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THE INFLUENCE OF THE DISPERSION METHOD ON THE MICROSTRUCTURE AND PROPERTIES OF MWCNTs/AA6061 COMPOSITES

The aim of this work was to study the effect of different methods of multi-walled carbon nanotubes (MWCNTs) dispersion, and their influence on the microstructure and properties of aluminium alloy matrix composites produced using the powder metallurgy techniques, such as powder milling/mixing and hot extrusion. The main problem in the manufacturing of nanocomposites is the homogeneous distribution of MWCNTs in the metal matrix. To achieve their proper distribution a high-energy and low-energy mechanical milling, using a planetary ball mill, and mixing, using a turbulent mixer, were applied. Studies have shown that composite materials prepared using milling and extrusion have a much better dispersion of the reinforcing phase, which leads to better mechanical properties of the obtained rods. The low-energy mechanical mixing and mixing using the turbulent mixer neither change the powder morphology nor lead to adequate dispersion of the carbon nanotubes, which directly affects the resulting properties.

Keywords: nanocomposites, powder metallurgy, mechanical milling, carbon nanotubes, aluminium alloys

1. Introduction

It is well known that there are different types of carbon nanotubes (CNTs) with respect to the number of layers (single-, double- and multi-walled), structure (straight, curled, branched, cup-stacked, herringbone) or surface chemistry (functional group, coating, oxidized) [1-3]. For nanocomposite application a considerable amount of CNTs is needed, which unfortunately generates high manufacturing costs. For this reason, low-cost multi-walled carbon nanotubes (MWCNTs) are mainly used as a reinforcing phase in MMCs. The efficient method of synthesizing MWCNTs at low cost is chemical vapour deposition (CVD), which is already used in their mass production [4-7].

The unique properties of CNTs like the Young's modulus of ~1.8 TPa, stiffness and high tensile strength of ~55.5 GPa make them promising reinforcements for synthesizing low-density, high-strength metal matrix composites (MMCs) [8]. MMCs, especially those with an aluminium matrix, are the most widely used composite materials in the industry. A homogeneous dispersion of CNTs in the metal matrix is a significant problem in the manufacturing of these composite materials. The expected mechanical properties of the composite will be achieved if the CNTs are homogeneously distributed throughout the volume of the matrix. The interfacial bonding between the CNTs and the metal matrix is also a crucial factor in obtaining enhanced properties of the composite. Unfortunately, due to the curled shape and influence of van der Waals interaction, carbon nanotubes have a strong tendency to agglomerate [9]. The successful development of a production process that allows a uniform dispersion of CNTs in the matrix without CNT damage, and an efficient load transfer between the CNTs and aluminium alloy matrix, are essential for obtaining the expected strengthening of nanocomposites. In recent years there has been a growing interest in carbon nanotubes used as reinforcement of aluminium matrix composites, as confirmed by the large number of publications related to this subject [8-15]. Most of them are targeted at different preparation processes by examining the impact of these techniques on the mechanical properties of the nanocomposite materials. The increase in mechanical properties by carbon nanotubes reinforcement is very promising, but the implementation of these composites on an industrial scale is only possible if they are produced in a simple and cost-effective way, using conventional procedures [16].

The study focused on investigation of the morphology of particles after mechanical milling and mixing, as well as on the effects of different methods of dispersion of nanotubes on the properties and structure of the resulting nanocomposite. To minimize the cold welding of the particles as well as to eliminate sticking of the powder to the milling balls, during preparation an amide wax was used as a process control agent (PCA) [17]. The aim of this study was to produce AlMg1SiCu/MWCNTs nanocomposite powders and to examine the influence of carbon nanotubes dispersion methods on the morphology of the obtained powders. Their particle sizes, phase composition and technological properties were measured as well. It has been found that the addition of MWCNTs results in a significant improvement in the mechanical properties of the AlMg1SiCu/MWCNTs composites.

