Microstructure and Thermal Conductivity of Al–Graphene Composites Fabricated by Powder Metallurgy and Hot Rolling Techniques

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Abstract The objective of this research is to improve the thermal conductivity and mechanical properties of Al/GNPs (graphene nanoplatelets) nanocomposites produced by classical powder metallurgy and hot rolling techniques. The microstructural evaluation confirmed the uniform dispersion of GNPs at low content and agglomeration at higher contents of GNPs. The structure of graphene was studied before and after the mixing and the Raman spectrum proofs that the wet mixing has a great potential to be used as a dispersion method. There was no significant peak corresponding to the Al_4C_3 formation in both the differential scanning calorimetry curves and X-ray diffraction patterns. The microstructural observation in both fabrication techniques showed grain refinement as a function of the GNPs content. Moreover, the introduction of the GNPs not only improved the Vickers hardness of the composites but also decreased their density. The thermal conductivity investigations showed that in both the press-sintered and hot-rolled samples, although the thermal conductivity of composites was improved at low GNPs contents, it was negatively affected at high GNPs contents.

KEY WORDS: Aluminum; Graphene; Thermal conductivity; Powder metallurgy; Microstructure

1 Introduction

Nanoparticle-reinforced metal-matrix nanocomposites (MMNCs) have been developed over decades and gradually formed an important part in material systems for use in the aerospace, defense, automotive and electronic packaging industries [1–4]. Recently, MMNCs have attracted the interest to develop new composite materials and new fabrication techniques. Canakci et al. [2] studied the effect of B_4C addition on the physical and mechanical properties of Al alloys fabricated by stir casting. They reported that coarser B_4C can be dispersed uniformly, while the

agglomeration of particles was observed in the case of fine particles. They also showed that the hardness of the composites decreased by increasing the particle content. In another research, Canakci et al. [5] investigated also the effect of different volume fractions of B_4C on the microstructure and hardness of 2024 aluminum alloy. They found that the density of the composites decreased with increasing particle content, while their hardness increased by increasing the particle content. However, Varol et al. [6] studied the effect of nanographite, graphene nanosheets and carbon nanotubes (CNTs) on the properties of Cu composites produced by flake powder metallurgy. They found that in all the composites by increasing the reinforcement content from 0.5 to 5 wt%, the hardness and electrical conductivity of the composites decreased dramatically. Among the MMNCs, aluminum matrix nanocomposites could attract much attention owing to their low density, high strength, good ductility and good wear resistance [7, 8]. Nevertheless, their mechanical performance needs to be improved more and it is hard to gain this

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improvement only through conventional processes such as heat treatment and deformation techniques. An alternative approach is to fabricate aluminum matrix nanocomposites reinforced with either carbon base reinforcements such as carbon nanotubes, graphene, or some other ceramic particles (SiC, B₄C) to improve the strength of the Al alloys [4, 9, 10].

On the other hand, the application of graphene has grown drastically due to its unique mechanical, electrical and thermal properties [11–13]. Graphene is an interesting reinforcement in the production of MMNCs because of its superior mechanical properties (Young's modulus of 1 TPa, a low density of 1.06 g cm^{−3} and a fracture strength up to 130 GPa) [14]. To date, findings of many studies indicate a positive influence of graphene on the final properties of graphene/metal-matrix nanocomposites [15–17]. Rafiee et al. [12] have reported the effect of graphene addition on the mechanical properties of polymer matrix nanocomposites. Their experimental results show a significant improvement in tensile strength, Young's modulus and fracture toughness of the fabricated composites. Indeed, the application of graphene as reinforcement in the polymer and ceramic matrix nanocomposites has been largely explored, while more investigations are necessary in the case of metal-matrix nanocomposites. One of the key problems which limit the application of graphene in MMNCs is the poor wettability between the graphene and the metal. This can lead to a low interface adhesion and as a consequence to poor mechanical and thermal properties [15, 16, 18]. Another main difficulty is to obtain a good dispersion of graphene within the matrix; the dispersion of graphene seems to be much more difficult than that of other reinforcements [15]. Different techniques such as stir casting, mechanical milling or wet methods were used to disperse the graphene homogeneously within the matrix [15–17, 19]. Therefore, it can be concluded that the production of graphene nanoplatelets (GNPs)/MMNCs still seems to be a great challenge.

