Synthesis of Graphite Reinforced Aluminum Nanocomposite by Mechanical Alloying

J. L. Hernández R.¹, J. J. Cruz R.², C. Gómez Y.³, O. Coreño A.⁴ and R. Martínez-Sanchez¹

¹Centro de Investigación en Materiales Avanzados, Laboratorio Nacional de Nanotecnología Miguel de Cervantes 120, C.P. 31109, Chihuahua, Mexico
²Facultad de Ingeniería-Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Sierra Leona 550, Lomas 2ª sección, C.P. 78210, S. L. P., Mexico
³ESIQE-IPN, Av. Instituto Politécnico Nacional s/n, C.P. 07051, Mexico D.F., Mexico
⁴Centro de Investigación en Materiales y Metalurgia, Universidad Autónoma del Estado de Hidalgo, CU carretera Pachuca-Tulancingo km 4.5 C.P. 42184, Hidalgo, Mexico

Aluminum nanocomposite was obtained through mechanical alloying process using elemental powders of aluminum, copper and magnesium of high purity with the aim to obtain the 2024 aluminum alloy composition. Elemental powders and reinforcement particles were milled in a simoloyer mill for different times from 1 to 5 h. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) results indicated that even for milling time of 5h some elemental copper remained in the microstructure and has not been incorporated completely in solid solution into the aluminum lattice. Furthermore, it was not observed formation of any second phase, however when the specimens were subjected to Differential Thermal Analysis (DTA), it was observed in the microstructure the presence of Al₃Cu, Al₆C₃ and some oxide of the type CuO and CuO₂. It was also demonstrated that average crystallite size of milled powders was refined to nanometric level while microhardness values were arising continuously with the milling time and were a maximum in the 2 mass% graphite specimen.

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1. Introduction

Aluminum alloys have a great diversity of applications in many industries because of their relatively low weight, good workability and excellent response to hardening by applying aging heat treatments.¹,² Recently several materials composites have been produced with matrix based in aluminum alloys, such as 2024 alloy which have been reinforced typically with ceramic materials including SiC, Al₃O₃, Be₃C, TiC and TiB₂. These composites have demonstrated to provide a beneficial combination of stiffness, strength, and relatively low density.³,⁴ 2024 Al alloy is one of the most attractive non-ferrous matrix material used particularly in aerospace applications where the relation strength/density of structural components is crucial. Besides, the unique thermal properties of aluminum composites, such as metallic conductivity with coefficients of expansion that can be tailored down to zero, add to its prospects in aerospace, automotive, and military industries. Mechanical alloying techniques have been one of the most promising processes to fabricate aluminum composites due to the homogenous microstructure obtained. Another great advantage for using this technique is that it is possible to obtain a nanocomposite material; it means a material on which the grain or crystallite size has been reduced under 100 nm, being the main cause that arrays of dislocations rearranges and annihilates to form small angle grain boundaries inside of powders, refining in this manner the microstructure.⁵ On the other hand, the advantages of using graphite as reinforcement in aluminum composites have been addressed by Warner et al.⁶ For example the addition of graphite has demonstrated to improve the relation strength/density because of low weight of C. Furthermore, the presence of graphite helped to reduce the wear and abrasive loads that cutting and die tools experimented during machining or stamping. However, when these composites are produced by melt methods, the intermetallic Al₆C₃ precipitates and almost all the benefits mentioned are lost. In this work it have been tried to take the advantages of using a solid state process such as mechanical alloying to produce 2024 Al nanocomposite starting from elemental powders and with graphite as a reinforcement because this route have not been documented in deep.

