

Study of Electrical, Mechanical and Microstructural Properties of Composites Based on Cu-Ni-Ag-Al₂O₃ Obtained By Powder Metallurgy

Waldemar Alfredo Monteiro^{1, 2, a}, Juan Alfredo Guevara Carrió^{2, b},
E. C. Oliveira^{2, c}, G. G. Previatti^{2, d}, L. C. E. Silva^{1, e}

¹Nuclear and Energy Research Institute, IPEN - CNEN/SP, Av. Prof. Lineu Prestes, 2242 - Butantã - Cidade Universitária - USP / SP, 05508-900, São Paulo, Brazil.

²Engineering School, UPM, R. da Consolação, 930, Consolação, 01302-907, São Paulo, Brazil.

^awamonte@ipen.br, ^bjgcarrio@mackenzie.br, ^cemerson.oliveira@mackenzie.br,

^dgabriel.previatti@hotmail.com, ^elcesilva@ipen.br

Keywords: metal alloys, composites, cermets, powder metallurgy, physical properties, electrical conductivity, hardness, copper.

Abstract. The synthesis, microstructural, electrical and mechanical properties characterization of composites based on Cu-Ni-Ag-Al₂O₃ is a work that exposes the investigation of the correlation of the microstructures formed in the material with its physical properties and its manufacturing method. Cermets based on copper, nickel and silver have been doped with alumina varying the proportions of these components to create, by powder metallurgy, a material that has good electrical conductivity and good mechanical strength compared with that of pure copper, together with a manufacturing process which is both cost and energy efficient. The conductivity values vary between 30 to 55% IACS showing that the thermal treatments were effective for electrical connector uses.

Introduction

The aim of this work gives the correlation between sintering processing of some composites of copper-nickel-silver-alumina (powder metallurgy) with increasing on mechanical properties comparing with pure copper without significant loss in electrical conductivity, principally in electrical contact application. In this work were synthesized composites of Cu-Ni-Ag-Al₂O₃ with the aim of obtaining a steadily composites production by sintering (powder metallurgy) in laboratory scale and optimizing the electrical and mechanical properties. The process offers the potential to produce a wide variety of alloys with different material properties such as high temperature toughness and hardness. These advantages reduce or eliminate costly machining processes and allow less scrap loss, compared to other forming methods. The elements are added to copper with purpose to improve its resistance, ductility and thermal stability, without causing considerable costs on its form, electric and thermal conductivity and its resistance to the corrosion, typical characteristic aspects of pure copper [1-3].

Metal-ceramic composites are recently being used as electrode materials in solid oxide fuel cell (SOFC), which have received much attention as alternative energy sources. Structural and electrical properties of the anode materials determine the long-term performance of fuel cells. High electrical conductivity and high activity of electrochemical reactions and hydrocarbon fuel reforming are the fundamental properties of these materials. It is mentioned in literature that in some cermets the dependence of the electrical resistance with the temperature can be similar to that of the metals. Some conductor composites are employed in high speed railways electrical systems. Powder production and mixing is a highly specialized and complex process which produces custom made powder mixes designed to satisfy the needs of a specific application. A good powder mix not only has the ability to produce the required properties of a specific alloy, but also needs to facilitate handling, compacting and sintering. Experimentally, for instance, the easy flow of powder and its capability to mix evenly with other powders is important for an even powder distribution before pressing, and ensures uniform properties of the finished part [4-7].

Experimental Procedures

Samples of Cu-Ni-Ag-Al₂O₃ composites (precursors of high purity; powder form; weight %), initially compressed, sintered and sometimes homogenized were characterized by optical metallography (microstructure), mechanical strength (Vickers hardness), electrical properties (electrical conductivity) for the study of the influence of sintering processing (powder metallurgy). Composites with different compositions of Cu, Ni, Ag and Al₂O₃ were prepared from high purity powders. They were mixed for an hour in an orbital mixer and then compacted under 50 MPa in a cold uniaxial pressing. Afterwards, the specimens were sintered during 2.16x10⁴s (6 hours) at 1073K (800°C) in a furnace with mechanical vacuum of 10⁻³ mBar. The electrical conductivity of all specimens was determined through resistance measurements by the four probe method. These measurements were performed repeatedly in all samples to avoid eventual errors; each test obtained twenty mean values employed sixteen individual measurements.

