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WEAR RESISTANCE ANALYSIS OF THE ALUMINUM 7075 ALLOY AND THE NANOSTRUCTURED ALUMINUM 7075 – SILVER NANOPARTICLES COMPOSITES

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Abstract

Nanostructured composites of the aluminum 7075 alloy and carbon-coated silver nanoparticles were synthetized by the mechanical milling technique using a high-energy mill SPEX 8000M; the powders generated were compacted, sintered and hot-extruded to produce 1 cm-diameter bars. The composites were then subjected to a wear test using a pin-on-disc device to validate the hypothesis that second phase-ductile nanometric particles homogenously distributed throughout the metal-matrix improve the wear resistance of the material. It was found that silver nanoparticles prevent the wear of the material by acting as an obstacle to dislocations movement during the plastic deformation of the contact surface, as well as a solid lubricant when these are separated from the metal-matrix.

***Keywords**: Nanostructured composites; Pin-on-disc; Silver nanoparticles; Aluminum; Wear*

1. Introduction

Aluminum is the second most employed metal in the world; several of its properties make it critical to many applications-among these are: good corrosion resistance, low density, high electrical conductivity, as well as good thermal conductivity. Pure aluminum exhibits poor mechanical properties, but by additions of alloying elements these properties can be substantially improved [1]. The combination of a relatively high resistance with a low density implies a higher efficiency of the several aluminum alloys and offers many opportunities to replace heavier metals without an overall loss, but perhaps improvement, of bearing higher loads. The 7xxx series, which are alloyed with zinc, especially when combined with copper and magnesium, provide the highest strengths of any commercial series [2].

The 7075 aluminum alloy has several applications: aircraft fittings, gears and shafts, fuse parts, meter shafts and gears, missile parts, regulating valve parts, worm wears, keys, aerospace and defense applications, bike frames, all-terrain vehicle (ATV) sprockets [3]. Some applications involve relative movement between surfaces of components, and in this way the wear resistance is an important property to take into account, this and other properties can be improved by producing metal matrix composites (MMC). A composite is obtained by combining two or more materials which in turn generates a unique arrangement of new properties. The final properties of the composite are generally better than those of the original alloy constituents [4]. Composites are not only applied for their structural properties, but also for tribological, electrical, thermal, and environmental applications [5].

A method of producing particle reinforced metal matrix composites (MMC) is mechanical milling (MM). MM is a technique that allows the production of homogenous materials by the mixture of powders; by using a high-energy mill the material deforms plastically, fractures and is cold welded several times by the milling media for the required time [6]. The wear resistance is a property that is improved with this technique. Adhesive wear occurs when material transfers from a surface to another during their relative movement; this happens when surfaces slide and a load between asperities in contact is enough to promote local plastic deformation. The hardness of an asperity is an important factor in evaluating the wear resistance of a material [7].

Composites reinforced with hard particles exhibit

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good adhesive wear resistance; these hard particles limit the plastic deformation of the metal matrix, thus promoting a higher resistance to wear. Several studies have been conducted regarding the behavior of the wear resistance of aluminum metal matrix composites reinforced with hard particles (SiC, Al_2O_3, TiC, TiB_2, $NiAl_3$, $FeAl_3$), and these have reported a general improvement of wear resistance compared to their base alloy [1, 8-10].

The aim of the present investigation is to evaluate the wear resistance of metal matrix composites reinforced with ductile nanoparticles. MMC were synthesized by an aluminum 7075 (Al_{7075}) reinforced with different amounts of carbon-coated silver nanoparticles (Ag-C NP). The effect of Ag-C NP on wear performance is evaluated and discussed.

2. Experimental procedure

The raw materials used were Al_{7075} alloy metal-shaving with a thin plate-like shape an average size of 5 mm long, 5 mm width, and 0.2 mm thickness and carbon-coated silver nanoparticles with an average size of 20 nm. Ag-C NP is a product obtained from Nanotechnologies Inc. (Austin TX), which are produced by arc discharge and stabilized with carbon from a hydrocarbon source, at the end of the production process the nanoparticles were surrounded by an amorphous graphite shell. Concentrations selected were 0.5, 1.0, 1.5, and 2.0 wt. % of Ag-C NP. MMC were synthesized by a milling process in a high-energy ball mill SPEX 8000M. The milling times selected were 0, 5, 10 and 15 h. The total milling load was 10 g and the milling ball-to-powder weight ratio was set at 4 to 1, the SPEX vials and milling media were made of hard steel. To avoid oxidation during milling, all runs were done under argon atmosphere, 0.25 ml of methanol as a process control agent (PCA) was used in all experiments [11]. Milling products were cold compacted in steel die with 4 cm diameter. Sintering under argon atmosphere was done first at 473 K for 2 h, then at 733 K for 4 h and then at 748 K for 18 h. Sintered products were hot extruded at 773 K. An extrusion ratio of 16 was selected to obtain 1cm diameter bars [12].