The Al nanocomposites reinforced with GNPs seem to present interesting properties compared to other composites [20, 21]. However, it was demonstrated that the GNPs/Al interface plays a key role in the final properties of the composite because it is through the interface that the applied stresses are transferred from the soft matrix to the reinforcement [22]. The formation of a chemical bond is one of the most favorable solutions to address this problem; however, this is a challenging solution. The most common phase that can form through an interfacial reaction in Al/GNPs systems is aluminum carbide (Al₄C₃), which has a low free energy of formation (−196 kJ mol^{−1} at 298 K); however, this phase can deteriorate the final properties of the composite [15]. Bartolucci et al. [15] reported that in a composite fabricated through ball milling, hot isostatic

pressing and extrusion, the hardness improved, while the ductility decreased significantly due to the formation of Al₄C₃. They showed that the aluminum carbide formed during the long period of ball milling. Li et al. [23] fabricated Al-0.5 wt% GNPs nanocomposites using cryomilling (at −181 °C), hot isostatic pressing and extrusion at a low temperature (300 °C). They reported that the fabrication through this technique could prevent the aluminum carbide formation and, as a consequence, it would be possible to obtain a significant improvement in the mechanical properties. However, the aforementioned production processes are substantially long and time-consuming and consequently not economical. Moreover, mechanical milling is not favorable in the present case (Al/GNPs nanocomposites) because it introduces defects in the graphene platelets. In addition, dispersants like stearic acid which are added during the ball milling cannot be eliminated easily and can lead to the formation of microholes [15, 16, 23].

A favorable candidate as a fabrication technique to produce Al matrix nanocomposites could be instead hot rolling of nanocomposite powders. In fact, hot rolling is a time-saving, low temperature, low pressure and high-quality technique to fabricate the MMNCs. However, to date, far too little attention has been paid to this technique.

Therefore, the main aim of the current research was to fabricate Al matrix nanocomposites reinforced with different GNPs contents using two separate techniques for consolidation: (I) a conventional powder metallurgy (press sinter) and (II) hot rolling. The effect of GNPs on the physical and mechanical properties, microstructure and thermal conductivity of aluminum matrix nanocomposites was also investigated in this research.

2 Experimental

The starting powders used to prepare the aluminum matrix nanocomposites with different percentages of GNPs are listed as follows:

- Aluminum powder, with average particle size of 44 μm and 99.5% purity. This powder had an irregular morphology with high aspect ratio and was supplied by Alfa Aesar, USA.
- GNPs with 99% purity, 1–2 μm lateral size and surface area of 700 m² g^{−1} were supplied by abcr, Germany.

The density of aluminum powder and GNPs was 2.7 and 2.1 g cm^{−3}, respectively.

Figure 1 presents the scanning electron microscopy (SEM) (a) and optical (b) images of the pure Al powder and the SEM image (c) together with the Raman spectrum (d) of the as-received GNPs. As shown in Fig. 1a, the Al particles have an irregular shape with a high aspect ratio.

Fig. 1 SEM image **a** and optical image **b** of pure Al, SEM image **c** and Raman spectrum **d** of as-received GNPs

Figure 1b shows the cross-sectional optical microscopy image of Al powders; some internal porosity can be observed inside the Al particles which are present in the final composite and might affect the final properties. Figure 1c shows the morphology of the as-received GNPs. From this image, it can be seen that the as-received multilayer GNPs have a flake shape with a thickness lower than 100 nm and a length in 7–10 μm range. As it can be seen in Fig. 1d, three main bands corresponding to the D, G (+D') and 2D vibrational modes are present in the Raman spectrum of GNPs.

