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EFFECT OF MILLING TIME ON MICROSTRUCTURE AND PROPERTIES OF AA6061/MWCNTs COMPOSITE POWDERS

WPŁYW CZASU MIELENIA NA STRUKTURĘ I WŁASNOŚCI PROSZKÓW KOMPOZYTOWYCH AA6061/MWCNTs

The main purpose of this work is to determine the effect of milling time on microstructure as well as technological properties of aluminium matrix nanocomposites reinforced with multi-walled carbon nanotubes (MWCNTs) using powder metallurgy techniques, including mechanical alloying. The main problem of the study is the agglomeration and uneven distribution of carbon nanotubes in the matrix material and interface reactivity also. In order to reach uniform dispersion of carbon nanotubes in aluminium alloy matrix, 5÷20 h of mechanical milling in the planetary mill was used. It was found that the mechanical milling process has a strong influence on the characteristics of powders, by changing the globular morphology of as-received powder during mechanical milling process to flattened one, due to particle plastic deformation followed by cold welding and fracturing of deformed and hardened enough particles, which allows to obtain equiaxial particles again. The obtained composites are characterised by the structure of evenly distributed, disperse reinforcing particles in fine grain matrix of AA6061, facilitate the obtainment of higher values of mechanical properties, compared to the initial alloy. On the basis of micro-hardness, analysis has found that a small addition of carbon nanotubes increases nanocomposite hardness.

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

Głównym celem podejmowanej pracy było określenie wpływu czasu mechanicznego mielenia na strukturę oraz własności technologiczne nanokompozytów o osnowie stopu aluminium 6061 wzmocnionych wielościennymi nanorurkami węglowymi (MWCNTs, ang. multi-walled carbon nanotubes) z wykorzystaniem technik metalurgii proszków, w tym mechanicznej syntezy oraz wyciskania na gorąco. Głównymi problemami podjętymi w badaniach były: aglomeracja i nierównomierny rozkład nanorurek węglowych w osnowie, a także reaktywność na granicy faz. W celu uzyskania jednorodnego rozmieszczenia nanorurek węglowych w osnowie stopu aluminium zastosowano wysokoenergetyczne mechaniczne mielenie w młynie planetarnym przez 5÷20 godzin. Stwierdzono, że zmiana czasu trwania procesu mechanicznej syntezy wpływa znacząco na morfologię materiałów proszkowych, umożliwiając uzyskanie zmiany ich morfologii ze sferycznej – charakterystycznej dla stanu wyjściowego – w odkształconą plastycznie (płatkową), następnie w powtarzających się procesach zgrzewania i pękania materiału umocnionego ponownie przyjmuje postać cząstek równoosiowych. Otrzymane w procesie mechanicznej syntezy materiały kompozytowe charakteryzują się strukturą równomiernie rozłożonych, rozdrobnionych cząstek fazy wzmacniającej, w drobnoziarnistej osnowie stopu AA6061, sprzyjających osiąganiu wyższych wartości własności wytrzymałościowych w porównaniu do stopu wyjściowego. Na podstawie badań mikrotwardości wykazano, że już niewielki dodatek nanorurek węglowych powoduje zwiększenie twardość nanokompozytu.

1. Introduction

The metal matrix composites (MMCs), especially this with the aluminium matrix are the most widely used composite materials in the industry due to their outstanding properties like light weight, high strength, low thermal expansion coefficient, high specific modulus and excellent wear resistance [1]. Among various reinforcements as SiC [2], Al_2O_3 [3], ZrO_2 [4], Ti(C,N) [5] used in aluminium matrix composites, carbonous materials have many attributes what makes them promising candidates as a reinforcement in MMCs, due to their mechanical, electrical and tribological properties. In recent years, there is growing attention in carbon nanotubes (CNTs) as reinforcement of aluminium matrix composites. A large number of publications shows an enormous interest in this field [6-10]. Most of them are focused on different processing methods investigating the effects of those techniques on mechanical properties of the composites [11]. Very limited studies are focused on the investigation of particle microstructure, as well as MWCNTs' evaluation during the mechanical milling [1,11]. Other important factors took into the consideration are the concentration of CNTs in the matrix and addition of process control agent (PCA) during the powder preparation, which was used to minimise cold welding of the particles, as well as to eliminate the powders sticking to the milling balls. In most of the publications methanol [8], stearic

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acid [7], heptane [11] were used as PCA. In this work for the first time, the micronised amide wax was used as process control agent.

