Rev. LatinAm. Metal. Mat.

Artículo Regular

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DUREZA Y PROPIEDADES ESTRUCTURALES DE COMPUESTOS BASADOS EN NANOTUBOS DE CARBONO Y ALUMINIO

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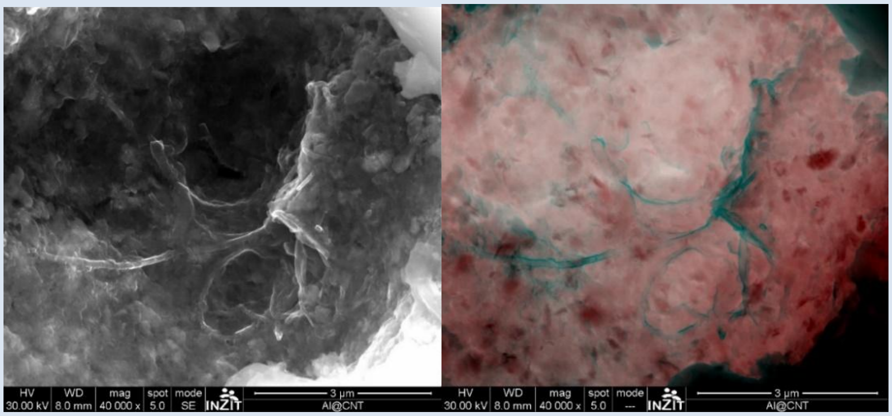


MWCNT inside the Al matrix

RESUMEN

Se prepararon compuestos de aluminio reforzados con nanotubos de carbono de pared múltiple (NTCPM) utilizando la técnica de pulvi-metalurgia. Los NTCPM se sintetizaron por deposición química de vapor (DQFV), utilizando C_2H_2 como gas precursor, Ar como gas de arrastre y Fe-Co / $CaCO_3$ como catalizador. El polvo de aluminio se mezcló con NTCPM en un dispositivo de molienda de bolas planetaria para diferentes relaciones de peso, de 0% a 2% y diferentes etapas de tiempo en el proceso de mezcla (3 min y 60 min). Los compuestos en polvo se prensaron en caliente, recocidos en atmosfera inerte y analizados usando un microscopio electrónico de barrido de emisión de campo (MEB-EC), difracción de rayos X en polvo y dureza Vickers. Se examinaron un total de 80 muestras para evaluar el efecto de los NTCPM sobre la dureza. Los resultados mostraron un aumento de la dureza para los compuestos de ~ 15% a 24%. Se consideró la desviación estándar de las medidas de dureza para evaluar la dispersión de MWCNT en los compuestos. Se aplicó un ajuste lineal a los datos de dureza para evaluar la influencia de la temperatura en el proceso de consolidación de granos y un análisis de varianza. Los resultados exhibieron una dispersión sustancial de la dureza de 13.13% a 24.57% de error. El análisis de los resultados obtenidos en varias condiciones sugirió condiciones óptimas para un tiempo de mezcla de 3 min y una temperatura de sinterización de 760 ° C.

Palabras Claves: *Reforzamiento de aluminio, matrices compuestas de aluminio, nano compuestos, nanotubos de carbono, dureza.*

Recibido: 04-12-2020 ; **Revisado:** 30-01-2020
Aceptado: 12-02-2021 ; **Publicado:** 24-07-2021
DOI: 10.5281/zenodo.7401910

pISSN: 0255-6952 | eISSN: 2244-7113
Rev. LatinAm. Metal. Mat. 2021; **41** (2): 100-120

HARDNESS AND STRUCTURAL PROPERTIES OF MULTIWALL CARBON NANOTUBES AND ALUMINUM-BASED COMPOSITES

ABSTRACT

Powder Metallurgy was used for the preparation of aluminum composite reinforced with multiwall carbon nanotubes (MWCNTs). The MWCNTs were synthesized by Chemical Vapor Deposition (CVD), using C_2H_2 as precursor gas, Ar as a carrier gas, and Fe-Co/$CaCO_3$ as a catalyst. The powder aluminum was mixed with MWCNTs in a planetary ball milling device for different weight ratios, from 0% to 2%, and different times stages in the mixing process (3 min and 60 min). The powders compounds were doubled hot-pressed and sintering and analyzed using a Field Emission Scanning Electron Microscope, X-ray powder diffraction, and Vickers Hardness. A total of 80 samples were examined to evaluate the effect of the MWCNTs on the hardness. Results showed a hardness-increasing for the compounds from ~15 % to 24 %. The standard deviation of hardness measures was considered to evaluate the dispersion of MWCNTs in the composites. We applied a linear fit to the hardness data to assess the influence of temperature in the grain consolidation process and variance analysis of data. Results exhibited a substantial dispersion of hardness from 13.13% to 24.57% of error. The analysis of the results obtained at several conditions suggested an optimal setting involving a mixing time of 3 min and a sintering temperature of 760 °C.

Keywords: *Aluminum reinforcement, aluminum matrix composites, nanocomposites, carbon nanotubes, hardness.*

1. INTRODUCCIÓN

The development of advanced materials with improved mechanical properties remains of considerable technological interest. Lighter, strengthened, and rigid materials are required in the aerospace and automotive industry to decrease fuel consumption and promote energy saving. In recent decades, materials science has focused on creating lightweight and ecological materials for high-performance devices. An alternative approach is the preparation of composite. Two chemically different materials separated by a defined interface constitute a composite. In these composite materials, one component transfers the mechanical or other physical properties to the bulk. Metal composites are essential in the development of advanced materials as alternatives to conventional ones. Lightweight materials with high specific strength, thermal expansion coefficient, and excellent damping properties are useful and desired. In this sense, Aluminum and MWCNTs are ideal materials to increase the strength without sacrificing the density. Lightweight properties, excellent corrosion resistance, and deformation make the aluminum alloys and its composites the most industrially used nonferrous structural materials.

The arising of carbon nanotubes (CNT)[1] and their properties have attracted scientific and technological interest in the reinforcement of Aluminum: high Young's modulus, low density, flexural modulus [2]. MWCNTs are also thermally stable when they are exposed to the air and under vacuum below ~660°C and ~2150 °C [3], respectively. The aluminum hardness in this kind of composites from the compaction is near 40-50 HV [4]–[6]. The useful properties of MWCNTs, combined with those associated with Al, are attractive for developing new materials. In this context, several studies have reported the improvement of the mechanical properties of Al/MWCNTs composites using different synthetic approaches [7]–[17]. One of these techniques, which has an industrial interest because of its potential scalability is ball milling. This approach is often combined with pressing and sintering to induce a consolidation of micro grains. In this milling method, the material undergoes collisions from steel balls in high-speed rotation. Subsequently, the hot pressing seeks to consolidate the compounds' inter grain boundaries to improve mechanical properties.

Using the ball milling powdering method, different authors [13,14, 18-24] reported improved mechanical properties (typically: hardness and ultimate tensile stress). Table 1 contains a resume of works in this area. All these studies considered a range between 2 to 4 Al/MWCNTs weight ratio concentration. In the studies of Bradbury et al. [18], however, they regarded an extended concentration range including 1 wt%, 3 wt%, 6 wt%, and 9 wt%, in a 20 h ball milling process and hot pressing of 570 MPa at 500 °C, obtaining a hardness which reached a maximum of HV= 151 at 6 wt% MWCNTs. On its side, Al-Aqeeli [19] developed two kinds of Al-based alloys with different concentrations of Si and, using MWCNTs from 0.5 to 2.0 wt%, the mixtures were ball milled for 1, 3, and 5 hours. For this study, three sintering techniques were used (Spark Plasma, Microwave Sintering, and Hot Isostatic Press Sintering) to consolidate the ball-milled powders varying the temperatures from 400 °C, 450 °C, and 500 °C. The sintering temperature of 500 °C was found to be the most suitable. A striking point of this study was the use of 36 samples to compare their results.

