Graphite nanoparticle dispersion in 7075 aluminum alloy by means of mechanical alloying

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Abstract

Dispersion of metallized graphite nanoparticle reinforcements in 7075 aluminum alloy (Al_{7075}) and composites were microstructurally and mechanically characterized. Al_{7075}-based composites were prepared by mechanical alloying in a high energy ball mill. Composites were cold compacted, sintered, and hot extruded in order to obtain samples for mechanical evaluation (hardness and tension). From a microstructural point of view, milling time and graphite concentration had an important effect on the refining sequence and mechanical properties of prepared composites. The results of tensile tests and hardness measurements show a significant increase in the maximum tensile strength and hardness values.

1. Introduction

Aluminum alloys have a wide diversity of industrial applications because of their light weight, high electric conductivity, and corrosion resistance. Generally, they are used more often than any other metal, except steel [1]. But, the use of aluminum and its alloys in certain applications are limited due to their low stiffness, resistance to wear and tear, and low yield strength. Furthermore, industry demands advanced materials and technology for the preparation of these materials, which include aerospace, automotive, and defense applications. The search for new methods and processing techniques for improving certain material properties of these alloys has

gained great importance in recent decades [2].

Metal aluminum-based matrix composites (MMC) are regarded as an excellent substitute material for obtaining better mechanical properties [3] as opposed to those of the constituent parts [4,5]. If enhanced mechanical properties are desired, very small particles must be used for reinforcement (~1 μm or even smaller) [7]; a decrease of the reinforcement particle size effectuates an increase in the mechanical strength of the composite [8,9]. These materials can be prepared by dispersing hard particles into the aluminum matrix by using techniques in a solid or liquid [6] state. Through the liquid route, reinforcement particles are added to liquid metal by stirring before casting [10], nevertheless, the resulting distribution is sometimes inhomogeneous [1,11].

On the other hand, MMCs can generally be easily fabricated in the solid state through the powder metallurgy techniques. Mechanical alloying (MA) is a process that uses repeated powder deforming, welding, and fracturing [2,11,9]. By using MA, it is possible to produce a fine and homogeneous distribution of hardening particles with a very fine particle distribution [14] which otherwise would be difficult or even impossible with most molten material techniques. The amount that the dispersoids strengthen the composite depends on particle type, size, morphology, volume fraction, and distribution.

The objective of this work was to produce an Al_{7075}-based composite doped with metallized graphite nanoparticles, and evaluate the effects of additive concentration and milling intensity on resulting powder characteristics.

2. Experimental procedure

The system studied in this work was an Al_{7075} alloy prepared from elemental powders [15] and reinforced with metallized graphite nanoparticles (GNP). The chemical composition (wt.%) of the alloy was Zn—5.6, Mg—2.5, Cu—1.6, Cr—0.23, Al (balance) and graphite nanoparticles (GNP) 0–2. The GNP (20–30 nm) were produced from graphite powder and metallized by MA in a high energy SPEX mill as according to a method already reported [16,17].

Composite mixtures were pre-mixed during 0.5 h in a Shaker mill without milling media in order to obtain good initial chemical homogeneity. The as-mixed