Table 1 - Sintering parameters of Cu-Ni-Ag-Al₂O₃ composites

Condition	premixed well done milled powders		
Compaction pressure	50MPa		
Chemical composite composition (wt %)	Cu-5% Al ₂ O ₃ ; Cu-10% Al ₂ O ₃ ; Cu-15% Al ₂ O ₃ ; Cu-5% Ni-5% Al ₂ O ₃ ; Cu-7% Ni-3% Al ₂ O ₃ ; Cu-5% Ni-3% Ag-2% Al ₂ O ₃ ; Cu-5% Ni-2% Ag-5% Al ₂ O ₃		
Sample dimensions	Cylinder: $\phi = 25.0 \times 10^{-3}$ m; $h = 4.00 \times 10^{-3}$ m		
Sample weight	0.010 kg		
Sintering temperature and conditions	Sintering temperature	Premixed condition	Vacuum pressure
	1073 K	Solid State Sintering	10 ⁻³ mBar
Sintering time	2.16 x 10 ⁴ s		

Results and Discussion

The mechanical behavior of Cu-Ni-Ag-Al₂O₃ composites shows an increase in microhardness principally due to the distributed alumina particles and relatively small grain size of the copper matrix. Fine dispersed ceramic particles introduction into the metal matrix have significant reinforcing effects which can be kept at elevated sintering temperatures. For such reinforcement ultra-fine oxide particles are appropriate, which, due to their hardness, stability and insolubility in the base metal also represent obstacles to moving of dislocations at the elevated sintering temperatures. The microstructural aspects of copper – nickel – silver - alumina composites are shown in figures 1 to 6. The above characteristics notably determine the later-stage processing and sintering properties and in time determine the final composite microstructure. The microstructural aspects utilizing optical microscopy are observed in samples of Cu-Ni-Ag-Al₂O₃ composites. Fine grain presences but with some porosity and second phases show that homogenization treatments will be necessary to overcome this situation and also investigations with scanning and transmission electron microscopy to identify the presence of second phase on these alloys. Sintering of fine dispersed powders occurs due to sliding of the particles along their boundaries; in that case a sliding mechanism is responsible for creation of additional vacancies. Number of supplementary vacancies can arrive at a value which corresponds to the density of vacancies in temperatures near the materials melting temperature. Then, it could be fulfilled that diffusion activity during sintering of dispersed particles in low temperatures (until 0.3 of melting temperature) is related by extra vacancies presence.

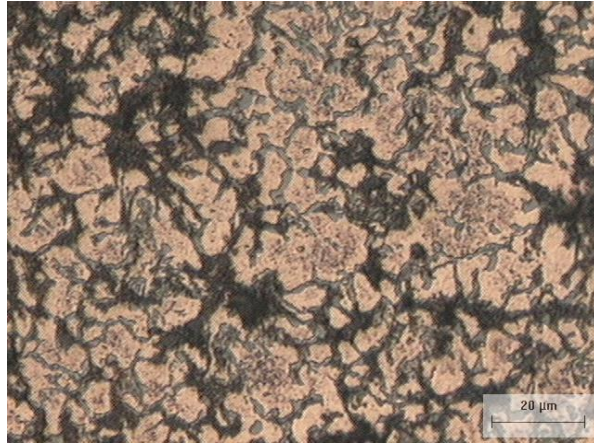


Fig. 1 Optical micrograph² of the composite Cu-15%Al₂O₃ cold compact (25MPa) and sintered at 1073 K for 2.16×10^4 s. Some porosities, presence of second phase in copper grain boundaries, small alumina particles inside the grains.

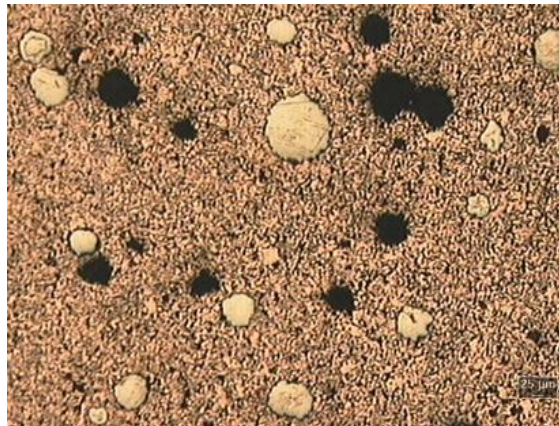


Fig. 2 Optical micrograph of the composite Cu-5%Ni-5%Al₂O₃ cold compact (50MPa) and sintered at 1073 K for 2.16×10^4 s. Some porosity, presence of second phases inside copper grains (Ni and Al₂O₃ particles). There is also missing of some Ni particles (dark areas) due to the metallographic polish processing.

