# **IMPROVING PROPERTIES OF COPPER BY SIC PARTICLES**

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#### Abstract

In this study, copper powder was precipitated by cementation method. In order to enhance some properties of copper, 5 µm SiC particles at amount of 0, 1 and 3% by weight were added in cemented and commercial copper matrix. Cu and Cu-SiC powder mixtures were pressed with an axial pressure of 280 MPa and sintered in an open atmospheric furnace at 700°C for 2h. Dominant phases and their morphology were analyzed by Scanning electron microscope (SEM-EDS) and X-ray diffraction (XRD) analysis techniques. SEM studies showed that SiC particles were dispersed homogenously in copper matrix. Effect of SiC addition on relative density, hardness and electrical conductivity were investigated. The highest electrical conductivity of 81% IACS (International annealed copper standard) and 87.9% IACS was obtained for cemented and commercial Cu-1wt.% SiC composites, respectively.

### **1** Introduction

Copper and gold are the earliest metals known to man and have been in use for about 10,000 years. The attractive properties which made copper so useful then - good corrosion resistance, attractive colour, excellent workability and good mechanical properties - are relevant today and, in addition, copper has the best electrical and thermal conductivity of any commercial metal. Today, over half of the copper produced is used in electrical and electronic applications [1]. The mechanical strength of copper can be increased dramatically either by age hardening or by introducing dispersoid particles in its matrix. The age-hardenable copper alloys are prone to precipitate coarsening at high temperatures, thereby reducing their strength drastically. In this respect, dispersion-strengthened copper has the ability to retain most of its properties on exposure to high temperatures. Dispersoid particles such as oxides, carbides, borides are insoluble in the copper matrix, and are thermally stable at high temperatures. The dispersion-strengthened copper alloys generally can be classified as the copper-based matrix composites [2]. Cu-based composites were feasible to be used as electrical contact materials in relays, contactors, switches, circuit breaks and other switch gear components [3]. The particle reinforced metal matrix composites can be synthesized by several methods. The PM processing route is generally preferred since it shows a number of product advantages. Powder metallurgy process (PM) lends itself well for economical mass production components. Different metal matrix composites are manufactured by this PM route The uniform distribution of ceramic particle reinforcements is readily realized. On the other hand, the solid-state process minimizes the reactions between the metal matrix and the ceramic reinforcement, and thus enhances the bonding between the reinforcement and the matrix [4-6]. In the present study SiC was selected as reinforcement for its superior mechanical properties of high hardness, high anti-wear stiffness during grinding operation, high electric conductivity to comply with the IACS's electrode standard, and high thermal conductivity to obtain higher thermal shock resistance [6]. Cu-SiC composites combine both the superior ductility and toughness of copper and the high strength and high modulus of SiC reinforcements [7]. In this study, copper powder was produced by cementation method and provided commercially. Powder metallurgy (PM) method was applied to synthesize a copper matrix composite containing SiC reinforcement, by which the reinforcement was homogeneously distributed in the Cu matrix. Furthermore, the microstructure, mechanical properties and electrical resistivity of the as-fabricated composite were studied.

### 2. Experimental

### 2.1 Materials and preparation of samples

Copper powders with a purity of 99.871 have been recovered from  $CuSO_4$  solution by cementation process and provided commercially for comparing. SiC powders with 99.9 percent (pct) purity from Struers and diameter of 5µm were used for reinforcement of copper. SiC particles were added into the cemented and also commercial Cu powders at amount of 1 and 3% by weight and mixed mechanically in order to manufacture Cu-SiC composites by powder metallurgy. The pure copper and mixed powders were then compacted in a cylindrical metallic mold with a diameter of 15mm and sintered in an open atmospheric furnace embedding into graphite powder at the temperature of 700°C for 2 h. Following sintering test samples were immediately pressed with a load of 850MPa.