In order to disperse the GNPs within the aluminum matrix, at first GNPs were dispersed in ethanol for 45 min via ultrasonication. At the same time, Al powders were dispersed by mechanical agitation in ethanol. After ultrasonication, GNPs were added dropwise to the aluminum powder slurry in ethanol to obtain the final dispersions containing 0.5 or 1.0 wt% GNPs. A control alloy consisting of pure Al was also considered for comparison. The mixtures were mechanically agitated for 60 min to improve homogeneity. Afterward, the mixtures were filtered and dried at 80 °C for 6 h.

Consolidation of the powders through die compaction is an economical and highly productive procedure to fabricate the MMNCs [8]. In order to fabricate the Al-xGNPs ($x = 0, 0.5, 1.0$ wt%) nanocomposites, dried powders of the composite mixture were compacted in a stainless steel die with 13 mm diameter at ambient temperature. 500 MPa

was chosen as the compaction pressure. The green cylindrical samples were sintered for 6 h at 620 °C under inert atmosphere (N_2) in a tubular furnace.

Consolidation of the composite powder mixture through the hot rolling process has been done by an OAM SM2001 duo rolling mill machine at 5 rpm speed. Before rolling, the powders were manually pressed inside the steel cans shown in Fig. 2a, b. Thereafter, hot rolling was performed at 600 °C. Four rolling passes were performed (15% reduction per pass) until the plates were reduced from 20 to 8 mm thickness. Finally, the outer steel can was removed after the last rolling pass (Fig. 2c, d).

The morphology, size and shape of the Al-GNPs powder mixtures were characterized by a Merlin-Zeiss FESEM (field emission scanning electron microscope). The X-ray powder diffraction patterns were recorded on a Philips X'Pert diffractometer using the $\text{CuK}\alpha$ radiation. The Raman analysis of graphene was carried out using a Renishaw InVia Reflex micro-Raman spectrometer (Renishaw plc, Wotton-under-Edge, UK) equipped with a cooled charge-coupled device camera. The laser beam ($\lambda = 514.5$ nm) was focused using a 50 $\times$ objective lens before irradiating the samples. The hardness of all specimens was measured by the Vickers hardness method, and the average of at least five measurements was reported at a load of 5 kg. Differential scanning calorimetry (DSC) tests were carried out in DSC 7 PerkinElmer apparatus with an argon atmosphere. The densities of the as-press-sintered

Fig. 2 **a** Dimensions of the can used for the consolidation process, **b–d** samples before and after the various steps of the hot rolling process (*RD* rolling direction, *TD* transverse direction)

and as-hot-rolled samples were measured by the Archimedes's method, and the results were averaged over three independent measurements. The laser-flash method was used in order to measure the thermal diffusivity, by using an FlashLineTM thermal diffusivity measurement system. The results are the average of three different measurements. Afterward, the thermal conductivities (k) were calculated by the following equation:

$$k = \alpha \times c_p \times \rho, \quad (1)$$

where α is the thermal diffusivity, c_p is the estimated value of the heat capacity of the composites, and ρ is the bulk density of the composite.

3 Results and Discussion

3.1 Powder Characterization

Figure 3 depicts the morphology of the Al-0.5 wt% GNPs powder mixture after wet mixing. The energy-dispersive spectroscopy (EDS) results show that during the mixing, GNPs adhere to the surface of the Al particles.

A similar effect was observed also on the Al-1.0 wt% GNPs nanocomposite powders. Figure 4 shows that the GNPs are homogeneously dispersed within the matrix. It is

evident not only that the dispersion of graphene within the aluminum matrix is uniform, but also that the structure of graphene remains unchanged.

Figure 5 shows the Raman spectra of the as-received GNPs and of the as-mixed composite powder (obtained by averaging 5.0 measurements at different points for each sample). Substantially, the Raman spectra of the graphene-based materials show several bands in the range of 1200–2800 cm^{-1} . The first peak (D band) at $\sim 1350 \text{ cm}^{-1}$ is due to a second-order scattering process which involves a graphene defect and a phonon. Actually, the D band is related to a disorder of graphene and graphitic-based materials. The second band at $\sim 1580 \text{ cm}^{-1}$ (G band) is related to the E_{2g} phonon at the center of Brillouin zone; such a vibrational mode is sometimes convolved with a weaker feature at $\sim 1615 \text{ cm}^{-1}$ which can be ascribed to the disorder-induced D' band [24]. The last important vibrational fingerprint deals with the 2D band (also defined as G' band), that is spectrally located at $\sim 2695 \text{ cm}^{-1}$ for single layers of graphene. This band shows a blue shift and a broadening due to multiple convolved components strictly dependent on the number of graphene monolayers and to the stacking order in multilayered graphene and graphitic materials [25]. Thus, according to the I_D/I_G ratio which is equal to 0.17, it can be concluded that the as-received GNPs contain a small amount of defects and the