Consolidated products were characterized by density determination by the Archimedes method. Microstructural characterization by XRD was done in a Panalytical X'pert PRO diffractometer with Cu Kα radiation operated at 40 kV and 35 mA in the 2θ range of 20 – 100°. Step size and collection time were 0.05° and 50 s, respectively, and by scanning electron microscopy (SEM) in a JEOL JSM 6610LV microscope operated at 20 kV and by transmission electron microscopy (TEM) in a JEOL 2200FS microscope operated at 200 kV. The chemical analyses were determined by energy dispersive spectroscopy (EDS), using an Oxford Inca X-Ray energy dispersive spectrometer attached to the microscope system.

The mechanical characterization was carried out by microhardness tests in a Micro Hardness Tester FM-07, using a maximum load of 200 g and dwell time 10 s. Tensile tests were performed based on ASTM E8M in a Universal Shimadzu machine with a constant crosshead speed of 0.066 mm/s.

The wear tests of extruded composites were carried out in a pin-on-disc device. Cylindrical pin specimens 10 mm in diameter and 20 mm long were prepared form the aluminum extruded bars. The tip of pin specimens were grounded and polished to keep up the surface uniformity, and to ensure a complete contact of the flat surface on the abrasive sandpaper. The arrangement consists of a container perpendicular to a rotating disc. Sand-paper of SiC with a 53.5 µm average size was used. The applied loads during the tests were of 1 N and 2 N, applied perpendicularly to the wear surface of the pin specimens. To corroborate the data experiments were carried out making two tests for each condition. Fig. 1 presents a schematic representation of the pin-on-disc device employed.

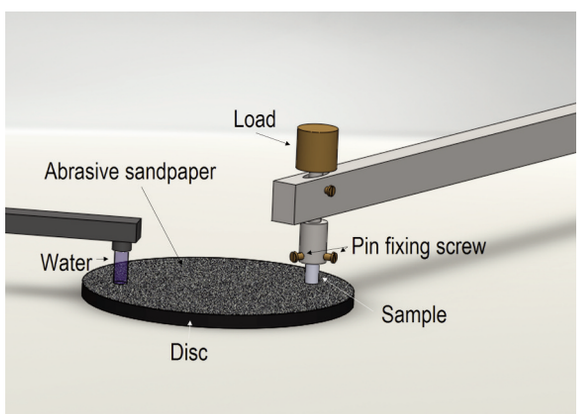

Figure 1. *Schematic process of the pin-on-disc apparatus to evaluate the wear behavior of the nanostructured composites Al_{7075} – Ag-C NP*

A constant sliding speed of 0.5 m s^{-1} was established. The total linear sliding distance during the tests was established at 600 m. Evaluations of weight loss were done each 100 m. The samples where cleaned in an ultrasonic bath of methanol, dried and weighed in an analytical balance of 0.0001 g precision to determine the weight loss in each interval. The tests were made at room temperature, using a continuous flow of water as a lubricating agent during each test. The abrasive paper was changed after each evaluation of the applied sliding distances.

The worn surfaces of the pin specimens were examined by scanning electron microscopy (SEM) in a JEOL JSM 6610LV microscope.

3. Results and discussion

Fig. 2 shows the density results for MMC as a function of milling time and Ag-C NP concentration. In Fig. 2a it can be observed that the density variation is minimal, presenting an average of 2810 kg/m^3 for the different applied milling times, this value corresponds with that reported in the literature for the Al_{7075} alloy [13]. Fig. 2b shows the density variation in terms of the overall nanoparticle concentration and at the different applied milling times. It can be noted that the density value increases slightly as the content of the nanoparticles dispersed inside the metal matrix increases, presenting a maximum at 1.0 wt. % of Ag-C NP concentration; at higher concentrations of nanoparticles (1.5 and 2.0 wt. %) a small decrease in its value is perceived. The small density increment in the nanostructured composites could be attributed to the silver nanoparticles, which are homogenously distributed in the aluminum matrix, acting as nucleation centers that promote the formation of the $MgZn_2$ phase [12]; the presence of different compounds produced during the processing of the nanostructured composite [14], i.e. Al_2O_3, MgO, Al_4C, also contributes to this effect.

