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EFFECT OF MILLING TIME ON MORPHOLOGY AND SIZE OF COPPER/CNT COMPOSITE POWDER

The development of a sintered copper matrix composite with a small addition of carbon nanotubes (CNTs), which improves its mechanical strength without a decrease in electrical conductivity is of practical importance. Therefore, in the present paper the parameters of ball milling of a Cu+CNT powder mixture were optimized in order to obtain the highest refinement of particles of such a composite material. Investigations carried out with the help of scanning electron microscopy and sieve analysis revealed that the average particle size of the powder decreases with an increase in the volume content of the carbon nanotubes. The presence of carbon material should limit grain growth during the hot pressing of composite material, allowing much smaller grain sizes and accompanying high hardness to be obtained of the resulting compacts, as compared with similarly processed copper powder.

Keywords: ball milling, copper powder, carbon nanotubes, SEM, sieve analysis, TEM

WPŁYW CZASU MIELENIA NA MORFOLOGIĘ I WIELKOŚĆ CZĄSTEK KOMPOZYTOWYCH PROSZKÓW MIEDŹ/CNT

Opracowanie spiekanych kompozytów na osnowie miedzi z niewielkim dodatkiem nanorurek węglowych, poprawiających ich własności wytrzymałościowe bez wyraźnego spadku przewodności elektrycznej, ma duże znaczenie praktyczne. Dlatego w ramach niniejszej pracy została przeprowadzona optymalizacja parametrów mielenia w młynku kulowym mieszanki proszkowej miedź + nanorurki węglowe w celu uzyskania możliwie największego stopnia rozdrobnienia cząstek takiego materiału kompozytowego. Badania przeprowadzone metodą skaningowej mikroskopii elektronowej oraz analiza sitowa wskazały, że średnia wielkość cząstek proszku generalnie spada wraz ze wzrostem zawartości nanorurek węglowych. Obecność nanorurek węglowych powinna zapobiegać rozrostowi ziarna podczas prasowania na gorąco takiego materiału kompozytowego, co pozwoli na uzyskanie znacznie mniejszego ziarna, a w konsekwencji wyższej twardości w porównaniu do wytwarzanego w ten sam sposób proszku miedzi.

Słowa kluczowe: mielenie w młynie kulowym, proszki miedzi, nanorurki węglowe, SEM, analiza sitowa, TEM

INTRODUCTION

Copper plays a key role in electrical and electronic industries due to its very good electrical conductivity [1, 2]. However, its mechanical properties may be insufficient for many practical applications. Therefore, strengthening a copper matrix with carbon nanotubes (CNTs were proposed as the latter show a very high ultimate tensile strength, Young's modulus and high electrical conductivity) [3-7]. Indeed, even the first experiments indicated that the sinters of copper powder with a small addition of CNTs exhibits better strength than that without such an addition, with only a slight decrease in electrical conductivity [8-10]. The exact size and shape of the sintered powder might significantly contribute to further improvement of the materials produced with such a method. The ball milling process used for mixing copper elemental powder and CNT strongly affects not only the average size but also the shape of the particles used later in the sintering process [11, 12]. During milling several stages may occur: flattening of the particles, cold-welding, fracturing or re-welding of fractured particles [13, 14]. Therefore, the microstructure of the processed powder strongly depends on the milling parameters like the total milling time or speed of vial rotation [15, 16]. It is also worth noting that the mechanical properties of the sintered Cu+CNT material is governed by the morphology of the milled powder. Therefore, it is of great importance to elaborate the milling parameters of such a mixture in a way allowing the highest mechanical properties to be obtained of the sintered composite.

The morphology and size of Cu+CNT powder mixture particles obtained using various ball milling parameters like the duration of the process or rotation speed of the mill, up to now have been investigated

mainly with the help of light (LM) or scanning electron microscopy (SEM) methods. Bor et al. [16, 17] showed that the average grain size of the Cu+CNT powder mixture particles generally increases with the milling process time, contrary to the same processing of a pure copper powder. The SEM observations together with laser particle size analyses carried out by Shukla et al. [15] allowed them to state that extending the ball milling process from 5 h up to 20 h resulted in a change in the morphology of the powders from spherical to a disk-like one. Additionally, in case of Cu+CNT mixtures milled for 20 h, the intiation of particle fracturing was also observed. However, the effect of longer processing times on the Cu+CNT powder particle size is still lacking.

