OPTIMIZATION OF COPPER-GRAPHITE COMPOSITE MATERIALS THROUGH SPARK PLASMA SINTERING: IMPACT OF VARIED POWDER SIZES ON PHYSICAL, MECHANICAL, AND ELECTRICAL PROPERTIES

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Abstract. *In this study, copper-graphite composite materials were meticulously prepared using spark plasma sintering (SPS), manipulating the size of graphite and copper powders to achieve an optimal ratio. The physical, mechanical, and electrical characteristics were found to be directly influenced by the initial powder sizes. Specifically, by selecting an optimal copper-graphite ratio (Cu-G) and employing different SPS sintering temperatures, samples were fabricated using graphite and electrolytic grade copper powder as source materials. Notably, when the particle size of the copper and graphite exceeded several microns, the resulting samples exhibited deteriorated mechanical and electrical properties, leading to a decline in overall quality. The fabricated composite samples underwent comprehensive examination using micro-hardness testing, Hall system analysis, density testing, optical microscopy, and FE-SEM to explore thermal, compositional, and structural parameters.*

Keywords: *copper-graphite composites, spark plasma sintering, planetary ball milling.*

INTRODUCTION

Composite materials based on copper-graphite are highly appealing for applications in high-speed electric railways due to their exceptional blend of mechanical and electrical properties, particularly notable thermal and electrical conductivities, and internal solid lubricating characteristics. In addition, these composites find widespread usage as brushes for motor technology, contact strips for pantographs, and collector shoes in electric railways [1-5].

The production of these composites typically employs a powder metallurgy technology. This approach is favored for its ability to yield uniform brushes and reduce the laborious and costly machining processes associated with other methods [6,7]. Despite its advantages, powder metallurgy encounters certain limitations, primarily attributed to the weak affinity between copper and graphite. This inherent drawback results in suboptimal interfaces, negatively impacting the structural, mechanical, and electrical properties of the material.

The ongoing popularity of copper-graphite composites in various railway components underscores their importance in modern transportation systems. Overcoming the challenges posed by the weak copper-graphite interface is crucial for further enhancing the efficacy and versatility of these composites in high-speed electric railways and other related applications. In the subsequent sections, we delve into strategies employed to address these limitations and advance the synthesis of copper-graphite composites, with a specific focus on spark plasma sintering (SPS) technology [8,9].

METHODOLOGY

Materials. Two sets of experiments were conducted with the aim of producing copper-graphite composite materials possessing enhanced thermal and electrical conductivity, as well as robust mechanical properties. The rationale behind these experiments lies in the significance of these properties for applications in high-speed electric railways and related components, such as brushes for motor technology, contact strips for pantographs, and collector shoes.

In the first set of experiments, the initial materials included spherical copper powder (CUSP50) characterized by an average particle size of 4.8-5μm and a density of 8.9000 g/cm³. Additionally, carbon and graphite powder (KB-3) with an average size of 30-40 nm and 99.9% purity were utilized. This choice of materials was made to explore the impact of specific particle characteristics on the resulting composite properties, with a focus on achieving fine-scale uniformity and enhancing overall conductivity.

For the second set of experiments, a different approach was taken. The initial materials consisted of graphite powder (SAMCHON Pure Chemical Co. Ltd) with an average size of 23 μm and 99.9% purity, along with copper powder (CUSP50) characterized by an average particle size of 4.8-5μm. This variation in particle sizes and sources aimed to investigate how different carbon materials, along with variations in copper powder characteristics, would influence the final composite properties.

Powder grinding. The ball milling process is a well-established and efficient method for grinding and mixing various materials into fine powder. This technique offers two main approaches: the dry process and the wet process, each exhibiting distinct advantages based on the desired outcomes. Additionally, ball milling can be categorized into tabular and flowing types, depending on the form of discharging material.

In the fabrication of a sub-stoichiometric copper-carbon composite powder, the ball milling process proves to be a highly effective tool for achieving fine dispersion. Specifically, the dry process of ball milling was employed using 5-6 mm size aluminum balls, conducted over a period of 24 hours at room temperature. In the initial stages of the milling process, the powders and balls are thoroughly mixed, subsequently impacting the inside surface of the metallic bowl. The separation of aluminum balls from the mixed powder is achieved through sifting in a thin metallic net, facilitating the creation of a finely dispersed composite powder with desirable properties.