Fig. 3 shows a TEM image from the nanostructured composite with 1.5 wt. % of nanoparticles. Fig. 3a) shows a silver nanoparticle with a size of ~30 nm, around which there are smaller phases corresponding to the $MgZn_2$ phase, this phase lead to the most significant improvement of mechanical properties in the Al_{7075} alloy [15]. The shield of carbon that surrounds the silver nanoparticles avoids this to dissolve into the aluminum. Fig. 3b) shows the morphology of the nanostructured composites, it can be seen that silver nanoparticles are dispersed homogenously into the aluminum matrix. Homogeneous dispersion of nanoparticles and $MgZn_2$ phase, are responsible of the increment in mechanical properties [12]. Table 1 gives the composition of the phases and particles. In Fig. 3, it can be observed that particle 1 is rich in silver, and phases 2 and 3 are rich in Mg and Zn, as shown in the EDS spectrum. The $MgZn_2$ phase precipitation is accelerated and stabilized when Cu is added to the alloy [16].

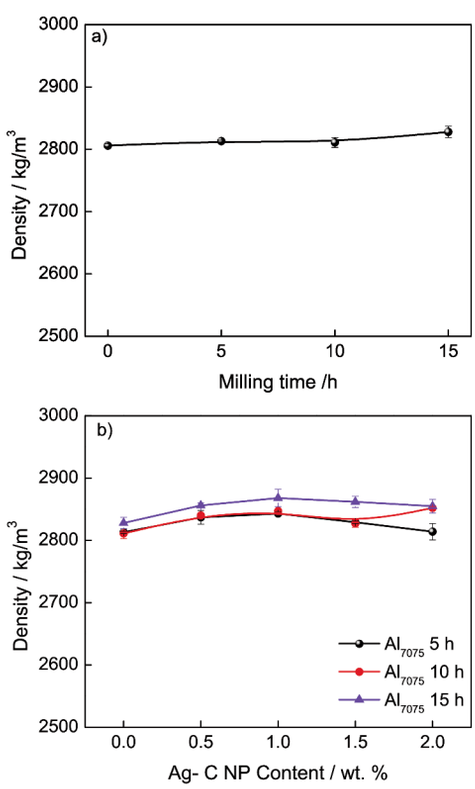

Figure 2. *Density of a) Al_{7075} alloy and b) nanostructured composites obtained at different milling times in the as-extruded condition*

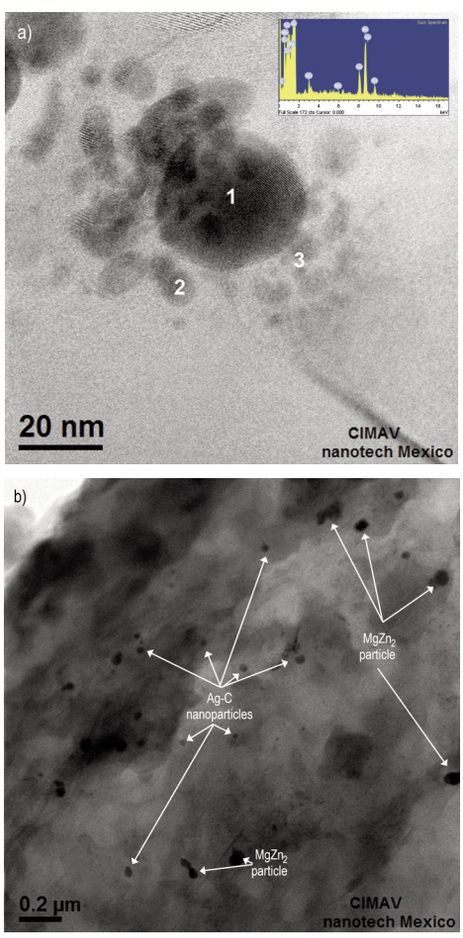

Figure 3. *TEM micrographs of the nanostructured composite obtained at 10 h of milling and 1.5 wt. % of silver nanoparticles in the as-extruded condition a) Ag-C NP surrounded by $MgZn_2$ particles and its EDS spectrum, and b) dispersion of silver nanoparticles into the aluminum matrix*

Table 1. *Average quantitative EDS analysis on the phases and particles shows in Fig. 3*

Position	Composition (wt. %)								
	C	O	Mg	Al	Mn	Cu	Zn	Ag	Total
Particle 1	0	0	0	60.61	0	3.04	5.02	31.34	100
Phase 2	0	3.31	3.63	60.44	0	7.84	24.79	0	100
Phase 3	0	1.81	1.43	89.45	0	1.22	6.09	0	100

Fig. 4 shows the XRD pattern of the hot extruded samples with 2.0 wt. % and without silver nanoparticles at the different milling time employed. It can be observed that the Al_{7075} alloy without additions of Ag-C NP´s exhibits sharp and high intensity peaks corresponding to the aluminum matrix, and small reflections of second phases corresponding to $MgZn_2$, MgO and Al_2O_3. These phases crystallize during sintering and hot extrusion processes probably due to the oxygen present in the milled products. On the other hand, the nanostructured composites present a high intensity peaks corresponding to the aluminum matrix and evident signals of $MgZn_2$, MgO, Al_2O_3 and Al_4C_3. It can be seen that the formation of the $MgZn_2$ and Al_4C_3 phases is favored for the Ag-C NP´s content.