Table 1. Compilation of different mixing techniques for the preparation of Al/MWCNTs composites

	MWCNTs weight ratio.	**Dispersion methodology**	**Secondary process**	**Mechanical properties**
Bradburry et al 2014.	1,3,6 and 9%.	Ball milling 20h.	Hot pressing + hot extrusion.	Hardness HV_{20}=151 with 6% of CNT.
Yoo et al. 2010.	1-3 %	Traction milling 4h.	Hot rolling.	Yield stress 456 MPa. Ultimate tensile stress 571 MPa.
Liao et al. 2010.	0,5 %	Horizontal rolling machine.	SPS Hot extrusion.	Increase of hardness.
Kuzumaki et al. 1999.	5% 10%	Compacting and hot pressing.	Hot extrusion.	An estimate of 40 MPa for the tensile strength lower than the theoretical one.
Deng et al 2006	Two weight ratios concentration	Mechanical agitation with an ultrasonic stirrer.	N/A.	Hardness of 136 HV.
George et al. 2006.	0.5 and 2% weight ratios concentration of MWCNT and 1 and 2% SWCNT.	Ball milling.	Compacted.	Ultimate tensile strength 138 MPa using MWCNT 134 MPa with SWCNT.
Chen et al 2016.	1 and 2%.	High energy ball milling (12h).	Consolidation by plasma spark.	tensile stress–strain Increased CNT/Al.
Liao et al. 2012.	2-4 %.	Ball milling.	Hot extrusion.	Increase the Vickers harness from 42.3 (Aluminum without CNT) to 60.3 HV.
Choi et al 2012.	9 weight ratios concentration.	Ball milling 12h.	Hot Rolling.	Vickers Hardness from 20 to 60 HV.
Al-Aqeeli 2013.	0.5-2 wt% MWCNT, 36 samples 3 times for Ball milling Al-Si alloys.	Spark Plasma Sintering (SPS), Microwave Sintering (MWS), and Hot Isostatic Press Sintering.		

Remarkably, the literature focuses on the discussion on how to improve the dispersion to enhance the mechanical properties. It is recognized that MWCNTs possesses a high surface area of ~200 m^2/g, and its natural trend is to agglomerate due to the Van der Waals attraction forces between them, avoiding the consolidation of the matrix grains and contributing to the brittleness of the final composite [2]. Thus, the formation of agglomerates is unavoidable in almost all processing techniques.

So, it still appears necessary to gain more information about the ball mixing time to improve the homogeneity of composite, the proportion of MWCNTs within the metal matrix, the interaction mechanism between the surface of the nanotube and the Al matrix, and the contribution of temperature to improve the grain consolidation to achieve increased mechanical properties.

Almost all of the work in the literature compares one or two weight ratio combinations for the

Al/MWCNTs composite. Only two works, [18], [19] to the best of our knowledge, are the exceptions. Herein, we present the results for a series of experiments that provide valuable information for the optimal ratio concentration and the mix conditions to improve the mechanical properties of carbon nanotubes reinforced aluminum matrix composites using a combination of ball milling and pressure mixing techniques. The mixing was performed in two stages. First, varying the energy supplied to the material during the ball milling (3 min and 60 min) to study the influence of this parameter in the final hardness-dispersion. Second, implementing a subsequent hot pressing followed for sintering to promote the micro grains consolidation. Sintering was accomplished using temperatures at 560 °C, 660 °C, 760 °C and 860 °C and weight ratio concentrations of Al/MWCNTs set up to 0.1%, 0.25%, 0.5%, 0.75%, 1%, 1.25%, 1.5 %, 1.75% and 2%. In total, the study was completed by 80 samples, allowing the statistical analysis of the experiments, and therefore gaining more insight into the fabrication of these important Al/MWCNTs composites.

2. EXPERIMENTAL.

2.1 Characterizations

The morphology of the MWCNTs and the final composites were determined in an FEI, Quanta 200 Field Emission Scanning Electron Microscope (FESEM), in which images were registered in Secondary Electron Mode (SE) and involving a combination mode (mix) between the SE signal and the Backscattering Electron Mode (BSE). This last function allowed achieving images with a contrast depending on the atomic number of the atoms in the samples, permitting to separate the contrast of each chemical phase with different colors and then identify its morphology. Also, a Raman spectrogram was performed over the purified MWCNT using a Jobin Yvon T64000 Raman system and a laser at 514.5 nm to measure the vibrational modes and consequently to evaluate the quality of the purified products.

The structure of the composite Al/MWCNT characterized by a polycrystalline Bruker AXS diffractometer model D8 Focus with a *K*α Cu-radiation (λ= 1.54056 Å). The XRD measurements for the samples containing the maximum and minimum weight ratio of MWCNT in composites were registered to corroborate the non-formation of any other sub-product like aluminum carbide phase (Al_4C_3) at temperatures 760 °C and 860 °C in 3 min and 60 minutes experiments.

The Vickers hardness was measured following the ASTM E 384 [20] procedure using a micro durometer Leitz Wetzlar. The load for this test was set to 50 gf (0.49 N). The hardness was computed by taking the measure on 20 different points randomly selected and calculating the arithmetic average for each sample. Besides, a statistical study was implemented by calculating each group's standard deviation, a power fit for each temperature, and the variance analysis (ANOVA) of the group of measurements. This procedure was considered for each of the 80 samples.

2.2 Synthesis of multiwall carbon nanotubes.

The Chemical Vapor Deposition (CVD) technique was used for the synthesis of the MWCNTs. The initial conditions were previously studied [21]–[24]. The synthesis was achieved in a Thermo Scientific Lindberg Blue M furnace, model TF55035 A-1, using a quartz tube with 2.3 cm external diameter. The gases setup was acetylene (C_2H_2) 120 ml/min and argon (Ar) 280 ml/min. The velocity flow of the gases was controlled with needle valves and a Cole-Parmer flowmeter with a precision of ±1ml/min.

Metallic salts of $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ in a 4:1 ratio supported on $CaCO_3$ were used as a catalyst. Synthesis of the catalyst was previously reported [21]. The temperature for the synthesis was set at 750 °C and a reaction time of 15 minutes. Subsequently, the MWCNTs purification was performed in four steps procedure [21]: First, the MWCNTs were subjected to reflux in HCl solution in proportions of 50:50 for 4 h to remove the metal catalyst and support. They were filtered and washed using distilled water. Second, the MWCNTs were dried in a Carbolite oven at 120 °C for 20 minutes. Third, the nanotubes were oxidized at 450 °C for 20 minutes. And fourth, sintering was performed at 800 °C, for 1 h under an Ar flow of 280 mL/min to remove the non-graphitic carbon material.

2.3. Fabrication of the Al/MWCNT composites.

The mixing process was set in four steps: First, the ball milling mixing was accomplished in a Restch PM100 planetary mill in two mixing times (3 min and 60 min) to study the mixing energy's influence. The speed used was set at 300 rpm.[11], [25]. The particle size of the Al powder was 20 mesh. The MWCNT weight ratios proportion were set to 0% (blank sample), 0.1%, 0.25%, 0.5%, 0.75%, 1%, 1.25%, 1.5 %, 1.75%, and 2%. Second, compaction at 124.7 MPa in 450 °C, and 60 min, in the air was performed. Third, the sintering was conducted in four different temperatures in an Ar atmosphere below and over the melting point of Al (560 °C, 660 °C, 760 °C, and 860 °C). Finally, in the fourth-step, samples were pressed at 152.5 MPa at room temperature for 30 s, to induce a final compacting.