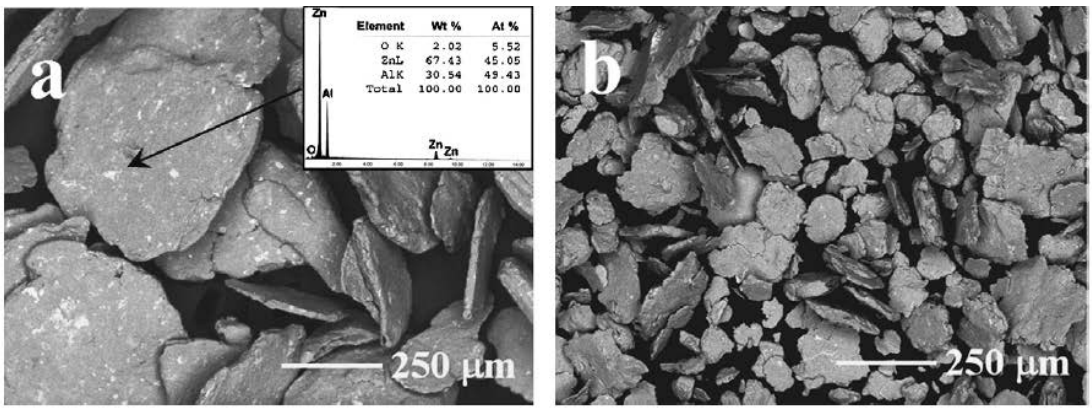

Fig. 1. SEM micrographs (backscattered electron) showing morphological evolution of the non-reinforced aluminum alloy as a consequence of milling intensity: (a) as-mixed powders, (b) 2.5 h processing time, (c) after 10 h of MA.

composites were then mechanically milled in a ZOZ CM01 Simoloyer high energy mill [15] for three milling intervals (2.5, 5 and 10 h) under argon atmosphere. Milling devices were made of stainless steel. The milling ball-to-powder weight ratio was set at 20:1

Consolidated bulk products were prepared by pressing the powder at 465 MPa under uniaxial load. Next, green samples were pressure-less sintered for

1 h at 523 K and 2 h at 773 K under a constant Ar flow. Sintered products were held for 0.5 h at 800 K and hot extruded by using an indirect extrusion method (extrusion ratio 16).

The density of the composites was determined by gas pycnometry using an Ultrapycnomerter 1000 (from Quantachrome Instruments) with high purity Nitrogen as the displacement gas.

Processed samples were characterized using a Siemens model D-5000 diffractometer in order to monitor crystallographic changes of the powders. Hardness tests were carried out in a Wilson Rockwell Instron hardness tester. Hardness were determined in the hardness Rockwell B (HRB) scale and then converted to Brinell using the ASTM E-140 standard. Additionally, tensile tests were carried out in an INSTRON universal tester at constant displacement rate of 0.0333 mm/seg.

3. Results and discussion

3.1. Morphological analysis of powders and size evolution

Fig. 1 shows the effect of mechanical milling on the morphology of the unreinforced Al_{7075}powder. The original particles were semi-spherical, typical of gas-atomized powders, and had small satellite particles attached to large particles. After 2.5 h of milling (Fig. 1a), the particles were severely deformed plastically by MA and exhibited a shape changes from nearly spherical to flake-like. Large aggregates formed due to their high ductility [12]. It is evident that small particles with high Zn concentrations were embedded into the large particles by cold-welding (Fig. 1a and EDS spectra). Forge hardening of the deformed particles reached a critical value which led to the activation of the fracture process. Particles presented sharp edges

and cracks near their borders (Fig. 1b). With further milling time, flattened particles were broken into smaller pieces [15].

Fig. 2 shows the general morphology of Al_{7075}-2GNP powders with 10 h of processing time. The sequence of milling steps is similar to the elemental powders mixture process (matrix deformation to flattered particles, cold welding and finally flake fragmentation) [9] (Fig. 1). The effect of reinforcement particle addition on final morphology of the sample [9,13] can be noticed. The image shows that particles were smaller when compared to the unreinforced Al alloy (under the same conditions). The formation of small flake size indicated that the milling approached the steady-state condition.

The reduction in the particle size after 10 h indicates that a strong conminution of the material [12] had occurred. The morphological results showed that the addition of graphite nanoparticles favor refining of particles during MA. It is important to mention that the powder density had a strong correlation with the physical morphology and size distribution of the particles [9,18].

To study the effect of graphite addition on the aluminum composites, it is possible to evaluate the variation in the density of samples as a function of processing time. Consequently a variation in the bulk density of powders during MA provides information about phenomena occurring during milling [8].

