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Testing of Sinters Made of Copper Powders Coated with Carbon Structure Containing Graphene

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Abstract. This paper presents the results of preliminary tests on specimens made from mixtures of dendritic copper powder (CuE) with the graphene-coated copper powder (CuG) in a range from 20% to 100% (CuG). The properties of the powder mixtures, green compacts and sinters were determined. To study the properties of the powder mixtures, the following tests were carried out: a measurement of the CuG powder grain size after the grinding process, measurements of the bulk density and tap density of the prepared powder mixtures. The porosity of the produced green compacts and the sinters was calculated as well as the densification capabilities of the powder mixtures by die pressing, cold isostatic pressing and sintering in a reducing atmosphere were tested. Moreover, the nature of the porosity formation was analysed using an optical microscope and the Brinell hardness was determined.

The measured Brinell hardness was in the range of 17 HB for sinters made from CuG to 34 HB for sinters made from a 20% CuG powder mixture. More than six hundred measurements that were made in this study show that the high CuG content in the powder mixture reduces the hardness of the sinters as well as increase their porosity.
Keywords: mechanical engineering, material engineering, powder metallurgy, sintered copper, graphene

1. INTRODUCTION

Graphene has become the subject of intense research since the late 20th century (especially after the 2010 Nobel Prize was awarded to the discoverers of graphene) in many research centres around the world [1]. It is a structure that can exist as a single layer of atoms. Graphene has good physical properties, including strength, electrical and thermal conductivity and very good mechanical properties. It is Young's modulus can reach 1 TPa and its tensile strength can reach 130 GPa [2]. It also has stable chemical properties. Research is in progress on the applications of graphene in medical devices, composites, conductive materials and supercapacitors.

Many publications report on the study of metal-graphene composites produced using powder metallurgy methods, including graphene-copper materials [1, 3, 4]. Such composites are usually made from a mixture of copper powder with the addition of graphene powder. Studies have shown the addition of graphene increases the strength properties of the composites [5, 6].

An innovative method for the production of graphene-copper powder, which is the starting material for sinters, was developed at the Łukasiewicz Research Network Institute of Precision Mechanics (formerly the Institute of Precision Mechanics) in Warsaw (Poland). It involves the deposition of graphene coatings on copper powder particles. The method of producing the material is based on the formation of a graphene layer on copper powder particles by vibro fluid thermo-chemical treatment in an active atmosphere containing an inert shielding gas, an impurity-reducing gas and a carbon precursor gas. The manufacturing technology of the material is protected by patent rights under Polish Patent PL.225890, "A method of production of carbon structures by chemical and heat treatment and with graphene-coated copper powder", dated 1 December 2016.

Attempts to use this material for the production of sintered shaped-charge liners were carried out at the Faculty of Mechatronics, Armament and Aerospace of the Military University of Technology in Warsaw (Poland) and described in [7, 8].

This article presents the results of optimisation of copper-graphene powder grinding processes and investigations of the effect of graphene on selected physical and mechanical properties of green compacts and sinters.

2. TEST METHODOLOGY

The test samples were made from powder mixtures composed of a dendritic electrolytic copper powder (CuE) and an electrolytic graphene-coated copper powder (CuG), that was produced at the Institute of Precision Mechanics. The mixtures were made with the following ratios: 100% CuG, 20% CuE and 80% CuG, and 80% CuE and 20% CuG.

The specimen preparation consisted of three steps: preparation of powder mixtures, making of green compacts, and sintering.

During the preparation of powder mixtures, it was important that before pressing green compacts, both components of the mixture should have similar grain sizes and shape similar to that of the starting powder. For this purpose, the CuG powder was ground in a mortar using different batches and mixing times: 15 g / 15 min, 15 g / 30 min, 15 g / 60 min, 30 g / 90 min, 50 g / 90 min, and 75 g / 90 min. One set of grinding parameters was selected to produce all types of powder mixtures. This selection was made based on the particle size of the CuG powder after the grinding process measured using a KAMIKA infrared light-emitting particle size analyser, model IPS-U, particle shape of powders analysed by Thermo Fisher Scientific electron microscope, model Phenom ProX, and the efficiency of the powder grinding process. During the particle shape study, photographs were taken of all powders at 500x magnification. In the particle size tests, 100,000 grains were included in each particle size measurement. Three measurements were made for the samples ground with each of the methods used.

The powder mixtures were then prepared and examined with Hall bulk density tests and tap density tests. In each test, the samples were measured three times and the density result was averaged.