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2. Experimental procedure

The morphology of powders obtained after 10 hours of milling or mixing was observed using scanning electron microscopy (SEM). The bulk density was determined as the ratio of the mass of loose powder to the volume of the filled cell in which it is located using a Hall flowmeter (PN-EN ISO 3923-1:2010 E). The flowability of the obtained powders was measured by using the Hall flowmeter as well. The microstructure of the obtained composite material was observed under the light microscope Leica MEF4A. X-ray diffraction (XRD) analysis of the composites with a Co radiation source was carried out. The microstructure of extruded composites was examined by the transmission electron microscope S/TEM TITAN 80-300. Microhardness measurements of the obtained composite materials were carried out using the Vickers tests, under a load of 1N. The wear behaviour was performed by the ball-on-plate test using the CSM instrument (Table 1). Friction coefficients were recorded at 5 Hz frequency.

TABLE 1

Conditions of the ball-on-plate test

Load	5 N
Sliding distance	25 m
Sliding speed	0.02 m/s
Ball material	Al_2O_3

3. Starting materials

An atomized aluminium alloy powder AlMg1SiCu supplied by ECKA (Germany) containing 0.95% Mg, 0.6% Si, 0.26% Cr, 0.22% Cu, 0.47% Fe, 0.11% Mn, 0.015% Zn, 0.006% Ti, was used as the matrix material (Fig. 1). The size of the powder particles was between 5-50 µm. Multi-walled carbon nanotubes, with a diameter between 30-50 nm and length >5 µm were produced by the CVD method at Cheap Tubes, Canada. Figure 2 shows the morphology of the MWCNTs.