Fig. 3 shows the density of initial and resulting milled powders as a function of time. High densities found in as-mixed samples were characteristic of spherical morphologies, where powders have a lower tendency to form bridges, and because of their relatively good mobility become densely packed. On the other hand,

flattened particles, in the early stages of milling, yield an extremely low density due to high friction and bridge formation. This explains the lower density of samples milled for 2.5 h. A gradual increase in density upon increasing milling time and GNP concentration of the composite was evident. With a 2%GNP addition and 2.5 h milling time, final density was reached in the sample. Nevertheless, with further processing, no significant difference in the powder composite density was noticed.

In Fig. 4, the average equivalent particle size ($d_{0.50}$) and size distribution is shown. Notice that the $d_{0.50}$ of unreinforced and milled Al powder (0%GNP) is larger than the $d_{0.50}$ of the composite powders.

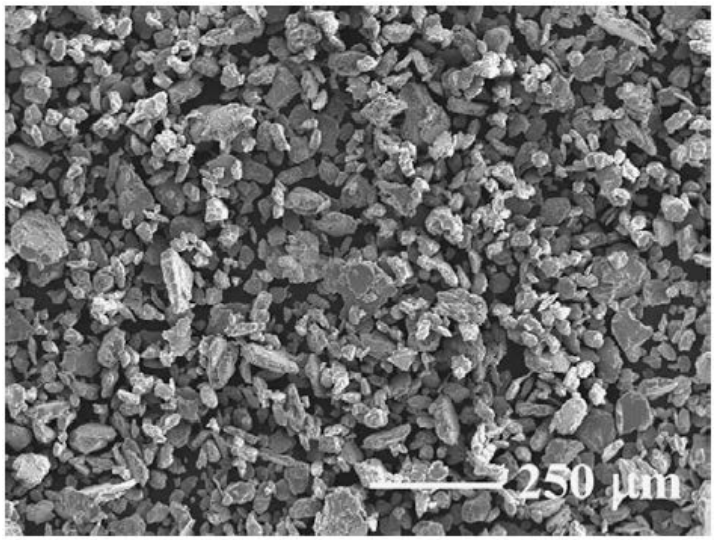

Fig. 2. SEM micrographs of Al_{7075} with 10 h of milling time at 2% GNP.

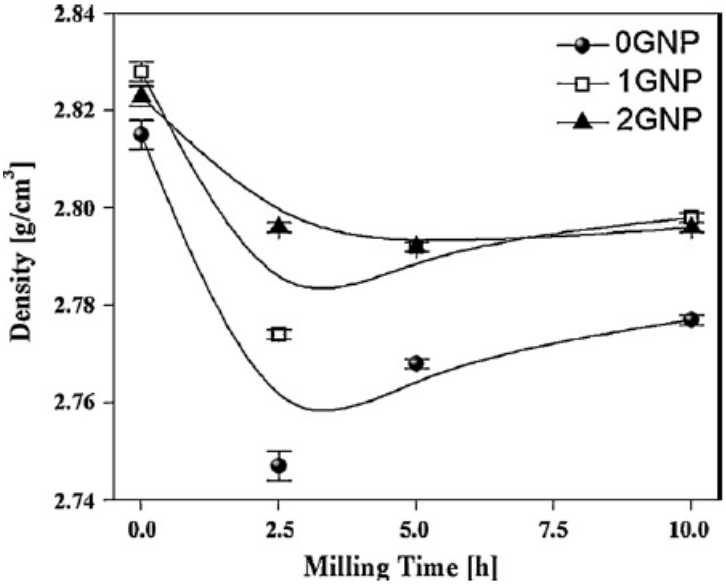

Fig. 3. Density curves of composites powders as a function of milling time.