Therefore, the main aim of the present work was to study the effect of the addition of CNTs on the particle refinement of the Cu/CNT composite powder during ball milling carried out for extended processing times. The task involved sieve analysis in order to determine the histogram of the particle size as well as SEM and TEM observations used to characterize their morphology.

EXPERIMENTAL PROCEDURE

Copper powder, with an average grain size of 42 μm and 99% purity was supplied by the Alfa Aesar company. Multi-walled carbon nanotubes, obtained by courtesy of the Nanostructured & Amorphous Materials company, were characterized by an outside diameter in the range of 30÷50 nm. 1 and 3 vol.% carbon nanotubes were added to the copper powder in an mBraun glove box under argon atmosphere.

Pure copper and Cu+CNT (1 and 3 vol.% CNT) powder mixtures were milled with the help of a Pulverisette 5/4 ball mill using zirconia containers and balls, at a rotation speed of 200 rpm. The weight ratio of the balls to powder was 10:1. The ball milling process was carried out for 1, 2, 4, 6, 8, 16 and 32 h for each powder mixture.

The microstructure observations of the milled Cu+CNT powder mixtures were carried out by means of scanning electron microscopy (SEM) in the secondary electrons (SE) mode operating at 10 kV and an FEI Technai G2 transmission electron microscope (TEM). The thin foils for TEM were prepared by cutting the milled powder with a Leica microtome, which were then were placed on nickel grids with an ultra-thin holey carbon support film. Sieve analysis was performed with an Analysette 3 PRO vibratory sieve shaker.

RESULTS

The SEM/SE observations of the as-supplied copper powder revealed that the largest particles were approx. 100 μm, while the smallest ones were even below 20 μm (Fig. 1a). The provided powder was characterized by an irregular-rounded shape of particles with a highly corrugated surface. The SEM/SE micrographs of the carbon nanotubes indicated that they are braided and able to form aggregates with a size up to even 10 micrometres (Fig. 1b). The sieve analysis of the pure copper powder revealed that it adheres to nearly symmetric Gaussian distribution with an average size of ~30 μm (Fig. 2). The maximum content of ~35% was observed for the particle size of 32 μm (with a median of ~345 μm^2). The contribution of particles with a size larger than 63 μm was omitted as negligible estimated at < 0.05 vol.%).

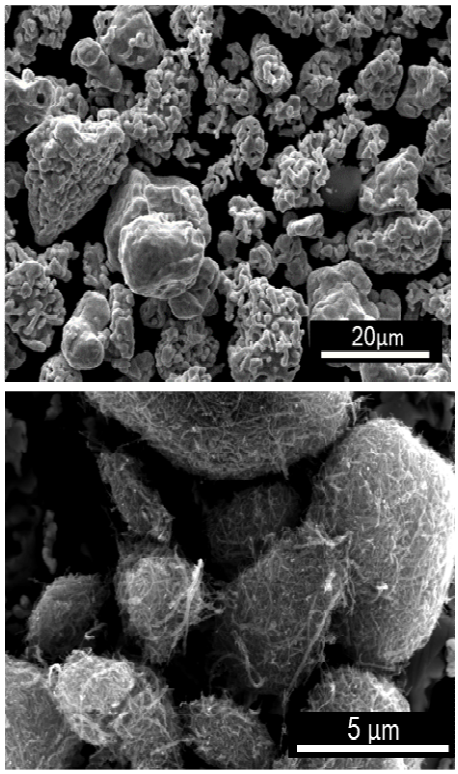

Fig. 1. SEM/SE micrographs of as-supplied copper powder (a) and CNTs (b)

Rys. 1. Obrazy SEM/SE mikrostruktury dostarczonego proszku miedzi (a) oraz nanorurek (b)