## 2.2. Characterization of the composites

Before characterization, sintered Cu and Cu-SiC composite samples were ground with consecutive finer SiC abrasive papers followed by polishing with an alumina suspension up to  $0.3\mu$ m. Scanning electron microscopy (SEM, model JEOL – JSM 6060 LV) was used to observe the surface and the cross-sectional microstructures of the copper matrix and SiC reinforcements. Energy dispersive X-ray spectroscopy (EDS) was used to evaluate the distribution of SiC particles in the matrix materials as well as to analyze the elements in the composite materials. XRD analysis was carried out with a Rigaku D/MAX/2200/PC model X-ray diffractometer scanning at a speed of 1°/min in the 20 range of 10–90°. The hardness of the samples were measured using a Vicker's microhardness indenter (Leica VMHT) with a load of 50 g. The relative densities of the sintered samples were measured by the water immersion technique (Archimedes' method). Electrical conductivity of Cu and Cu-SiC composites was measured by GE model electric resistivity measurement instrument.

### 3. Results and Discussions

In this study copper powder was produced by cementation method and provided commercially for comparing. SEM images and EDS analysis of commercial and cemented copper powder are shown in Fig 1,2. It is seen from the Fig.1 that commercial copper powder is in spherical shape with particle size of  $10\mu m$  and does not include any oxygen. The copper powder which was produced by cementation method is of spherical shape and significant

powder agglomeration was observed (Fig.2). SEM image of cemented copper powder at higher magnification shows that the size of these agglomerations are between  $2-6\mu m$ , while the real size of particles are submicron (Fig.3).



Figure 1. a) SEM images and b) EDS analysis of commercial copper powder.



Figure 2. a) SEM images and b) EDS analysis of cemented copper powder.

For the SiC reinforced copper matrix composites, it is very important to obtain homogeneous reinforcements in the matrix phase in order to enhance mechanical properties without decreasing electrical properties. The distribution of SiC particles in the matrix phase is homogeneous. Homogeneous distribution of the reinforcements ensures the isotropic mechanical properties and uniform distribution of stresses in the sintered composite [8]. If reinforcement particles in the composites do not disperse uniformly, this affects mechanical and electrical properties of composites negatively [9]. A very important factor influencing the structure and properties of the composite is the ceramic metal interface. In the present study it was observed that there is a good wettability between Cu matrix and reinforcing SiC particles. Also, previous study done by Uddin et al.[10] revealed that the matrix phase and reinforcement do not show interfacial debonding, indicating the good wettability of SiC particles with the binder phase. Figure 4 shows the distribution of SiC particles in the polished and unetched cemented and commercial copper based SiC reinforced composites. It is seen

that the distribution of SiC particles in copper matrix is uniform and they are surrounded by the matrix phase.



Figure 3. SEM images of cemented copper powder at higher magnification.



Figure 4. SEM images of a) commercial, b) cemented Cu-SiC composites including 3wt.%SiC.

In Fig. 5, the light regions are representative of the Cu matrix, while the dark and cornered regions reflect the SiC particles. The SiC particles were near cornered in morphology with an average size of about  $5\mu$ m. In SEM micrograph of cemented Cu-SiC composite, dark grey and shapeless zones shows iron rich areas (Fig. 5b). SEM-EDS analysis of commercial and cemented Cu-SiC composites performed so as to analyze the presence, morphology and distribution of components. From the EDS spectra given in Fig.6,7, it was concluded that black and cornered particles indicate SiC particles, light grey free areas show Cu matrix and there is a good bonding between reinforcement and matrix phase. No oxygen was detected on the surface of SiC particles, Cu matrix and Cu-SiC interfaces. In Fig. 7 cauliflower like and grey zones marked with number 2, 3, 4 and 5 include slight iron and oxygen. This probably originated from the cementation process of copper powder. It is possible to claim that, iron comes from cementation process oxidize at the sintered temperature. During polishing process alumina entered into the matrix from the polishing agent depending on this Al was detected in the EDS analyses and seems as white points in the matrix.



Figure 5. SEM images of a) commercial, b) cemented Cu-SiC composites including 1wt.%SiC.



Figure 6. EDS analysis of commercial Cu-3wt.%SiC composites.



Figure 7. SEM-EDS analysis of cemented Cu-1wt.% SiC composite.