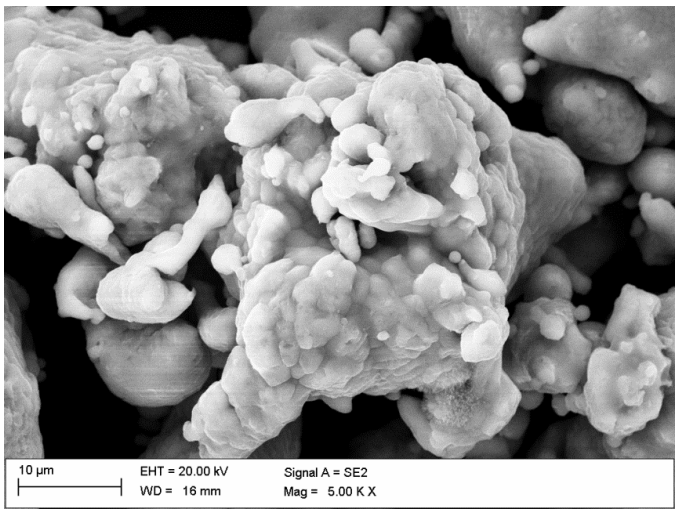

Fig. 1. Morphology of the as-received AA6061 powder; SEM

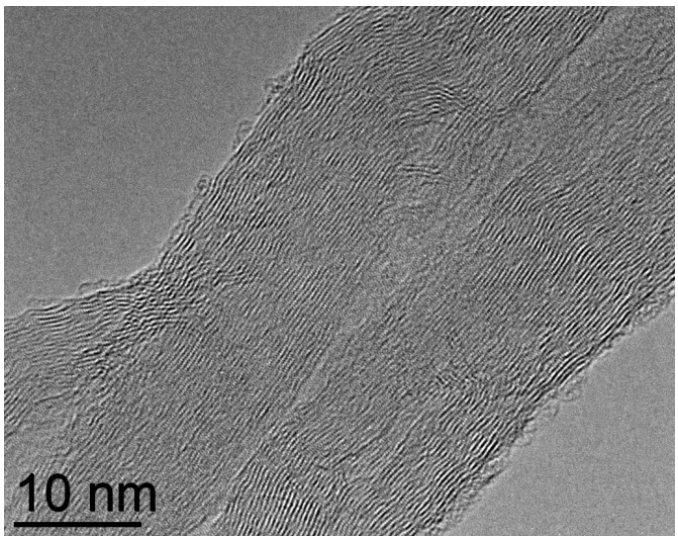

Fig. 2. Morphology of the as-received multi-walled carbon nanotubes; TEM

The MWCNTs were dispersed in the aluminium alloy matrix using three methods, i.e. a high-energy powder milling (HEMM), a low-energy powder milling (LEMM) in the planetary ball mill, and by mixing using a turbulent mixer (TM). All the composite samples contained 2 vol.% of MWCNTs and were milled/mixed for 10h. The milling and mixing parameters are summarized in Table 2. Unreinforced aluminium alloy powder was fabricated under the same high-energy milling condition for comparison. Subsequently, the milled powders were compacted in a uniaxial hydraulic press in a mould 25 mm in diameter, under a pressure of 300 MPa and then extruded at 480°C, to yield near fully densified bars of 6 mm in diameter. During the extrusion process, the extrusion force was registered. The highest extrusion force was needed to obtain composites from the HEMM powders.

TABLE 2

Parameters of MWCNTs dispersion methods

Milling/mixing conditions	**Dispersion method**		
	TM	**LEMM**	**HEMM**
MWCNTs content	2 vol.%	2 vol.%	2 vol.%
Ball diameter	x	10 mm	20 mm
Ball material	x	Zirconia	AISI steel 420
Ball to powder weight ratio	x	5:1	20:1
Milling time	10 h	10 h	10 h
Milling speed	25 rpm	200 rpm	200 rpm
PCA (process control agent)	x	1 wt.%, amide wax	1 wt.%, amide wax

4. Results and discussion

It has been found that the different ways of dispersing carbon nanotubes in the matrix powder have an influence on the morphology of the powder as well as on the degree of dispersion of carbon nanotubes in the metal matrix. In the case

of the powders subjected to milling, changes in particle shape were observed. The particle shape changes from globular, in the as-delivered condition, to plastically deformed flakes, and then during repeated welding and cracking processes the particles become equiaxed (Fig. 3a). No clusters, agglomerates or individual carbon nanotubes are seen (Fig. 3d), which probably indicates that during milling the nanotubes stuck between the welded aluminium particles. The powders obtained using low-energy mechanical milling do not show any morphological changes (Fig. 3b). The shape of the alloy particles after 10 hours is still globular, and the carbon nanotubes are arranged in an irregular manner to form clusters on the surface of aluminium particles (Fig. 3e). In the TM and LEMM powders, CNTs agglomerations are easily visible. In turn, the use of turbulent mixing for particles dispersion admittedly retains their shape but the particles, differ from the powders obtained after low-energy mechanical milling, form agglomerates (Fig. 3c). Smaller particles adhere to the larger ones. Moreover, without effort, spherical agglomerates of entangled carbon nanotubes ranging in size from a few to several microns can be seen. This shows that for both of these methods of dispersion the generated energy is not sufficient to break up agglomerates of nanometer particles or less to achieve adequate dispersion.

Extruded composites prepared from HEMM powder, due to a very homogeneous distribution of the carbon nanotubes, are characterized by good cohesion of the matrix particles (Fig. 4a).