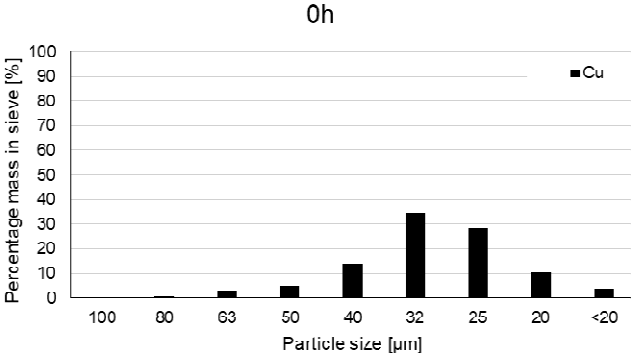

Fig. 2. Histogram of particle size of as-supplied copper powder obtained by sieve analysis

Rys. 2. Histogram wielkości ziaren dostarczonego proszku miedzi uzyskany za pomocą analizy sitowej

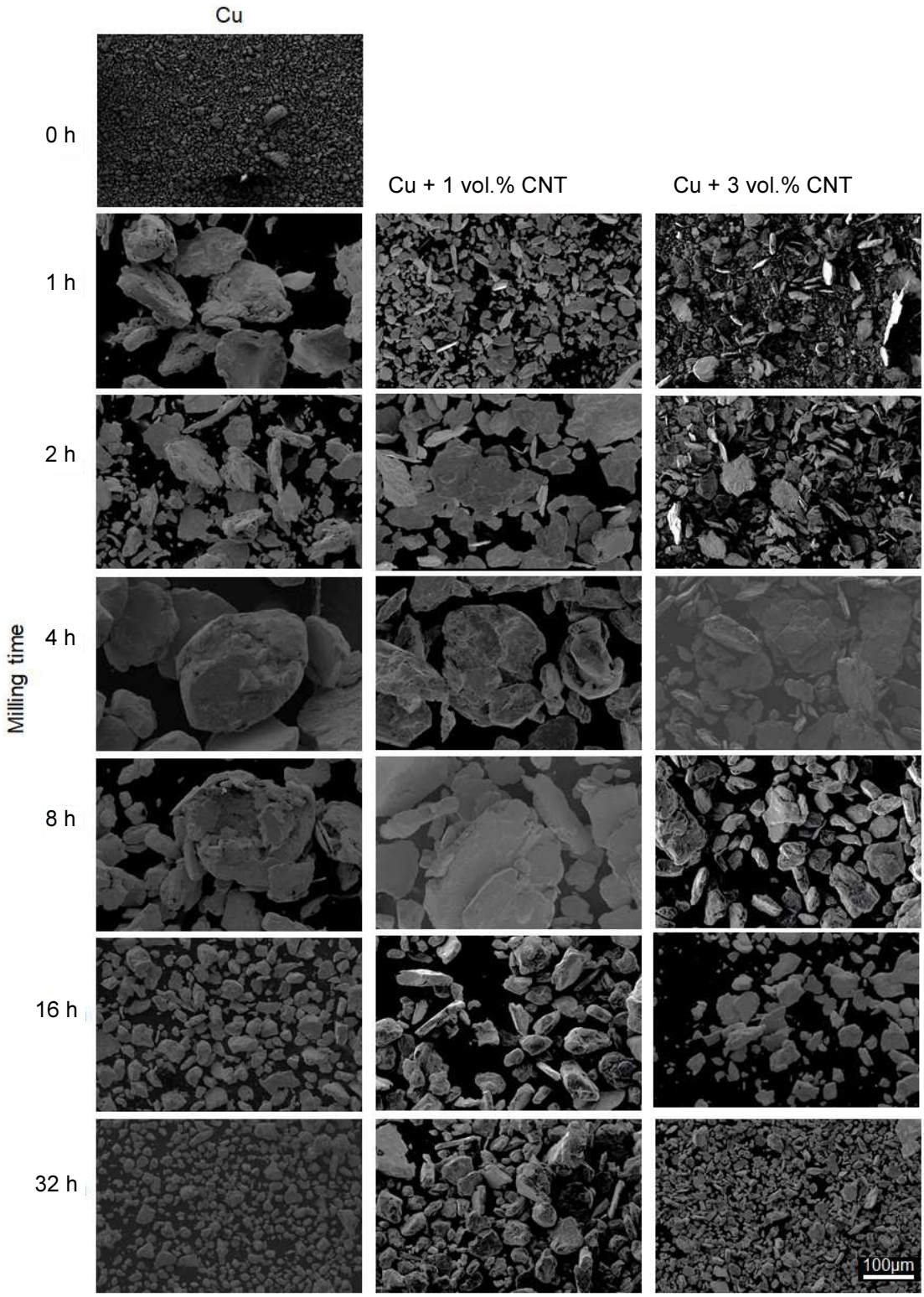

Fig. 3. SEM/SE micrographs of copper powder with addition of CNTs after various milling times

Rys. 3. Obrazy SEM/SE przedstawiające proszek miedzi z dodatkiem nanorurek węglowych dla różnych czasów mielenia

The SEM/SE micrographs of the Cu and Cu+CNT (1 and 3 vol.% of CNTs) powder mixtures after various milling times are presented in Figure 3. The mean size of the powder particles estimated from their area presented in 2D SEM micrographs is shown in Figure 4. In the case of the pure copper powder, milling for 1 h resulted in a sharp increase in the average particle size as compared to the as-supplied one. Next, milling for one additional hour caused significant particle refinement, while a further 2 hours of milling raised it significantly. Longer milling times of the copper powder caused only a decrease in their average particle size. The additions of 1 and 3 vol.% carbon nanotubes initially resulted in a gradual increase in the particle size, but after 8 hrs it