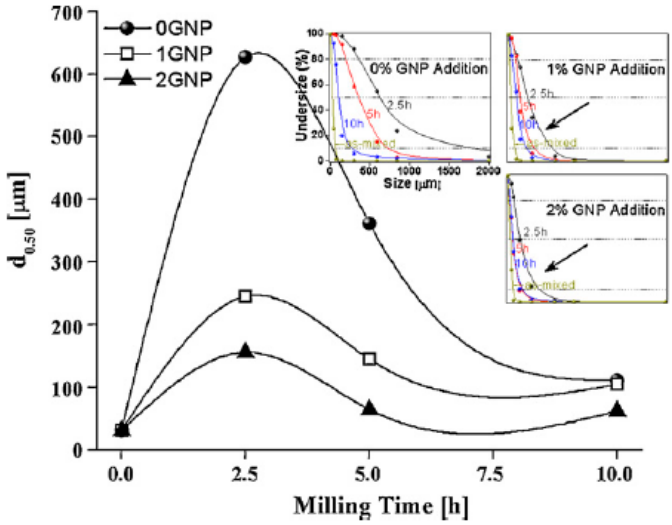

Fig. 4. Size distribution curves as a function of milling time.

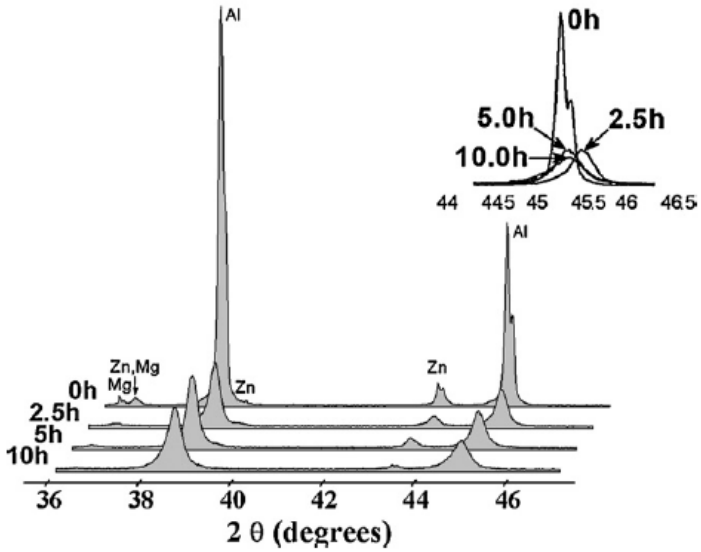

Fig. 5. X-ray diffraction pattern of composites with 1% GNP (36–47° and 44–46.5° zoom).