The green compacts were made using two methods: die pressing and cold isostatic pressing (CIP). Both pressing processes were carried out at a constant pressure of 200 MPa and for a target pressure holding time of one minute. The obtained green compacts had a diameter of 9±0.2 mm and were subjected to hydrostatic density tests, from which their porosity was calculated.

The sintering of the produced green compacts was carried out in a single batch in a reducing atmosphere of dissociated ammonia with one-hour stops at the temperature of 350°C, 650°C and 920°C (to reduce the oxide layer on the surface of powder particles). The sintering process is shown in Fig. 1. The produced sinters, like the green compacts, were subjected to hydrostatic density testing, from which their porosity was calculated.

The next test was a Brinell hardness measurement. The tests were carried out on selected cross-sections of sinters, each time at three locations within one cross-section. A 2.5 mm diameter ball indenter and a 62.5 kg load were used for the Brinell test.

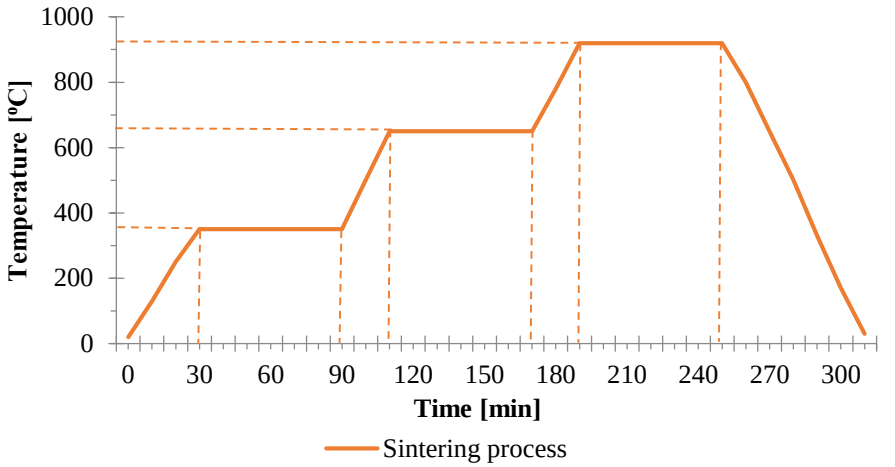

Fig. 1. The course of the sintering process in a reducing atmosphere

The test locations were determined as follows: at the centre of the cross-section (test point designated as 1), at a distance of four indentation diameters from the centre of the specimen (designated as 2) and at a distance of two and a half indentation diameters from the edge of the specimen (designated as 3), as shown in Fig. 2. Each of the die-pressed samples was divided into five parts, making in total fifteen parts for each mixture, while the CIP-ed samples were divided into twelve parts for each mixture.

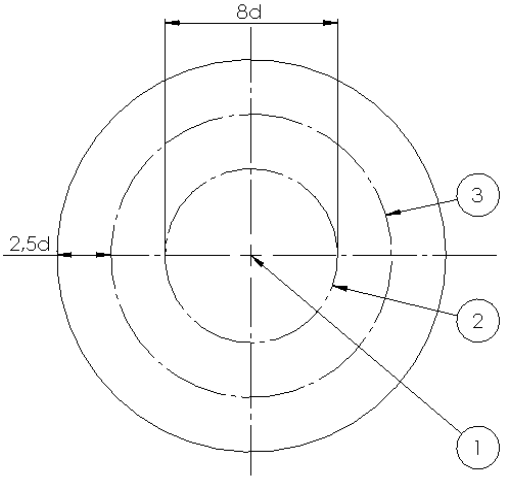

Fig. 2. Distribution diagram of places on the cross-sections of samples where hardness measurements were performed

The last examination was to analyse of the sintered microstructure using microscopic images taken with a ZEISS optical microscope, model ARIO Observer.Z1m.

3. TEST RESULTS

The results of the CuG powder particle size tests crushed in the mortar with different mixing parameters showed that 50% of the powders grains tested were in the range from 10.3 to 32.3 μm, while 75% of them were in the range from 23.5 to 54.3 μm. By examining the grain size, it was found that powders from the 15 g batch crushed for 60 min and the 30g batch crushed for 90 min resulted in receiving powders consisting of 75% particles smaller than 35 μm. The results are shown in Fig. 3.