Table 2 shows the microhardness results as a function of the silver nanoparticle content and milling times. It can be observed in the Al_{7075} alloy that the microhardness value increases with higher milling times. Additionally, for nanostructured composites an increment in microhardness is observed with nanoparticles additions at the same milling time, reaching a maximum value at concentrations of 1.0 wt. % of Ag-C NP, decreasing slightly at higher concentrations. The reduction in the microhardness value is attributed to the agglomeration of silver nanoparticles [17].

Table 3 shows the ultimate tensile strength (UTS) values for the nanostructured Al_{7075} – Ag-C NP composite as a function of the silver nanoparticle content and milling times. Notice that the UTS

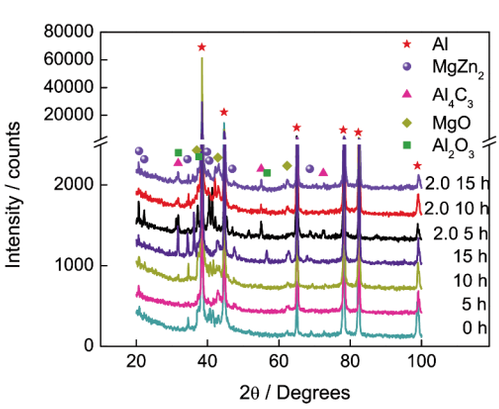

Figure 4. *XRD spectra of the nanostructured Al_{7075} – Ag-C NP composites showing the effect of milling time in the as-extruded condition and the effect of Ag-C NP´s*

Table 2. *Microhardness as a function of silver nanoparticles content for 5, 10, and 15 h of milling*

Ag-C NP	Microhardness (HVN)		
Content (wt. %)	5 h	10 h	15 h
0	88.48 ± 2.30	93.98 ± 2.77	101.27 ± 1.95
0.5	104.07 ± 5.92	105.57 ± 4.81	112.33 ± 1.85
1	116.50 ± 4.81	122.08 ± 1.13	113.02 ± 2.08
1.5	111.95 ± 1.14	112.60 ± 4.04	111.25 ± 2.41
2	106.10 ± 1.08	104.20 ± 2.98	116.28 ± 1.42

Table 3. *Ultimate tensile strength as a function of silver nanoparticle content and milling time*

Ag-C NP	Ultimate tensile strength (MPa)		
Content (wt. %)	5 h	10 h	15 h
0	305.0 ± 19.1	332.2 ± 48.6	239.0 ± 6.6
0.5	358.0 ± 6.3	347.8 ± 7.8	281.6 ± 57.2
1	328.9 ± 10.0	375.1 ± 26.4	337.2 ± 17.1
1.5	400.5 ± 16.3	396.5 ± 9.3	356.0 ± 21.3
2	353.7 ± 18.6	323.8 ± 0.5	353.9 ± 22.5

generally increases as the nanoparticles content increases. This behavior is observed in all milling times used, reaching a maximum at 1.5 wt. % of Ag-C NP, but then shows a small decrease with a higher content. This enhancement in the mechanical resistance is due to the homogenous dispersion of silver nanoparticles, as well as to the presence of different phases ($MgZn_2$, Al_4C_3, MgO, and Al_2O_3) formed during the synthesis of nanostructured composites. The existence of both, nanoparticles and secondary phases in the material arrests the movement of dislocation lines. This is a well-known strengthening mechanisms present in MMC [18].

During the relative movement of the surfaces, the hard SiC surface asperities move across the softer aluminum surface acting as a cutting tool, generating the detachment of the aluminum matrix, presence of different particles formed or introduced into the matrix obstruct the cutting effect of the SiC hard surface. Fig. 5 displays the wear behavior of the reference alloy as a function of milling times. The effect of the different loads employed, 1 N and 2 N, is presented in Fig. 5a and Fig. 5b, respectively. For both conditions, the wear rate is almost the same at any sliding distance, a higher

applied load, a higher wear rate is observed. Furthermore, it can be seen that the alloy with 0 h of milling presents the lower wear rate; with a higher milling time a higher wear occurs.