tended to decrease, even as finally the latter powder is characterized by an evidently smaller particle size (comparable with the copper powder milled without the CNT addition). The sieve analysis of the Cu and Cu+CNT (1 and 3 vol% CNTs) powder mixtures after various milling times is presented in Figure 5. The contribution of copper powder particles (for the mixture without CNTs) with a size of at least 100 μm remains higher than 60% for 16 hours of processing time. Milling for 32 h resulted in notable flattening of the particles (nearly uniform distribution). In case of the Cu powder with additions of 1 and 3 vol% carbon nanotubes, an increase in the fraction of particles with a size larger than 100 μm was observed after 8 hours of processing time. Continuing the milling for longer times resulted in particle refinement as in the case of the pure copper powder. Simultaneously, particle refinement is more significant with a rising content of CNTs in the Cu+CNT powder mixture.

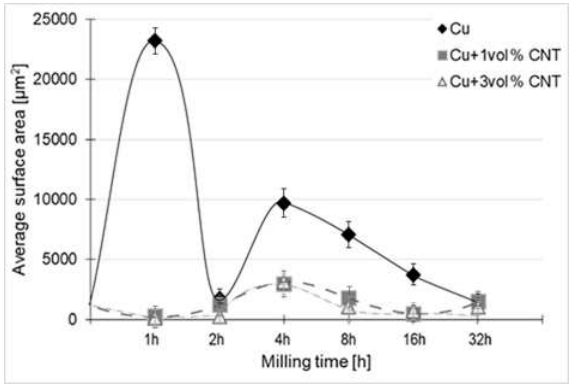

Fig. 4. Mean surface area of Cu+CNT powder mixture particles after various milling times. Untypical scale of milling time (neither linear, nor logarithmic) was chosen to make it easier for the reader to follow particle surface area changes

Rys. 4. Średnia powierzchnia cząstek mieszanki proszkowej miedź + nanorurki węglowe dla różnych czasów mielenia. Wybrano nietypową skalę dla czasu mielenia (ani liniowa, ani logarytmiczna) w celu ułatwienia czytelnikowi śledzenia zmian powierzchni cząstek

