*Science of Sintering,* **42** (2010) 81-90

doi: 10.2298/SOS1001081K

UDK 622.785:546.56:661.183.8

# Sintered Materials Based on Copper and Alumina Powders Synthesized by a Novel Method

**M. Korać[1*)], Ž. Kamberović[1], Z. Andjić[2], M. Filipović[1], M. Tasić[2]**
[1]Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[2]Scientific Research Center, Nikole Pašića 26, Užice, Serbia

***Abstract:***

*This paper presents the production of sintered materials from nano-composite powders obtained by a novel synthesis method, which represents a combination of thermo-chemical synthesis and mechanical alloying. Produced powders were characterized by an average individual particle size of 30nm, with the presence of a small number of aggregates with a size of 150nm. The positive effect on dispersion strengthening of the copper matrix occurred up to 1 wt.% $Al_2O_3$, whereas a further increase of the $Al_2O_3$ content showed a negative effect on hardness. The new synthesis method is more suiTab. for composite materials containing maximum 1wt.% $Al_2O_3$. By this novel method it is possible to produce composites possessing a good combination of hardness and electrical conductivity.*

***Key words****: Copper, Alumina, Nano-composite powders, Sintering, Dispersion strengthening*

## Introduction

Research on nanostructural materials in recent years has been intensified due to their attractive potential, primarily their mechanical and physical properties, which are significantly improved compared to the conventional grain materials. Nanostructural materials can be synthesized in controlled processes by the following methods: highly energetic reactive milling [1], precipitation from solution (sol-gel [2], hydrothermal synthesis [3], electrochemical synthesis [4]), internal oxidation [5] etc.

Introduction of fine dispersed particles into the metal matix has significant reinforcing effects, which can be kept even at elevated temperatures. For such reinforcement nano-particles of oxides are suiTab.. Due to their hardness, stability and insolubility in the base-metal they represent obstacles to dislocation and grain boundaries motion at elevated temperatures without a significant effect on thermal and electrical conductivity [6-8]. Results of research on dispersion reinforced materials point out the significance of properties of the starting powders and of the starting structure, which even though suffers certain changes in further processing, basically remain preserved in the structure of the final product [9]. A very important aspect of dispersion strengthening is introduction of low volume fraction of dispersed oxide particles into the volume of the base-metal, a uniform distribution of oxide particles and their fine dispersion especially in nanometer scale [10].

Copper is very often chosen as a base-metal due to its high electrical and thermal conductivity and relatively low mechanical properties. Copper-based composite materials are

*) Corresponding author: marijakorac@tmf.bg.ac.rs

widely applied in the field of electronics and electrical engineering as highly conductive materials for operation at elevated temperatures, as electrodes for resistance spot and seam welding, different contact materials, various switches, thermal and electric conductors, microwave tubes, etc [11].

Alumina is known for its exceptional properties such as high melting point, high hardness, excellent thermal stability and chemical inertness. Also, addition of alumina particles can increase the temperature of recrystallization by pinning grain and sub-grain boundaries of the copper matrix and blocking the movement of dislocations and thus highly improving strength at elevated temperatures [12,13]. The usual amount of alumina used for dispersion strengthening is from 0.5-5.0 wt.% [14], but significant results regarding particle size could be achieved with even higher amounts ranging up to 50 wt.% alumina [15].

The objective of this research was to investigate strengthening of the copper matrix by a fine dispersion of alumina particles applying a new synthesis route representing a combination of two processes: thermo-chemical route and mechanical alloying. A series of experiments which were previously performed on mechanically alloyed commercial copper powder with alumina synthesized from a solution by the sol-gel method [16] did not give satisfactory results due to the high degree of agglomeration of alumina. On the other hand, the possibility of production of Cu-$Al_2O_3$ nano-powders with 3 and 5 wt.% $Al_2O_3$ by thermo-chemical method was investigated [17,18] and the results obtained were promising.

## Experimental

The route used for synthesis of composite powders may be regarded as new, irrespective it has arisen from previous research on different synthesis methods of composite materials.