The minimal and maximal wear rate correspond to 0 and 15 h milling time, with an applied load of 1 N the values at 100 m was $2.55x10^{-4}$ and $4.17x10^{-4}$ mg/m respectively, and for the 600 m of sliding distance the values was $2.08x10^{-4}$ and $3.61x10^{-4}$ mg/m, respectively. While for an applied load of 2 N the values were $4.94x10^{-4}$ and $7.96x10^{-4}$ mg/m and $4.65x10^{-4}$ and $7.24x10^{-4}$ mg/m, in that order, at 100 m and, for the extreme values at 600 m of sliding distance, respectively. The values of wear rate for 5 and 10 h of milling time lies between the minimal and maximal (0 and 15 h, respectively).

Comparing these results with the microhardness results reported in Table 2, (87.65 ± 2.56 HVN at 0h milling), it can be noted that at higher microhardness the wear resistance is lower; this is ascribed to a higher milling time that dissolves and/or fragments the $MgZn_2$ phase [11], producing a metal matrix with a few particles. Although the $MgZn_2$ phase can be formed during the synthesized processes, the amount of this phase would be present in a minor quantity at higher milling times, thus during the surface relative movement a lower quantity of particles will prevent the dislocation line motion generating a greater wear rate.

With short milling times the synthesized alloys contain larges $MgZn_2$ particles in the aluminum metal matrix, and during the relative movement of surfaces these particles reduce the dislocation movement in the surfaces asperities. At longer milling times the alloys produced contain a smaller quantity of smaller particles imbedded in the metal matrix, causing a two-body abrasion effect where the hard surface asperities move across the softer surface as a cutting tool [19].

Figs. 6, 7, and 8 show the wear behavior of the nanostructured Al_{7075} – Ag-C NP composite obtained by mechanical milling with 5, 10, and 15 h of milling and at different silver nanoparticle content under the action of two loads: 1 N (Figs. 6a, 7a, 8a) and 2 N (Figs. 6b, 7b, 8b). As it can be noted in the various graphics, there is a similarity with the behavior shown by the Al_{7075} alloy (Fig. 5) obtained by mechanical milling and without the addition of nanoparticles.

From Fig. 6 it can be observed that, for a 5 h milling and a total displacement of 600 m, the alloy without silver nanoparticles shows a wear rate, for both applied loads, of $2.59x10^{-4}$ and $5.47x10^{-4}$ mg/m respectively, the nanostructured composite treated with 2.0 wt. % of nanoparticles has values of $2.14x\ 10^{-4}$ and $4.74x10^{-4}$

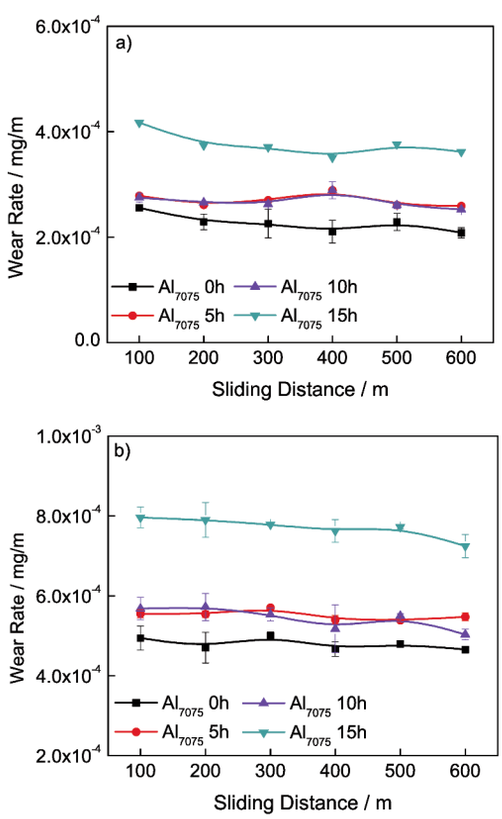

Figure 5. *Graphs showing the effect of the milling time, displacement and load in the wear rate, a) 1 N and b) 2 N*