2. Experimental Procedure

The raw powder materials used were Al, Cu, Mg (99.5% purity and ~325 mesh in size) and graphite microparticles previously milled. The impurities consisted of Mn, Si, Cr, Ti and Zn. The graphite content was 1 and 2 mass%. Each mixture was blended in spex mill without balls for 5 min to obtain an adequate and homogenous mix and then was mechanically alloyed in simoloyer mill ZOZ CM01 for 1, 3 and 5h in an argon atmosphere. Differential Thermal Analysis (DTA) tests were conducted to find phase transformations that could occur when milled powders were subjected to continuous heating. The heating rate was 15°C/min and the sample weight was 0.035 kg. The heating cycle was done until the Al melting. In Table 1 it is shown the average samples composition while in Table 2 nomenclature used is explained. Samples without reinforcement were prepared for comparison purposes. Microstructure observations and chemical analysis were done using a SEM Phillips XL-30 coupled with an Energy Dispersive Spectroscopy (EDS) and a Transmission Electron Microscope.
(TEM) JEM-1230 operated at 100 kV. XRD tests were carried out in a diffractometer Rigaku DMAX-2200, using at 40 kV, 36 mA, and monocromatic radiation of Cu Kα. Average crystallite sizes were obtained from the XRD peaks broadening when the difractograms were refined and analyzed using MAUD software. The structural parameters that were refined by this way were diffractograms background, texture and strain. Iterative refinement finished when the indicators sigma and Rw converged to acceptable values according to Lutterotti et al.7)

### Table 1 Average composition of the Al alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>92.67</td>
</tr>
<tr>
<td>Cr</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>4.26</td>
</tr>
<tr>
<td>Mg</td>
<td>1.49</td>
</tr>
<tr>
<td>Mn</td>
<td>0.59</td>
</tr>
<tr>
<td>Si</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.24</td>
</tr>
</tbody>
</table>

### Table 2 Nomenclature used for milled powders.

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Milling Time (h)</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Without</td>
<td>SR0</td>
<td>SR1</td>
</tr>
<tr>
<td>reinforcement</td>
<td></td>
<td>SR3</td>
</tr>
<tr>
<td>1% Graphite</td>
<td>R1G0</td>
<td>R1G1</td>
</tr>
<tr>
<td>2% Graphite</td>
<td>R2G0</td>
<td>R2G1</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

#### 3.1 Scanning electron microscopy

In micrographs shown in Figs. 1 and 2, aluminum particles can be seen in a light gray color while the white films that are observed inside aluminum particles are copper (Fig. 2(a)). On the other hand, magnesium films have a dark gray appearance and were located also inside of aluminum powders (Fig. 2(c)). The array observed of powder particles is a consequence of continuous cold welding and fracture events that ductile particles experimented when are processed by mechanical alloying.

In a qualitatively way particle size in the non reinforced powders was decreased slightly at higher milling times while in the reinforced ones it was not evident (Figs. 1 and 2). The morphology of the non reinforced powders was equiaxed for 1 h and changed to slight flake-flattened for 5 h, while in the case of the graphite reinforced ones, it seems to be flake-flattened for 1 h and it changed to more equiaxed particles with further milling of 5 h. In the last case it is important to take into account the role that graphite plays during milling. It has been reported by Fognanolo et al.8) that graphite tend to act locally as a process control agent promoting as a consequence that steady state, could be reached in shorter time comparing with non containing graphite powders. According to Aikin et al.9) steady state on mechanical alloying describes the step process on which there is no more reduction in particle size and alloy elements lamellae shows random distribution inside the particle. Graphite particles were documented by EDS and found to appear in a similar mode like alloying elements as thin films inside aluminum particles (Fig. 3). It seemed that graphite was deformed and trapped between Al powders when mechanical alloying process taken place, behavior that is typical in a

![Fig. 1 SEM micrographs for different milling times.](a) (b) without reinforcement. (c), (d) with 2% graphite.}
ductile phase. The signal of Au was of the coating used for avoiding electrical charge.

Lamellas of Cu and Mg shown a more homogenous distribution when milling time was higher. The latter fact could be demonstrated by observing the decrease in the interlaminar spacing between the copper lamellas. Additionally, SEM micrographs evidenced that alloy elements lamellas exhibited preferred orientation in both cases, in the reinforced and nor unreinforced powders.

3.2 X-ray diffraction

Figures 4(a) and (b) shown the XRD pattern of as-milled products. Characteristic reflections from elemental powders (Al, Cu and Mg) were observed for samples without reinforcement and with 2 mass% of graphite. No reflections from graphite were found in the reinforced specimen, it could be because of the content was not enough to enhance XRD peaks intensity and also because the atomic scattering factor...
for graphite is so low.\(^\text{10}\) Also, it is evident that Mg peaks disappeared and the Cu persisted for a 3 h of mechanical alloying.