Homogeneous dispersion of CNTs in metal matrix is the main problem during the composite powder preparation. Uniform dispersion of CNTs in the matrix caused the increase of the composite hardness compared to the unreinforced aluminium alloy. It has been observed that during the mechanical milling of CNTs with aluminium alloy powder, the CNTs are damaged to some extent [12,13].

The aim of this study was to obtain nanocomposite powders with a matrix of aluminium alloy AA6061 reinforced with MWCNTs and to analyse the influence of the milling time on the particles morphology, size, phase composition and properties. It has been investigated that the addition of MWCNTs causes significant improvement in mechanical properties of AA6061/MWCNTs nanocomposites.

2. Experimental procedure

The morphology of the obtained powders after different ball milling time, i.e. 5÷20 h were observed using scanning electron microscopy (SEM). The structure of MWCNTs was investigated by Raman spectroscopy using inVia Reflex f microscope, Renishaw. Phase composition analysis of the milled powders with was made using PANalytical X'Pert PRO X-ray diffractometer with cobalt radiation source. The density of the obtained composite powders was measured using automatic gas pycnometer Micrometrics AccuPyc 1340. Bulk (apparent) density was determined as the ratio of the mass of powder in a loose condition to the calibrated volume of a buried cell in which it is located using the Hall funnel (according to PN-EN ISO 3923-1:2010 E).

3. Material for investigations

As the reinforcement, multi-walled carbon nanotubes with the diameter of 20÷50 nm and length > 5 µm were used. Carbon nanotubes were produced by Chemical Vapour Deposition (CVD) using Ni as a catalyst by Cheap Tube (USA) (Fig. 1). As the matrix material, the powder of gas atomised aluminium alloy EN AW-AlMg1SiCu (AA6061) supplied by the ECKA Company (Germany) was used with the average size of the particles < 63 µm (Fig. 2). The chemical composition of the AA6061 alloy was summarised in Table 1.

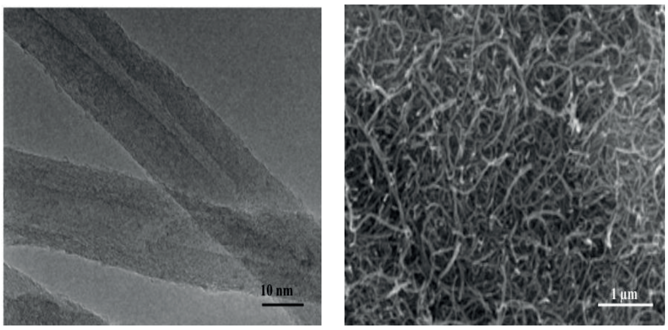

Fig. 1. Morphology of the as-received multi-walled carbon nanotubes: a) HRTEM, b) SEM

TABLE 1

The chemical composition of AA6061

Mg	Si	Cr	Cu	Fe	Mn	Zn	Ti	Al
0.95	0.6	0.26	0.22	0.47	0.11	0.015	0.006	Bal.

In order to achieve uniform dispersion of MWCNTs in aluminium alloy matrix, 5÷20 h of mechanical milling in planetary ball mill was made with an addition of 0, 2 and 5 vol.% of MWCNTs. Each powder was milled under the rotation speed of 200 rpm, with the ball to powder weight ratio 20:1. 1 wt.% of micronised amide wax as a process control agent (PCA) was added as well.

4. Results and discussion

As has been shown in Fig. 1. the as-received multi-walled carbon nanotubes are curved and tangled. MWCNTs forms big clusters, most likely due to the Van der Waal force between long tubes. The nanoparticles agglomeration is the important problem in the metal matrix composites reinforced with carbon nanotubes. Clusters of reinforcing particles can lead to crack initiation and fracture. Uniform dispersion of the carbon nanotubes was the main problem to solve. The shape and morphology of the AA6061 powder in the initial state have been shown in Fig. 2. Aluminium particles have globular shape and smooth surface, what decide that during low-energy agitation, MWCNTs cannot attach to them. The smooth particles allow MWCNTs to separate from AA6061 powder for the longer milling time, which can lead to an increase of dislocation and defects. Due to severe collisions of a high speed of milling balls, carbon nanotubes can be harmed or damaged. However, gas-atomised aluminium powder particles are relatively ductile, which exposes MWCNT to get stuck between cold-welded aluminium particles. In the result of ball-milling collisions, carbon nanotubes can be also thrust into the matrix particles. Overall mechanical milling of ductile powder, involves two opposing processes: cold welding and fracturing. Cold welding creates large particles, while – as a result of fracturing – small particles can be obtained. To reduce cold welding as a dominant process in the aluminium powder ball-milling, micronized amide wax was used as process control agent.