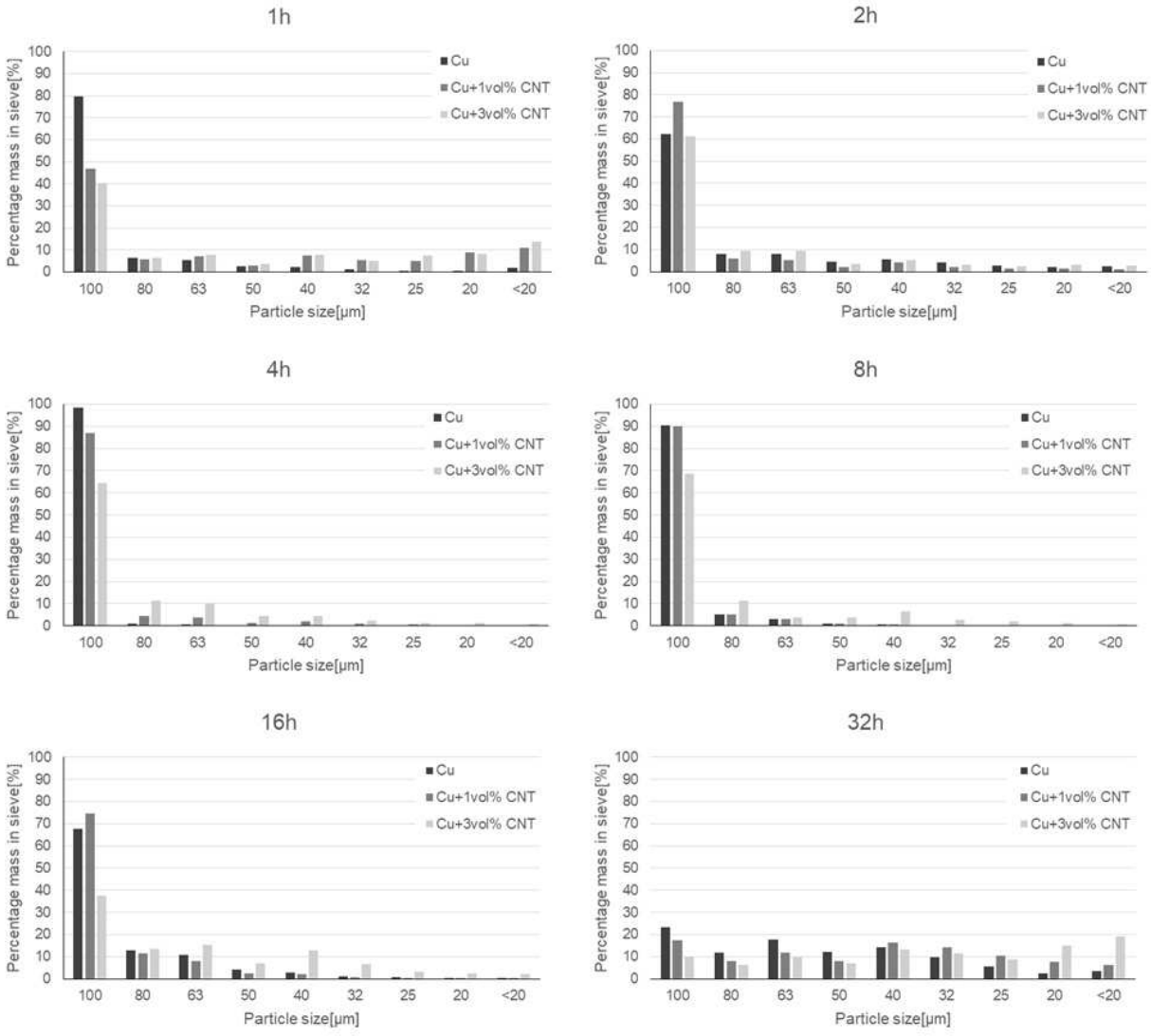

Fig. 5. Histograms of Cu+CNT powder mixture particle size (1 and 3 vol.% CNTs) obtained by sieve analysis

Rys. 5. Histogramy wielkości cząstek proszku miedzi wraz z dodatkiem 1 oraz 3% obj. nanorurek węglowych uzyskane za pomocą analizy sitowej