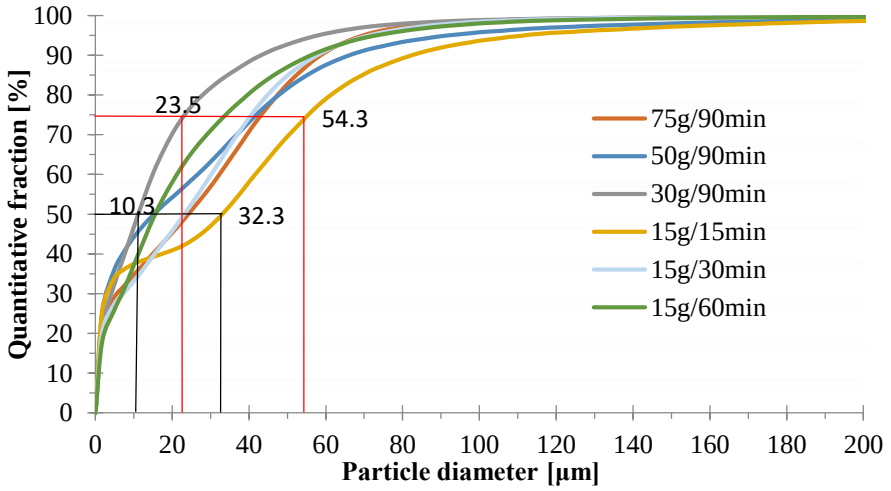

Fig. 3. Cumulated particle size distribution of CuG powders ground in a mortar, for various weights and mixing time

Another criterion for the selection of a suitable grinding method for the CuG powder was the shape of the particles after processing. Images showing the shape of the CuG powders ground with each method and the CuE starting powder image are presented in Fig. 4.

It can be seen that by increasing the grinding time of the powder in the mortar, as well as decreasing the batch weight, the fragmentation of the powder increased(Fig. 4 a-f). The use of a method other than grinding in a mortar affected both particle size and shape. Powders ground in a ball mill (Fig. 4g) were flake-shaped only, but their fragmentation was greater compared to other methods. The heat generated during grinding in a high-energy mill (Fig. 4h) causes the formation of large agglomerates.

The powders crushed in the mortar, which were characterised by the highest degree of fragmentation (Fig. 4c and 4d), contained no agglomerated particles.

In addition, the 30 g batch powder ground for 90 min (Fig. 4d) consisted mainly of globular particles and, as can be seen in images, particles were similar in size to those of the CuE starting powder (Fig. 4i).