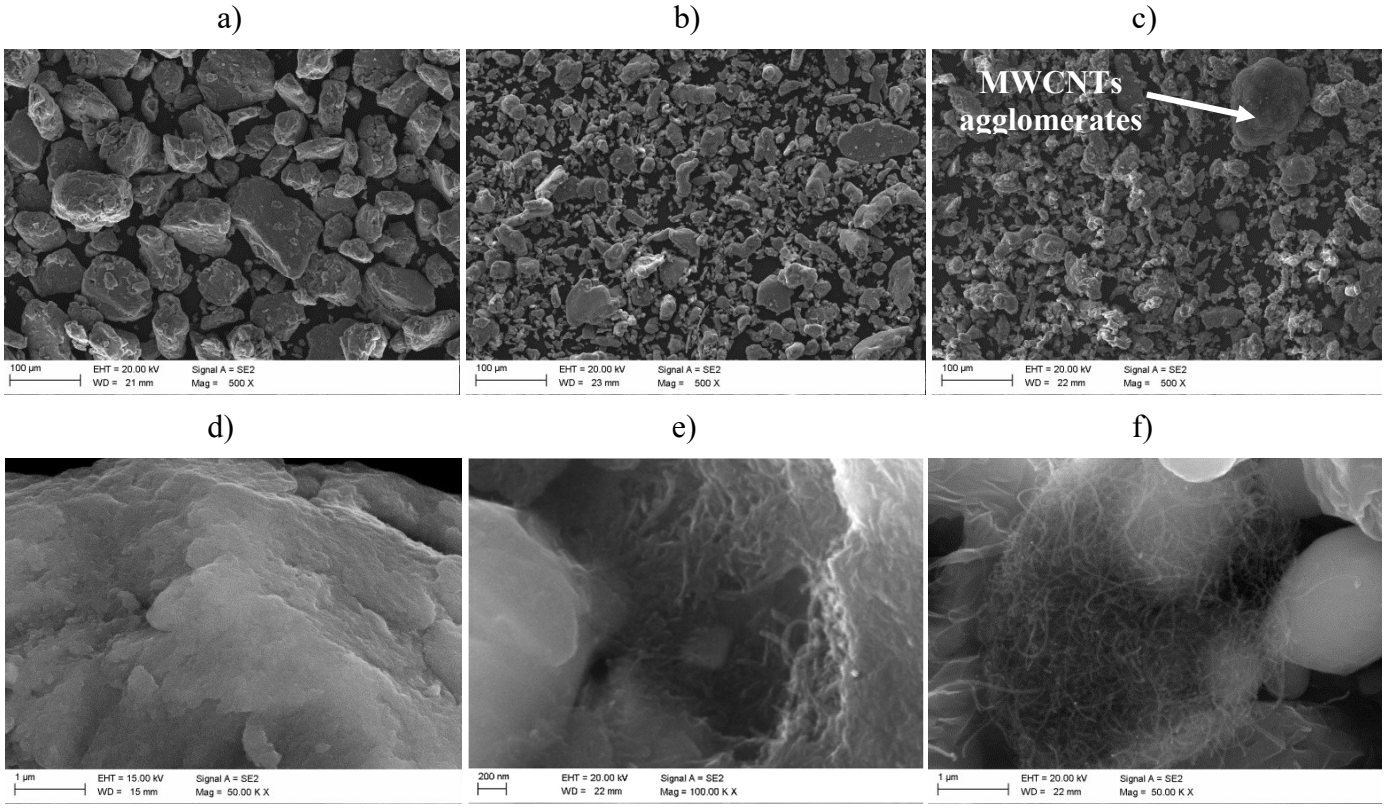

Fig. 3. Morphology of the AlMg1SiCu powder with 2 vol.% addition of multi-walled carbon nanotubes after 10 hours of: (a,d) high-energy mechanical milling, (b,e) low-energy mechanical milling and (c,f) mixing using turbulent mixer; SEM