XRD patterns of composites were drawn in logarithmic scale to see the very small SiC peaks Fig. 8 shows the XRD patterns of cemented (left side) and commercial (right side) sintered pure Cu and Cu-SiC composites. XRD patterns of cemented and commercial Cu and Cu-SiC composites consist of Cu and SiC dominantly and similar to each other. No oxide peaks were detected in the XRD results. The measured densities of the pure copper and metal matrix (Cu-SiC) composites are presented in Fig. 9. As expected, the density decreases linearly with SiC reinforcement since the total density is the volume fraction average of the density of the matrix and reinforcements. As it is known well, the relative density plays a major role on the mechanical properties of the sintered composite, it is important to have it as high as possible. Experimental works about the densification of powder mixtures during free sintering have been performed by different authors. In most cases the materials were composed of metal matrix particles mixed with much larger ceramic inclusions. These studies demonstrated that even a very small amount of inclusions (typically 3 vol.%) can significantly affect the densification. This effect has been attributed to different phenomena such as inclusion induced stresses, heterogeneity and network formation. In any case, the addition of inert inclusions to the metal powder consistently results in lower densification. This reduction becomes even more significant as the amount of inclusions is increased. On the other hand, particles having dendritic shape should have less density (the more regular the shape, the denser the powder) compared to that of spherical structure [10, 11]. Similarly, in the present study it was observed that commercial copper powders are in more regular and spherical shape thus, sintered commercial copper and Cu-SiC composites have higher relative density than cemented ones.



Figure 8. XRD patterns of cemented (left side) and commercial (right side) sintered Cu and Cu-SiC composites.

The results of Vickers hardness tests of sintered Cu and Cu-SiC compacts are given in Figure 10, from which it is evident that hardness markedly increases with the addition of ceramic SiC particles. The improved hardness due to the increased SiC content was highly correlated to the volume fraction of SiC. The microhardness of the sintered commercial and cemented Cu-SiC composite including 3wt.%SiC was 177 HV and 173HV respectively whereas the microhardness of a pure sintered commercial and cemented Cu was 133 HV and 127 HV respectively. Generally hardnesses of commercial Cu and Cu-SiC composites are a little higher than that of cemented Cu-SiC composites. This can be attributed to higher relative densities of commercial Cu and Cu-SiC composites. The enhanced hardness of the composite can be attributed to the contribution from the soft matrix and to some extent, from the SiC particulates. The amount and size of the particles define two kinds of reinforcing mechanisms in MMC materials, namely dispersion strengthening and particle strengthening. When the dispersed particle size is higher than 1µm the strength of the metallic matrix is increased predominantly due to load carrying capacity of the reinforcement phase. A dispersion strengthened composite is characterized by a dispersion of particles with a particle diameter ranging from 0.01 to 1µm through a dislocation-particle interaction Orowan hardening mechanism [12]. In this case, the matrix carries the load, and the fine particles impede the motion of dislocations [13]. Thus, for the Cu-SiC composite in this study, the enhancement was related to the particle strengthening effect [14]. Improvement of electrical conductivity of a highly conductive metal is still a big question of science. In a sintering body of powder metallurgy, it is difficult to achieve 100% density of the theoretical density. There will be a certain amount of porosity inside the composite. These porosities are in fact the insulation sites which reduce the conductivity of the composites. Fig. 11 shows the electrical conductivity of the sintered pure copper and Cu-SiC composite. Increasing SiC contents in the Cu-SiC composites decreases the electrical conductivity for both commercial and cemented copper. The electrical conductivity scale established in 1913 was based on a copper standard defined as 100%, and the electrical conductivity of any material is still expressed as percent IACS (International Annealed Copper Standard), equal to 100 times the ratio of the volume resistivity of the annealed copper standard (0.017241 $\mu$ Ω.m) at 20°C (68°F) to the value measured for the material concerned [10, 15, 16]. The electrical conductivity decreases with increasing SiC content because the volume fraction of nonconducting particles increases. The higher electrical conductivity of sintered commercial Cu and Cu-SiC composites can be attributed to the purity and higher relative density when compared to sintered cemented Cu and Cu-SiC composite.





Figure 9. Relative density variation of cemented and commercial Cu and Cu-SiC composites depending on SiC weight percentage.

Figure 10. Hardness variation of cemented and commercial Cu and Cu-SiC composites depending on SiC weight percentage.



Figure 11. Electrical conductivity variation of cemented and commercial Cu and Cu-SiC composites depending on SiC weight percentage.