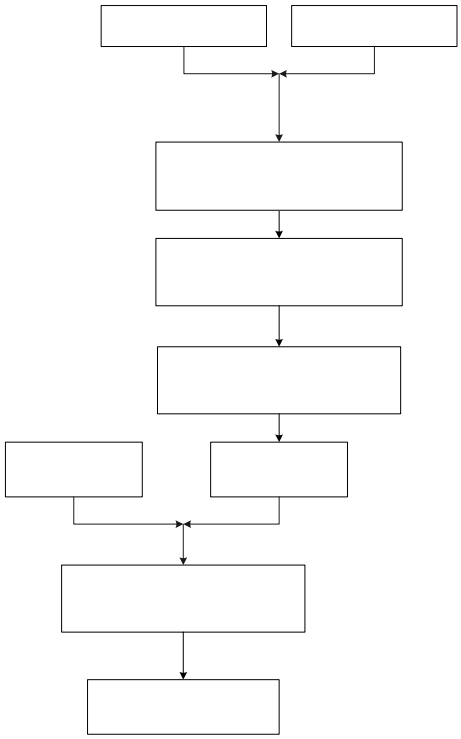

**Fig. 1** Schematic preview of novel method for synthesis of copper-based composite materials

Starting raw materials for powder synthesis by the thermo-chemical route were as

follows: soluble salts, nitrates of copper and aluminum of p.a. quality, dissolved in distilled water (50wt.% solution) in a suiTab. ratio for the final powder to contain 50wt.% of $Al_2O_3$ in its structure. The synthesis of powders underwent several stages as schematically presented in Fig. 1.

Stages of the synthesis process included the following processes:

1. Spray drying of the nitrate solution using a Spray Dryer Büchi B-290 Advanced [19] with the inlet/outlet temperature 190/143°C and the solution flow rate was 10% of pump power,
2. Dried nitrates were subjected to heat treatment in a laboratory electroresistant tube furnace [20] in air at 900°C for 1h in order to form oxides of copper and aluminium,
3. Oxides were then reduced in the same furnace in hydrogen atmosphere (flow rate 20L/h at 350°C for 1h) in order to obtain metallic copper. Previously formed sTab. $Al_2O_3$ remained unchanged during reduction [20],
4. Mechanical alloying was the next step in the synthesis process. Atomized copper powder (size approximately 45μm) was mechanically alloyed with the produced composite powder with 50wt.% $Al_2O_3$ in a ceramic ball mill, with dimensions ø180×160mm. Milling media were corundum balls (≥99% $Al_2O_3$ with 30mm in diameter) in order to prevent contamination of the material; the ball to powder ratio was 1:30. The optimal milling time was fixed at 5h for a mill rotation speed of 300$min^{-1}$. Quantities of added copper powder were adjusted so that the final amount of alumina $Al_2O_3$ in the composite powder would contain 1, 1.5 and 2 wt.%.

After mechanical alloying the obtained powders were compacted by a uniaxial pressing force in tooling with the basal dimensions 8×32mm and height 3mm, applying a compacting pressure of 500 kN. Sintering of samples was performed in hydrogen atmosphere in isothermal conditions at five different temperatures in the range from 725-925°C for 15 to 120 min.

Produced powders were characterized by X-ray diffraction analysis (XRD) and analytical Electron Microscopy (AEM). XRD was performed using APD 2000-Ital structures with CuKα radiation, 2θ=0-100°. AEM was carried out on a JEOL 200CX microscope on powders spread on conductive carbon tape.

Characterization of sintered samples (referred as composite in the following text) included Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), HRF hardness measurements and electrical conductivity.

SEM analysis was performed on a JEOL JSM-T20 on polished samples subsequently etched with 40 vol.% $HNO_3$ solution. EDS analysis was conducted on unpolished composites using an Oxford system attached to a JEOL SEM JSM-5800.

An Ames PorTab. Hardness Tester was employed for hardness measurements using a 1/16" ball with an applied load of 60kg. For electrical conductivity measurements a Foerster Sigma Test 2.069 operating at 120 kHz and with 8mm electrode diameter, was used. The values of hardness and electrical conductivity represent the mean value of at least six measurements conducted on the same composite.