Fig. 3 Al-0.5 wt% GNPs powder mixture **a**; Al-0.5 wt% GNPs powder mixture, magnified **b**; EDS spectrum corresponding to the mentioned point **c**

Fig. 4 EDS maps of Al-1.0 wt% GNPs composite, showing the homogeneous dispersion of GNPs

GNPs have a high quality. Moreover, the ratio of I_{2D}/I_G shows clearly that the as-received GNPs were multilayer.

As it can be seen, three main bands corresponding to the D, G (+D') and 2D vibrational modes are present in the spectra. Actually, the intensity ratio of the D band to the G band which is related to the disordering and defect density is not significantly altered by the process ($I_D/I_G \sim 0.17$ for both the bare GNPs and the GNPs in the Al-1.0 wt% GNPs nanocomposite powder mixture). This proves that the wet-mixing method does not introduce any defect in GNPs. The 2D band shows a certain asymmetry, which can be justified with the interplanar stacking order of the graphene layers, showing a certain degree of three-dimensional order [25].

3.2 Differential Scanning Calorimetry

In order to study the possible Al_4C_3 formation, differential scanning calorimetry (DSC) tests were performed on the pure Al powder and on the composite powder mixtures. The compacted powders were heated from 30 to 700 °C in an alumina crucible with a heating rate of 20 °C min⁻¹. Figure 6 shows the DSC curves of pure Al and Al-1.0 wt% GNPs nanocomposites. The curves exhibit a large endothermic peak which is corresponding to the melting of Al.

The DSC curve of the composite powder did not show any clear transformation occurring during heating up to

Fig. 5 Raman spectra of as-received GNPs and mixed composite powder

Fig. 6 Differential scanning calorimetry of pure Al and Al-1.0 wt% GNPs

700 °C. In previous studies, it has been reported that in Al-2024 containing 5.0 wt% CNTs, an exothermic peak corresponding to the aluminum carbide formation was detected as soon as aluminum melted [26, 27]. On the other hand, since the amount of GNPs in our samples is very low, the exothermic effect could be lower than the resolution of the DSC, preventing the detection of the Al_4C_3 formation.

3.3 X-ray Diffraction Patterns of the Composites

During the fabrication of the Al-based nanocomposites reinforced by carbon nanotubes or graphene, the aluminum carbide formation is the most energetically favorable phase transformation. As mentioned before, Al_4C_3 is a harmful phase in the Al/C nanocomposites because it deteriorates the mechanical properties. From the thermodynamic point of view, this reaction strongly depends on the fabrication temperature [15, 16]. Substantially, the prismatic planes of

carbon with the highest surface free energy are the favorable place for the Al_4C_3 formation, while aluminum carbide does not form, even at very high temperatures, in the highly stable defect-free graphitic planes of graphene. Thus, the aluminum carbide formation will be promoted at higher temperatures and where the density of defects is higher on graphitic planes [15, 16]. The XRD patterns of the powders and sintered composites are shown in Fig. 7. According to the Raman spectra of the Al/GNPs composites (Fig. 5), there was no increment in the level of defects in the GNPs during the preparation process and the level of defects is quite low. By considering the XRD patterns, it can be concluded that the level of defects in the Al/GNPs composites was not sufficient to promote the reaction in the solid state. If something formed, its amount was very low so that it was difficult to be detected by XRD. Thus, no peak corresponding to the Al_4C_3 phase was found. On the other hand, in the XRD patterns of the Al/GNPs systems, also the peaks related to the carbon were not detected, which could be attributed to the size, the crystallinity and the low percentage of the GNPs [28].