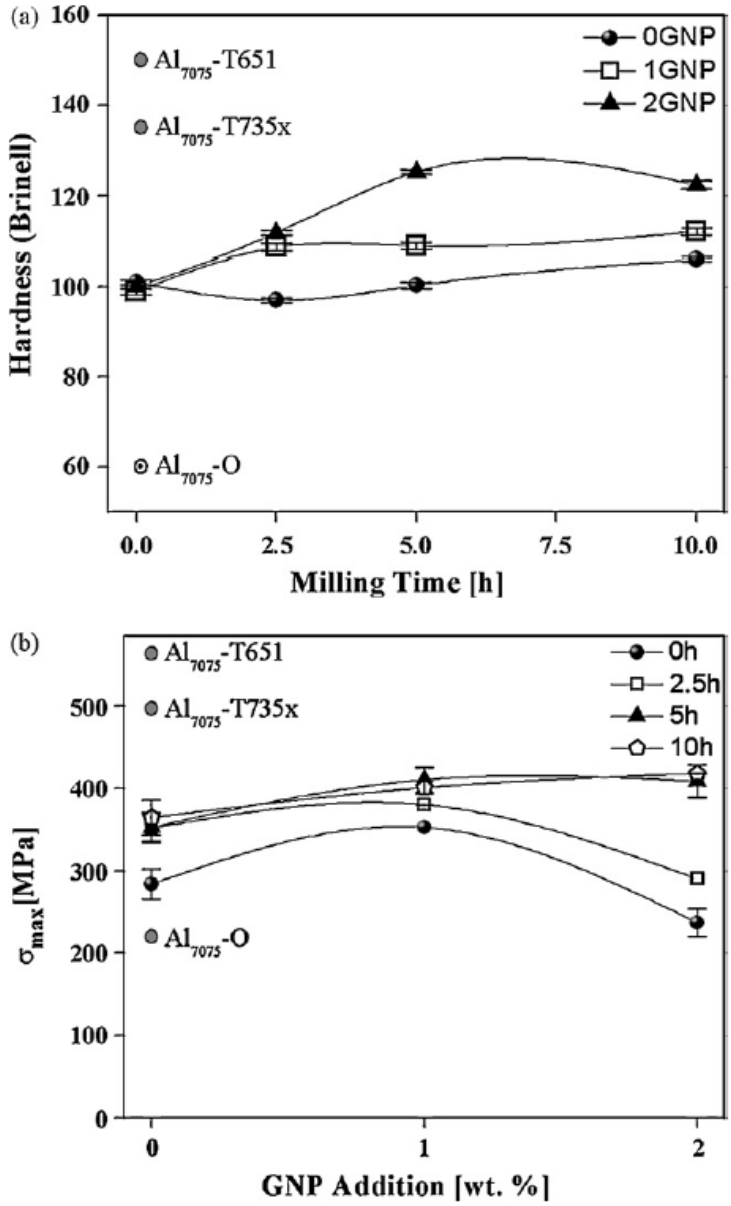

Fig. 6. Mechanical properties of Al-based composites as a function of milling time and GNP additions (a) Hardness Brinell vs. milling time, (b) σ_{max} vs. GNP concentra-tion.

This is consistent with flake-like shape and low density of the composites.

The smaller $d_{0.50}$ of composite powders was a result of the early fracture stage reached with lower processing time. Such premature formation and fracturing of irregular-shaped particles from large aggregates result in smaller particles which finally enhance the bulk density of powders (Fig. 4). These results suggest that the

steady-state milling condition for composite powders occurs after shorter milling times [8].

3.2. X-ray diffraction patterns

MA of composite powders was accompanied by morphological and micro-structural changes. Severe plastic deformation of the particles can lead to grain refining, variation in the crystallite size, accumulation of internal stress and variation of the lattice parameter, and in some alloy systems, an amorphous phase formation [1].

Fig. 5 shows the differences in diffraction peaks for samples with 1% GNP; all spectra from milled samples show a decrease in peak intensity and appreciable widening which indicate varying crystalline size [12]. In samples with 1%GNP variations was reached after 5 h of milling and were kept constant after 10 h of processing and achieved a stable state.

Table 1
Tensile strengths of the extruded bars as a function of the milling time.

Sample (% GNP)	Milling time (h)	Yield strength (MPa)	Max. strength (MPa)	Hardness (Brinell)
0	0	185.25	283.71	101.0
0	2.5	225.46	351.48	99.2
1		229.97	352.92	100.8
2		238.01	364.59	97.0
0	5	182.56	352.66	108.5
1		197.17	380.28	111.7
2		214.82	410.50	100.3
0	10	211.97	400.86	108.8
1		167.40	236.94	125.2
2		206.14	289.97	106.0

A probable source of the displacement could be Fe contamination due to wear and tear of media and milling container; however, EDS analyses determined low Fe concentrations in milled samples even for samples milled for 10 h, which

showed Fe contents less that 0.8 wt. %. Therefore, the Fe contamination effect of peak shifting was discarded. Suryanarayana [19] reported, in ductile–ductile systems, a small quantity of powder gets welded onto the ball surface and prevents excessive wear of grinding medium, but does not contaminate the powder.

3.3. Mechanical properties of extruded composites

The results of the tensile tests and hardness measurements for the composites, after the sintered and hot extruded sequences, are reported in Table 1 and Fig. 6.