Detailed microstructure investigations of the powders after the chosen milling times in which morphology changes are significant, i.e. after 4, 8 and 32 hours, were performed by transmission electron microscopy (TEM). Figure 6 presents bright field (BF) micrographs taken at two different magnifications, the corresponding selected area diffraction pattern (SADP) and dark field (DF) micrograph of the powder mixture with 3 vol.% CNTs after 4 hours of milling. As can be seen in the BF micrographs, a typical band structure appears in the early stages of milling. The SADP has an annular character, which already indicates the high refinement of the copper crystallites. The respective rings correspond to the respective atomic planes of Cu, Cu_2O and graphite. Thus, it can be seen that after 4 hours of milling the copper powder oxidizes, although the process was carried out under argon. The clear ring corresponding to the (002) plane of graphite confirms the presence of CNT. The microstructure in DF made from (111) Cu reflection (indicated by the circle on the SADP micrograph) indicates that after 4 hours of milling, the size of the copper crystallites ranges from 100 to 200 nm and they have an elongated character.

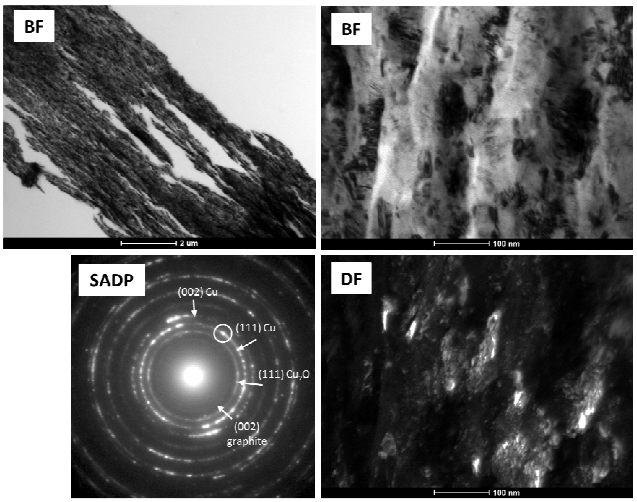

Fig. 6. TEM/BF micrographs taken at two different magnifications, corresponding SADP and DF micrograph of Cu+3%CNT powder mixture after 4 hours of milling

Rys. 6. Obrazy TEM w jasnym polu przy dwóch powiększeniach, odpowiadający obraz dyfrakcji elektronowej (SADP) oraz obraz w ciemnym polu DF kompozycji proszkowej Cu+3%CNT po 4 godzinach mielenia

Figure 7 presents a set of TEM micrographs of the microstructures of the powder mixture containing 3 vol.% CNTs after 8 hours of milling. Furthermore, the band structure can be seen inside the particle, but not as pronounced as in the powder milled for 4 hours. The bands are very thin and there is often a lack of them in selected areas of the particle. The size of the copper crystallites estimated from the DF micrograph ranges from 50 to 100 nm, and they are characterized by much less directionality than in the case of after 4 hours of milling.

The electron diffraction also indicates a higher refinement of the Cu crystallites, the rings are almost continuous around the entire circumference (no single reflections), however, the phase composition is identical to that of the powder after 4 hours of milling. Figure 8 shows a set of TEM micrographs of the powder mixture containing of 3 vol.% CNTs after 32 hours of milling. The band structure of the powder particles has completely disappeared and they have been highly refined. The size of the copper crystallites determined on the basis of the DF micrograph is about 50 nm and they have a regular shape. The electron diffraction rings are almost continuous around the circumference and there is no (or barely visible) pronounced ring of planes (002) graphite which may indicate a high level of structural defects or amorphisation of the carbon nanotubes. The strong ring from Cu_2O is still visible, which can testify to an increase in the proportion of this oxide in the powder composition.