3.4 Microstructure of the As-Press-Sintered and the As-Hot-Rolled Composites

Optical microscopy (OM) was used to study the microstructure of Al and the Al/GNPs nanocomposites after the press-sinter or hot rolling processes. Figure 8 shows the OM images of (a) pure Al, (b) Al-0.5 wt% GNPs and (c) Al-1.0 wt% GNPs. With increasing weight percentage of graphene, the mean grain size decreases from 13 to 10 and 8 μm for Al-0.5 wt% GNPs and Al-1.0 wt% GNPs, respectively. The dark gray areas are the consequence of oxidation during the sintering or polishing step, while in the composites the small black wire-like structure (at the grain boundaries) are GNPs; it seems that in some

Fig. 7 XRD patterns of **a** as-received GNPs, **b** pure Al, **c** Al-0.5 wt% GNPs, **d** Al-1.0 wt% GNPs nanocomposites after sintering at 620 °C

Fig. 8 Optical microscopy images of press-sintered **a** pure Al, **b** Al-0.5 wt% GNPs, **c** Al-1.0 wt% GNPs, **d** SEM image of Al-1.0 wt% GNPs, **e** EDS analysis at a grain boundary, **f** a representative grain boundary of Al-1.0 wt% GNPs after sintering at 620 °C for 6 h in N₂ flow

regions the GNPs do not have a strong chemical bonding with aluminum (Fig. 8d). Figure 8b, c confirms the uniform distribution of the GNPs within the Al matrix; however, in the sample containing 1.0 wt% of graphene some agglomerates of graphene are present. Figure 8e, f shows the presence of graphene at the grain boundaries, and it is evident that a weak interfacial bonding was formed between Al and graphene. Generally speaking, in the Al/C system the adhesion can be affected positively by aluminum carbide formation so that Al₄C₃ can facilitate the adhesion because of the similarity between the metallic and the covalent bonding. However, as explained before, Al₄C₃ is a harmful phase inside the Al matrix nanocomposite and this brittle phase can deteriorate the final properties of the composite; thus, a lower sintering temperature was chosen to avoid this reaction. Since there was no wetting agent inside the composite and also the aluminum carbide formation was prevented by sintering at lower temperatures, a

poor interfacial bonding could be expected. Moreover, due to the significant mismatch between the coefficients of thermal expansion of Al and graphene, debonding could have taken place.

The SEM images of press-sintered nanocomposites with different GNPs contents are shown in Fig. 9. As can be seen, the GNPs distributed between the grain boundaries in both cases; however, the extent of agglomeration increased by increasing the GNPs content. It is believed that when the reinforcement size is smaller than the matrix size, they can agglomerate very easily in the matrix [29]. Moreover, it is evident that by increasing the graphene content the grain boundary spacing increased and consequently the sinterability of the composite was negatively affected. Varol *et al.* [29] have shown that the agglomeration regions acted as a resistant barrier to grain boundary diffusion during the sintering process and thus the sintered density of composite was negatively affected. Figure 10 shows the

Fig. 9 SEM images of press-sintered **a** Al-0.5 wt% GNPs, **b** Al-1.0 wt% GNPs after sintering at 620 °C for 6 h in N₂ flow

Fig. 10 Optical microscopy images of as-hot-rolled **a, b** pure Al, **c, d** Al-0.5 wt% GNPs, **e, f** Al-1.0 wt% GNPs

microstructure of hot-rolled Al and Al/GNPs nanocomposites after rolling along the transverse direction (RD–TD). By increasing the weight percentage of GNPs, the grain size decreased from 11 to 9 and 7 μm for Al-0.5 wt% GNPs and Al-1.0 wt% GNPs, respectively, while the

amount of agglomeration in the Al/GNPs increased. In these images, the GNPs agglomerations are shown by yellow-dash circles and microvoids by red-dash circles. In comparison with the press-sintered nanocomposites, it seems that the distribution of the GNPs is more uniform, a

fact that could be attributed to the high area reduction during the hot rolling process. In principle, due to the rolling compressive force, the GNPs will be aligned along the rolling direction and the GNPs agglomerates will be broken due to the weak bonding between the GNPs layers. However, it was reported that during the nanocomposites fabrication, the plastic deformation can cause some defects such as interfacial decohesion, reinforcement fracture and microvoid growth [30].