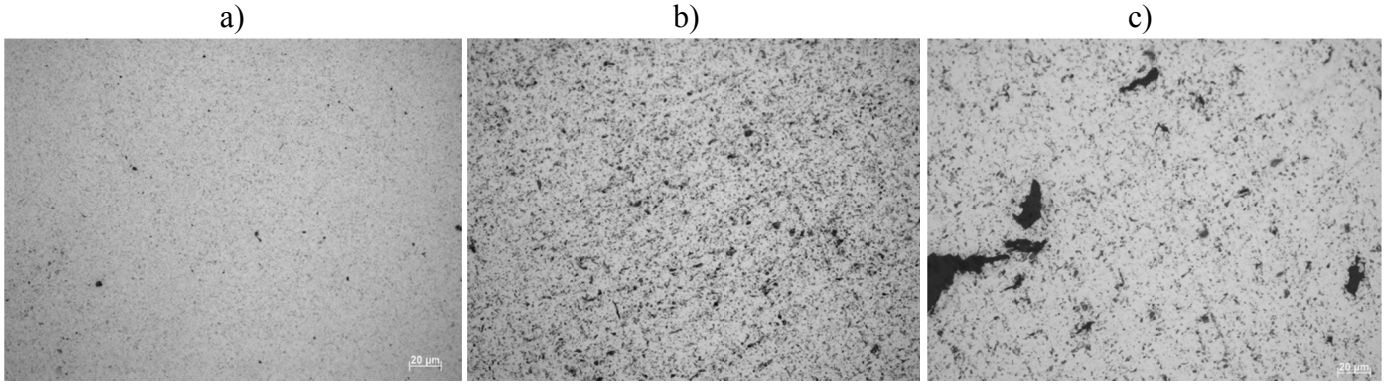

Fig. 4. Microstructure of the nanocomposites made of the AlMg1SiCu powder with 2 vol.% content of multi-walled carbon nanotubes after hot extrusion of powders prepared by using: a) high-energy mechanical milling, b) low-energy mechanical milling, c) mixing using turbulent mixer; light microscope

The lack of pores, large voids and close adherence of the phases to each other proves the proper connection between the matrix and reinforcement particles during both the powder milling and hot extrusion. Although the composite powders obtained using LEMM and TM are not strengthened by the milling process, their plastic consolidation by hot extrusion is difficult. This is probably caused by the occurrence of MWCNTs agglomerations, which makes powder compacting much more difficult. During powder compacting these agglomerations disturb the movement of single particles and, together with the smaller level of extrusion force, lead to inhomogeneous consolidation. Therefore after hot extrusion LEMM and TM composites are characterized by a lot of easily visible pores and discontinuities, especially in the case of the TM powder (Fig. 4b,c).

X-ray analysis proves that the dispersion method affects the phase composition of the manufactured composite material (Fig. 5). Plastic consolidation of composite powders fabricated by LEMM and TM does not cause the appearance of additional phases. However, in the extruded composites manufactured by HEMM, in addition to α-Al phase, aluminium carbide (Al_4C_3) was also identified (Fig. 5). This phenomenon is caused by the fact that high deformation during the ball milling process causes structural defects in the CNTs and aluminium carbides can easily precipitate in those places.

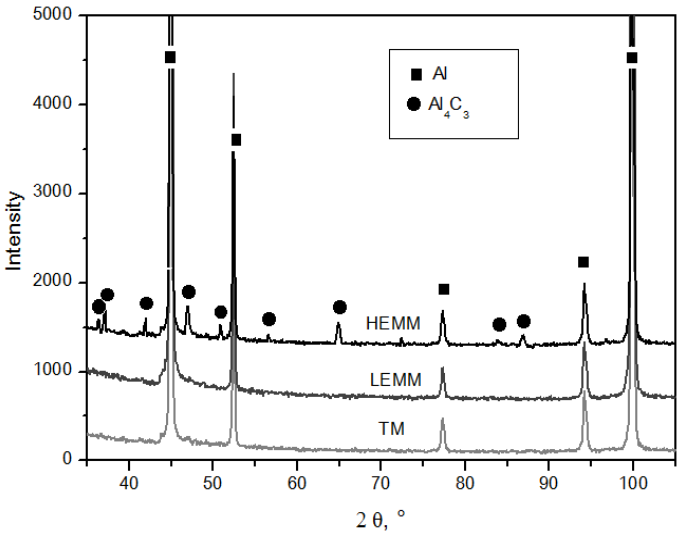

Fig. 5. X-ray diffraction patterns of the nanocomposite materials

The X-ray analysis results have been confirmed by transmission electron microscopy observations (Fig. 6). The microstructure of thin foils of composite materials prepared from HEMM powder, consisting of fine grains of aluminium, dispersed MWCNTs and aluminium carbides.