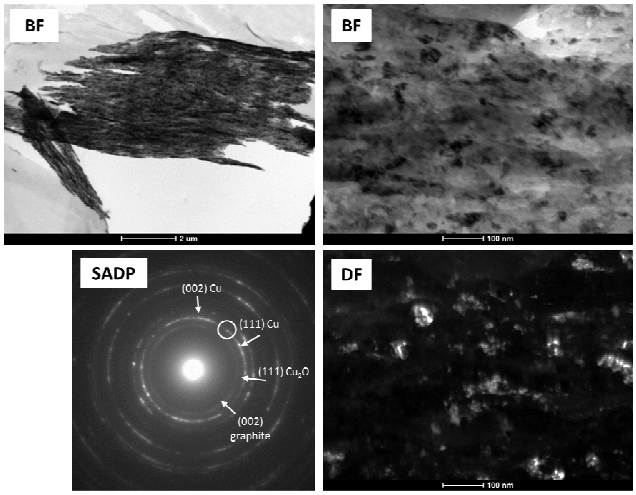

Fig. 7. Set of TEM micrographs of microstructures of Cu+3%CNT powder mixture after 8 hours of milling

Rys.7. Zestaw mikrostruktur TEM kompozycji proszkowej Cu+3%CNT po 8 godzinach mielenia

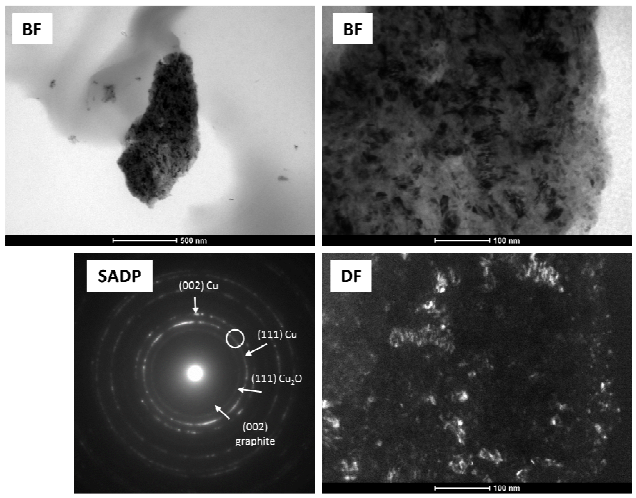

Fig. 8. Set of TEM micrographs of microstructures of Cu+3%CNT powder mixture after 32 hours of milling

Rys. 8 Zestaw mikrostruktur TEM kompozycji proszkowej po 32 godzinach mielenia

Summarizing the TEM results, we can stated that with an increase in the milling time, the Cu crystal sizes gradually decrease, however, it should be noted that after 8 hours the crystallites are below 100 nm, and extending the grinding time to 32 hours does not drastically reduce their size. Moreover, longer milling times cause a stronger defect of the carbon nanotubes and a greater oxidation state of the milled copper powders. Therefore, when selecting the final milling time after which the powders will be compacted, all the above factors (particle size, crystallite size, CNT degradation rate, oxidation state of the powder mixture) should be taken into consideration in order to provide adequate properties of the bulk composites.

SUMMARY AND CONCLUSIONS

In the present work, SEM observations together with sieve analysis were applied in order to investigate the evolution during milling of the Cu powder mixture containing different additions of CNT. The performed experiments allowed the authors to show the role of CNTs in the particle refinement of the copper powder during extended high energy milling with ceramic balls.

The performed experiments indicated that even a 1 to 3 vol.% addition of CNTs to the copper powder strongly affected particular stages of the ball milling process. Measurements of the average particle size of the copper powder carried out by means of the SEM observations and sieve analysis indicate that it goes through strong rise, decrease, and rise stages to a final decrease. This corresponds to the cold welding, fracturing, re-welding and re-fracturing of blended powder particles, as described by Shukla et al. [15]. In the case of the copper powder with the addition of carbon nanotubes the size variations were much smaller and were limited to a moderate rise, followed by a slow decrease in the particle size. It could be related to welding stages and subsequent fracturing of them. The above indicates that the added CNTs are very rapidly distributed in the copper matrix acting as fine defects reducing its plasticity. The larger addition of CNTs initially acts in a similar way as the smaller one, but finally it helps to cause a higher refinement of milled powder particles.

