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TEM characterization of Al–C–Cu–Al_2O_3 composites produced by mechanical milling

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Abstract

Novel Al-based composites (Al–C–Cu–Al_2O_3) obtained by mechanical milling (MM), were characterized by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Analyses of composites were carried out in both, the as-milled and the as-sintered conditions. C nanoparticles were found in the as-milled condition and Al_2O_3 nanofibers were found in as-sintered products, as determined by EELS. C and Cu react with Al to crystallize in Al_3C_4 and Al_2Cu structures, respectively.

Keywords: Metal matrix composite; Transmission electron microscopy; TEM; Electron energy loss spectroscopy

1. Introduction

Aluminum-based metal matrix composites (MMC) reinforced with ceramic particles are demanded because of their low density and high specific stiffness [1–3]. In addition, the ceramic particles increase significantly the wear resistance and the high temperature strength. Different processing techniques can be used for the production of MMC, which can be grouped into two main routes depending on the state of the matrix during the synthesis process, these are the liquid and solid routes [4]. Dispersion strengthened materials belong to the group of composite materials, which are made mainly by the techniques of powder metallurgy (PM). Their microstructure is composed by a polycrystalline matrix, in which dispersed particles are incorporated (mainly oxides, carbides and nitrides).

The strengthening effect of dispersoids is based on the blockage of the matrix dislocation movement. The dispersoids increase the density of dislocations and refine the grain and subgrain structure. The strengthening effectiveness of the dispersoids depends on their type, size, morphology, volume fraction and distribution. Their resistance against dissolution in the matrix and coalescence is an important factor in their strengthening effect, mainly at high temperatures. By PM methods it is possible to produce unique MMC materials, with very fine reinforcement particle distribution, which otherwise would be impossible to produce by conventional ingot metallurgy. The mechanical alloying (MA) and mechanical milling (MM) processes have been widely recognized as alternative routes for the formation of metastable phases for selected applications [5]. MA and MM processes are convenient techniques to synthesize advanced materials with unusual properties, due to the refinement of the microstructure, even in immiscible systems. The MM technique was originally developed to produce a fine and homogeneous dispersion of oxide particles in a nickel-base super alloy for producing oxide-dispersion strengthened (ODS) super alloys [6–7]. The same principle can be applied to produce particle-strengthened Al-based composites. Thus, by combining PM and MM a new generation of materials can be produced. On the other hand, the interactions between the hardening particles and the matrix include atomic-level effects that are responsible for the new and novel properties of final composites.

By using electron energy loss spectroscopy (EELS), it is possible to characterize the electronic structure of the materials [8–9]. EELS allows the study of precipitates, grain boundaries, internal interfaces and other atomic interactions through the analysis of the energy loss near edge structure (ELNES) [10–12].

The aim of this work is to characterize the particles present in an Al-based composite produced by mechanical milling and

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sintering process from microstructural and electronic point of view by TEM and EELS techniques.

2. Experimental

The raw materials were Al powders (99.5% purity, mesh −325) and pre-milled graphite with Cu. Pure Al and mixtures of Al–C, Al–Cu and Al–C–Cu were employed to produce the composites. Each one was mechanically processed in a high energy SPEX mill for 4 h. Argon was used as the milling atmosphere. Devices and milling media used were made of hardened steel. The milling ball to powder weight ratio was 5:1. The sample weight was 5 g and no process control agent was required due to the short milling time employed.

Consolidated products were obtained by pressing the milled powders for two minutes at ∼1250 MPa in uniaxial load. Consolidated samples were pressureless sintered for 1 h at 823 K under vacuum (∼1 Torr). Transmission electron microscopy (TEM) characterization was performed using a Philips CM-200 microscope operating at 200 kV, equiped with a DX4 energy dispersive spectrometer (EDS) and a parallel electron energy loss spectrometer (digi-PEELS model 666).

EELS spectra were obtained with a Gatan parallel electron energy loss spectrometer (PEELS model 666) attached to the TEM. Spectra were taken in diffraction mode with 0.3 eV/channel dispersion, an aperture of 3 mm and a collection semi-angle of 10 mrad. The resolution of the spectra was determined by measuring the full width at half-maximum (FWHM) of the zero-loss peak and this was typically close to 1.6 eV at 200 kV. Spectra from the ionization edges were acquired for all Al-based composites. The EELS spectra were corrected for dark current and readout noise. The channel to channel gain variation was minimized by normalizing the experimental spectrum with independently obtained gain spectrum of the spectrometer.

