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Effect of metallic addition on mechanical properties in an aluminum–graphite composite synthesized by means of mechanical milling

I. Estrada-Guel[a,b], C. Carreño-Gallardo[a,b], J.L. Cardoso-Cortés[b], E. Rocha-Rangel[c], J.M. Herrera-Ramírez[a], R. Martínez-Sánchez[a,*]

[a] *Centro de Investigación en Materiales Avanzados (CIMAV), Laboratorio Nacional de Nanotecnología, Miguel de Cervantes No. 120, CP 31109, Chihuahua, Chih., Mexico*
[b] *Universidad Autónoma Metropolitana, Departamento de Materiales, Av. San Pablo # 180, Col Reynosa-Tamaulipas CP 02200, México DF, Mexico*
[c] *Departamento de Mecatrónica, Universidad Politécnica de Victoria, Luis caballero No. 1200, Col. del Maestro, CP 87070, Cd. Victoria, Tamaulipas, Mexico*

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ABSTRACT

The increase on mechanical properties of different graphite dispersions in aluminum-based composites was studied. Al composites with metal-coated graphite (MCG) were prepared by mechanical milling route. Selected MCG couples were C–Cu, C–Ni and C–Ag while uncoated graphite was used as reference. As-milled products were consolidated by uniaxial cold compression followed by pressure-less sintering, hardness and compression tests were carried out on a longitudinal direction. Experimental values showed a significant increment on yield strength and hardness values in synthesized composites with respect to the blank (pure milled Al) processed under same conditions. Metal type and its concentration have an important effect on mechanical properties of prepared composites.

1. Introduction

The interest to increase aluminum strength for applications in demanding industries especially in aerospace and automotive applications [1] where the light weight of these alloys would be an advantage over the parts made of cast iron [2] has motivated the study of reinforced aluminum composites. For different ceramic/metal composite couples the incorporation of a ductile metal phase is known to improve mechanical properties compared to monolithic ceramic performs, due to the fact that metal is more ductile, metal phase provides a significant resistance to crack propagations in composites [3]. The principle of the strength enhancement in these materials lies in the introduction of high strength dispersed phase into the matrix [4–6], without losing the benefit of a low density value [7]. Aluminum composites can be prepared by dispersing insoluble particles like carbides, oxides [2,6], nitrides, silicon, graphite [5–14] into the aluminum matrix by using techniques in a solid or liquid state [1]. Graphite fibers have long been recognized as high strength, low density material. Because of its high strength to mass ratio, graphite has been used extensively as a reinforcement material in epoxy and polymer based composites [6]. Other important advantages are its excellent structural stability, mechanical performance at high temperatures [7] and high thermal conductivity, all of them, are reasons to consider graphite as a potential candidate for its use in composites [5], in addition graphite acts as an excellent lubricating agent under friction conditions [8], reducing the metal to metal contact area, producing a low friction coefficient [9]. The amount that the dispersoids strengthen the composite depends on particle type, size, morphology, volume fraction and distribution. The extent to which the particles withstand dissolution in the matrix and coalescence is an important factor of composite strengthening. The interactions between the reinforcing particles and the matrix include atomic-level effects which are responsible for the raise on mechanical properties of synthesized composite. So the quality of the bond aluminum/graphite (Al/C) is limited by the process of integration of the particles into the metal matrix. Besterci [10] in his study, concluded that volume fraction of carbide phase $A1_4C_3$ are in good agreement with resulted microstructure and achieved mechanical properties and the best strengthening is obtained with carbon types with a high transformation rate to Al carbide content and low subgrain size like electrographite on the contrary, Rodríguez-Guerrero et al. [11] mention in his work, that aluminum carbide is an unstable compound with very poor mechanical and thermal properties and needs to be avoided by silicon additions. Unfortunately, due to poor wettability of graphite particles they cannot be easily integrated into aluminum matrix due to an inadequate bonding Al/C [6]. Hence, to facilitate the wetting process, an intermediate layer known to be wetted by aluminum is deposited on the surface of the graphite particles.