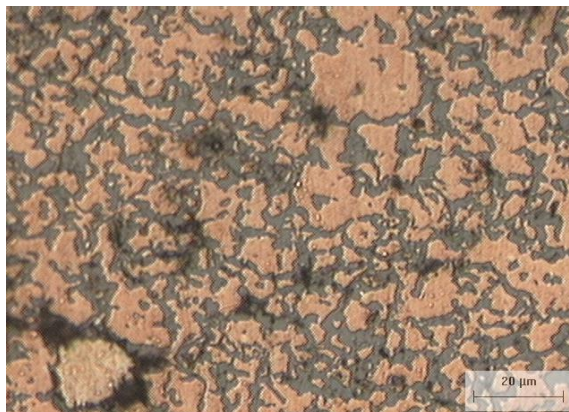


Fig. 3 Optical micrograph of the composite Cu-7%Ni-3%Al₂O₃ cold compact (25MPa) and sintered at 1073 K for 2.16×10^4 s. Presence of nickel second phases surround copper grains and also small alumina particles.

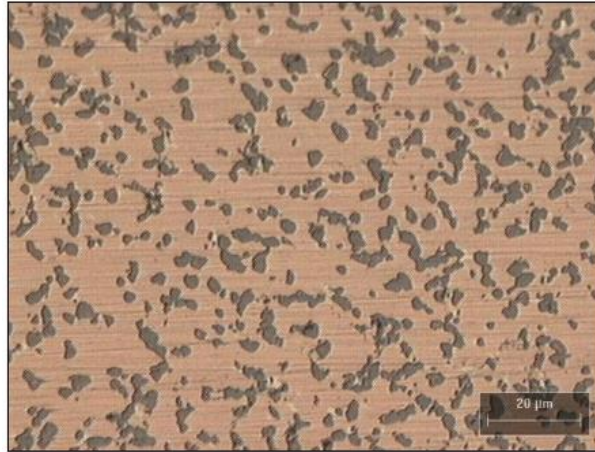


Fig. 4 Optical micrograph of the binary Cu-5%Ag, cold compact (50MPa) and sintered at 1073 K for 2.16×10^4 s. Presence of silver second phases distributed in copper grain boundaries.

Such obtained nanocomposite powders, with the structure preserved in the structure of the final product, have provided production of the sintered system with special effects of reinforcement and a good combination of mechanical and electrical properties. Consequently, the results of the hardness examination of the sintered samples show that the growth of the hardness value is due to the lessening specific electric resistance, which is a system structural stabilization, confirmed by the microstructural investigation.

Table 2: Electrical conductivity and Vickers hardness for Cu-Ni-Ag- Al_2O_3 composites

Composite Chemical Composition (wt %)	Electrical Conductivity (% IACS)	Vickers Hardness (MPa)
100%Cu	96 ± 3	369 ± 8
Cu-5% Al_2O_3	43 ± 3	650 ± 8
Cu-10% Al_2O_3	39 ± 3	670 ± 8
Cu-15% Al_2O_3	35 ± 3	620 ± 8
Cu-5%Ni-5% Al_2O_3	46 ± 3	660 ± 8
Cu-7%Ni-3% Al_2O_3	36 ± 3	650 ± 8
Cu-5%Ag	47 ± 3	632 ± 8
Cu-5%Ni-5%Ag	35 ± 3	645 ± 8
Cu-5%Ni-3%Ag-2% Al_2O_3	37 ± 3	725 ± 8
Cu-5%Ni-2%Ag-3% Al_2O_3	31 ± 3	735 ± 8

The mechanical resistance in MMC composites depends on the second phase distribution to obtain comparable electrical conductivity of pure copper (matrix). To increase the strength, ductility and formability keeping good electric conductivity of these alloys, have been used special thermal treatments as well as variations in the chemical composition. Initial powder diffraction data indicate that the utilized amounts of dopants do not distorted the copper matrix structure significantly.