Figure 5 evidenced that Mg has been incorporated into solid solution because aluminum peak corresponding to (111) shifted clearly its position. In order to confirm this fact, centroid of each peak was obtained and it was found a variation in \(2\theta\) of 0.04°, which translated to lattice parameter, means an increment from 0.4048 nm to 0.4052 nm. As has been stated, the change found in peak position combined with the absence of magnesium peaks for a processing time of 3 h implied that a supersaturated Al solid solution was formed at a 5 h of mechanical alloying. Similar results have been published by Jafari \textit{et al.}\(^\text{11}\) who reported a variation on the lattice parameter of aluminum of 0.0005 nm when a material with similar composition was mechanically alloyed for 5 h and all Mg was incorporated into Al lattice.

On the other hand, it is evident that no intermetallic phases were formed during mechanical alloying in this work. Different results have been documented by Zhou \textit{et al.}\(^\text{12}\), who found that formation of Al\(_4\)C\(_3\) is possible for 60 h of aluminum and graphite powders in a planetary mill.

Another observation that is important to point out is that Al peaks presented slight broadening as the milling time was increased. According to literature\(^\text{13}\) this behavior was caused by two events.

The first one was because of the intense deformation that have been imparted to powders during milling process and the defects generated inside of Al lattice. Second was the decrease of crystallite size that occurred in powders leading to a nanometric sized material formation. Combined effect of these two contributions was clearly visible at higher angles because aluminum peaks (as stated before) were wider. Also, the possible formation of an Al solid solution caused that the diffraction peaks position changed slightly.

In this work it was obtained a microstructural refinement in function of the milling time achieving a minimum value of around of 50 nm corresponding to the Al average crystallite size (Fig. 6(a)). Abdoli \textit{et al.}\(^\text{14}\) have obtained a crystallite size of 66 nm after a mechanical milling for 25 h of pure aluminum reinforced with AlN. Comparing this result with the one obtained in this work, it can be seen that similar refinement was reached with lower milling time.

On the other hand Fig. 6(b) shown continuous increment in powder microhardness values when the milling time was increased. This increment was associated with the powders internal strain ought to the more lattice defects generated in the microstructure. The specimen that contains 2% of graphite reached the higher microhardness values.

### 3.3 Transmission electron microscopy

The micrographs obtained in TEM studies are shown on Figs. 7 and 8. The contrast observed in bright field images shown the general morphology of milled powders and also some regions that appeared in dark contrast, corresponded to microstructural defects such as shear bands, which have been reported to occur during mechanical alloying due to the high deformation rates experienced.\(^\text{15,16}\) Shear bands contained a high dense network of dislocations and preceded the formation of substructure inside of crystals. Different stages of mechanical alloying process have been established by observing these defects and the latter decomposition into low angle boundaries causing the decrease of crystallite size.\(^\text{16}\)

Selected Area Diffraction Patterns (SADP) consisting of spot rings were obtained and together with dark field images helped to found phases present in milled powders and also were useful to describe in a qualitatively way the average crystallite size.

For example on Figs. 7(b) and 8(a), the bright areas on the images corresponded to Aluminum crystallites that were oriented to electron beam and were obtained from the (100)
ring. SADPs evidenced that besides aluminum, there were present some spots corresponding to (200) and (311) copper planes in the case of Fig. 7(a) while in the Fig. 8(a) the (200), (311) and (222) copper planes were identified. In the case of Aluminum, (111), (200), (220) and (222) planes were found in both figures. It is important to remember that copper remained in the microstructure as dispersed particles and have not been incorporated as solid solution into the aluminum lattice, do to the last fact there existed copper signals.

As has been said, dark field images were useful to show that crystallite size of aluminum powders have been reduced to nanometric level for 5 h of milling time in both reinforced and non reinforced powders. This result agreed well with the average sizes obtained by XRD tests reported in the preceding section.