* Corresponding author. Tel.: +52 614 439 11 46; fax: +52 614 439 48 23.
E-mail address: roberto.martinez@cimav.edu.mx (R. Martínez-Sánchez).

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Table 1
Nomenclature and chemical composition of studied MCG in atomic and weight percent.

MCG	Element	at.%	M [wt.%]	C [wt.%]
C	C	100	0.00	100.00
LC	C	90	37.02	62.98
	Cu	10		
HC	C	85	48.28	51.72
	Cu	15		
LN	C	90	35.19	64.81
	Ni	10		
HN	C	85	46.30	53.70
	Ni	15		
LS	C	90	49.95	50.05
	Ag	10		
HS	C	85	61.32	38.68
	Ag	15		

Coating materials that have been evaluated include Ni [6]. Ni, which reacts with the aluminum matrix to form an Al_3Ni intermetallic improved the load carrying ability of the alloy and contributed to the hardness [2] and strength [6] of the composite. Good wetting is achieved when the contact angle θ (angle measured from the substrate surface on the liquid side to the tangent on the drop profile drawn at the triple junction) is low. The θ for Al/C is 140°, whereas Al/Ni is 31°. On the other hand, θ for Al/nickel coated graphite is only 4°, showing that coating graphite with nickel is an effective way to promote wetting of graphite on aluminum [6]. Moreover, Cu–C couples have been studied even through graphite is not soluble in the melting copper alloy [9]. Powder metallurgy (PM) is an important supporting technique for composites preparation which includes: mixing the integrant powders, compacting processes, sintering and sometimes a final step of thermical treatment [12]. The porosity concentration can be eliminated or reduced by subsequent hot extrusion or rolling [13]. Methodology used in the present work lies with the introduction of graphite particles into the aluminum matrix by mechanical milling (MM) and PM processing. Through MM, it is possible to produce a fine and homogeneous distribution of hardening particles with a very fine particle distribution, which otherwise would be difficult or even impossible with most material techniques [8,10].

The aim of this work is the Al-based composite synthesis and the subsequent study of the effect of metal-coated graphite (MCG) on the mechanical properties (strength and hardness) of consolidated and sintered composite materials. The effect of different metals on the graphite adhesion to Al matrix is presented and discussed as a result of microstructural and mechanical characterization.

2. Experimental procedure

Raw materials (Alfa Aesar) were gas atomized aluminum (99.8% purity), copper (99.5%), nickel (99.8%), silver (99.9%) and graphite (99.9%) powders. MCG couples were prepared from graphite and some metals in the ratio indicated in Table 1, as the chart shows, two metal concentrations were used: LOW (LX with 10 at.% of metal) and HIGH (HX 15 at.% metallic concentration); where X = Cu, Ni or Ag.

The first step was the MCG's preparation by milling graphite with the corresponding quantity of metal powder in a high energy SPEX 8000M connected a hardened steel container with 13 mm (Ø) balls as milling media and an inert Ar atmosphere. The milling ball to powder weight ratio was kept 5 to 1 for all experimental runs. Methanol was used as process control agent (PCA-1 ml). Milling intervals were 1, 4 and 8 h using alternate cycles of 30 min milling and 30 min rest to avoid sample's overheating. In the second step; Al-based composites (1 wt.%) were prepared by mixing 9.9 g of Al powder and 0.1 g of previously synthesized MCG, using the same milling device for 1 h with the addition of 3 drops of methanol as PCA in order to avoid excessive aluminum agglomeration. Un-milled and milled pure aluminum samples (without MCG addition) processed under same conditions were used as reference for comparison purposes. Green (consolidated) products were obtained by pressing milled powders into a circular die at 950 MPa under uniaxial load. Compacted samples were then sintered for 3 h at 823 K under a constant inert Ar flow (150 cm^3/min) and a heating rate of 10 K/min. Pressed samples were mounted, grinded, polished and etched using standard metallographic techniques in order to carry out the microstructural observations by using a scanning electron microscope JEOL-JSM 7401F. Hardness tests were carried out in a Wilson Rockwell Instron hardness meter using a 1/16″ ball indenter and 60 kg of load, obtaining values in Rockwell B scale and were transformed to Brinell hardness using an Instron conversion chart, average value of 5 indentations and its standard error were present. On the other hand, compressive stress of the aluminum composites was measured using an Instron testing machine at room temperature with a constant displacement rate of 0.03333 mm/s. Yield stress was measured at elastic limit, meanwhile the maximum stress was measured at arbitrary condition of ε = 20%.