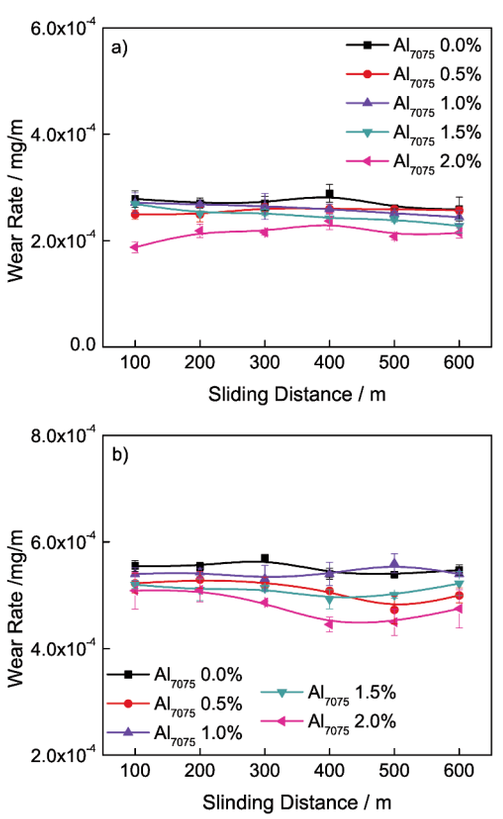

Figure 6. *Wear rate as a function of total displacement with load of a) 1 N and b) 2 N. MMC were synthesized with 5 h of milling*

mg/m for 1 N and 2 N, respectively.

In Fig. 7 the wear rate of the alloy without nanoparticles produced at 10 h of milling is determined at $2.52x10^{-4}$ and $5.02x10^{-4}$ mg/m for the respective applied loads, and with a total displacement of 600 m; the reported values for the nanostructured composite with 2.0 wt. % of nanoparticles are $2.19x10^{-4}$ and $4.35x10^{-4}$ mg/m for 1 N and 2 N, respectively.

Finally, Fig. 8 shows that the alloy without nanoparticles produced at 15 h of milling present a wear rate of $3.61x10^{-4}$ and $7.24x10^{-4}$ mg/m for the respective applied loads and at a total displacement of 600 m; the nanostructured composite with 2.0 wt. % of nanoparticles reports a wear rate of $2.22x10^{-4}$ and $4.73x10^{-4}$ mg/m for 1 N and 2 N, respectively.

As the silver nanoparticles content increase in the nanostructure composites produced at the different milling times, the wear rate decrease indicating that silver nanoparticles has a valued effect on the wear resistance of the material, it is interesting to note that the highest wear resistance value corresponds to that of the nanostructure composite obtained at 10 h of milling, material that exhibits the higher ultimate tensile strength values.

The results imply that with an increment in mechanical strength of the nanostructured composite, a higher wear resistance is obtained. This occurs because nanostructured composites will support higher loads before they raise the fracture stress of the asperities in the material between the surfaces in relative movement, due to the presence of silver nanoparticles as well as the phases $MgZn_2$, Al_2O_3, MgO, and the Al_4C_3 that form during the synthesis of the nanostructured composite [14]; thus it can be concluded that the addition of silver nanoparticles has a positive effect on the whole wear resistance of the Al_{7075} – Ag-C NP composites. Despite the fact that the nanostructured composites are constituted by ductile particles, the wear resistance is enhanced by the addition of carbon-coated silver nanoparticles to the Al_{7075} alloy. This shows that ductile particles can improve the wear resistance of nanostructured composites by two mechanisms: *i* acting as obstacles to dislocation movement during the plastic deformation of the contact surface, and *ii* acting as a solid lubricant when these are separated from the metal-matrix.

Fig. 9 shows SEM images of the worn surface morphology of the Al_{7075} alloy obtained at different milling times; wear scars products of the surface relative movement can be observed in the material. Fig. 9a) corresponds to the unmilled sample; $MgZn_2$ phase can be seen inside the aluminum metal matrix, which confers a higher wear resistance slowing the dislocations motion of the contact surfaces during the

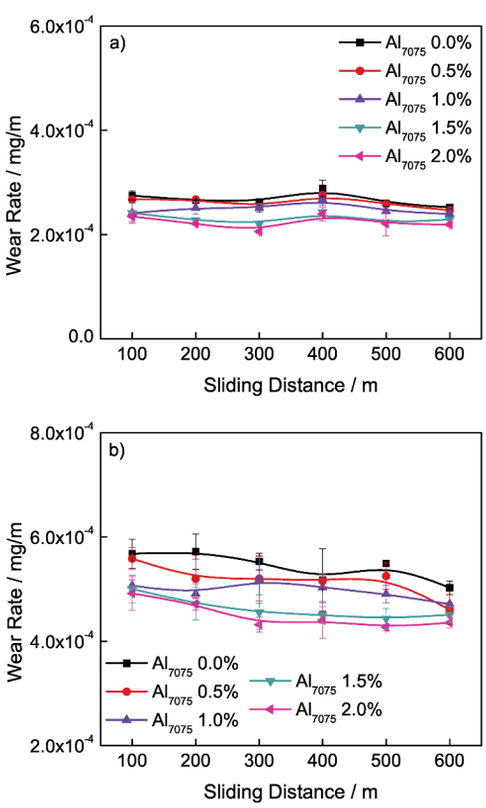

Figure 7. *Wear rate as a function of total displacement with load of a) 1 N and b) 2 N. MMC were synthesized with 10 h of milling*