From the tensile data shown in this table, it can be seen that the milling process led to a 40% increase in maximum tensile strength (compared with non-milled and pure samples) and an important

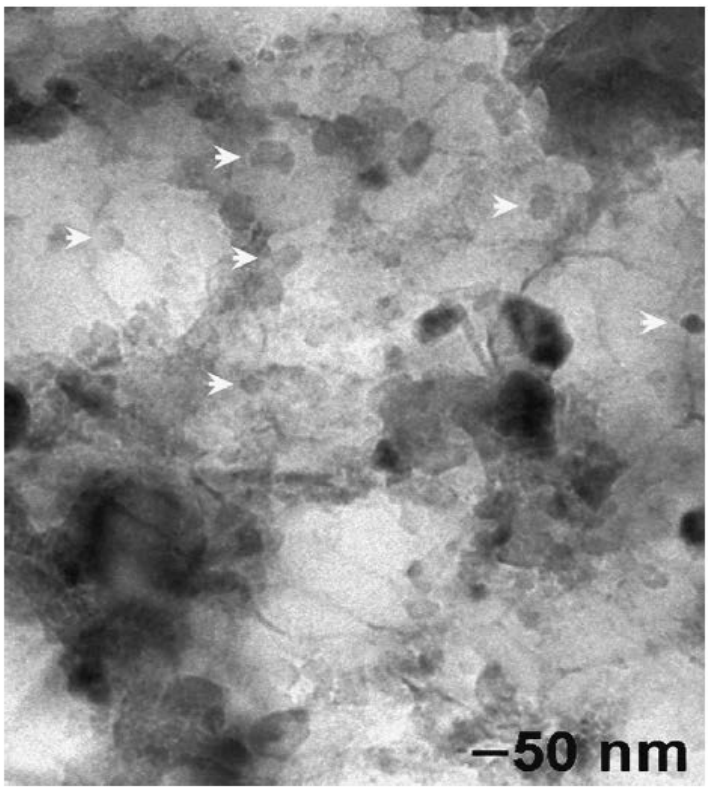

Fig. 7. TEM BF image of Al_{7075}–2% GNP–10 h composite in sintered and extruded condition.

Reduction in elongation, possibly caused from the stress concentration produced by the hardened phases [6] in the aluminum matrix.

The mechanically milled and extruded sample was almost 20% harder than the as-mixed sample; the differences between the milled powders are significant [11, 15,10,13,20].

It is evident that the tensile properties of the composites in as-milled condition were lowered by the addition of graphite and were found to be the lowest for extruded samples from the milled powder at 2.5 h.

The poor tensile properties for the as-mixed composites could have possibly resulted from low contact area between matrix alloy powders, required for suitable plastic deformation during milling, as well as the elongated shape of the powders. Dolata-Grosz et al. confirmed that porosity is also an important factor in the decrease of mechanical properties [7].

Fig. 7 shows a transmission electron microscopy (TEM) bright field image of Al_{7075}–2% GNP–10 h sample. The contrast corresponds to bend contours and grain boundaries. Grain size of the Al-based matrix was in the range of 70–250 nm. GNP reinforcement particles (white arrows) have about 20–30 nm sizes and are homogeneously dispersed onto the matrix. This homogeneous and fine dispersion of the reinforcement is more likely to have contributed to improved tensile strength [13].

4. Conclusions

The correlation among the different stages of MA with the powder morphology, particle size, and apparent density is clear. In accordance to morphological results, density variation versus milling time indicates severe plastic deformation of the aluminum powder during milling which form flake-like particles with low density during the early stages of processing; when the hardening particles were added, they accelerated the milling process of the aluminum matrix, reached a stable state condition, and; consequently, the density rate increases considerably. The results of the tensile test and hardness measurements for the prepared composites show a significant increase (40%) in maximum tensile strength and in hardness (20%) as compared to the blanks (as-mixed and extruded sample). Nevertheless, some samples show an important decrease in mechanical properties, probably caused by poor contact between the matrix alloy and the reinforcing particles.

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