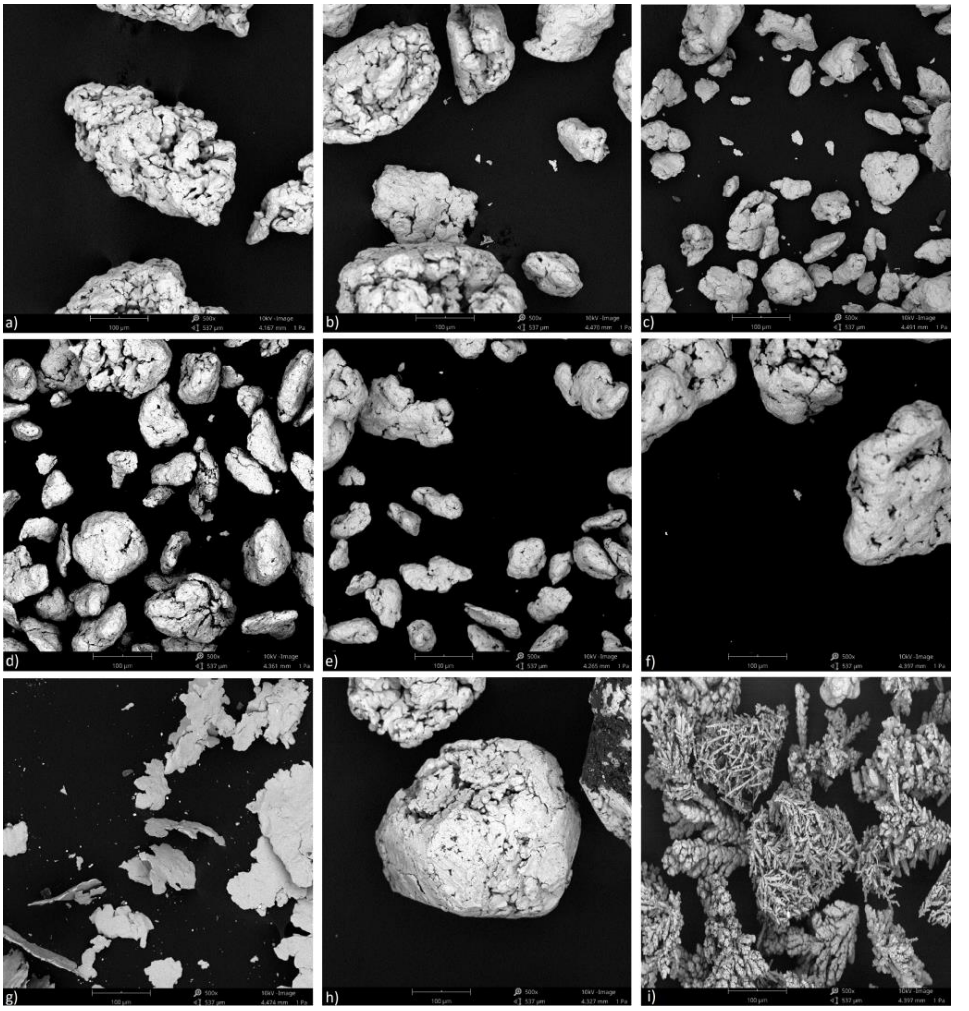

Fig. 4. SEM analysis of copper powders: (a) 15 g ground for 15 min in the mortar, (b) 30 g ground for 15 min in the mortar, (c) 15 g ground for 60 min in the mortar, (d) 30 g ground for 90 min in the mortar, (e) 50 g ground for 90 min in the mortar, (f) 75 g ground for 90 min in the mortar, (g) ground in the ball mill, (h) ground in the high-energy blade mill (i) initial powder CuE (magnification: 500x)

Also taking into account the grinding efficiency aspect of the CuG powder, the 30 g batch powder ground for 90 min in the mortar was chosen to make the powder mixtures, as the same amount of ground powder was obtained in 25% less time than the 15 g batch powder ground for 60 min.

The powder mixtures were subjected to a bulk density test and a tap density test, the results of which are presented in Table 1. The bulk density ranged from 1.95 to 3.86 g/cm^3, while the tap density ranged from 2.39 to 4.66 g/cm^3.

Table 1. Test results for bulk density and tap density

Graphene-coated copper content [%]	Mass [g]	Volume [cm^3]	Density [g/cm^3]
Bulk density test results			
100	97.5	25.28	3.86
80	86.5	25.28	3.42
20	49.3	25.28	1.95
Tap density test results			
100	50.1	10.75	4.66
80	50.08	12.25	4.09
20	50.13	21	2.39

The green compacts and sinters were subjected to a hydrostatic density test. On this basis, the porosity of the tested specimens was calculated. The test results are shown in Figs. 5 and 6.

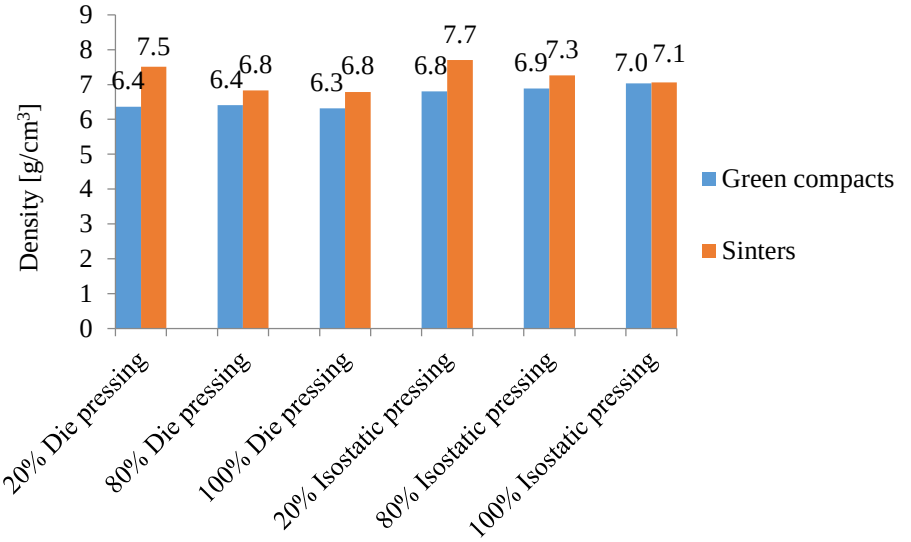

Fig. 5. The density of green compacts and sinters depending on the CuG content and pressing method