The Aluminum was obtained from Fisher Scientific Company with a particle size of 833 μm and 99.99 %. Each sample weighed 4 gr. The pressing was performed in a Buehler Bakelite model Suplimet II up to 11 Tons, with a homemade modification to achieve a heating up to 450 °C. The samples obtained were discs with 3 cm of diameter. A total of 10 samples for a mixing time of 3 minutes and 10 samples for 60 min of mixing were obtained. Each of these samples was cut into 4 pieces for a total of 80 samples. Each piece was treated in 4 different sintering temperatures, 560 °C, 660 °C, 760 °C, and 860 °C. The sintering was conducted for 60 min in an Ar atmosphere in a flow of 180 mL/min to avoid MWCNTs oxidation.

3. RESULTS AND ANALYSIS

3.1. Synthesis of MWCNTs.

The MWCNTs were observed in the FESEM. Figure 1 shows the presence of MWCNTs with an average external diameter of 62 nm after the purification process.

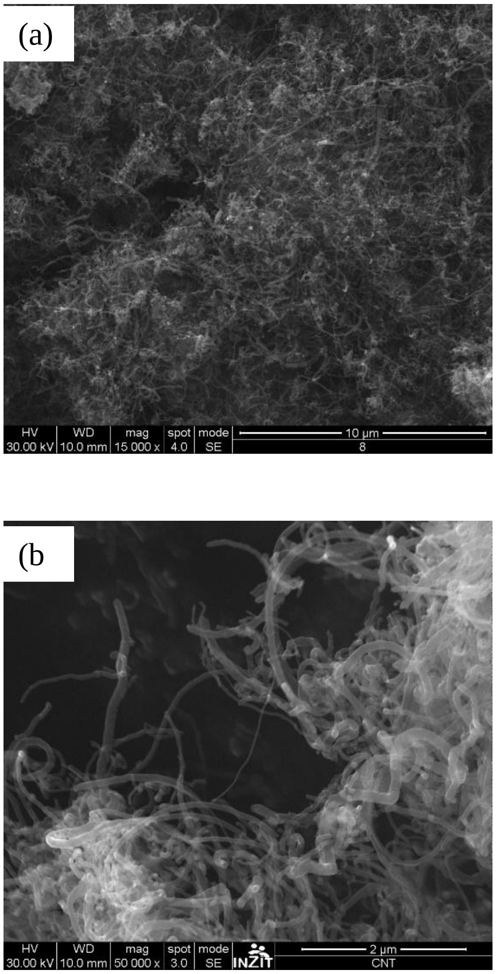
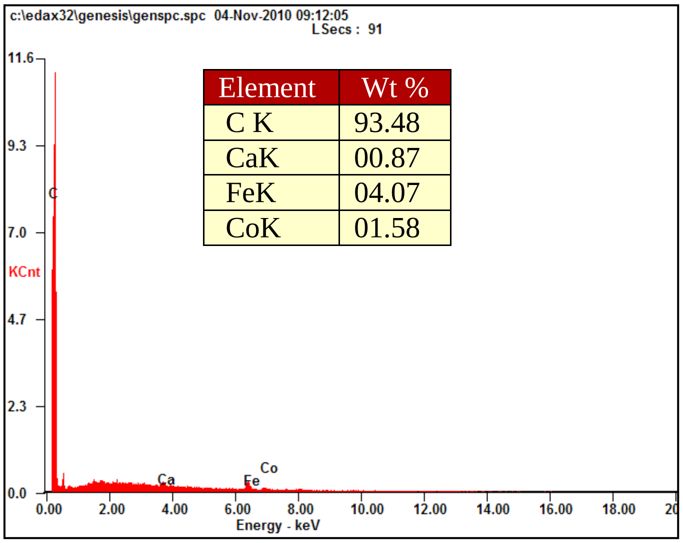


Figure 1. Micrograph of MWCNTs obtained by the CVD technique. (a) The micrograph was taken at 15 kx of magnification, from which the MWCNTs are observed. (b) The micrograph was taken at 50 kx showing the MWCNTs more in detail.

Figure 2 shows the quantitative and qualitative analysis of X-ray Dispersive Energy (EDX) of the MWCNTs (analysis performed over the selected area on Figure 1a) and the percentage of impurities after purification. The larger peak in the left area of Figure 2 corresponds to the presence of carbon. The table within the figure presents the elemental analysis and the % by weight per element (C, Ca, Fe, and Co). The carbon corresponds to the MWCNTs, with 93.48% of the total weight, and the other elements are associated with the catalyst remaining after purification. The small amount of catalyst still present is related to the fact that the acid treatment cannot remove the metals of the inner tube of MWCNTs.



Element	Wt %
C K	93.48
CaK	00.87
FeK	04.07
CoK	01.58

1

Figure 2. Qualitative and quantitative elemental analysis for purified MWCNTs. Small quantities of the catalyst are still present in the composite after purification.

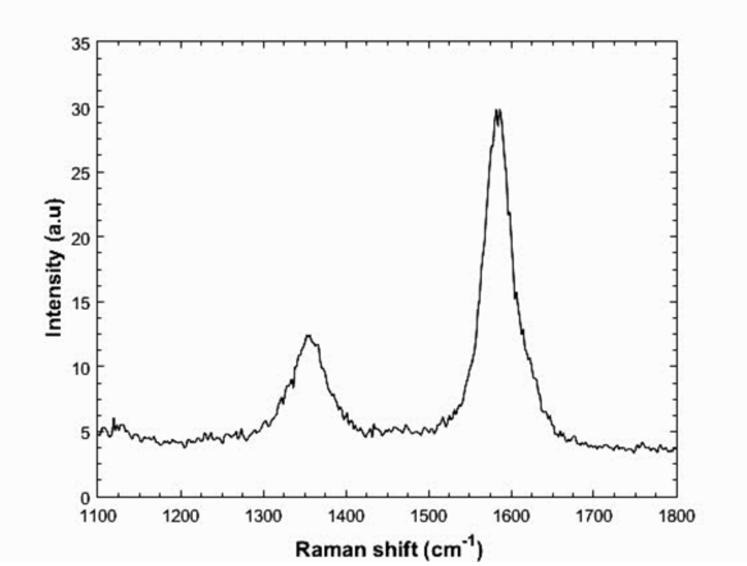


Figure 3. Raman spectrogram of purified MWCNT. The graph presents the G around 1350 cm-1 whose origin is related to disorder and defects in the structure of nanotubes and "G" band around 1600 cm-1 from vibrations within the plane of the graphite sheets.

Figure 3 present the Raman spectrogram of the purified MWCNT. Observing the presence of an intense band between 1500 and 1600 cm^{-1} corresponding to the fundamental vibration of the tangential elongation of the sp^{2} carbon-carbon bonds that form the walls of the MWCNT, this band is called the "G" band and provides information on structural purity and crystallinity of MWCNT. An intense band is also observed near 1350 cm^{-1} called "D", this band is not allowed in Raman when there is the case of a perfect graphite sheet. However, the presence of vacancies, defects, and the loss of symmetry in the crystalline lattice makes it possible to observe in Raman. Therefore, this band offers information on defects in the walls of the MWCNT with hybridization other than sp^{2}. This information confirms the presence of the MWCNT in the products of purification [18, 31, 32].

3.2. Composites Fabrication.

Characterization by FESEM.

The set of FESEM images collected in Figures 4(a-d) shows the presence of MWCNTs in 3 minutes experiments, the second set of FESEM images displayed in Figures 5(a-d) shows the micrographs in mix mode SE+BSE all of them for different sintering temperatures 560 °C, 660 °C, 760 °C, and 860 °C, respectively and 1% of weight ratio, performed over the previous areas of Figures 4(a-d). In the mix mode (Figure 5), as the blue color contrast gives evidence of carbon material (smaller atomic number), the red color is the evidence for Al, showing the well-defined phases of Carbon and Aluminum. Comparing figures 4-b and 5-b, it appears a covered MWCNTs because of the mixing process.