Spark plasma sintering. The consolidation of all the obtained powders was executed utilizing the Spark Plasma Sintering (SPS) technique, specifically employing the Dr. Sinter 1030 apparatus from Sumitomo Coal Mining Co. Ltd., Japan. In both the first and second sets of experiments, different weight ratios of copper and graphite powders were utilized, with the specific amounts detailed below.

For the consolidation process, the mixture of copper and graphite powders was placed inside a 20 mm diameter mold, and a carbon paper was employed to separate the powders from the upper and lower punches. The total powder amount in each consolidation was within the range of 8-10 grams. The Spark Plasma Sintering process involved a heating rate of 200°C/min and a pressure of 40 MPa. Notably, the samples were categorized into groups based on powder composition at 850°C, for a duration of 5 minutes under a flowing Ar-4%H_2 gas atmosphere. The resulting copper-graphite composite samples exhibited dimensions of approximately 20 mm in diameter and 4 mm in thickness.

Table 1. Summary of the sample composition (carbon and graphite powder (KB-3) with average size 30-40 nm and 600 mesh graphite powder with average size 23 μm) and used experimental sintering condition (T- temperature; P-pressure; t_{hold} - holding time).

Sample name	**Composition (wt%) KB-3 carbon & graphite**	**SPS**			**Sample name**	**Composition (wt%) 600 mesh graphite**	**SPS**		
		T(°C)	P(MPa)	t_{hold}(min)			T(°C)	P(MPa)	t_{hold}(min)
Cu-Gr0.5	99.5%Cu+0.5%C&Gr	850	40	5	Cu-Gr0.5	99.5%Cu+0.5%Gr	850	40	5
Cu-Gr1	99%Cu+1%C&Gr	850	40	5	Cu-Gr1	99%Cu+1%Gr	850	40	5
Cu-Gr2	98%Cu+2%C&Gr	850	40	5	Cu-Gr2	98%Cu+2%Gr	850	40	5
Cu-Gr4	96%Cu+4%C&Gr	850	40	5	Cu-Gr4	96%Cu+4%Gr	850	40	5

RESULTS

Copper-graphite composites were prepared using graphite and copper as reinforcement by spark plasma sintering at different temperature. Two types of graphite, with different composition, morphology and grain size were used: carbon and graphite powder (KB-3) with average size 30-40 nm and 600 mesh graphite powder with average size 23 μm. The differences in morphological structure and distribution of graphite particles at different composition as shown by the optical images in Figure 1 (a – d'). Images of the obtained structures show distribution of graphite on copper composite, where darker areas represent higher graphite content and yellow areas represent higher content of copper.

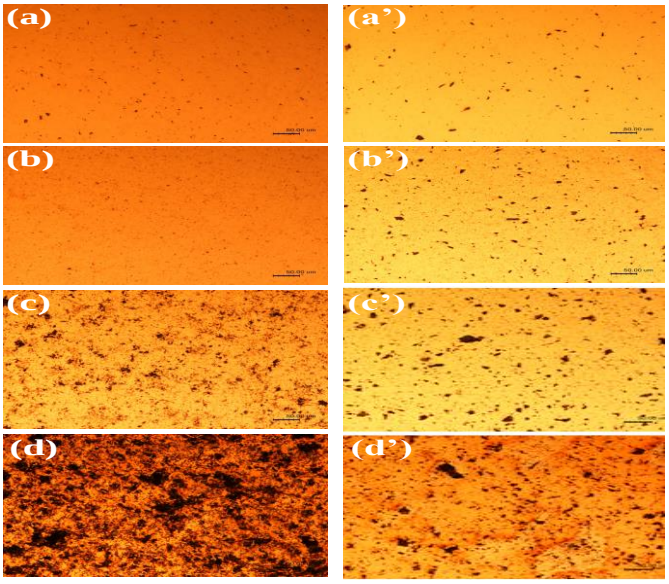

Figure 1. Representative optical images of sintered samples : for copper and KB-3 carbon & graphite composite at T=850 °C: (a) 99.5%Cu+0.5%C&Gr; (b) 99%Cu+1%C&Gr; (c) 98%Cu+2%C&Gr; (d) 96%Cu+4%C&Gr; for copper and 600 mesh graphite composite at T=850 °C: (a') 99.5%Cu+0.5%Gr; (b') 99%Cu+1%Gr; (c') 98%Cu+2%Gr; (d') 96%Cu+4%Gr.