Therefore, the performed SEM observations and sieve analysis allowed us to conclude that:

a) the addition of CNTs to copper powder changes the four stage cold welding/fracturing/re-welding /re-fracturing process to a two stage cold welding and fracturing one,
b) milling of the mixture of copper and increased CNT addition from 1 to 3 vol.% goes along the same path of the two-stage mode, but eventually helps to obtain a more refined product. Highly refined powder with larger CNT additions and the presence of remnants of carbon material in the milled composite particles should block any extensive grain coarsening during their hot pressing, offering a possibility to form a bulk composite characterized by a much higher mechanical strength as compared to copper processed in the same way. The TEM observations of the microstructure showed that in order to select the proper milling time prior densification of the powders, several factors like particle size, crystallite size, CNT degradation rate, and oxidation state of the powder mixture should be taken into consideration in order to provide adequate properties of the bulk composites. We found that the powder milled 8 hours best meets the above criteria.

REFERENCES

[1] Davis J., Copper and copper alloys, ASM International 2001.
[2] Amruthalari S., Synthesis of copper carbon nanotube composite and its electrical conductivity measurment, FIU Electronic Theses and Dissertations 2008.
[3] Paradise M., Goswani T., Carbon nanotubes - Production and industrial applications, Materials and Design 2007, 28, 1477-1489.
[4] Chen T., Dai L., Carbon nanomaterials for high-performance supercapacitors, Materials Today 2013, 16, 272-280.
[5] Thostenson E., Ren Z., Chou T.-W., Advances in the science and technology of carbon nanotubes and their composites - review, Composites Science and Technology 2001, 61, 1899-1912.
[6] Tjong S., Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets, Materials Science and Engineering R 2013, 74(10), 281-350.
[7] Shokrier M., Rafiee R., A review of the mechanical properties of isolated carbon nanotubes and carbon nanotube composite, Mechanics of Composite Materials 2010, 46, 155-172.
[8] Koppad P., Ram A., Ramesh C., Kashyap K., Koppad R., On thermal and electrical properties of multiwalled carbon nanotubes/copper matrix, Journal of Alloys and Compounds 2013, 580, 527-532.
[9] Uddin S., Mahmud T., Wolf C., Glanz C., Kolaric I., Volkmer C., Höller H., Wienecke U., Roth S., Fecht H.-J., Effect of size and shape of metal particles to improve hardness and electrical properties of carbon nanotube reinforced copper and copper alloy composites, Composites Science and Technology 2010, 70, 2253-2257.
[10] Wang H., Zhang Z., Zhang H., Hu Z., Li S., Cheng X., Novel synthesis and characterization of copper matrix composites reinforced with carbon nanotubes, Materials Science & Engineering A 2017, 696, 80-89.
[11] Ahn J., Shin H.-S., Kim Y.-J., Chung H., Structural modification of carbon nanotubes by ball milling, Journal of Alloys and Compounds 2007, 434 428-432.
[12] Stolarska J., Dutkiewicz J., Maziarz W., Pstruś J., Wójcik A., Ozga P., Copper composites strengthened with carbon nanotubes or graphene platelets prepared by ball milling and vacuum hot pressing, Composites Theory and Practice 2015, 3, 174-180.
[13] Suryanarayana C., Mechanical alloying and milling, Progress in Materials Science 2001, 46, 1-184.
[14] Benjamin S., Volin T., The mechanism of mechanical alloying, Metallurgical Transactions 1974, 5, 1929-1934.
[15] Shukla A., Nayan N., Murty S., Sharma S., Chandran P., Bakshi S., George K., Processing of copper-carbon nano-

tube composites by vacuum hot pressing technique, Materials Science & Engineering A 2013, 560, 365-371.

[16] Bor A., Ichinkhorloo B., Uyanga B., Lee J., Choi H., Cu/CNT nanocomposite fabrication with different raw material properties using a planetary ball milling process, Powder Technology 2018, 323, 563-573.

[17] Bor A., Jagralsaikhan B., Lee J., Choi H., Surface coating copper powder with carbon nanotubes using traditional and stirred ball mills under various experimental conditions, Particuology 2018, 40, 177-182.