Substructure developed inside aluminum powders are shown in Fig. 9. The network observed in dark gray area consisted of arrays of low angle boundaries that formed when the density of dislocations inside of shear bands reach a limit and then rearranged and annihilated it forming in that way the boundaries mentioned. According to literature, before all shear bands disappeared, powder microhardness is highest and crystallite size is reduced to their minimum value. According to the results obtained in the present work, it is expected that for a milling time of 5 h, the decomposition of shear bands into substructure have not been completed since they were visible in Fig. 7(a) and 8(a). In addition to this, average crystallite size has not reached a constant value and microhardness have not experienced any decrease (Fig. 6).

On the other hand, it has been reported that in systems where melting temperature is low, some recovery phenomena could occur and as a consequence, the reduction in crystallite
size will reach its minimum values. These are smaller compared with high melting point materials. In the same reference the minimum value for Aluminum crystallite size was established to be of approximately 22 nm. Taking this value into account it can be considered that nanocomposite crystallite size in the present work could be decreased even more if the milling time were increased.

3.4 Differential thermal analysis

DTA results for the milled powders with graphite and without it are shown in Fig. 10. These graphs were obtained when the milled powders were subjected to a continuous heating in order to find microstructural changes that could appeared. In order to give a better understanding about the thermal events that DTA curves registered, XRD tests of these annealed powders were done and also included in Fig. 10.

First of all, it could be seen that there were 2 thermal events that appeared during heating this nanocomposite. The first event was an endothermic peak which occurred near to 660°C and which was associated to melting of aluminum as it has been reported elsewhere. Temperatures at which melting was recorded for each curve appeared in Fig. 10(a) and 10(b) at the top-right side. It was found that the tendency of the melting temperature value was to decrease when milling time increased in both compositions, with graphite and without it. It is known from phase diagrams theory that when a solid solution is formed, it has a lower melting point compared with the starting pure elements. As a consequence, the continuous decrease observed in the melting point of composites studied here, validated the assumption that a supersaturated solid solution formation was being formed as milling time increased.

The second event was an exothermic peak that appeared at 550°C in the non reinforced and at 592°C in the reinforced powder. It is assumed that it was due to the incipient CuO and CuO\textsubscript{2} formation in powders that were not mechanically alloyed, while for the milled powders with and without reinforcement this event was absent. In the literature\textsuperscript{20} it has been stated that formation of oxides always generates exothermic peaks in the DTA tests. A deficient protective atmosphere could be the cause that oxide formation was possible to occur in the composite powders studied here.
On the other hand, XRD of these powders evidenced that intermetallic Al$_2$Cu was formed in both compositions with graphite and without it. The absence of elemental copper peaks was evidence that almost all present in milled powders was consumed in the formation of this phase. In a similar mode, in the graphite reinforced powders it was also detected the Al$_4$C$_3$ presence and it seems that the milling time promoted the formation of this phase, because when the milling time increased the peaks intensity were higher.

It is important to remember that milled powders were in a highly reactive state ought to the high deformation experienced during milling and also because of large new surfaces created. Both conditions, combined with temperature, enhanced diffusion between elements and as a consequence, new phases were formed during DTA tests.

4. Conclusions

XRD results shown that Mg peaks disappeared at 3 h of mechanical alloying. Furthermore, Al peaks evidenced a slightly shift in their original position, so it is thought that Mg has been introduced as a solid solution into aluminum lattice, contrary to what happened with copper which for 5 h of mechanical alloying did not incorporate.

SEM observations allowed to conclude that steady state step of mechanical alloying was not achieved at any time in reinforced and non reinforced powders, since the morphology developed was equiaxed with a Cu lamellas oriented preferentially.

It was demonstrated that intermetallics such as Al$_3$C$_4$ and Al$_2$Cu were not able to precipitate during mechanical alloying mainly because of short processing times. However, when milled powders of both compositions were subjected to DTA analysis these phases were formed easily due to the thermal energy input.

High microstructural refinement in the nanometric level was obtained in powders during processing which was clearly evidenced through the values of crystallite size obtained by XRD test and TEM observations. Also, microhardness values helped to conclude that there was not an important amount of recovery phenomena in the milled powders since the microhardness continuously increased as the milling time did.

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REFERENCES