As the appearance of the as-received copper-graphite composite under the optical microscope images are similar (Figure 1 (a-b) and (a'-b')) for each copper-graphite composition at sintering temperature 850 ^{o}C. However, these similarities have not strong correlation for distribution graphite powder with different particles sizes. In particular, none uniform distribution of 600 mesh carbon-graphite powder with average size 23 μm (Figure 1 (c)) were observed in comparison with carbon and graphite powder (KB-3) which have average size 30-40 nm (fig 1. c) each sample have the same content 98%:2%. In all cases, the graphite dispersion observed was homogeneous, with exception of small agglomerates for both 0,5% and 1% of graphite content (fig 1 a,b and a',b'). The mainly difference was observed when graphite content was increased up to 4%. The samples, for instance, with 4% content of carbon graphite powder (KB-3) with average size 30-40 nm were observed accumulation of the large size (~120 μm) the graphite agglomerations (Figure 1 (d)), while for graphite powder with average size 23 μm the agglomerates were observed less frequently (Figure 1 (d')) and their size also smaller (50 μm). In fact, amount and size of agglomerations in the composition is directly related to graphite content and its powder size. A possible explanation for the graphite agglomerated structure might be the fact that the fine particles size of graphite lead to irregular dissolution of graphite in the Cu matrix and probably would have detrimental effect on the mechanic properties. Consequently, their electrical properties also diminish strongly with type of graphite composite.

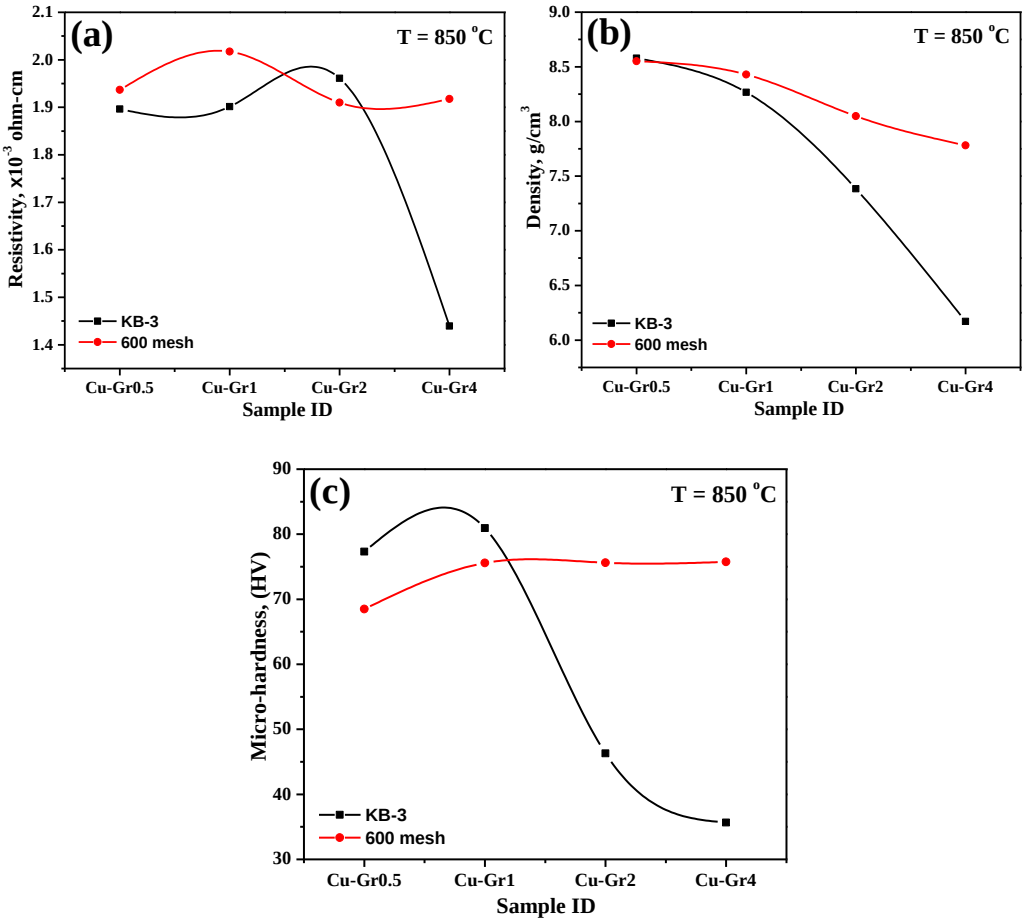

Figure 2. Electrical and mechanical properties of Cu-Gr composites prepared at 850 ^{o}C by spark plasma sintering: (a) resistivity, (b) volume density, and (c) micro-hardness.