The size of utilized powders is sited between 2 and 10 μm with noticeable presence of agglomerates. Nowadays the mechanical strength (650 MPa) and electrical conductivity (until

50% IACS) media values indicate a fine appliance for these composites utilizing powder metallurgy as a substitute of conventional metallurgy processing.

The results of electrical conductivity and Vickers hardness measurements for Cu-Ni-Ag-Al₂O₃ composites of the samples are resumed on Table 2. Apparently composites with the highest conductivity and highest hardness are that with copper and nickel and it seems that the silver amount of 5wt% (weight) was enough to elevate the electrical conductivity. The presence of nickel increases the hardness and also contributes to a good electrical conductivity, possibly due to a precipitation mechanism.

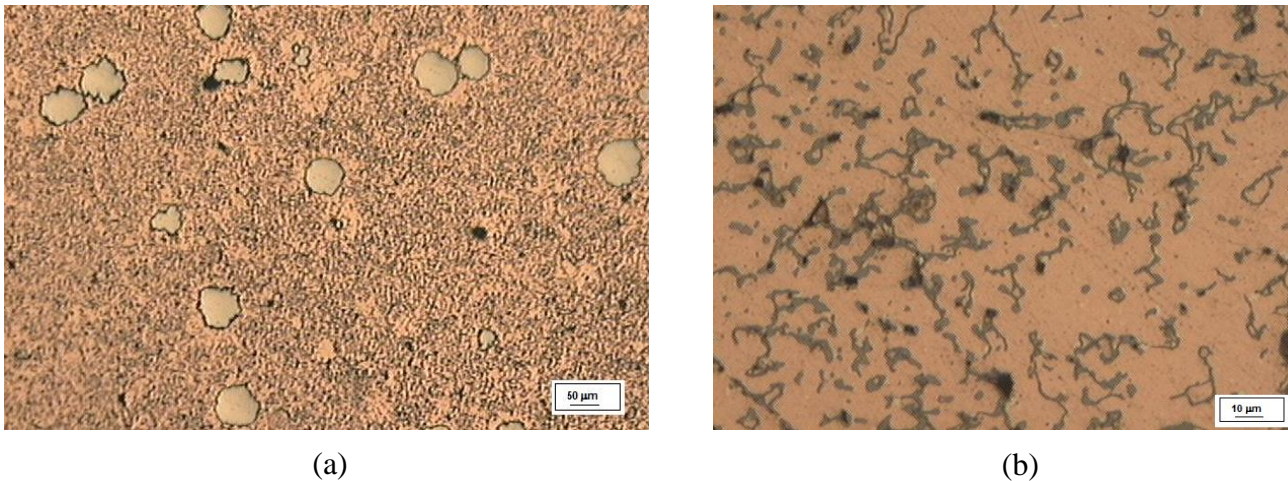


Fig. 5 Optical micrographs of the composite Cu-5%Ni-5%Ag, cold compact (50MPa) and sintered at 1073 K for 2.16×10^4 s. (a) Presence of some porosity (scale = 50 μm); (b) nickel and silver second phases in copper grain boundaries and inside the copper grains (scale = 10 μm).