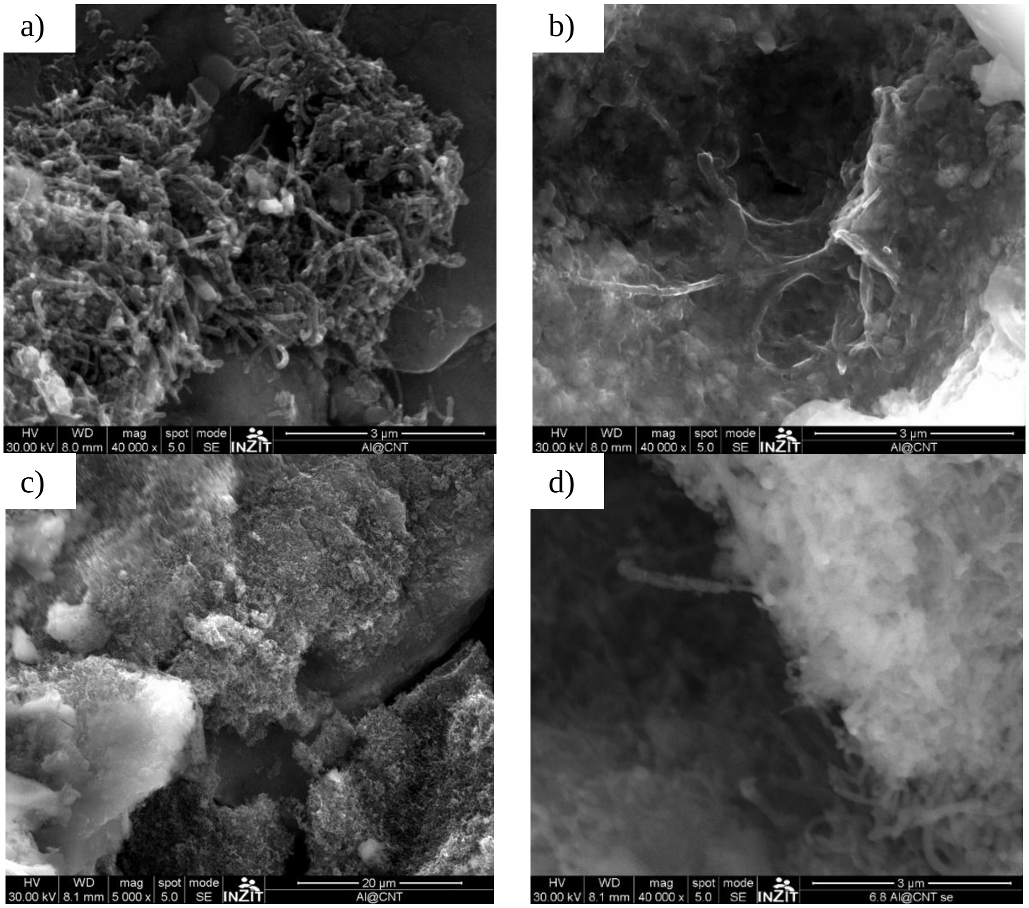


Figure 4. FESEM micrograph for the Al/MWCNT composites samples in the 3 min mixing time in SE mode. Each of these images corresponds to different temperatures of sintering. The upper left image (a) corresponds 560 °C degrees, the right upper to 660 °C (b), lower left 760 °C (c), and lower right 860 °C (d).

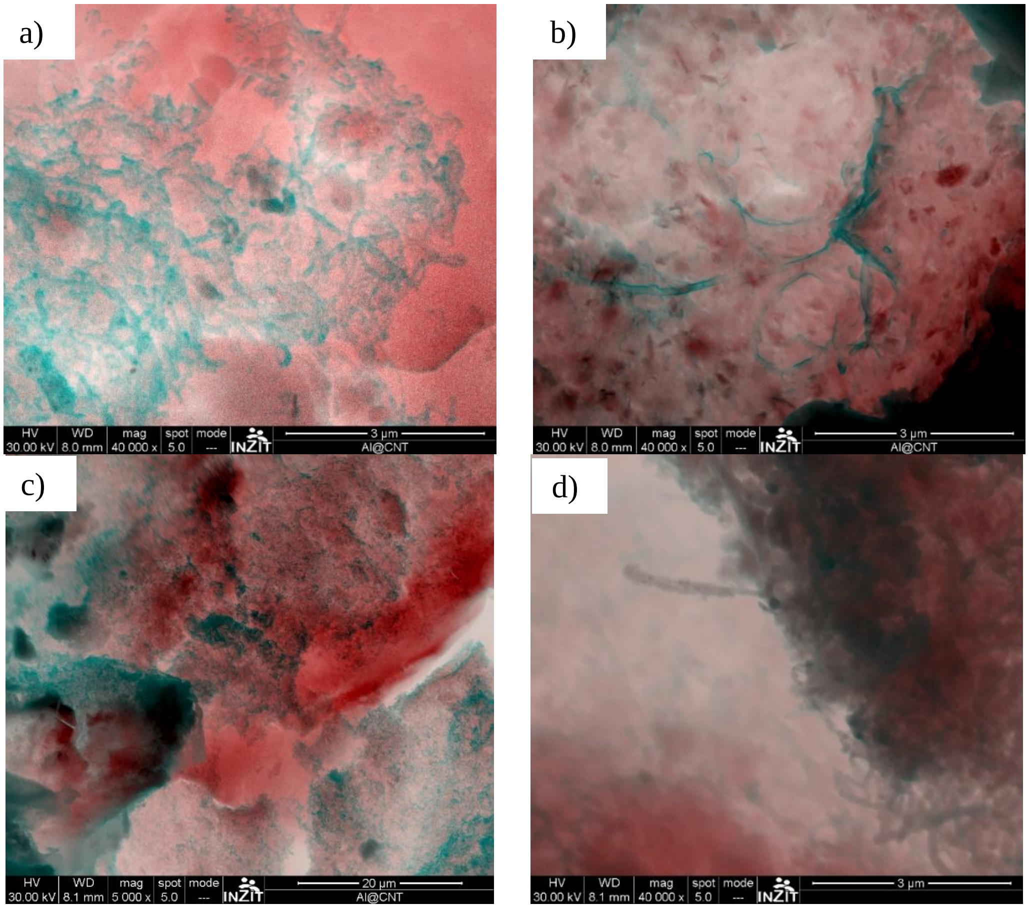


Figure 5. FESEM micrograph for the Al/MWCNTs composites in mix mode SE+BSE for the 3 minutes mixing time. By this mode, it is possible to observe the morphology and the contrast from atomic numbers combined in an image. This micrograph matches the same areas as those in figure 3. The upper left image corresponds to 560 °C (a), the upper right to 660 °C (b), lower left 760 °C (c), and lower right 860 °C (d).

The set of FESEM images collected in Figures 6(a-d) shows the composites of Al/MWCNT in 60 min experiments in SE mode. The photos displayed in Figures 7(a-d) shows the micrographs in mix mode SE+BSE, all of them for different sintering temperatures 560 °C, 660 °C, 760 °C, and 860 °C, respectively and 1% of MWCNT weight ratio, these images were performed over the area of Figures 6.

These images show the presence of carbon material; however, comparing with Figure 7(a-d) the red contrast is diffuse, it appears some blue lines in figures which can be assumed as shorter MWCNTs, in contrast to the previous 3 minutes mixing time cases. These results can be interpreted, as more energy is given to the mixing process, more damage (shortening by breaking the tubes) in the MWCNTs will be obtained.