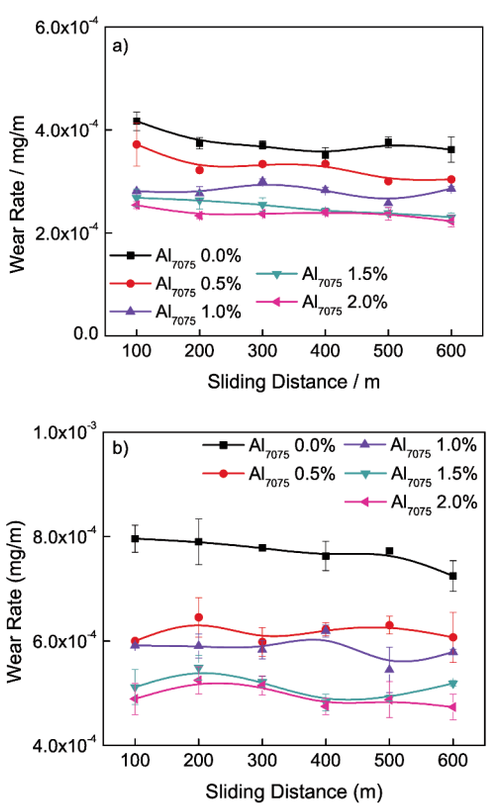

Figure 8. *Wear rate as a function of total displacement with load of a) 1 N and b) 2 N. MMC were synthesized with 15 h of milling*

relative movement. In the case of Fig. 9b), the alloy with 15 h of milling has an apparently particle-free surface, which explains its lower wear resistance. This confirms the previous discussion that with higher milling times the alloy obtained has a lower wear resistance, despite the fact that higher microhardness values ensue from increasing milling time. The absence of the $MgZn_2$ phase can be explained by the fragmentation/dissolution of this as the milling time increases, which enters in solid solution with the material during the mechanical milling process, and therefore a smaller number of these phases are presented in the aluminum matrix after the synthesis of the material.

Fig. 10 shows SEM images of the wear surface morphology of the nanostructured Al_{7075} – Ag-C NP composite. Fig. 10a) displays the composite with 10 h of milling and 1.5 wt. % of Ag-C NP, the condition that exhibits the best mechanical properties as reported elsewhere [13]. It presents a smoother surface compared to that of the base alloy (Fig. 9), having flakes in its surface, which indicate that the material was not severly abraded, but gradually worn away. Fig.10b) shows the same condition for the nanostructured composite at a higher magnification, in which superficial layers at different levels of depth are observed.

Fig. 11 shows SEM images of the wear surface morphology of the nanostructured Al_{7075} – Ag-C NP composite obtained at 5 h of milling and 2.0 wt. % of Ag-C NP. At this nanoparticles concentration, it was observed a nanoparticles agglomeration [17]. In Fig. 11a) a worn surface can be observed with a flake morphology and, besides this, some silver nanoparticles seem to have been smeared along the displacement direction, giving up a spherical hollow.

Fig. 11b) is a magnification of the material surface, in which the presence of spherical hollows along the metal matrix are more evident, having an average size of 90 nm; this suggests that the silver nanoparticles were separated from the metal matrix during the surface´s relative movement, and thereby acted as wear debris [7].

Comparing images 9, 10 and 11, it is evident that the silver nanoparticles act as a solid lubricant when separated from the aluminum metal matrix by producing a more even surface, in contrast to a rougher surface generated when no solid lubrication is applied.

From the information that these images provide, it is observed that nanostructured Al_{7075} – Ag-C NP composites exhibit a higher wear resistance due to: i) the presence of silver nanoparticles that have an strengthening effect as second phase [14], ii) these nanoparticles arrest the movement of dislocation lines during the plastic deformation at the material surface, iii) when these nanoparticles are separated from the aluminum metal matrix, they act as a solid lubricant between two surfaces in contact, improving thereby the wear behavior of the material; recent studies in the field of lubrication that concern silver nanoparticles dispersed in oils have shown that these improve the wear resistance of surfaces [20], and at last, but not the least, iv) the carbon shell has an additional lubricant effect during wear test [21].