One of the important characteristics of contact composite material is electrical resistivity. The electrical resistivity's of sintered copper-graphite composition at different content of graphite

powder were calculated from resistance measurement of the Hall mobility and shown in Figure 2 (a). The copper-graphite samples with carbon and graphite powder (KB-3) which have average size 30-40 nm (Figure 2 (a)) have resistance curve for different composition is similar for different contain of graphite. However, it was observed when used graphite powder with relatively big size 23 μm the resistance curve start decrease at 2% and 4% containing of graphite powder. The decreasing of the electrical resistivity of composite samples with big and small powder size of both phases is shown in Figure 2 (a). This is caused that resistivity of both metallic powder and carbon powders in matrix composite strongly dependent also from the shape of the carbon powders (long or short fibres, spherical particles, etc.) and their orientation with respect to the current flow. The average densities of the as-received copper graphite composite with content of carbon graphite powder (KB-3) with average size 30-40 nm determined by the water immersion technique were Table 2: 8,58 g/cm^3, 8,27 g/cm^3, 7.38 g/cm^3 and 6,17 g/cm^3, for the 0,5%, 1%, 2% and 4% respectively. The measured average densities for the 0,5%, 1%, 2% and 4% content of 600 mesh graphite powder with size 23 μm are equal 8,55 g/cm^3, 8,43 g/cm^3, 8,04 g/cm^3 and 7,78 g/cm^3, respectively. The graphite content in samples is strongly affected to average densities. As expected, the density decreases linearly with increasing of carbon graphite content for both types of graphite materials (see Figure 2 (b)).

Table 2. Hardness, volume density of the copper graphite samples with different composition of graphite. Samples sintered by spark plasma sintering at 850 ^{o}C during 5 minutes under flowing Ar-4%H_2 gas atmosphere at pressure 40 MPa respectively.

Sample name	**Composition (wt%) KB-3 carbon & graphite**	**Mechanical Properties**			**Sample name**	**Composition (wt%) 600 mesh graphite**	**Mechanical Properties**		
		Volume density, (g/cm^3)	Resistivity, (ohm-cm)x10^{-3}	Hardness, (HV)			Volume density, (g/cm^3)	Resistivity, (ohm-cm)x10^{-3}	Hardness, (HV)
Cu-Gr0.5	99.5%Cu+0.5%C&Gr	8.58	1.896	77.32	Cu-Gr0.5	99.5%Cu+0.5%Gr	8.55	1.936	68.5
Cu-Gr1	99%Cu+1%C&Gr	8.27	1.901	80.94	Cu-Gr1	99%Cu+1%Gr	8.43	2.017	75.58
Cu-Gr2	98%Cu+2%C&Gr	7.38	1.961	46.3	Cu-Gr2	98%Cu+2%Gr	8.04	1.909	75.62
Cu-Gr4	96%Cu+4%C&Gr	6.17	1.439	35.66	Cu-Gr4	96%Cu+4%Gr	7.78	1.917	75,76

Hardness testing is most frequently used method for characterization mechanical properties of composite. An indenter of well-defined round shape geometry is pressed into surface of sample under predefined load. Therefore, the micro-hardness indentations are micron size scale and have been extensively applied at the microstructure when Vickers diamond pyramid indenter are usually applied. The hardness values for all copper-graphite specimens are given in Table 2. The results show that maximum hardness value was obtained for the 1% of contamination of carbon-graphite 23 μm powder. The results also show that increase of content for carbon graphite powder (KB-3)

with average size 30-40 nm lead to slightly increasing of the hardness where the hardness for the graphite powder content with size 23 μm the hardness greatly decreased Figure 2 (c).

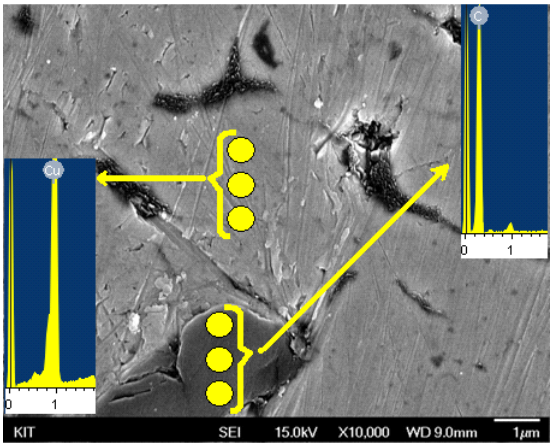

Figure 3. FE-SEM image of copper-graphite composite surface and insets EDS images taken for each elements.