Spectra were background-subtracted by fitting the pre-edge backgrounds with a power-law function and then Fourier-ratio deconvoluted to remove multiple scattering components.

3. Results and discussion

Fig. 1 shows a TEM micrograph of the Al–C–Cu composite in the as milled condition. Graphite nanoparticles are present in the Al matrix whose dimensions are ∼2 nm in thickness and ∼10–15 nm in length. The graphite interplanar distance (0 0 2) is appreciable in the inset.

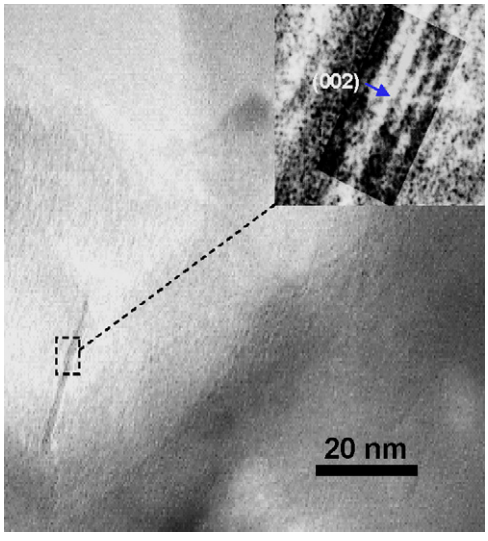

Fig. 1. HRTEM image from an Al–C–Cu composite in the as-milled condition showing the shape of carbon nanoparticles.

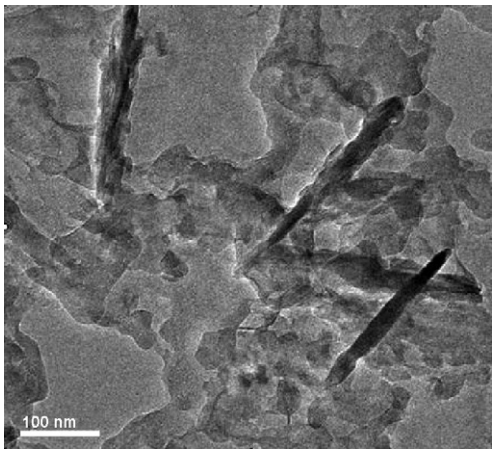

Fig. 2. TEM image from an Al-based composite showing the distribution and shape of Al_2O_3 nanofibers.

Fig. 2 shows typical nanofibers found in the Al–C–Cu composite in the as-sintered condition. Nanofibers show asymmetrical shape, irregular surface and the dimensions are ∼20–40 nm in thickness and ∼200–300 nm in length. Nanofibers are randomly distributed, and the composition is mainly Al_2O_3, however, it has been found graphite presence along all fibers according to previous analysis [12]. The oxygen comes from oxidized powder surface, it seems, the atomic O penetrates and is located at interstitial sites of the Al structure due to the diffusion phenomena occurring during the milling process. During the sintering process Al react with O and form Al_2O_3, which present a fiber shape. Additionally, during HRTEM observations it was found Al_2Cu and Al_3C_4 nanoparticles (Fig. 3). At present deep characterization on these nanoparticles is being carried out.

During TEM characterization, EELS analyses were carried out for all Al-based composites. Figs. 4 and 5 show the Al–K ionization edge for metallic Al, Al–C and Al–C–Cu composites in the as-milled and sintered condition, respectively. Fig. 4(b) and (c) present changes with respect to metallic Al (a). These changes are due to the presence of Al_2O_3, formed during the milling; similar results were reported before [13] for Al–Al_2O_3 samples. It is expected C have two routes of reaction during