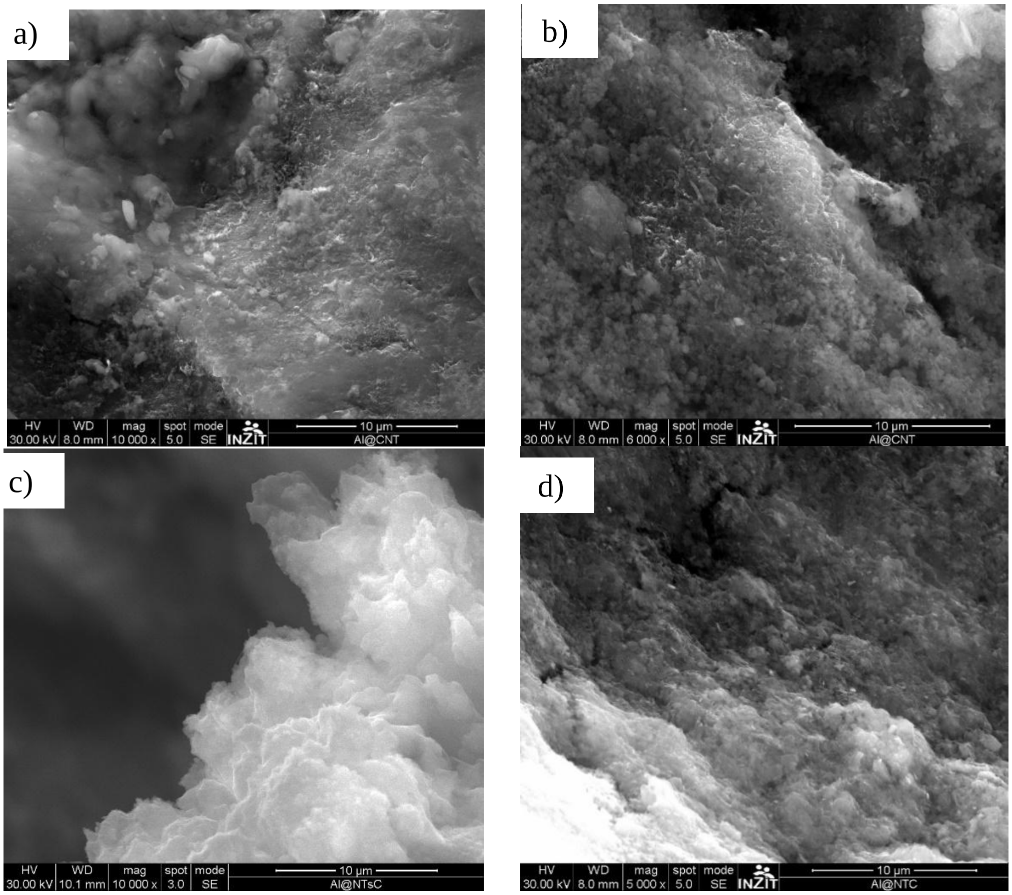


Figure 6. FESEM micrograph for the Al/MWCNT composites samples in the 60 min mixing time in SE mode. Each of these images corresponds to different temperatures of sintering. The upper left image (a) corresponds 560 °C degrees, the right upper to 660 °C (b), lower left 760 °C (c), and lower right 860 °C (d).

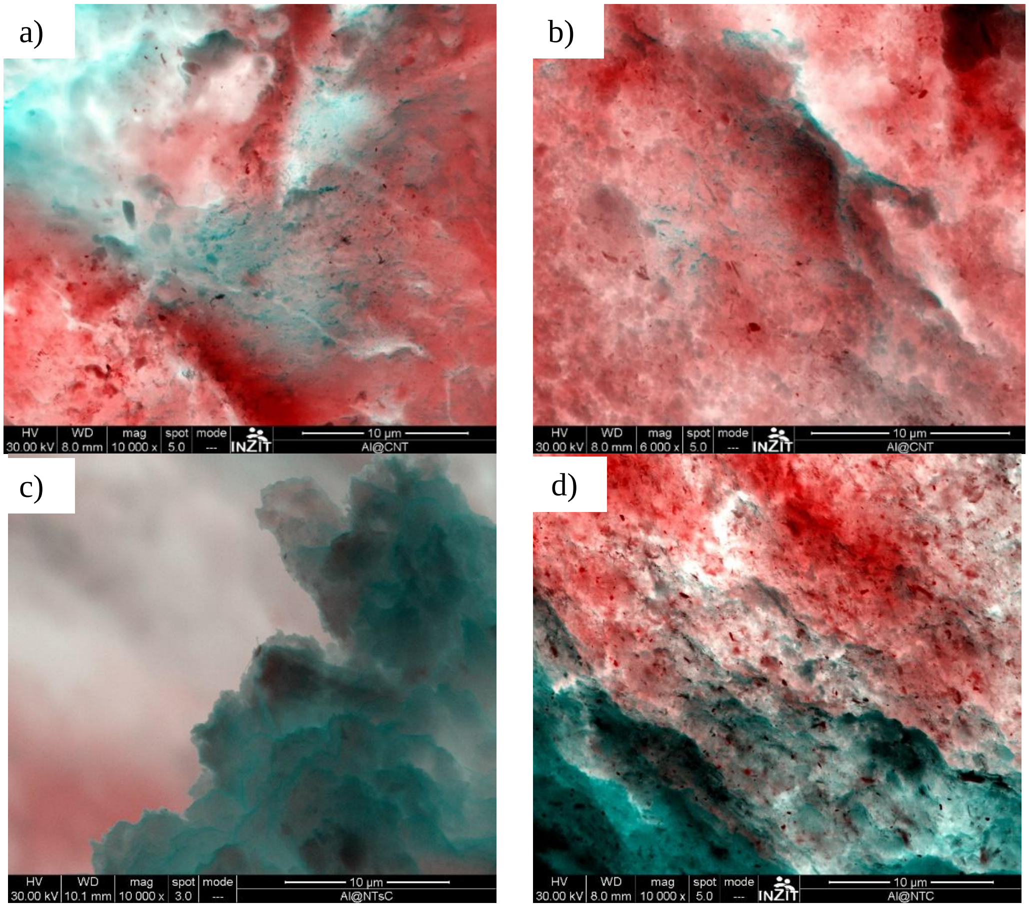


Figure 7. FESEM micrograph for the Al/MWCNTs composites in mix mode SE+BSE for the 60 minutes sintering samples. By this mode, it is possible to observe the morphology and the contrast from atomic numbers combined in an image. This micrograph matches the same areas as those in figure 5. The upper left image corresponds 560 °C (a), the upper right to 660 °C (b), lower left 760 °C (c), and lower right 860 °C (d).

X-ray diffraction characterization.

XRD patterns are collected in Figure 8 (a-d) for 3 min in 760 °C and 860 °C respectively and 0%, 0.1, 1% and 2% of weight ratio. The powder X-ray diffractograms were compared versus the Crystallography Open database [28]. The absence of the reflections corresponding to the diffraction angles ($2\theta \approx 32°, 53°, 55°, 58°$) supports the inexistence of Al_4C_3 phases. These results agree with those reported by R. Martínez-Sánchez [29].

Characterization by Vickers Microhardness.

The left columns of Figures 9 and 10 show the results for the Vickers Microhardness values (HV) as a function of the MWCNTs weight ratio concentrations, in different sintering temperatures, and for the mixing time of 3 min and 60 min, respectively.

The right column of both figures presents the standard deviation of HV for each of the 80 samples.