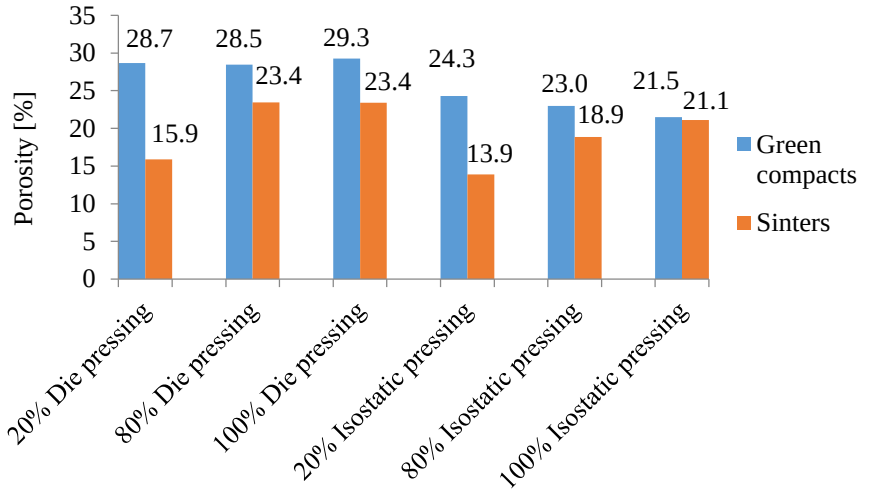

Fig. 6. The porosity of green compacts and sinters versus the CuG content and pressing method

Figure 7 shows the averaged results of the Brinell hardness test. The density of green compacts ranged from 6.3 to 7 g/cm^3, while the density of the sintered samples ranged from 6.8 to 7.7 g/cm^3. The porosity of the tested specimens ranged from 21.5 to 28.7% for the green compacts and 13.9 to 23.4% for the sinters.

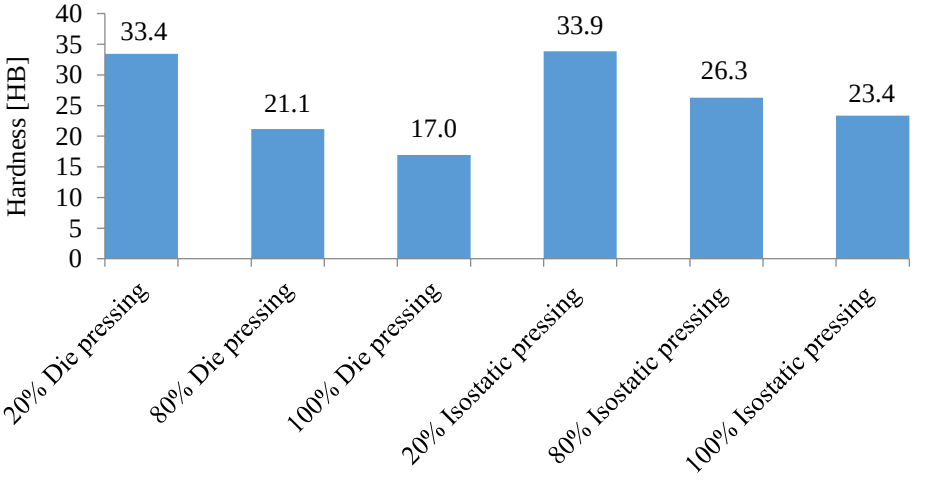

Fig. 7. The hardness of sinters versus the CuG content and pressing method

The average hardness of the die pressed specimens ranged from 17 HB for the sinters with the highest CuG content to 33.4 HB for the sinters with the lowest CuG content. The CIP-ed sinters had an average hardness ranging from 23.4 HB for the sinters with the highest CuG content to 33.9 HB for the sinters with the lowest CuG content.