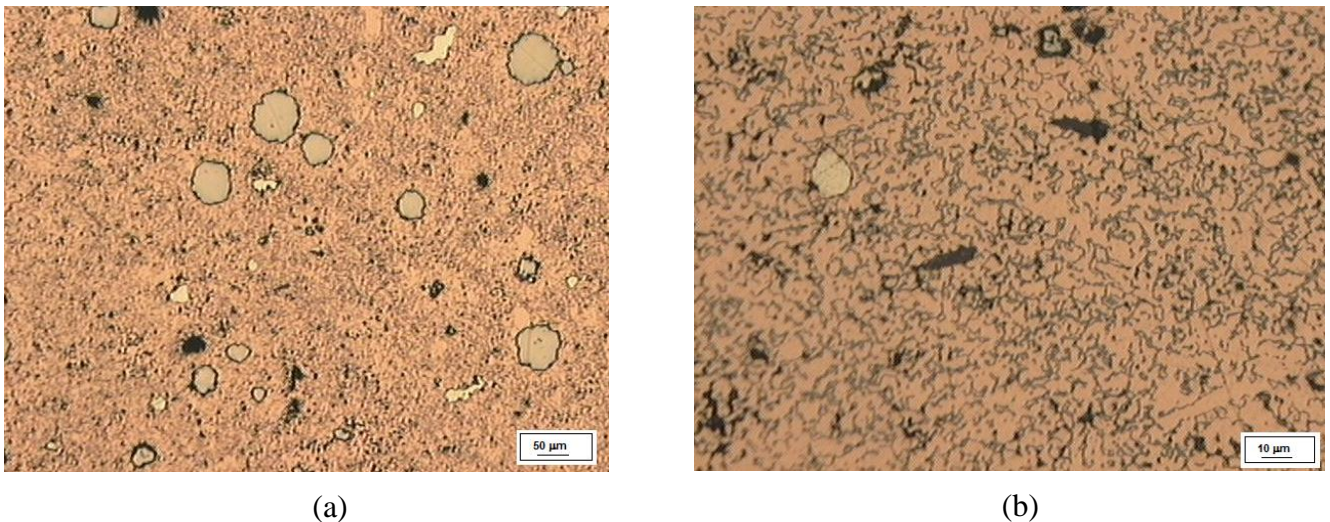


Fig. 6 Optical micrographs of the composite Cu-5%Ni-2%Ag-3%Al₂O₃ cold compact (50MPa) and sintered at 1073 K for 2.16×10^4 s. (a) There is missing of some nickel and silver particles due to the metallographic polish processing (scale = 50 μm). (b) Presence of second phases inside copper grains (nickel, silver and small alumina particles) (scale = 10 μm).

Conclusions

The highest conductivity and highest hardness were obtained for the composition with copper and nickel. Therefore it can be affirmed that nickel increases the hardness and could contribute to the

higher conductivity through a precipitation mechanism. The practical powder metallurgy processing steps on the copper-nickel-silver-alumina composites uphold a first-rate mechanical strength and electrical conductivity values that indicate a good quality employment for these alloys utilizing powder metallurgy instead conventional metallurgy processing. The possibility to search and make fine grained homogenous structures, the skill to form complicated shapes with close dimensional tolerances and the capacity to produce parts with a superior surface finish with close dimensional tolerances encourage this metallurgical application.

The study of dispersion reinforced materials emphasizes the importance of properties of the starting powders, magnitude of the starting structure, respectively, which, although suffer certain changes in further processing, basically remains preserved in the structure of the final product. Important facet of dispersion strengthening is the introduction of possible amount of dispersed particles into volume of base material. The presence of Al_2O_3 could increase the corrosion resistance of the metallic copper alloys. This result could be related to the fact that the copper crystalline structure presents internal strengths and possibly crystallites with different cell parameters due to the effect of thermal and mechanical treatments in presence of some percentage of Al_2O_3 .

Acknowledgements

The authors would like to thank to UPM (PIBIC and Mackpesquisa), IPEN, CNPq, FAPESP and CAPES (Brazil) for financial support.

References

- [1] W.A. Monteiro, J.A.G. Carrió, M.A. Carvalhal, A.K. Okazaki, C. R. Silveira, M. V. S. Martins, “Sintering of ternary copper alloys (powder metallurgy) – electrical and mechanical properties effects”, Sintering Applications, ed. Burcu Ertug, INTECH, ISBN 980-953-307-914-6, <http://dx.doi.org/10.5772/53258>, chapter 9, p. 145-163, 2013.
- [2] ASM Specialty Handbook: Copper and Copper Alloys, Metal, chapter 1, section 1, ASM International, 2001.
- [3] W.A. Kaysser, Solid State Sintering. The Institute of Metals Series on Powder Metallurgy - an overview. London, p. 45-53, 1991.
- [4] K. Haberko, M. Jasinski, P. Pasierb, M. Radecka, M. Rekas, Structural and electrical properties of Ni-YSZ cermet materials, Journal of Power Sources 195 (2010) 5527–5533
- [5] T.S. Srivatsan, N. Narendra, and J.D. Troxell, “Tensile deformation and fracture behavior of an oxide dispersion strengthened copper alloy”, Materials & Design , Volume 21, Issue 3 (2000) 191-198
- [6] R.J. Barker and E. Schamiloglu, High-Power Microwave Sources and Technologies, chapter 10, IEEE Press, New York, (2001).
- [7] T. Kobayasi, Y. Fujihasi, T. Tsuburaya, J. Satoh, Y. Oura and Y. Fujii, RTRI, Japan Electrical Engineering in Japan, Vol. 124, No. 3, 1998