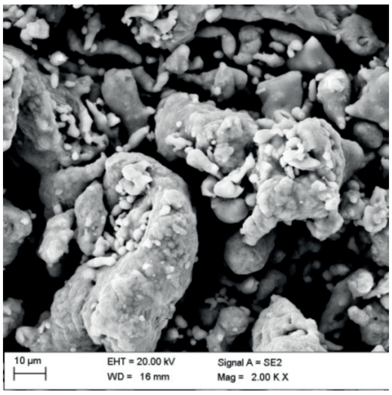

Fig. 2. Morphology of the as-received AA6061 powder, SEM

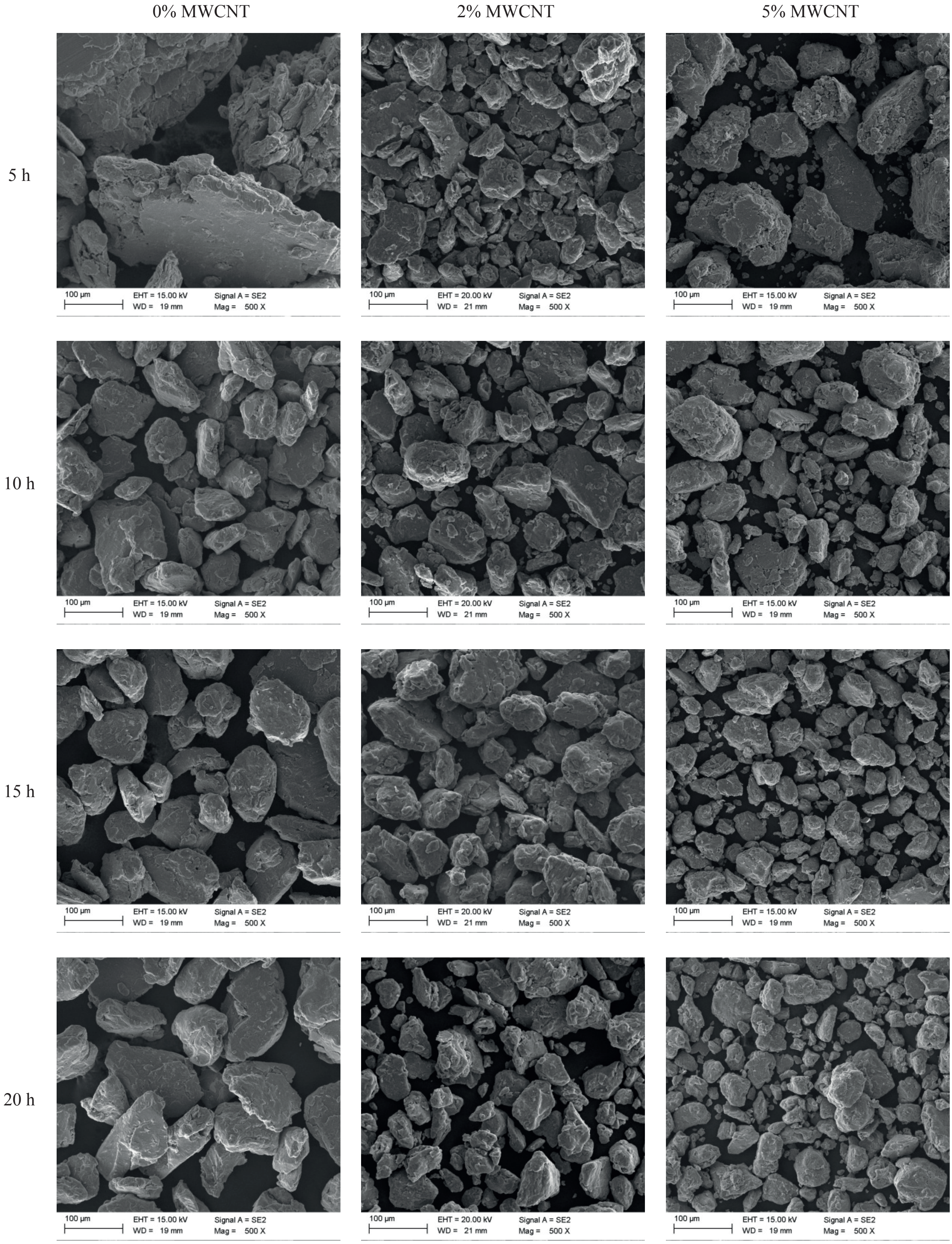

Fig. 3. The morphology of milled powders with: a) 0, b) 2% c) 5% vol. MWCNTs after different times of mechanical milling, SEM

The morphology evolution of ball-milled AA6061 powder with and without an addition of MWCNT is shown in Fig. 3. It is well known that the primary globular aluminium powder particles are deformed and flattened in the early stage of mechanical milling. The flat particles are welded together as a result of ball-milling and such particles form plate, much bigger structures. Changes in the particle size and shape of the base powders are caused due to collisions with milling balls or with the milling container walls. The conglomerates of laminar particles, formed as a result of welding, become much more reinforced, simultaneously more brittle. As milling advances, the particles are crumbled and re-welded, what in the end gives a quite regular shape of the milled particles and tells that the milling process has reached the steady-state. In contrast to the milled AA6061 alloy powder, it was found for the composite material powder, that the deformed particles were tightly joined, in consequence creating homogenous composite particles free of pores. Variations in the morphology of particles after 5 hours of milling can be explained by differences in properties of composites powders. Due to the predominant ductility of AA6061 powder and possibly dynamic recovery or dynamic recrystallization taking place, a cold-welding mechanism is the dominant in the ball-milling process, leading to the large particles formation observed in Fig. 3a. With an addition of MWCNTs, the powders become less ductile and much smaller particle sizes can be obtained (Fig. 3b, c). Longer milling leads to decreasing difference in particles size and shape. However, at every stage influence of carbon nanotubes content can be easily noticed: the size of the particles decreased with the increasing of MWCNTs