3. Results

3.1. Morphological analysis

Fig. 1a presents a micrograph of composite prepared from metallized-graphite milled 8 h prior addition to aluminum matrix, Fig. 1b shows an image of a composite prepared under same conditions, after milling and sintering process. It is noticeable the presence of small pores on the surface of samples as a result of

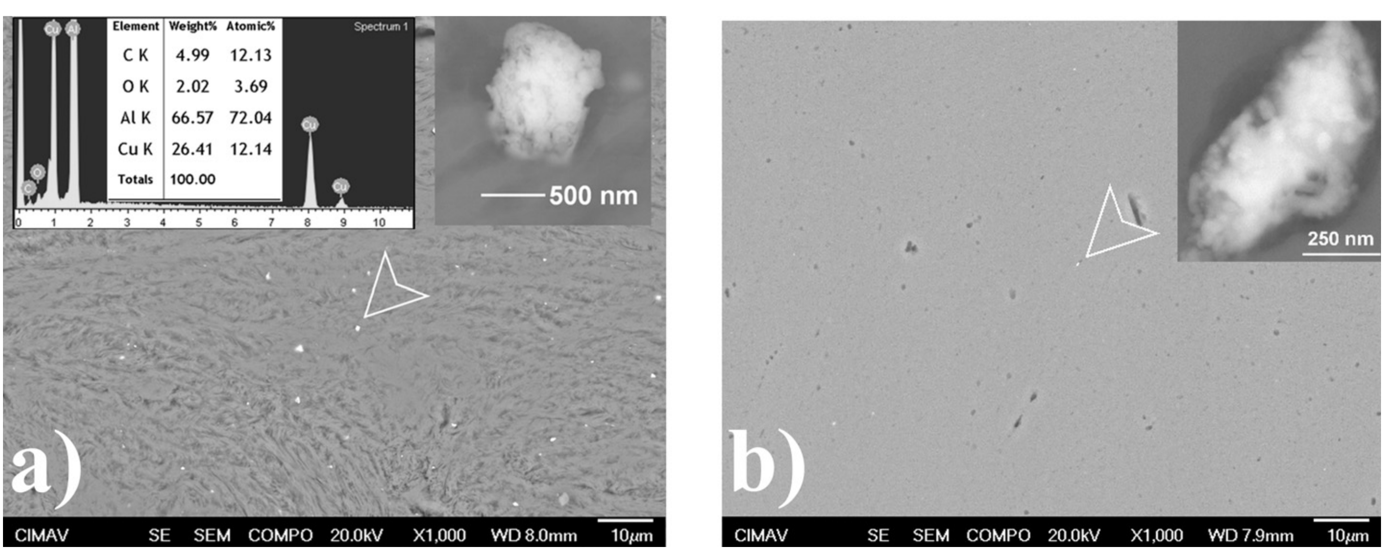

Fig. 1. SEM backscatter electron (BE) micrographs and EDS chemical analysis of some Al–CuC composites prepared with (a) HCu–graphite milled 8 h, (b) previous composite pressed and sintered.