Besides the homogeneous dispersion of the reinforcement in the matrix, the porosity and the interface between the matrix and the reinforcement play significant roles in the final properties of the composite. A perfect bonding in a metal-matrix composite should protect the reinforcement and facilitate the load transfer from the soft matrix to the hard reinforcement. However, the presence of porosity at the interface deteriorates the properties by acting as a barrier for thermal transport, reducing thermal conductivity and as a crack initiation source reducing the mechanical performance [31]. It has been reported that among all the metal-forming techniques, the rolling technique has a unique merit due to the presence of compressive radial force and tangential shear stress, while in hot extrusion samples undergo hydrostatic compressive stresses [32]. However, as shown in Fig. 11, in Al/GNPs nanocomposites it seems that the microvoids located at the Al/Al interface were eliminated during the rolling process, while the porosities near to GNPs agglomerates were not removed and the voids were entrapped inside the hard agglomerates of GNPs. Figure 11b shows a typical interface between Al and GNP, indicating a poor interfacial bonding between Al and graphene and confirming the presence of voids close to the GNPs due to poor adhesion between Al and GNPs. Surprisingly, the grain orientation, which is one of the significant effects of hot rolling, could not be seen in the microstructure due to the consolidation mechanism during rolling. In fact, during hot rolling, because of the very low green density of the compacted samples, the particle

rearrangement is the dominant mechanism and consequently the compacted powder starts to flow instead of undergoing a plastic deformation.

3.5 Surface Analysis

The surface of the samples was also observed by optical microscopy after hot rolling at 600 °C, after polishing down to 9 µm. This analysis confirmed the uniform dispersion of the GNPs and the formation of a higher number of graphene clusters when increasing the GNPs content (Fig. 12).

3.6 Density and Vickers Hardness Assessment

Density is a basic physical property of a composite. Therefore, in order to calculate the theoretical density of the composites, the following equation can be used [33]:

$$\rho_c = \frac{1}{\frac{m_{Gr}}{\rho_{Gr}} + \frac{m_{Al}}{\rho_{Al}}}, \quad (2)$$

where ρ_c , ρ_{Gr} and ρ_{Al} represent the densities of GNPs/Al composites, graphene and Al matrix, respectively, and m_{Gr} and m_{Al} are the mass fractions of graphene and Al. The measured and theoretical densities of pure Al and the composites are listed in Table 1. It can be seen that the density of Al and the composites lies in the range of 2.55–2.64 g cm^{−3} depending on the graphene content. The GNP reinforcement has a density of 2.1 g cm^{−3} which is lower than that of Al (2.7 g cm^{−3}). Therefore, the increase of the GNPs content will reduce the theoretical density of the composite.

In comparison with the hot-rolled samples, the samples fabricated by the conventional press-sinter technique have higher densities because, as mentioned before, microvoid growth is one of the defects that can occur during the plastic deformation (hot rolling) and, as a consequence, it causes density reduction. Moreover, it is clear from

Fig. 11 SEM images of **a** hot-rolled Al-1.0 wt% GNPs, **b** magnification of an Al/GNPs interface

Fig. 12 Polished surface of as-hot-rolled **a** pure Al, **b** Al-0.5 wt% GNPs, **c** Al-1.0 wt% GNPs

Table 1 Density and Vickers hardness of Al-*x*GNPs (*x* = 0, 0.5, 1.0 wt%) produced by conventional powder metallurgy and hot rolling

Composition	ρ_c (g cm ⁻³)	Press sintered		Hot rolled	
		ρ (g cm ⁻³)	HV ₅	ρ (g cm ⁻³)	HV ₅
Pure Al	2.7	2.646	44 ± 2.1	2.557	42 ± 1.1
Al-0.5 wt% GNPs	2.695	2.628	51 ± 1.4	2.526	43 ± 1.5
Al-1.0 wt% GNPs	2.690	2.556	57 ± 4.2	2.441	42 ± 2.3