A friction coefficient recorded during the ball-on-plate wear test is shown in Fig. 7. For the first 2 m of sliding distance, the friction coefficient of HEMM composites decreases abruptly. Beyond 2 m, it stabilises at an average value of about 0.5 for the remaining distance. Only a number of temporary increases of the friction coefficient can be observed. These may be attributed

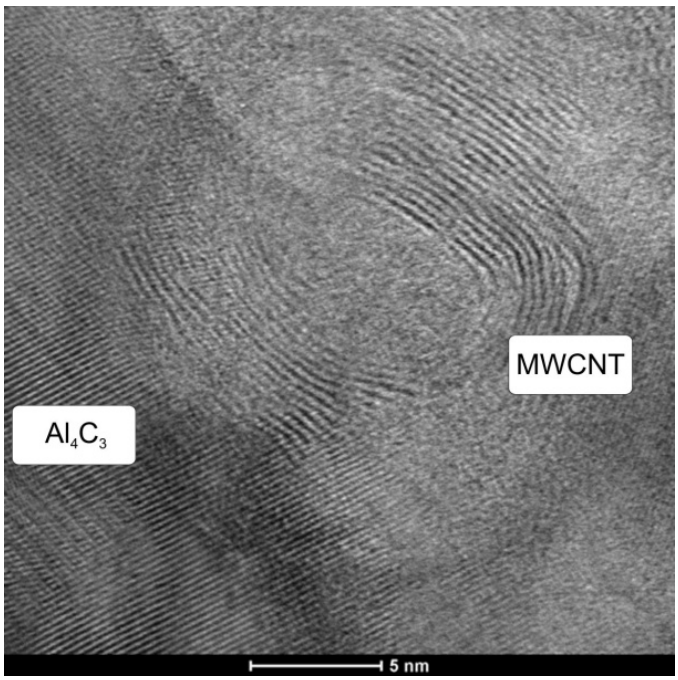

Fig. 6. Microstructure of nanocomposite material with 2 vol.% content of MWCNTs prepared from HEMM powder; HRTEM

to micro-fracturing and delamination. However, for the TM and LEMM composites, the friction coefficient presented considerable variation during the whole test. It is also obvious that the friction coefficient of the HEMM composite is smaller and less prone to fluctuations compared to the remaining composites. This may be attributed to the efficient powder densification during the extrusion process, stable lubricating action of well-dispersed MWCNTs and formation of aluminium carbide. In the TM and LEMM composites, the higher value and fluctuation of the friction coefficient is probably due to the removal of material by surface delamination and fracturing.

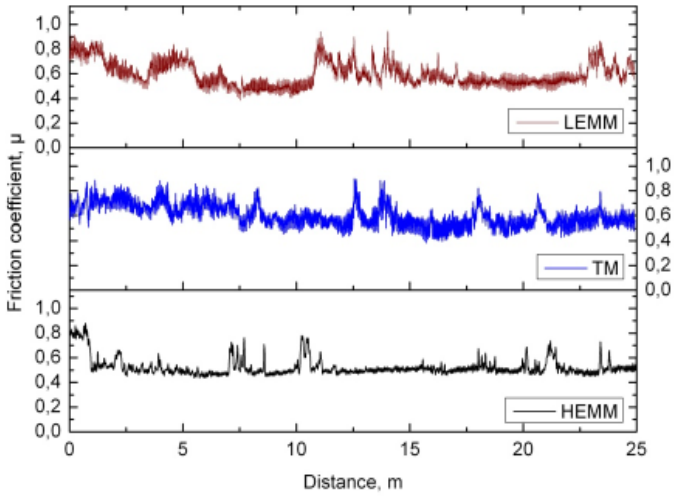

Fig. 7. Friction coefficient registered during ball-on-plate test

The wear volume for the obtained composites as a function of the dispersion method is shown in Fig. 8. These results