content for the same milling time. After 20h of mechanical milling, the AA6061 powder is characterised by much bigger particles in comparison with those with MWCNTs addition. Simultaneously, it is very hard to notice any differences in composite powders, what can be explained that in this time every mixture of powder has reached steady-state. Furthermore, it was very difficult to analyse the dispersion of MWCNTs in the AA6061 matrix. A large MWCNTs agglomerates randomly exist on the surface of AA6061 particles in the shorter milling time. Individual carbon nanotubes and their clusters cannot be seen on the aluminium particle surface after 5 hours and more. Most likely all of the carbon nanotubes has been embedded in the metal matrix particles. It has been assumed that MWCNTs were well dispersed and then wrapped in aluminium particles or just covered by a ductile matrix. It indicates the homogeneous distribution of MWCNT in the aluminium powder that also proves that the mechanical milling is an effective technique in carbon nanotubes dispersion in a metal matrix.

X-ray analysis of the mechanically milled composite powders has shown no phase composition change and presence of only α-Al phase (Fig. 4). The occurrence of aluminium carbides has not been detected. Even though, the maximum content of MWCNTs in composite fabrication was 5 vol.%, there are no carbon reflections from XRD patterns, regardless of milling time. Formation of the Al4C3 in the result of the reaction between carbon nanotubes and the aluminium alloy has been earlier described by many other authors [6,9,15]. It has been suggested that the formation of the Al4C3 carbide has a strong dependence on the processing time and temperature. The reference AA6061 alloy powder after the same milling time demonstrated sharp peaks in comparison with the composites powders reinforced with MWCNTs. Broadening of the α-Al peaks can be ascribed to the structure refinement, the lattice strain affected by its distortion due to the plastic deformation and attendance of MWCNTs.