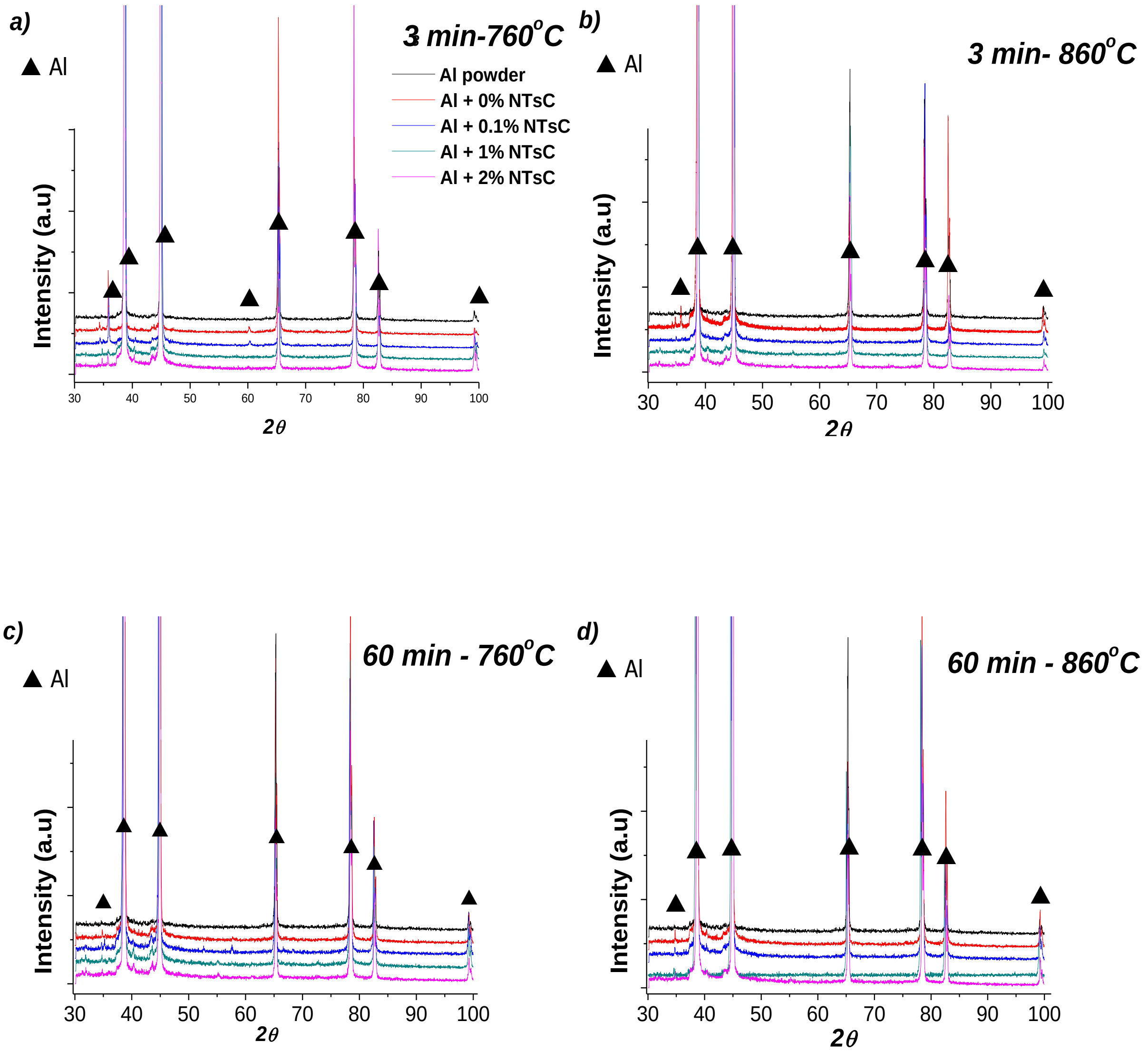


Figure 8. Diffractogram (a-d) for the Al/MWCNT composites. XRD patterns displayed correspond only to the cases for 3 min and 60 min of mixing time and ratio concentrations of 0%, 0.1%, 1%, and 2% at a sintering temperature of 760 °C and 860 °C.

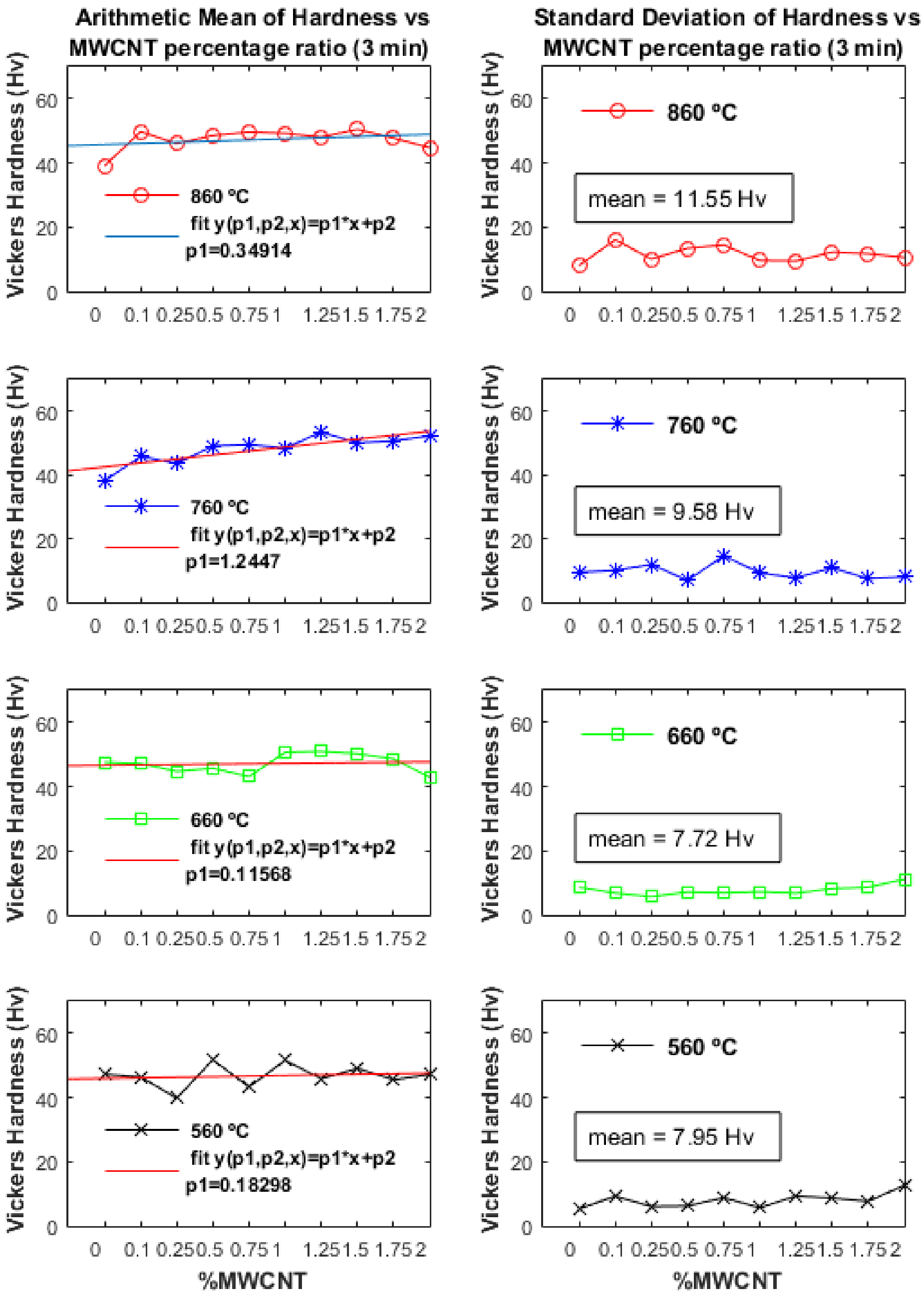


Figure 9. The graphs in the left column represent the measure of the hardness using 4 sintering temperatures (560 °C, 660 °C, 760 °C, and 860 °C) for the mixing time of 3 min, and 10 different weight ratios concentration in Al/MWCNT composites from 0% to 2%. Also, a linear fit of this data is presented to evaluate the increasing trend of hardness. The graphs on the right column show the compute of each measure's dispersion by using the Standard Deviation. The arithmetic means of this dispersion is presented as a measure of homogeneity of the composite.