of the ball-on-plate wear test show that application of the high energy milling process improves the wear resistance. For the LEMM and TM routes, pores existing in the composite as well as MWCNTs agglomerates perform as crack nucleation sources and generate severe surface destruction resulting in reduced wear resistance of the composite as compared to the fully consolidated material. Furthermore, weak bonding between CNTs and AA6061 particles in the extruded rods is another possible reason for excessive subsurface fracturing. The wear resistance of a composite material manufactured using powder metallurgy is very susceptible to the presence of pores. Porosity increases the wear rate because pores acts as crack nucleation and propagation sites, leading to surface fracturing. The better wear resistance of the composite compared to the bulk alloy at lower loads is in line with other studies [18].

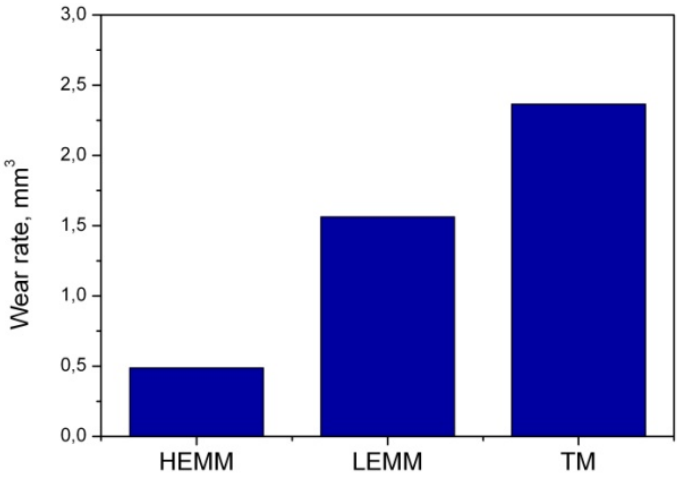

Fig. 8. Wear rate as a function of dispersion method

Figure 9 shows the wear surfaces of the nanocomposites samples being worn under a load of 5 N. In Fig. 9a on the worn surface of the composite prepared from HEMM powder a significant delamination and the presence of scratches can be easily seen. Probably the partially delaminated flakes could be particular layers of joint particles during high-energy powder milling. In contrast, Fig. 9b and c show severe surface fracturing and deep pits and grooves in the worn surface of the composites fabricated from powders subjected to low-energy milling/mixing. The presence of pores is the main reason for crack initiation and propagation during sliding. It looks as if propagating cracks lead to extensive delamination and therefore a high wear rate for the composite fabricated using low energy processes is observed. The deep grooves and pits have been formed due to continuous abrasion.

Composite materials prepared using HEMM powder are characterized by a uniformly distributed particulate reinforcement phase in a fine-grained alloy matrix AlMg1SiCu, which enables the highest microhardness numbers to be achieved (Table 3).