FESEM images of the obtained structures show distribution of graphite on copper composite, where darker areas represent higher graphite content and yellow areas represent higher content of copper. Especially for graphite KB-3 Carbon & Graphite powder with size 30-40 nm the dispersion in copper composite was homogeneous with uniformly distribution of graphite Figure 3.

CONCLUSIONS

- The density of copper-graphite composites decreased linearly with increasing of carbon graphite content for both types of graphite materials. At the same time, the volume density and micro-hardness of copper-graphite composites decrease gradually with increased powder size, in particular, increase of content for carbon graphite powder (KB-3) with average size 30-40 nm lead to slightly decreasing of the hardness where the hardness for the graphite powder content with size 23 μm the hardness greatly decreased.

- It was observed decreasing the electrical resistivity of copper-graphite composite samples with different particle size. It is shown that increasing particle size and graphite content lead to reducing of the samples resistance. While for the carbon graphite powder (KB-3) with average size 30-40 nm resistance almost similar.

- According the images optical microscope the surface morphology of the as-received copper-graphite composite are dependent from graphite content and sintering temperature. Besides it was found when graphite content was increased up to 4% for samples with carbon graphite powder (KB-3) with average size 30-40 nm were observed accumulation of the large size (~120 μm) the graphite agglomerations while for graphite powder with average size 23 μm the agglomerates were observed less frequently and their size also smaller (50 μm).

- Copper-graphite composite with 0,5%wt and 1%wt and particle size 30-40 nm show higher density, micro-hardness and lower porosity than other composite copper-graphite materials with different contents of graphite.

The selection of these optimal ratio composite materials was driven by the goal of achieving a comprehensive understanding of the fabrication process and tailoring the composite materials to meet the specific requirements of high-speed electric railway applications.

REFERENCES

1. J.M. Garcia-Marquez, N. Anton, A. Jimenez, M. Madrid, M.A. Martinez and J.A. Bas, "Viability study and mechanical characterization of copper-graphite electrical contacts produced by adhesive joining," *J. Mater. Process. Technol.* vol. 143/144, pp. 290-293, 2003.
2. D. Hai He and R. Manory, "A novel electrical contact material with improved self-lubrification for railway current collectors," *Wear,* vol. 249, pp. 626-636, 2001.
3. C.H. Stoessel, J.C. Withers, C. Pan, D. Wallace and R.O. Loufty, "Improved hollow cathode magnetron deposition for producing high thermal conductivity graphite-copper composite," *Surf. Coat. Technol.* vol. 76/77, pp. 640-644, 1995.
4. C. Schrank, C. Eisenmenger-Sittner, E. Neubauer, H. Bangert and A. Bergauer, "Solid state de-wetting observed for vapor deposited copper films on carbon substrates," *Thin Solid Films,* vol. 459, pp. 276-281, 2004.
5. E. Hammel, X. tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder and P. Ṗotschke, "Carbon nanofibers for composite applications," *Carbon,* vol. 42, pp. 1153-1158, 2004.
6. M. Kestursatya, J.K. Kim and P.K. Rohatgi, "Wear performance of copper-graphite composite and a leaded copper alloy," *Mat. Sci. Eng.* vol. A339, pp. 150-158, 2003.
7. Kim, S. J., etc. "The Fabrication of Porous Hydroxyapatite Including of Nano-Sized TiNx by Spark Plasma Sintering," *7th Pacific Rim Conference on Ceramic and Glass Technology*, Nov., vol. 14, 2007.
8. Ullbrand, J.M., Cardoba, J.M., Ariztondo, J.T., "Thermomechanical properties of copper-carbon nanofiber composites prepared by spark plasma sintering and hot pressing," *Composites Science and Technology*, Vol. 70, pp. 2263-2268, 2010.
9. Kim, S. J., Oh, Y. H., Park, S. B., "Fabrication of Sputtered TiO_{2-x} N_x Photocatalyst Using Spark Plasma Sintered Targets," *Materials Science Form*, Mar., vol. 30, pp. 539-543, 2007.