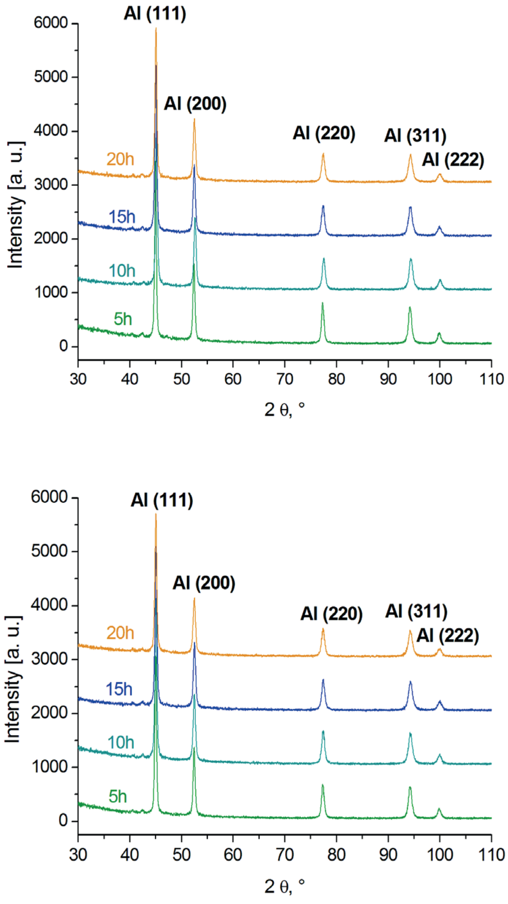

Fig. 4. XRD patterns of the milled powders with an addition of: a) 2% and b) 5% vol. MWCNTs

The occurrence and structural changes of MWCNTs after mechanical milling from 5 to 20 h were analysed using Raman spectroscopy. The change in the two band intensities can be quantified with the ratio ID/IG [12,13]. The Raman spectra of the initial MWCNTs used in this study is shown in Fig. 5. It can be seen that D band and G band are typically located at 1570 cm^{-1} and 1345 cm^{-1} respectively, what gives I_D/I_G ratio equal to 0.85. In D and G bands are due to sp2 sites. D band occurs due to the breathing modes of sp2 atoms in rings. G band is due to the bond stretching of all pairs of sp2 atoms in both rings and chains. G band is observed for perfect hexagonal graphite and, therefore, will appear wider and smaller for badly structured and defect containing nanotubes, what can be noticed in the Fig. 5. On the other hand, D band is attributed to lattice defects and finite crystal size, which cause a breaking of the 2D translational symmetry, so that it will increase and broadened with increasing number of defects in the nanotubes. Table 2 shows the ID/IG ratio of the milled powders after different milling time. The D band and G band peaks were detected in any powder with the addition of MWCNTs, what proved the existence and dispersion of the nanotubes in aluminium alloy powder. It can be seen that the ID/IG ratio for all the mixed powders is higher than the one for initial MWCNTs. For the samples with 2% MWCNTs addition, the ratio slightly increases to 1.20. It means that damages of the MWCNTs occurred during the ball milling process. Higher ratios are obtained after milling since the creation of lattice defects increases the D band intensity while decreasing the G band intensity. The broadening of the G and D peaks during milling observed here also indicates an amorphization of the nanotubes. Probably, this amorphization has been accentuated by the presence of Al.

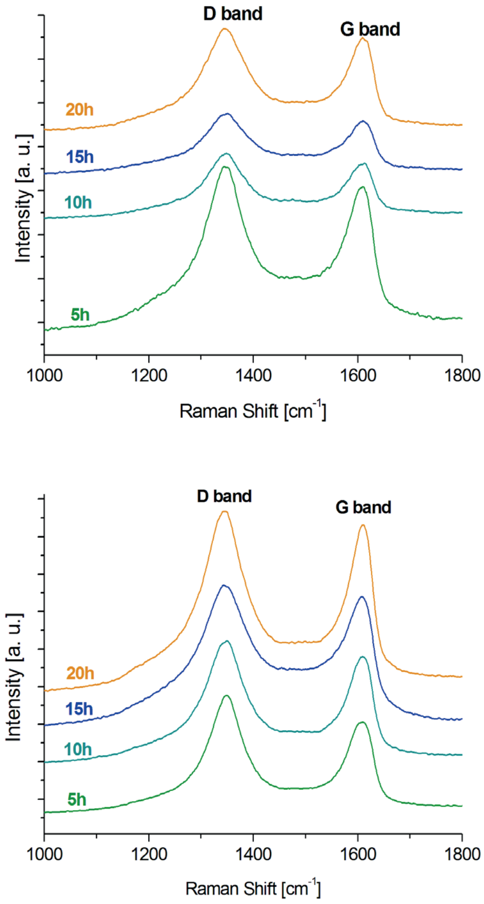

Fig. 5. Raman spectra of the milled powders with the addition of: a) 2%, b) 5% vol. MWCNTs for different milling time