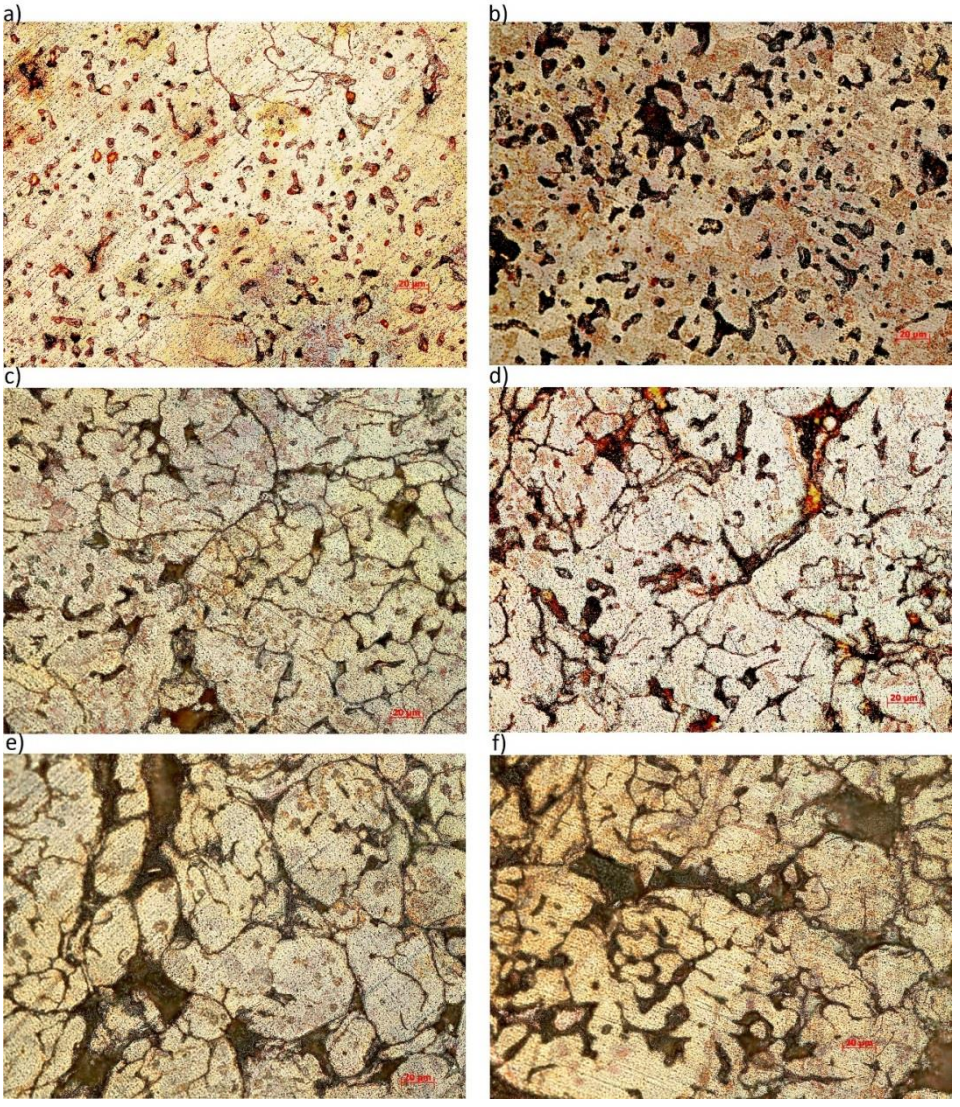

Fig. 8. Microstructure of the sinters with a graphene copper content of: 20% (a and b), 80% (c and d), 100% (e and f), cold isostatic pressed (a, c and e) and die pressed (b, d and f) (magnification: 500x)

In addition, a micro-analysis of the sinter surface was performed based on the cross-sectional images of the specimens. As the CuG content in the powder mixture increased, the ratio of pores visible on the surface of the examined cross-sections increased (Fig. 8).

It can also be noticed that in the case of samples made of 100% CuG powder mixture, the microstructure exhibits the presence of powder particles which the shape and size changed only to a low extent during the pressing and sintering processes, and thus the migration of the boundaries of individual particles occurred only into a small extent. This may indicate that the diffusion processes occurring during sintering were partially inhibited, which probably resulted in a deterioration of the mechanical properties of the materials thus produced.

4. ANALYSIS OF RESULTS

The tests showed that both the appropriate choice of the CuG powder mass and the grounding time can significantly influence the size and shape of the particles obtained. By optimising the parameters of this process, it was possible to produce a CuG powder that was the most appropriate during pressing and sintering. Results of bulk and tap densities tests of the powder mixtures showed that their density increased with the CuG powder content. This may have been since globular CuG particles have a greater ability to fit together than dendritic CuE particles, which facilitated the densification of the mixtures with higher CuG content.

During the pressing process, the CuG powder content in the mixture had no significant effect on the density of the resulting green compacts. For die pressing, the density between samples differed by a maximum of 1.5%, while for CIP, it was by a maximum of 3%. In the case of CIP, the density minimally increased with the CuG content.

Significant changes in the density of the samples could be observed after the sintering process. The maximum difference in density between die-pressed samples and CIP-ed samples was 9% and 7%, respectively. In addition, it is noticeable that as the CuG powder content in the mixture increased, the density of the sinters obtained from it decreased.

The Brinell tests of the sinters showed that the hardness of the samples tested decreased with the increase of the CuG powder content. This was due to the higher porosity of the samples which had more CuG.

In addition, it can be seen that the CIP-ed specimens were characterised by the highest hardness at the edge of the specimens (Fig. 9-11b), while the die-pressed specimens did not show any defined change in hardness in their cross-sections (Fig. 9-11a).

The spread between the smallest and largest measured values within one test location for die pressing was 12.2 HB. This measurement was made for a sample with 100% CuG, at test location 3 (Fig. 9a).