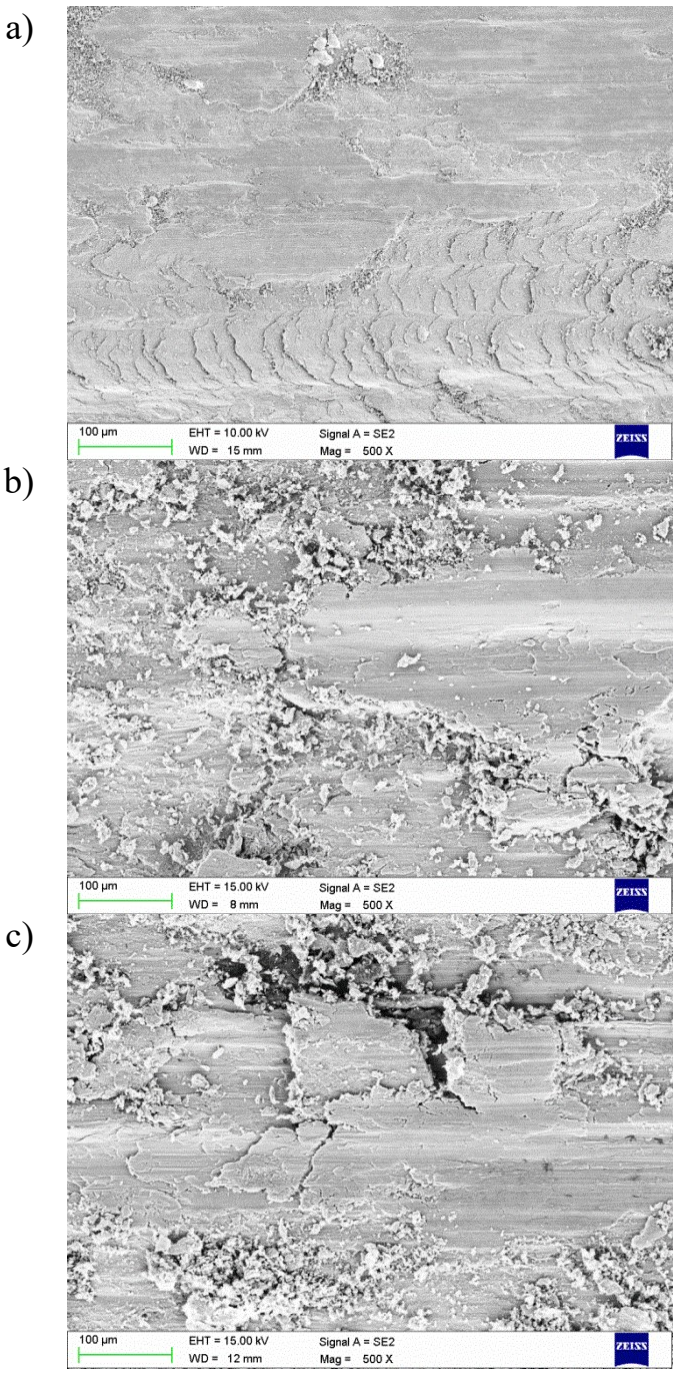

Fig. 9. SEM micrographs of the worn surfaces of composites after hot extrusion of powders prepared by: a) high-energy mechanical milling, b) low-energy mechanical milling, c) mixing using turbulent mixer

TABLE 3

Microhardness of composites

Powder	MWCNTs dispersion method	Microhardness, $HV_{0.1}$
AlMg1SiCu	unmilled	61
AlMg1SiCu	HEMM	98
AlMg1SiCu/2%MWCNTs	HEMM	129
AlMg1SiCu/2%MWCNTs	LEMM	66
AlMg1SiCu/2%MWCNTs	TM	63

Based on the outcomes of the bulk density analysis (Table 4) of the obtained powder, it was found that the addition of carbon nanotubes increases the bulk density, with a simultaneous decrease in flow time. At the same time, the composite powders subjected to low-energy powder milling and turbulent mixing in a mixer are characterized by lack of flowability, which can be regarded as a characteristic discrediting this type of material for industrial applications.

TABLE 4

Flow time and bulk density of the powders

Powder	MWCNTs dispersion method	Flow time, s	Bulk density, g/cm^3
AlMg1SiCu	unmilled	16	1.13
AlMg1SiCu	HEMM	16	1.15
AlMg1SiCu/2%MWCNTs	HEMM	20	1.20
AlMg1SiCu/2%MWCNTs	LEMM	Do not flow	1.05
AlMg1SiCu/2%MWCNTs	TM	Do not flow	0.98

5. Conclusion

The studies accomplished have shown that the composite materials produced by the use of high energy mechanical milling and hot extrusion have satisfactory dispersion of the reinforcing phase, which leads to improved mechanical properties of the obtained nanomaterials. Therefore HEMM is a promising method which can be used to disperse carbon nanotubes in the material matrix, although they may be involved in the formation of aluminium carbide during consolidation of the material. The microhardness of all the nanocomposite materials reaches a higher value than the raw material. It has also been found that the addition of MWCNTs to the AlMg1SiCu powder prior to HEMM slightly increases its bulk density.

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