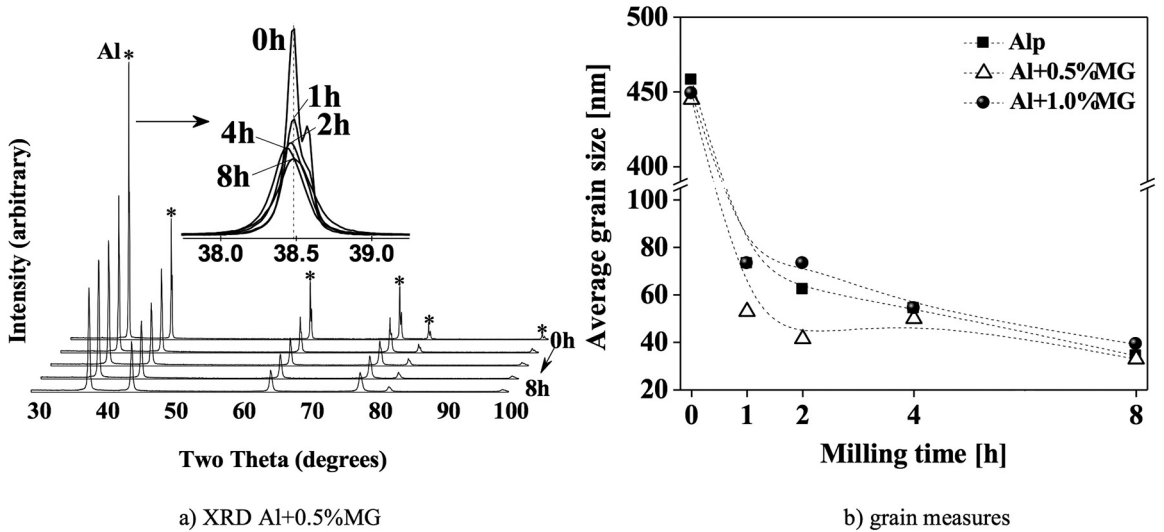


Figure 4. a) XRD patterns of Al+0.5%MG composite after milling time with a close up on aluminum (111) main diffraction peak and b) composites grain measures calculated from Al (111) plane.

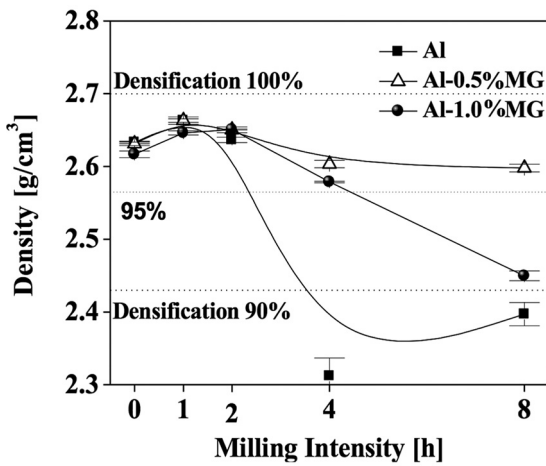


Figure 5. Density variation of sintered samples as a function of the milling time and MG addition.

times ( $< 2$ h). 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 deformation<sup>27</sup>, this behavior has been previously reported<sup>28</sup>. 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

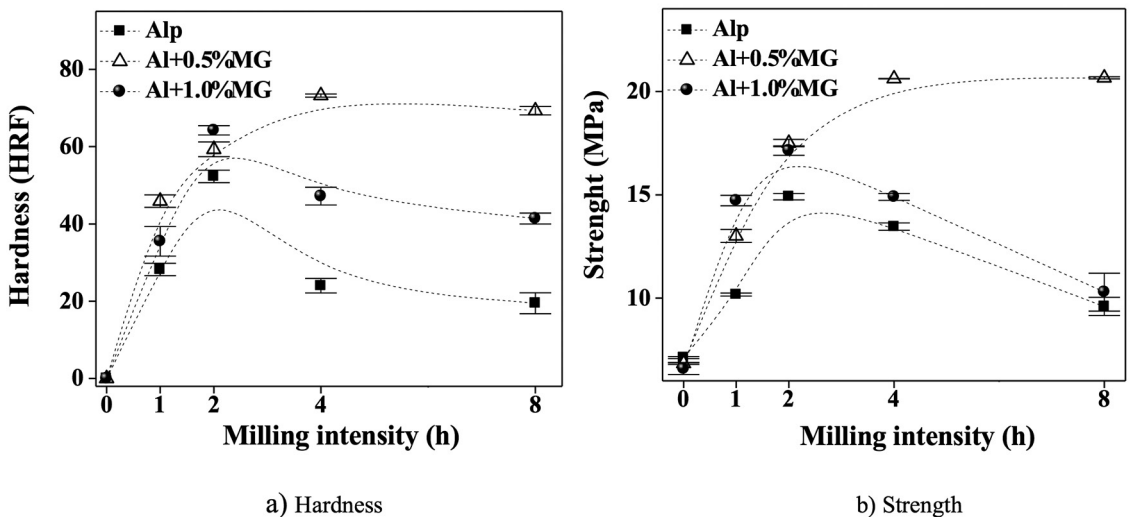


Figure 6. Mechanical response of composites: a) Hardness and b) strength as a function of milling time.

density is negatively affected when the powder particles are severely deformed by further milling resulting 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 HRF 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-1.0%MG composite, in both cases the best mechanical properties were observed in the samples milled for 2 h. On the other hand, the composite Al-0.05%MG presented the highest strength of all (20.6 MPa) with 4 h of milling. This represents a 37 % and a 24 % improvement in strength with respect to pure aluminum and the Al-1.0%MG composite.

## 4. Conclusions

The Al-MG composites produced herein demonstrated that milling improves homogeneity, grain size reduction and strength. The X-ray results show that there is no solid solution between Al and the added reinforcements, which is observed by the lack of shifting of the Al (111) reflection. The SEM studies show the microstructure changes as a function of the milling time and MG particles concentration. The TEM results demonstrated that the reinforcement particles (MG) are core-shell structures where the core is copper and the shell carbon, which prevents the dissolution of copper

by Al; however, this does not prevent the integration of the MG particles in the matrix having clear improvements in mechanical characteristics. The composite with the best mechanical properties is Al-0.50%MG milled for 4h having a hardness of 73 HRF 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 Al-0.5%MG. For Al (52 HRF/14.9 MPa) and Al-1wt%MG the (64 HRF/17.1 MPa) best mechanical properties were found in the samples milled for 2h.

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