## Results and discussion

Using the proposed synthesis method it was expected that atomized copper powder particles would be compactly surrounded by nano-composite Cu-$Al_2O_3$ produced by the thermo-chemical route. In this way a ductile, highly conductive core with a high strength shell layer of composite**,** will be achieved. In later stages this microstructure would provide dislocation blocking and prevent grain boundary motion as well as an increase of the recrystallization temperature.

An X-ray diffraction pattern of powder containing 50 wt.% $Al_2O_3$ is presented in Fig. 2. Identified peaks correspond to Cu and $CuAl_2O_4$. The $CuAl_2O_4$ phase represents the metasTab. equilibria, developed in the microstructure during powder synthesis process, heat treatment and reduction.

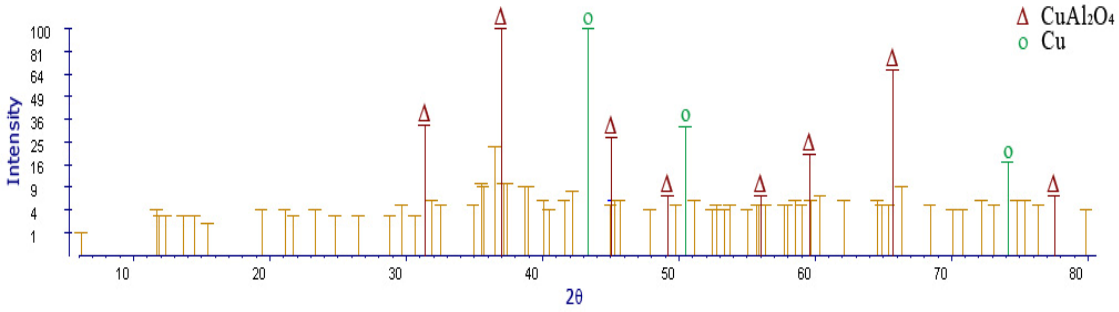


**Fig.** 2 X-ray diffraction of Cu-$Al_2O_3$ powder with 50 wt.% of $Al_2O_3$

X-ray diffraction patterns of powders containing 1, 1.5 and 2 wt.% $Al_2O_3$ show only peaks corresponding to copper.

Produced powders were characterized by AEM as presented in Fig. 3. It could be noticed that average individual particle size is around 30nm. The particle shape is irregular with a rough surface morphology. Sponge-shaped agglomerates are also registered, with the mean size around 150nm. Large black spots originate from conductive carbon tape.