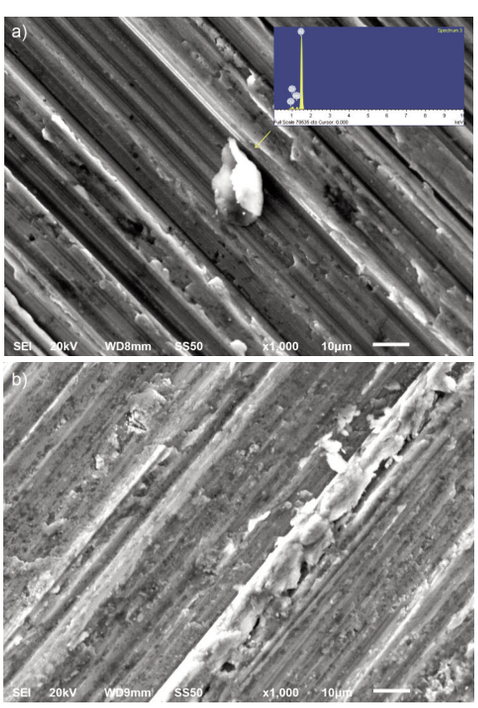

Figure 9. *Conventional SEM images of the Al_{7075} alloy with a) 0, and b) 15 h of milling, and its EDS spectrum*

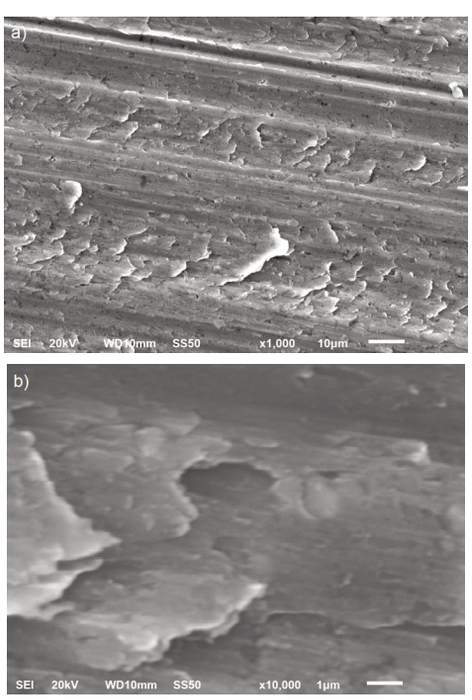

Figure 10. *Conventional SEM images of the nanostructured composite obtained at 10 h of milling and 1.5 wt. % of silver nanoparticles*

Due the silver nanoparticles are carbon coated, this shield of graphite helps to improve the wear resistance, first as a promoter of the hard phase Al_4C_3 during synthesis of the nanostructured composite [14], and second as a lubricant during the slide of the surfaces in contact [20].

It is observed that the nanostructured Al_{7075} – Ag-C NP composites milled at 10 h and with 1.5 and 2.0 wt. % of nanoparticles presents the best wear resistance and also have the best mechanical properties [14]. The analysis for the wear behavior of the nanostructured composites was realized without a heat treatment, this means in the as-extruded condition. Because this alloy is susceptible to strengthening by precipitation [2], it is expected to obtain better results after applying a heat treatment to the nanostructure composites (e.g. T6 temper).

4. Conclusions

The nanostructured Al_{7075} – Ag-C NP composites synthetized by mechanical milling show a higher wear resistance that the base alloy. The original alloy has a higher wear resistance in the condition of 0 h of milling. In the nanostructured composites wear resistance increases with increasing nanoparticle concentration.

Ductile particles, as in the case of the carbon-coated silver nanoparticles, enhance the wear resistance due to, in part, an obstacle to plastic deformation during the relative movement of surfaces in contact, and also by acting as a solid lubricant when separated from the metal matrix.

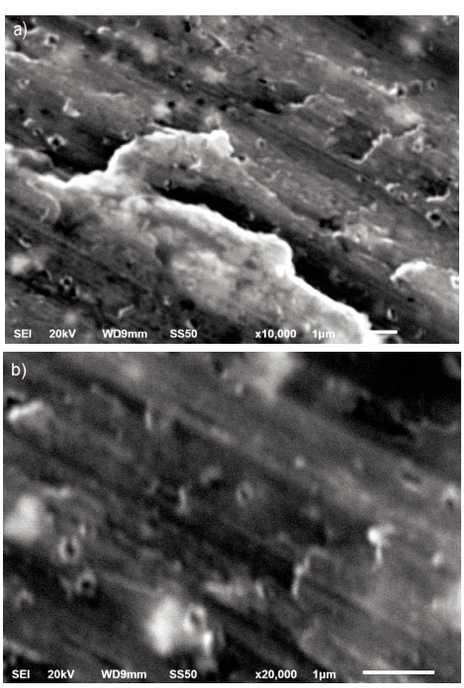

Figure 11. *Conventional SEM Images of the nanostructured composite obtained at 5 h of milling and 2.0 wt. % of silver nanoparticles*

Acknowledgments

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