TABLE 2

The I_D/I_G ratio of the milled powders

Milling time	5h	10h	15h	20h
2% MWCNTs	1.15	1.20	1.15	1.10
5% MWCNTs	1.14	1.16	1.09	1.09

Results of flowability, bulk density and pycnometric density analysis are gathered in Table 3. The bulk density of obtained powder is determined mostly by the shape and size of particles, as well as chemical composition (oxidisation of the surface) and possibility of gas absorption on the surface of such particles. The MWCNTs have a larger specific surface, an oblong shape and form porous clusters, therefore, have a much lower bulk density in comparison to spherical particles. However, very small reinforcing particles may cause the contradictory effect, which can be described by a phenomenon of small particles being located in the spaces between bigger particles. Additionally broad particles size distribution is decreasing the volume maximally as compared to e.g. spherical particles, what results in a valuable increase in the packing effect. Used MWCNTs were mainly characterised by much smaller particles than the AA6061 alloy matrix powder but also exhibit a high agglomeration tendency. However, during mechanical milling, all of the MWCNTs were well dispersed and embedded in the aluminium alloy particles. Due to higher carbon nanotubes content, composite particles became much more reinforced and simultaneously less ductile, what results in a higher level of fragmentation (Fig. 3). Smaller particles sift between bigger ones affect the higher bulk density of composite powders. Based on results of the bulk density of the obtained powder, it was observed that the highest bulk density was achieved for the sample with 5 vol.% of MWCNTs. Additionally, it is a typical feature when ductile powders are undergoing the mechanical milling process: the bulk density value is changing with the passing

TABLE 3

Technological properties of the milled powders

MWCNTs content in AA6061alloy matrix, % vol.	Milling time, h	Flowability, s	Bulk density, g/cm^3	Density, g/cm^3
0%	5	16	1.15	2.65
	10	16	1.15	2.66
	15	16	1.16	2.66
	20	16	1.16	2.68
2%	5	19	1.20	2.63
	10	20	1.20	2.63
	15	18	1.20	2.64
	20	18	1.20	2.65
5%	5	31	1.22	2.61
	10	24	1.21	2.61
	15	23	1.22	2.62
	20	23	1.23	2.62

of milling time. It was found that with the increase of the MWCNTs fraction, the dependency between apparent density and milling time is changing, reaching the values higher than in the primary condition.

The mechanical milling of AA6061/MWCNTs powders also has the significant influence on the flow rate. Used powders are not flowing out of a standard funnel before and at the beginning of milling, due to the flattened particles shape. Powders are estimated by flow rate only at a later stage when cold-welding processes are principal and bulk density is rising. The flow rate of powder increases with the growth of particle size, and there seems to be a critical size range over which flow rate does not show any improvement, in this case, 16 s for unreinforced AA6061 powder. It was found that flow rate is decreasing with increasing MWCNTs content in composite powders, what can be explained by that small particles generate a lot of inter-particle friction. But it has to be taking into account that other factors determining the powder flow rate are also particle size distribution, particle structure, particle surface, humidity, chemical composition and lubrication. The outcomes achieved confirm the information presented in the following works [16,17].

5. Conclusions

Completed studies have confirmed that a homogeneous dispersion of MWCNTs into the Al alloy was obtained obtainet by mechanical milling. It has been shown that mechanical milling time has an influence on particle morphology and size: the increased milling time affects the particle size reduction. From the Raman spectra was found that damages of the MWCNTs occurred during the ball milling process. The ID/IG ratio for all the milled powders is higher than the one for initial MWCNTs. Increasing milling time results that the bulk density of produced composite materials powders slightly increases, as well as the powders density.

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