Table 1 that the GNPs content has a negative influence on the density of the composites. As revealed in the optical images (Fig. 10), by increasing the GNPs content the number of agglomerates increases and there will be a higher percentage of porosity inside the composite. Moreover, it has been reported that by increasing the reinforcement content the grain boundary spacing increases and consequently the sinterability of composite decreases [29]. In fact, as discussed earlier, by increasing the GNPs content, due to their inherent tendency to form the agglomerates, the GNPs clusters are formed mainly at the grain boundaries. These agglomerates interrupt the grain boundary diffusion during the sintering process and cause lower sinter densities in the case of composites.

Table 1 shows also that for press-sintered samples the hardness of the composite increases as the weight percentage of the GNPs increases, probably due to the microstructure refining effect of the addition of GNPs. For hot-rolled samples the increase of hardness is masked by the reduction of density, but it is evident that both phenomena occur since the increase of porosity always leads to a hardness reduction, while in this case the hardness is more or less constant for all samples. Rashad et al. [7] studied the effect of the addition of multilayer graphene on the microstructure and mechanical properties of Al/GNPs composites produced by extrusion. They also reported that the addition of GNPs inside the aluminum matrix not only decreases its density but also improves the hardness of the

aluminum matrix composites. According to their investigation, the improvement of hardness could be attributed to the inherent strength of GNPs which offers high constraint during the indentation. This kind of improvement in hardness of MMNCs as a consequence of GNPs addition has been also reported in AZ31/GNPs composites [34]. However, Varol et al. [29] showed that the hardness of multilayer graphene (MLG)/copper nanocomposites decreased by increasing the MLG content.

3.7 Thermal Conductivity Evaluation

The thermal conductivities of the Al/GNPs nanocomposites with different graphene contents and produced by the two techniques are shown in Fig. 13. The thermal conductivity of the composites was measured along the *z*-direction, and a few models were used to compare the experimental data with the theoretical ones, using for graphene the thermal conductivity value of 5000 W m⁻¹ K⁻¹. It is possible to observe a slight increase in thermal conductivity for Al-0.5 wt% GNPs with respect to the base alloy, while at 1.0 wt% GNPs the thermal conductivity of the composite decreases significantly. By comparing the two techniques, it can be seen that hot rolling gives slightly lower results than press sintering.

It is known that during high strain processes graphene tends to be oriented in the plane of maximum strain [35], i.e., in this case in the *x*-*y* plane. Due to this anisotropy,

Fig. 13 Thermal conductivity of GNP/Al produced by **a, b** press-sintering process, **c, d** hot rolling

different theoretical models were chosen for an analysis of the experimental data. The thermal conductivity in different directions (x – y and z plane direction) can be predicted by the layers-in-parallel and layers-in-series or geometrical mean models. In the layers-in-parallel model, the thermal conductivity is estimated along the basal planes. In order to calculate the thermal conductivity in the x – y plane direction the following equation can be used [21]:

$$K_c = V_f K_f + V_m K_m, \quad (3)$$

where K is the thermal conductivity, V is the volume fraction, and the subscripts “c,” “f” and “m” refer to composite, reinforcement and matrix, respectively. However, in the thermal conductivity calculation along the z plane direction, the thermal conductance of the GNP/Al interface should be taken into account. Thus, to estimate the thermal conductivity along the z plane direction the following equation can be used [21]:

$$\frac{1}{K_c^z} = \frac{V_f}{K_f^z} + \frac{V_m}{K_m}. \quad (4)$$

In order to calculate the thermal conductivity enhancement through the addition of a conductive second phase by the geometrical model, the following formula can be used [36]:

$$K_c = K_f^{V_f} K_m^{(1-V_f)}. \quad (5)$$

The predictions of the different models are shown in Fig. 12 together with the experimental data. For the press-sintered samples, the good agreement of the parallel model with the experimental data for the 0.5 wt% GNP composites is evident, while in the case of 1.0 wt% GNP the experimental data are much lower than the model predictions. This discrepancy is likely to be related to three main reasons: (1) porosity that increased with increasing graphene content due to the clustering of graphene, (2) grain boundaries, which increased as a consequence of grain refinement due to the addition of a second phase, (3) poor bonding between Al and graphene.