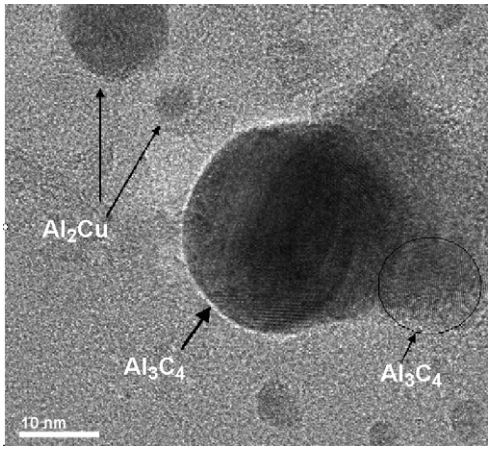

Fig. 3. HRTEM image from an Al–C–Cu composite after sintering showing different of Al_2Cu particles and the presence of Al_3C_4.

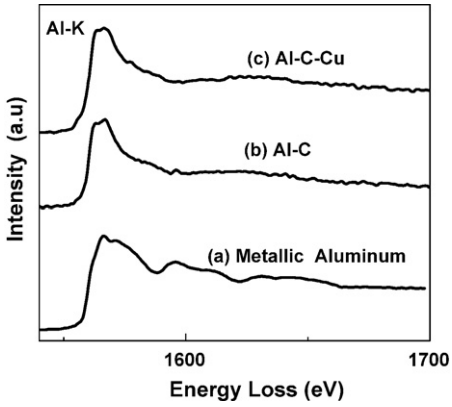

Fig. 4. EELS spectra from Al–K Ionization edges in Al–C, Al–C–Cu composites and metallic aluminum in the as-milled condition.

milling and sintering process, one of them is a preferential reaction with oxidized shell in aluminum powders and the second one is the reaction with aluminum matrix to crystallize Al_3C_4. On the other hand, Fig. 4a shows Cu has not relevant influence on ionization edge of Al. By comparing Figs. 5(a) and 4(a), it was found that Fig. 5(a) presents Al_2O_3 presence which is not perceptible in Fig. 4(a), this means Al and oxygen still react during sintering process to crystallize Al_2O_3. Analyzing Figs. 4(b) and 5(b) we found differences in the Al–K ionization edge of Al–C components, these differences could be the result of changes in Al_2O_3 structures. An analysis by HRTEM, developed on the alumina nanofibers in the as-sintered samples revealed that alumina is Al_2O_3-κ type. We assume that the alumina formed during the milling is Al_2O_3-α and it is transformed in the metastable Al_2O_3-κ during sintering.

Figs. 6 and 7 present the O–K ionization edge from composites produced in as-milled and sintered condition, respectively.

Fig. 6(b) shows a slight displacement of about 4 eV (from 552 to 556 eV) in the second peak respect to the EELS spectrum of O–K ionization edge of the Al–C composite of Fig. 6(a). This behavior is most likely due to reactions between the O and Cu to form CuO during the milling process. However, CuO particles were not found during HRTEM observations, due to small particles size or due to the CuO reduction by Al during sintering process. After sintering the O–K ionization edge of

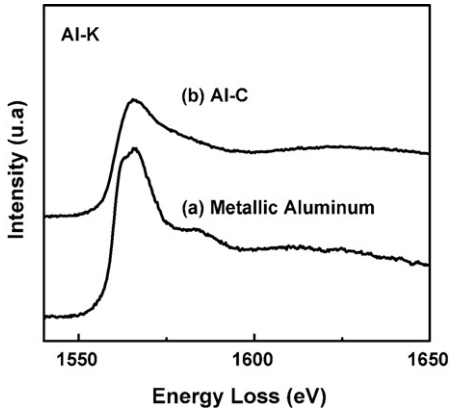

Fig. 5. EELS spectra from Al–K Ionization edges in Al–C composites, metallic aluminum in the as-sintered condition.

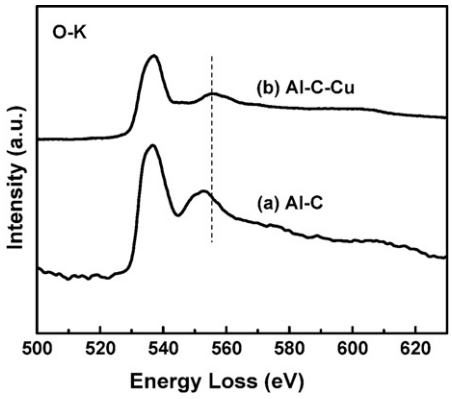

Fig. 6. EELS spectra from Al–K Ionization edges in Al–C and Al–C–Cu composites in as- milled condition.