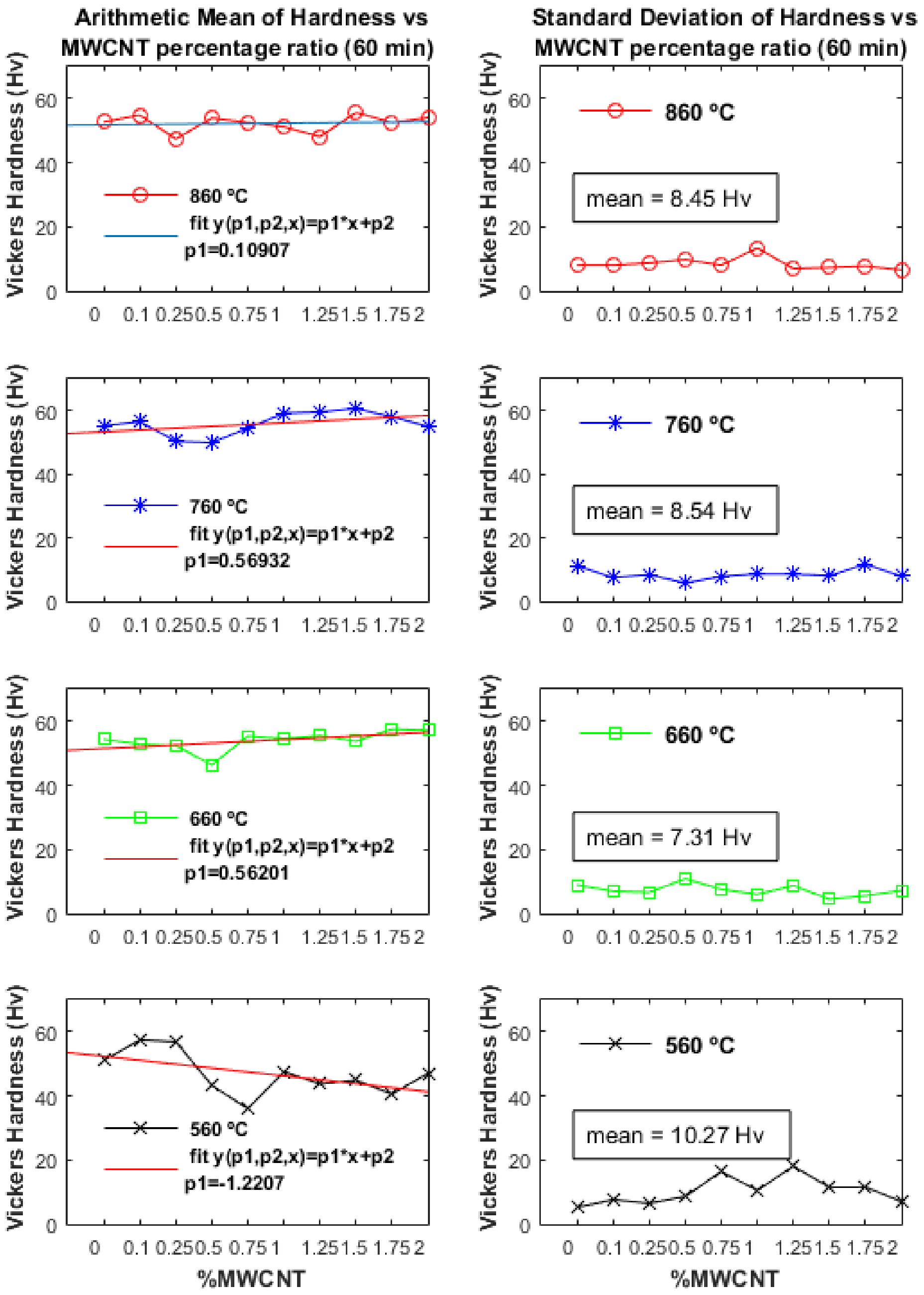


Figure 10. The graphs in the left column represent the measure of the hardness using 4 sintering temperatures (560 °C, 660 °C, 760 °C, and 860 °C) for the mixing time of 60 min and 10 different weight ratios concentration in Al/MWCNT composites from 0% to 2%. Also, a linear fit of this data is presented to evaluate the increasing trend of hardness. The graphs on the right column present the compute of the dispersion of each measure by using the Standard Deviation. The arithmetic means of this dispersion is presented as a measure of homogeneity of the composite.

Hardness trend

For the analysis of the hardness data in Figures 9 and 10, a linear fit on the graph was performed at each sintering temperature. The positives slope coefficients approximately represent a trend of increase of hardness as a function of weight ratio. We found positive coefficient values in both cases of mixing (3 min and 60 min), except for the example of sintering at 560 °C and mixing time of 60 min. In the 3 min case and for the sintering temperatures of 860 °C, 760 °C, 660 °C, and 560 °C the slopes were 0.34, 1.24, 0.11, and 0.18, respectively. Whereas at 60 min the slopes were 0.10, 0.57, 0.56, and -1.22, respectively. These results suggest an increase of the hardness as a function of the weight ratios of MWCNTs in composites. These trends can also indicate the more efficient temperature for the consolidation of the compounds. The 760 °C temperature has the largest slope (1.24) in the 3 minutes mix case. In contrast, at 560 °C, the slopes were small (0.18) or negative (-1.22) in the 3 min and 60 min cases, respectively.

Several studies have shown that the interval for the increase of hardness in Al compaction is in the order of 40-50 HV [4], [5], [30]. In Table 2, a resume of the hardness values measured for this study is presented. These results show arithmetic mean of 42.99 HV in the 3 min and 52.57 HV in 60 min, for pure Aluminum mixing. These values observed difference is attributable to the compaction, and the energy exerted to the Al powder. These kinds of results for pure Al are also reported by Kawasaki [4] and attributable to the energy exerted to the mix process. From now on, we use these values as blank sample references for the 3 min (42.99 HV) and 60 min (52.57 HV) cases. In this study for the Al/MWCNT composites, the maximum value for the hardness was achieved for the 60 min and 760 °C samples, obtaining 60.56 HV. This result corresponds to a relative increase of 14% compared with the compound's referential value without MWCNTs (52.57 HV). In the case of 3 min, the maximum value for hardness was 53.40 HV, also at 760 °C, which corresponds to an increase of 20.35% compared with the referential value without MWCNTs (42.99 HV).

Table 2. A resume of hardness values and its standard deviation for Al/MWCNTs composites in different sintering temperatures.

	60 minutes of mixing time Referential value HV Pure Al 52.57 HV			**3 minutes of mixing time Referential value HV Pure Al 42.99 HV**		
Temperature	Mean <HV>	Standard Deviation HV	Maximum hardness HV	Mean <HV>	Standard Deviation HV	Maximum hardness HV
860 °C	52.28	8.45	55.64	47.31	11.55	50.44
760 °C	55.89	8.54	60.64	48.09	9.58	53.40
660 °C	54.02	7.31	57.57	47.17	7.72	50.27
560 °C	46.82	10.27	57.47	46.76	7.95	51.74

In the Vickers hardness tests, micro indentation calculation is a function of the following variables: force, indenter geometry, and diagonal measurement. Therefore, the test depends on the superficial properties of materials. If the penetrator acts on a particular agglomerate of MWCNTs, this leads to considerable resistance to being penetrated due to the high Young modulus of the tubes, affecting the data measure and its dispersion hardness. This can be graphically represented in Figure 11. Typically, the error of the measures in a homogeneous composite is near to 1%. However, in Al/MWCNTs composites developed by powder metallurgy, it is frequently to find a broad interval for dispersing the data. This dispersion can be attributed to flakes of material, which are not consolidated by the pressure process. So, this dispersion can be assumed as a consequence of inhomogeneous composites [4], [8], [30]–[32].