The interfacial thermal resistance of the GNP/Al interface can be calculated by means of the acoustic mismatch model (AMM) model [37],

$$h = \frac{1}{2} \rho_{in} c_{in} \frac{\rho_{in} \rho_{tran} v_{in}^4}{v_{tran} (\rho_{in} v_{in} + \rho_{tran} v_{tran})^2}, \quad (6)$$

where C , ρ and v are the specific heat, density and phonon velocity, respectively. “in” and “tran” as subscripts are the incident and transmission sides of the phonon. Since the transversal waves contribute to heat transfer, their velocities were taken into account. By using the data in Table 2

Table 2 Properties of structure elements of the models used in the current work

	ρ (kg cm ⁻³)	C (J K ⁻¹ kg ⁻¹)	ν (m s ⁻¹)	References
Al	2700	895	3595	[39]
Graphene	2100	710	14,500	[39]

and Eq. 6, the interfacial thermal resistance in the Al/GNPs system could be calculated. The interfacial thermal resistance calculated in this study is $h = 4.7 \times 10^7$ W m⁻² K⁻¹, which is consistent with the literature data (5×10^7 W m⁻² K⁻¹ [21, 38]).

Regarding the hot-rolled samples, they have lower thermal conductivity than the press-sintered ones. This is likely to be the result of the higher porosity level in these samples with respect to the press sintered. According to the previous microstructure observations, by increasing the graphene content the porosity of samples increases due to porosity and agglomeration of the GNPs. These agglomerates have a negative effect on the thermal conductivity of composites.

4 Conclusions

1. Microstructural observations and Raman spectra of GNPs show that the wet-mixing method could be used as the appropriate mixing method. In fact, it is possible to disperse the GNPs within the matrix not only without damaging the structure but also homogeneously, in particular at low GNPs contents. By increasing the weight percentage of the GNPs, the number of GNPs agglomerates increased.
2. According to the DSC curves and the XRD patterns, it could be concluded that there was no significant carbide formation reaction during the fabrication of the composites.
3. Microstructural evaluations revealed that with both techniques a grain refinement occurred as a consequence of the GNPs addition, so that, by increasing the weight percentage of graphene, the mean grain size decreased from 13 to 10 and 8 μ m for Al-0.5 wt% GNPs and Al-1.0 wt% GNPs, respectively, in the case of press-sintered samples. Moreover, in the case of the hot-rolled samples, by increasing the GNPs content, the mean grain size decreased from 11 to 9 and 7 μ m for Al-0.5 wt% GNPs and Al-1 wt% GNPs, respectively.
4. A maximum sintered density of 2.646 g cm⁻³ was found for pure aluminum fabricated by conventional powder metallurgy which was equal to a relative

density of 98%. The density of pure Al after hot rolling was 2.557 g cm⁻³ which was equal to a relative density of 95%. In all cases, by increasing the GNPs content the density of Al/GNPs decreased and the minimum density was found for Al-1.0 wt% GNPs after hot rolling.

5. Mechanical characterization showed a Vickers hardness improvement in GNPs/Al composites by increasing the graphene content. This improvement can be attributed to the grain refinement effect.
6. The thermal conductivity results show clearly that a maximum thermal conductivity of 224 W/(m K) was achieved for Al-0.5 wt% GNPs which is 5% higher than that of the same composite produced by the hot rolling technique. This discrepancy could be related to their porosity content after fabrication processes so that the density of press-sintered Al-0.5 wt% GNPs sample was 3% higher than that of the hot-rolled one. However, in all the Al-1.0 wt% GNPs samples produced by press sintering and by hot rolling a minimum thermal conductivity was achieved mainly due to their higher porosity content with respect to the other composites.
7. In general, it could be concluded that GNPs/Al interface, porosity content, agglomeration of graphene and grain refinement can play significant roles in the final properties of the Al/GNPs composites.

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