For the CIP-ed samples, the difference between the smallest and largest measured values within one of the diameters was 6.8 HB. This measurement was taken for a specimen made from a mixture of 80% CuG and 20% CuE, at test location 3 (Fig. 9a). Careful analysis of the individual hardness test results shows that the spread between the maximum and minimum tested hardness values within one test location for the die-pressed samples ranged from 12.2HB to 6.3HB. Hardness decreased with the distance from the centre of the specimen and with the content of CuG powder in the mixture. For the CIP-ed specimens, the spread ranged from 6.8HB to 3.6HB, but in this case, no distinct character of change could be observed.

It is also important to note that for the CIP-ed specimens, 75% of the Brinell hardness is in the range around 3HB as can be seen in Figs. 9 and 11 (b) or, as in the case of the specimen with 80% CuG content, 50% of the tests around the median were in the range around 1.5HB (Fig 10b).

Die-pressed samples in each case showed a large spread between the 50% of the tests near the centre value and the remaining 50%. These results suggest that not only does the hardness of the specimen decrease while increasing the CuG content in the sinters but also that the porosity of the die-pressed specimens was higher and affected the accuracy during attempts at the determination of the final hardness value of the tested material.

The analysis of the microstructure of the sinters allowed us to conclude that the size of pores on the surface of the cross-sections examined increased with the CuG content. As already mentioned, the specimens with 100% CuG powder underwent only minor consolidation during sintering, which might have been since graphene coatings hinder the diffusion processes during sinter formation.

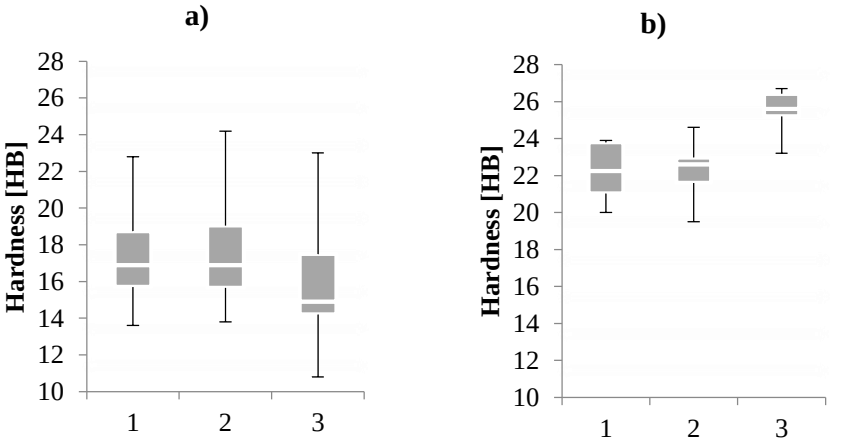

Fig.9. The hardness of the sinters with 100% CuG content measured at test locations 1, 2 and 3 of the specimens: (a) after die pressing, (b) after CIP

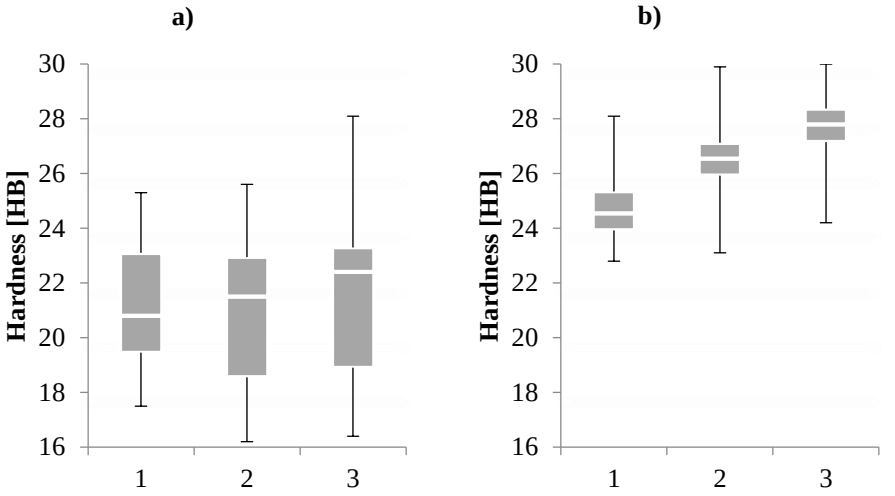

Fig.10. The hardness of the sinters with 80% CuG content measured at test locations 1, 2 and 3 of the specimens: (a) after die pressing, (b) after CIP