## 4. Conclusions

Cemented and commercial Cu-SiC composites were successfully fabricated by powder metallurgy method. XRD patterns of commercial and cemented Cu-SiC composites are similar to each other and consist of Cu and SiC peak dominantly. For cemented Cu-SiC composites more complex microstructure was observed related with the agglomerated grain structure of cemented copper. Related with this slightly higher relative density, electrical conductivity and hardness were achieved for commercial Cu-SiC composites. For both cemented and commercial Cu-SiC composites relative density and electrical conductivity was

decreased and hardness increased with increasing weight percentage of SiC particles. It can be said that cemented copper matrix can replace instead of commercial copper matrix.

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### References

[1] <u>http://www.copperinfo.co.uk/alloys/copper/</u>

- [2] Tjong S.C., Lau K.C., Tribological behaviour of SiC particle-reinforced copper matrix Composites, *Materials Letters*, 43, pp. 274-280 (2000).
- [3] Zhang R., Gao L., Guo J., Temperature-sensitivity of Coating Copper on Sub-micron Silicon Carbide Particles by Electroless Deposition in a Rotation Flask, *Surface and Coatings Technology*, 166, pp. 67-71 (2003).
- [4] Moustafa S.F., Hamid Z.A., Elhay A.M, Copper matrix SiC and Al<sub>2</sub>O<sub>3</sub> particulate composites by powder metallurgy technigue, *Materials Letters, Elsevier*, 53, pp. 224-249 (2002).
- [5] Wanga H., Zhanga, R., Hua, X., Wangb, C.A., Huangb, Y., Characterization of a powder metallurgy SiC/Cu–Al composite, *Materials Processing Technology*, 197, pp. 43-48 (2008).
- [6] Shu K.M., Tu G.C., Study of electrical discharge grinding using metal matrix composite electrodes, *Machine Tools and Manufactures*, 43, pp. 845-854, (2003).
- [7] Efe G., Altinsoy I., Yener T., Ipek M., Zeytin S., Bindal C., Characterization of Cu-SiC Composites, 4th International Conference on Powder Metallurgy, Craiova, Romania, July 8-11, 2009.
- [8] Akhtara F., Askaria S., K. Shaha A., Dua X., Guoa S., Microstructure, Mechanical Properties, Electrical Conductivity and Wear Behavior of High Volume TiC Reinforced Cu-Matrix Composites, *Materials Characterization*, 60, pp. 327-336 (2009).
- [9] Efe G., Altinsoy I., Yener T., Ipek M., Zeytin S., Bindal C., The Effect of Sintering Temperature on Some Properties of Cu–SiC Composite, *Journal of Alloys and Compounds*, 509, pp. 6036-6042 (2011).
- [10] Uddin S., Mahmud T., Wolf C., Glanz C., Kolaric I., Volkmer C., Höller H., Wienecke U., Roth S., Fecht H., 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*, 70, pp. 2253-2257 (2010).
- [11] Olmos L., Martin C., Bouvard D., Sintering of Mixtures of Powders: Experiments and Modeling, *Powder Technology*, 190, pp. 134–140 (2009).
- [12] Zhou Y., Zhang H., Qian B., Friction and wear properties of the co-deposited Ni-SiC nanocomposite coatings, *Appl. Surf. Sci.* 253, pp. 8335–8339 (2007).
- [13] Muller B., Ferkel H., Al<sub>2</sub>O<sub>3</sub>- nanoparticle distribution in plated nickel composite films, *Nanostruct. Mater.* 10, pp. 1285 (1998).
- [14] Xue Y. J., Jia X. Z., Zhou Y. W., Ma W., Li J. S., Tribological performance of Ni-CeO<sub>2</sub> composite coatings by electrodeposition, *Surf. Coat. Technol.* 200, pp. 5677-5681 (2006).
- [15] Akhtara, F., Askaria, S. J., Shaha, K. A., Dua, X., Guoa, S., Microstructure, mechanical properties, electrical conductivity and wear behavior of high volume TiC reinforced Cumatrix composites, *Materials Characterization*, 60, pp. 327-336 (2009).
- [16] Richerson, D.W., Modern ceramic engineering, Taylor & Francis CRC Press, 2006.