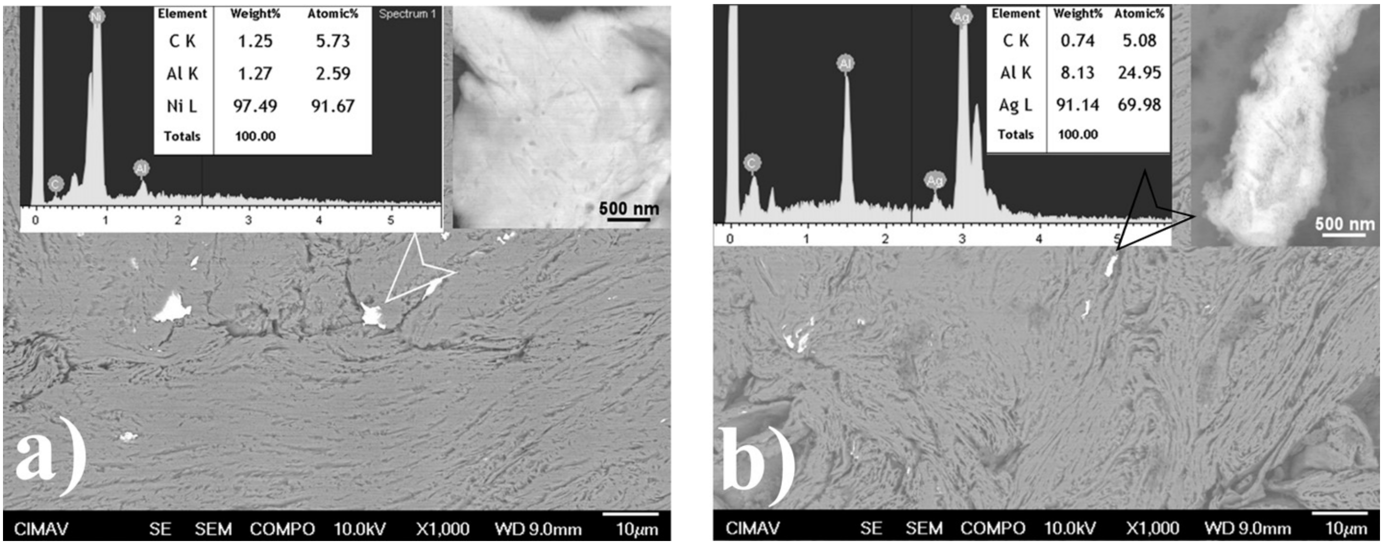

Fig. 2. SEM-BE images of composites prepared with Al powder and (a) Ni–C milled 8 h, (b) Ag–C milled 8 h. Additionally particle EDS analyses are presented.

defective array of irregular milled particles and gas inclusions. Matrix was plastically deformed due to impact forces by the collision between milling media and metallic powder particles and they exhibit a change in shape from nearly spherical (from atomized powders) to flake-like, because of the aluminum ductility. Chemical analysis presented in Fig. 1a showed the presence of a particle with high Cu and C concentration embedded between matrix layers. Contrary to this evidence, Akhlaghi et al. [12], using stir casting method for Al/C composite preparation found coarse reinforcement particles of graphite with particle size >100 μm, due mainly to an ineffective melt disintegration during preparation. AlHC-0h composite image (not shown) presents large size Cu particles compared with AlHC-8h sample, this is due to further milling time breaking the Cu–C particles to small parts and facilitating the particle integration into metal matrix. After 8 h of milling time particles are smaller and rounded and homogeneously distributed into the layers of aluminum matrix (Fig. 1a). The Cu–C distribution along the Al matrix is more homogeneous and those particles present a lower final size. With particle size constant, the influence on strength corresponds to the subgrain size and the mean dispersed interparticle distance [10]. Fig. 1b shows an evident change from lamellar (characteristic of ductile MM'ed samples) to homogeneous morphology with Cu–C particles randomly distributed, due to the sintering process. It is noticeable that the Cu particles were not dissolved into Al matrix by thermal treatment and they stayed as remnant. These characteristics have an important effect on the mechanical performance of the composite [8]. Homogeneous and fine dispersion of the reinforcement is more likely to contribute to the improvement of the compression strength; because the homogeneous stress dispersion is associated with a favorable microstructural arrangement [8]. On the other hand Fig. 2a and b shows micrographs of Al–HN and Al–HS composites processed under the same conditions, it is evident a very different array of the MCG particles, compared with composites with Cu reinforcements addition. Al–HN and Al–HS samples present particles with bigger sizes, poor homogeneity and a coarse dispersion into the metallic matrix. Some chemical analyses carried out on the particles (Fig. 2a and b) show low graphite contents. Morphological and chemical evidence could confirm that these systems (Ag and Ni) do not produce an efficient interphase of graphite and this adverse arrangement causes a poor mechanical performance that will be presented forward.