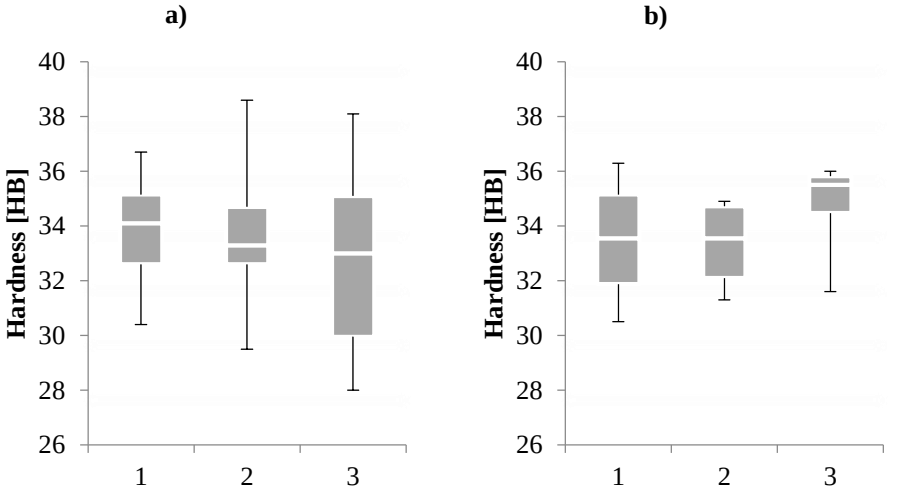

Fig.10. The hardness of the sinters with 20% CuG content measured at test locations 1, 2 and 3 of the specimens: (a) after die pressing, (b) after CIP

This could have been the cause of the deterioration of the mechanical properties of the sinters, as confirmed by the hardness test results, which showed that their value decreased with the increase of the graphene powder content in the mixture.

5. CONCLUSIONS

The study helped determine that the most efficient way of grinding CuG powder, assuming that the shape of its particles is to be maintained, is to grind a 30 g batch in a mortar for 90 min.

This results in a powder similar in particle size to the CuE powder and eliminates most of the particle agglomerates present in the CuG input powder.

Investigations of the density of the green compact and the sinters showed that with increasing CuG powder content in the mixture, the porosity of the samples increased and in most cases exceeded 20%.

The Brinell hardness tests also showed that as the content of CuG powder in the mixture increased, the hardness of the sinters obtained decreased. It is worth noting that after CIP, the hardness spread was about 50% of that achieved after die pressing. The hardness of the sinters after CIP at the edge of the specimens was the highest, but the hardness spread irrespective of the test location showed no clear fluctuations. This may indicate a more uniform distribution of the properties of the materials throughout their volume.

The examination of the microstructure of the specimens confirmed the results of previous studies, additionally revealing the nature of the pores present on the sinter cross-sections.

It can be seen that as the CuG powder content increased, particle diffusion was impeded, which might have been due to the presence of the graphene coating on adjacent particles.

The experiments showed that the use of powder mixtures with a high CuG content was unfavourable. Further studies are planned to use mixtures with 1% to 20% CuG and to carry out strength tests, also under high strain rate conditions.

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Badania spieków wykonanych z zastosowaniem proszków miedzi pokrytej strukturą węglową zawierającą grafen

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Streszczenie. W artykule zostały przedstawione wyniki wstępnych badań próbek wykonanych z mieszanin proszku miedzi dendrytycznej (CuE) z proszkiem miedzi pokrytym strukturą węglową zawierającą grafen (CuG) w przedziale od 20% do 100% (CuG). W ramach badań określone zostały właściwości mieszaniny proszków, wyprasek oraz spieków, składające się na opis badanego materiału. W celu zbadania właściwości mieszanin proszków zostały wykonane następujące badania: pomiar wielkości ziaren proszku CuG po procesie rozdrabniania, pomiar gęstości nasypowej oraz nasypowej z usadem przygotowanych mieszanin. Obliczono porowatość wytworzonych wyprasek, a następnie spieków oraz sprawdzono możliwości zagęszczania się otrzymanych mieszanin poprzez zastosowanie prasowania matrycowego, prasowania izostatycznego na zimno oraz spiekania w atmosferze redukującej. Dokonano również analizy powierzchni wykonanych próbek pod kątem charakteru powstałych porów za pomocą mikroskopu optycznego oraz określono twardość próbek metodą Brinella. Zmierzona twardość próbek mieści się w zakresie od 17HB dla spieków wykonanych wyłącznie z CuG do 34HB dla spieków wykonanych z mieszanki zawierającej 20% CuG. W ramach badań wykonanych zostało ponad sześćset pomiarów, których wyniki pokazują, że duża zawartość CuG w mieszaninie proszkowej zmniejsza twardość otrzymanych z niej spieków oraz zwiększa ich porowatość.
Słowa kluczowe: inżynieria mechaniczna, inżynieria materiałowa, metalurgia proszków, miedź spiekana, grafen