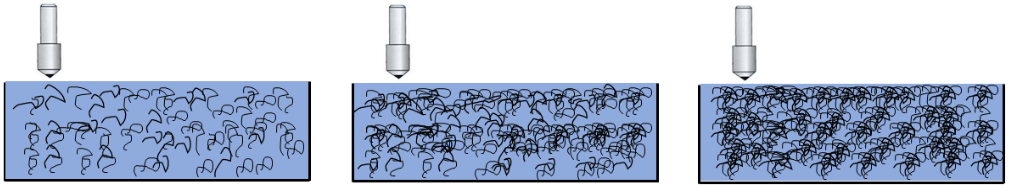


Figure 11. Several concentrations of MWCNT will induce zones with different hardness, this information can be useful to describe the dispersion of hardness in the Al-MWCNT compounds.

Statistical analysis of results.

We implement the Analysis of Variance or (ANOVA), also called the Fisher analysis of variance using the MATLAB function ANOVA1, over hardness data. The test was performed comparing the data for hardness in each temperature versus the percentage ratio of MWCNT. [33].

The ANOVA analysis determines whether data from several groups (hardness and temperatures in our case) have a common mean. The function tests the hypothesis that the samples in the columns (mean of hardness) are drawn from populations with the same mean against the alternative hypothesis that the population is not equal. So, the null hypothesis for ANOVA is that all population means are precisely identical. This is weighed by the F parameter. The groups compared were the hardness in each temperature. Each temperature will have 10 hardness results for the 3min and 60 min. The results are presented in Figure 12(a-b) and tables 3 and 4.

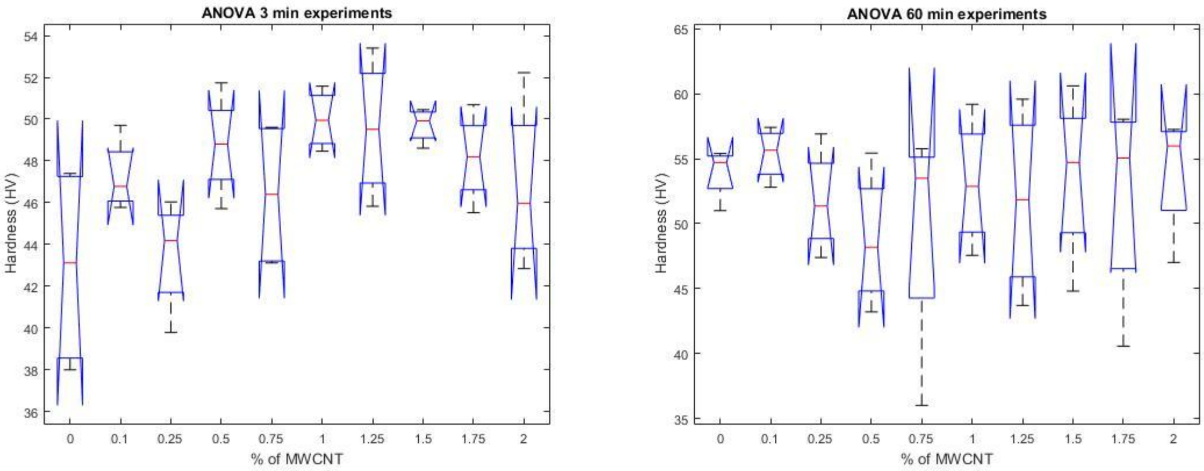


Figure 12 ANOVA analysis of hardness, for each temperature, and for the group of different weight ratio concentration of MWCNT.

The ANOVA tables 3 and table 4 shows the variation between-groups (percentage ratio of MWCNT) and within-groups variation (hardness for each temperature). SS is the sum of squares, and df is the degrees of freedom. In the 3 minutes example, the total degrees of freedom are the total number of observations minus one, which is 40 - 1 = 39. The between-groups degrees of freedom are the number of groups minus one, which is 10 - 1 = 9. The within-groups degrees of freedom is total degrees of freedom minus the between-groups degrees of freedom, which is 39 - 9 = 30. MS is the mean squared error, which is SS/df for each source of variation. The F-statistic is the ratio of the mean squared errors (24.6891 /8.9789). The p-value is the probability that the test statistic can take a value greater than or equal to the value of the test statistic. The small Prob-value of 0.018 in the case of 3 min indicates that differences between column means are significant. The same analysis was applied to the 60 min case achieving a value of Prob-value of 0.8721. The graphics in figure 12 show how the variance is dispersed between the groups.

Table 3. ANOVA results for 3 min experiments.

Source	SS	df	MS	F	Prob>F
Columns	222.202	9	24.6891	2.75	0.018
Error	269.368	30	8.9789		
Total	491.569	39			

Table 4. ANOVA results for 60 min experiments.

Source	SS	df	MS	F	Prob>F
Columns	151.13	9	16.7928	0.49	0.8721
Error	1035.68	30	34.5225		
Total	1186.81	39			

The results for the 3 min case and the small value of P indicate that the variation inside the group is significative, so we have a dispersion in the data and therefore a less homogeneous compound. This in contrast to the case of 60 minutes where the result of p indicates a compound with more similar means, and therefore more homogeneous.

4. CONCLUSIONS.

The fabrication of reinforced Al/MWCNT composites using ball milling, hot compression, and sintering mixing technique reports a maximum relative increase of Vickers microhardness of 24.21% for the time of 3 minutes of mixing and 15% for 60 minutes, compared to the average of the referential values of Al without MWCNT 42.99 HV and 52.57 HV, respectively. We compare hardness trends by computing slopes of data for each temperature graph. Hardness trends increase in almost all cases, reaching a maximum slope value of 1.24 for the 3 min and 760 °C. In the composites Al/MWCNT the temperature must induce a diffusion between the grains surface, helping the homogenization of the composite and improving their mechanical properties. In both cases (3 min and 60 min) results show the largest slope (HV measures) for temperatures of 760 °C.The influence of mixing by ball milling technique was characterized by FESEM. In the ball milling, the composite's energy can improve or not mechanical properties. This is because if energy is too high, the MWCNT will be brokens. The FESEM results show damage in the tubes (shorter) at 60 min compared to the 3 min case. Also, our results show a very slight increase of hardness when the ratio concentration of MWCNT increase in the composite, this increase can also related to the optimal temperature. The larger slope coefficient was obtained for the 760 °C in the 3 min and 760 °C and 660 °C in the 60 min. Although the dispersion associated with the standard deviation in hardness measures for the two cases of mixing time (3 min and 60 min) is similar, the ANOVA analysis allowed us to observe that the compounds mixed for 3 minutes are less homogeneous than those mixed for 60 minutes. So, we propose an optimal setup for this kind of experiment, which is the case of the 3 min for mixing time in ball milling at 760 °C. Despite the improvement of the mechanical properties, the Al/MWCNT composites still have dispersion issued that can be explored by chemical approaches (to improve diffusion between grains) or extremely high pressure to enhance the final mechanical properties.

5. AGRADECIMIENTOS

Eduardo Cedillo agradece al Consejo Nacional de Ciencia y Tecnología (CONACYT-México) por la beca proporcionada para la realización de sus estudios de posgrado.

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