3.2. Mechanical properties

The results of compressive tests and hardness measures for the prepared composites are reported in Table 2 and complemented with Fig. 3a and b. Milled Al sample without MCG addition presents a higher yield strength (σ_y), maximum strength (σ_{max}) and hard-

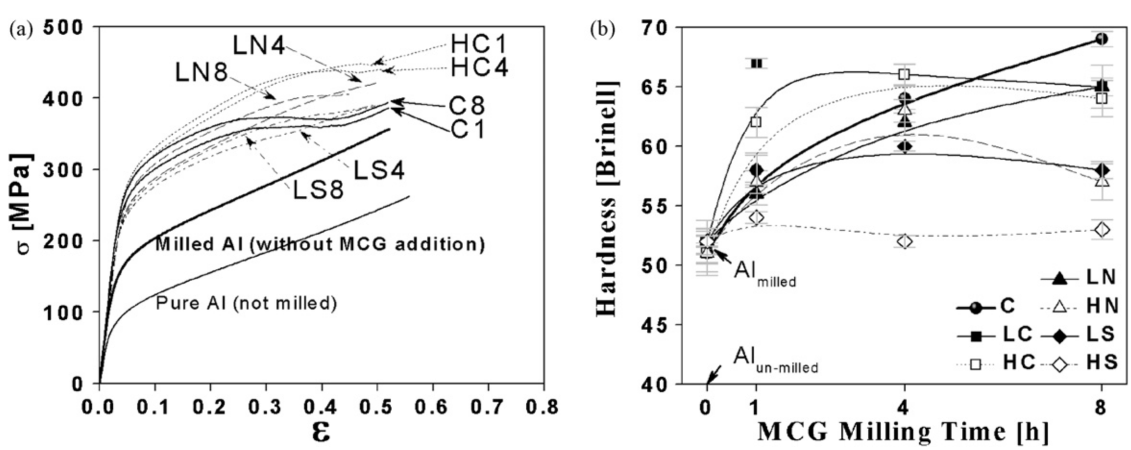

Fig. 3. (a) Stress–strain curves in composites with the best mechanical response, (b) Hardness values found in the composites as a function of type, concentration and milling intensity of MCG.

Table 2
Tabulated chart from evaluated mechanical properties (yield strength and hardness) from composites samples. INC are the property increment (in %) compared to pure milled aluminum sample.

Sample	T	σ_y	INC	σ_{max}	INC	HB	INC	Sample	T	σ_y	INC	σ_{max}	INC	HB	INC
Pure Al	–	67.31	–	166.74	–	23	–	Al–LN	0	189.30	57.6	342.02	22.1	58	12.6
									1	168.45	40.2	308.65	13.4	56	7.2
Milled Al	–	120.13	–	262.85	–	52	–		4	199.20	65.8	352.58	29.1	62	20.3
									8	218.07	81.5	373.63	31,4	65	26.1
Al–C	0	203.55	69.4	283.90	8.0	63	21.1	A1–HN	0	205.19	70,8	362.49	26.7	59	13.5
	1	210.06	74.9	350.62	30.9	58	12.6		1	175.70	46.3	333.72	19.6	57	10.6
	4	199.73	66.3	352.60	25.6	64	24.2		4	204.50	70.2	364.12	30.3	63	20.8
	8	228.79	90.4	369.68	30.3	69	32.4		8	170.57	42.0	321.26	16.0	57	9.2
Al–Lt	0	185.99	54.8	347.65	22.9	61	17.9	Al–LS	0	175.28	45.9	329.63	20.8	55	6.8
	1	197.56	64.4	361.13	28.3	67	29.5		1	179.20	49.2	329.17	20.1	58	12.1
	4	188.39	56.8	356.50	25.9	66	27.5		4	188.78	57.1	332.30	21.1	60	15.9
	8	175.11	45.8	328.62	18.4	65	26.1		8	193.39	61.0	339.77	23.1	58	12.6
Al–HC	0	214.72	78.7	392.76	39.5	63	21.1	Al–HS	0	145.27	20.9	299.43	10.8	55	6.3
	1	215.09	79.0	396.15	33.9	62	19.3		1	144.81	20.5	293.29	10.2	54	3.4
	4	225.88	88.0	407.56	36.5	66	26.6		4	140.23	16.7	289.26	9.0	52	0.0
	8	190.50	58.6	358.92	23.6	64	23.7		8	161.27	34.2	304.66	14.5	53	2.4