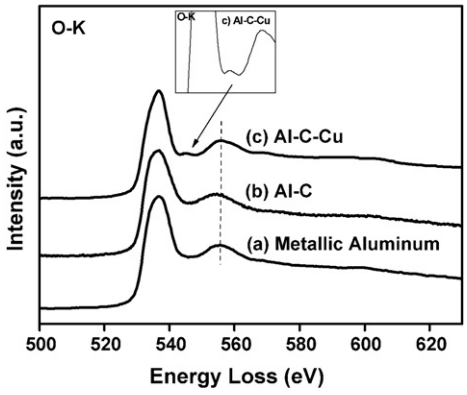

Fig. 7. EELS spectra from O–K Ionization edges in pure aluminum and in Al-based composites in as-sintered condition.

Al–C–Cu (Fig. 7c) shows a small peak at 545 eV (see inset) due to the Cu presence, while the Al–C spectrum (Fig. 7b) kept the same morphology after sintering and similar to metallic Al spectrum (Fig. 7a).

Fig. 8 shows EELS spectra from C–K ionization edge of Al–C composite in as-milled (b) and as-sintered condition, (c), which are compared with graphite spectrum (a) taken from EELS spectra atlas [14].

From Fig. 8 it is expected that there is an amorphous C structure produced by the intense milling process. On the other

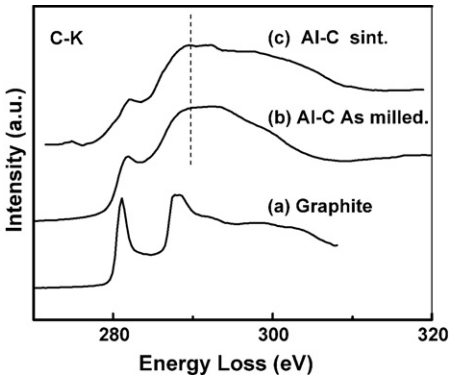

Fig. 8. EELS spectra from C–K ionization edges in Al–C both as-milled and sintered condition and graphite as reference.

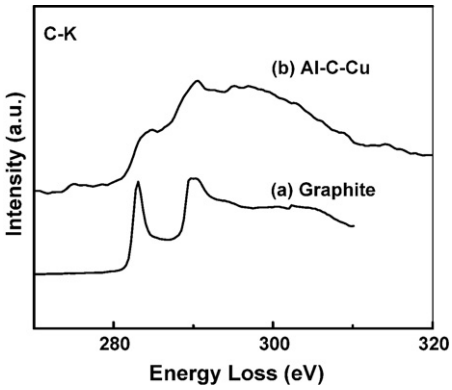

Fig. 9. EELS spectra from C–K ionization edges in graphite and Al–C–Cu in as-sintered condition.

hand, Fig. 8(c) shows the changes in fine structure in second peak (∼290 eV) on the C–K ionization edge with respect to (b), which can be attributed to Al_3C_4 crystallization during sintering process.

Fig. 9 shows EELS spectra from C–K ionization edge for graphite (a) and Al–C–Cu composite in as-sintered condition (b). From Fig. 9(b) it is observed that the peak structure has a tendency to restore the structure present in graphite (Fig. 9a), indicating that Cu presence apparently favors the crystallization of amorphous C into Al_3C_4 carbide or Al_2O_3–C nanofiber.

4. Conclusions

Al–C–Cu composites were produced by mechanical milling, cold compaction and pressure-less sintering sequence. From the analyses of EELS spectra we conclude that the addition of C–Cu to the Al matrix promote the formation of Al_2O_3 particles during the milling process which transform to metastable Al_2O_3-κ during the sintering process. Al_2Cu and Al_3C_4 crystallization during sintering process were corroborated by TEM and EELS techniques. Cu has not relevant influence on ionization edges analyzed, however Cu makes easier the C incorporation to Al-matrix and avoid in certain way the amorphization of the C. It has been confirmed that EELS is a reliable technique in the study of composites at nanometer scale.

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