T = MCG milling time [h] σ_y and σ_{max} = [MPa] INC = increment compared with milled aluminum HB = hardness [Brinell].

ness compared with un-milled pure Al sample, due cold worked and high internal stress caused by the increment of dislocation density and grain size reduction [8] achieved during milling. From the data in Table 2, the best σ_y values are presented in composites with HCu–C and pure C addition, meanwhile HS–C composites exhibit only modest increments on this property. The best response was found with AlC-8h (INC = 90.4) and AlHC-4h (88.0) composites. It is noticeable that non-metallized-graphite composites have apparent good mechanical properties but, its graphite concentration is 37–60% higher than some MCG composites (see Table 1), and the increment on mechanical properties is low (~2%) if we compare AlC-8h vs. AlHC-4h. It can indicate a synergic effect of graphite with metal on the integration of reinforcement particles and finally on mechanical properties. Besides, the highest increment in σ_{max} was found in AlHC-0h and AlHC-4h composites with almost 40%, unfortunately this produce a reduction of the elongation rate, possibly caused by the high stress concentration produced by hardened phases in the aluminum matrix. Contrary to this evidence, Son et al. [8] in their study on Al-6061 alloy reinforced with graphite particles prepared by ball milling established that addition of graphite to metal matrix composites decreases the compression strengths due to the significantly lower strength of graphite compared with the matrix alloy. On the other hand, Yılmaz et al. [13] in their study of the effects of Al_2O_3 on the abrasive wear resistance of Al-MMC prepared by casting method concluded that the presence of hard dispersed particles will cause additional strain hardening and the strength of the composites increases with the volume percentage of particles in the composite. Complement studies showed that it is true, but higher particle concentration (>5%) decreases the strength of the products by matrix saturation effect.

Fig. 3a shows that increment in studied properties is notable, but it has an important relation with type of metal in MCG used and the milling intensity. AlHC-1h and AlHC-4h showed the highest levels in the plot, meanwhile AlLS-8h and AlLS-4h were the lowest (even though they are superior compared with pure Al). Macro-hardness tests were done instead μ-hardness assay due to the fact that small MCG particles have different hardness values compared with metal matrix; a punctual measure could induce a high scattering in results [4]. Hardness results are presented in Table 2 and Fig. 3b, higher response was found in all composites containing graphite pure and metallized with copper, peak was found with AlLC-1h sample; the differences between composites with same MCG additions and different milling time were significant. Hardness markedly increases with the addition of ceramic particles [14]. Changes on hardness were a function of type metallized agent and milling intensities (with except Al–HS composites, which presented a constant behavior).

4. Conclusions

Strengthened Cu–graphite particles are sub-micrometric size and are homogeneously distributed into the aluminum matrix. Contrary to this, graphite metallized with Ag and Ni presented larger size, poor homogeneity and coarse dispersion into the matrix. The tests showed a significant increment in the yield strength and hardness values of composites with respect to pure aluminum sample. Metal type, milling time and its concentrations have an important effect on mechanical properties of composites and it has a synergic effect with graphite integration into the Al matrix. Al–HC composites were the best options as reinforcement medium. On the contrary, graphite–silver composites present the lower mechanical properties. Differences in mechanical behavior among composites with same MCG addition and different milling time were significant and did not show a clear correlation.

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