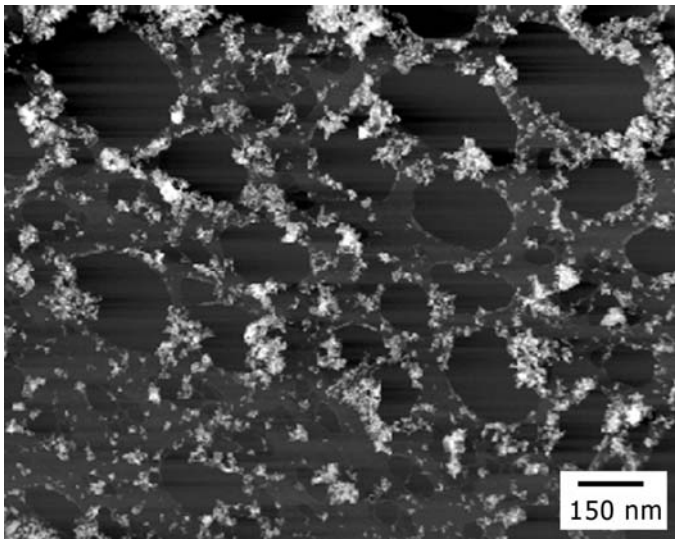


**Fig. 3** AEM of Cu-$Al_2O_3$ powder with 1 wt.% of $Al_2O_3$

During further processing of powders, such as cold pressing and sintering, the shell layer of the composite diffuses into the copper core producing an $Al_2O_3$ concentration gradient, additionally contributing to improvement of properties. Also, during the period of sintering, formation of a third phase is expected [13], due to the thermodynamically possible eutectic reaction of ($Cu+Cu_2O$) with $Al_2O_3$ at the contact surface. Through this reaction the eutectic tends to expand and reacts with $Al_2O_3$ forming the $Cu_xAl_yO_z$ phase, compatible with both phases at the interface [21,22]. The formed third phase influences the dislocation structure resulting in improvement of mechanical properties, whereas good electrical conductivity is retained. According to literature [23] the chemical formula of this compound might be derived as $CuAlO_2$ or $CuAlO_4$.

The presence of this phase in the structure and especially at the interface could impede crack propagation and result in higher interface fracture energy [24].

The sintered composite with 1wt.% $Al_2O_3$ (Fig. 4) produced by powders synthesized by novel route exhibits annealing twins and sub-grain boundaries. Twinning might have occurred during the high temperature sintering stage.

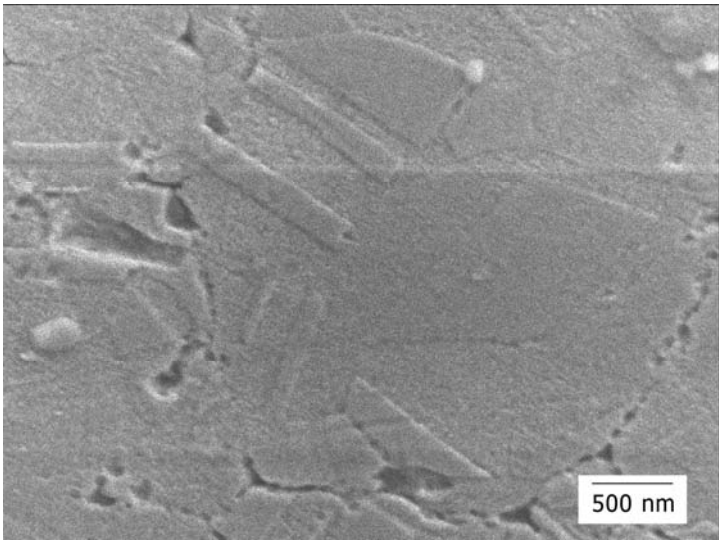


**Fig. 4** SEM micrograph of composite Cu-$Al_2O_3$ 1wt.%

Conditions for twin formation are achieved when a large number of obstacles is formed in the crystal, blocking dislocation movement. Dislocations are accumulated on obstacles causing increase of internal strain in local areas, which together with external strain induce twin formation. The presence of twins indicated a lower mobility of dislocations, in other words stabilization of the dislocation structure, which is the primary condition for improvement of mechanical properties of dispersion strengthened materials.

The size of sub-grains similar to that in Fig. 4 is expected to be preserved under the influence of temperature as a result of dispersed $Al_2O_3$ particles blocking sub-grain boundaries and increasing the recrystallization temperature, rendering these materials suiTab. for exploitation at elevated temperatures.

Fig. 5 presents EDS analysis of produced composites with 1, 1.5 and 2 wt.% $Al_2O_3$. The presented EDS results in Fig. 5 show that in the composites with 1wt.% $Al_2O_3$ aluminum was not detected in the structure, indicating that the whole amount of $Al_2O_3$ is incorporated in the copper matrix. With increase of $Al_2O_3$ content, aluminum is detected which suggests the occurrence of segregations in the structure and formation of aluminum-rich regions. These results suggest that the new synthesis method is more suiTab. for composite materials containing maximum 1wt.% $Al_2O_3$. This amount could be fully incorporated in the base-metal matrix playing a role as an obstacle to dislocations, grain and sub-grain boundaries movement. However, this role is diminished with increase of $Al_2O_3$ content by formation of aluminum-rich regions. Furthermore, Fig. 5 shows better compaction for sintered compacts with lower $Al_2O_3$ content.

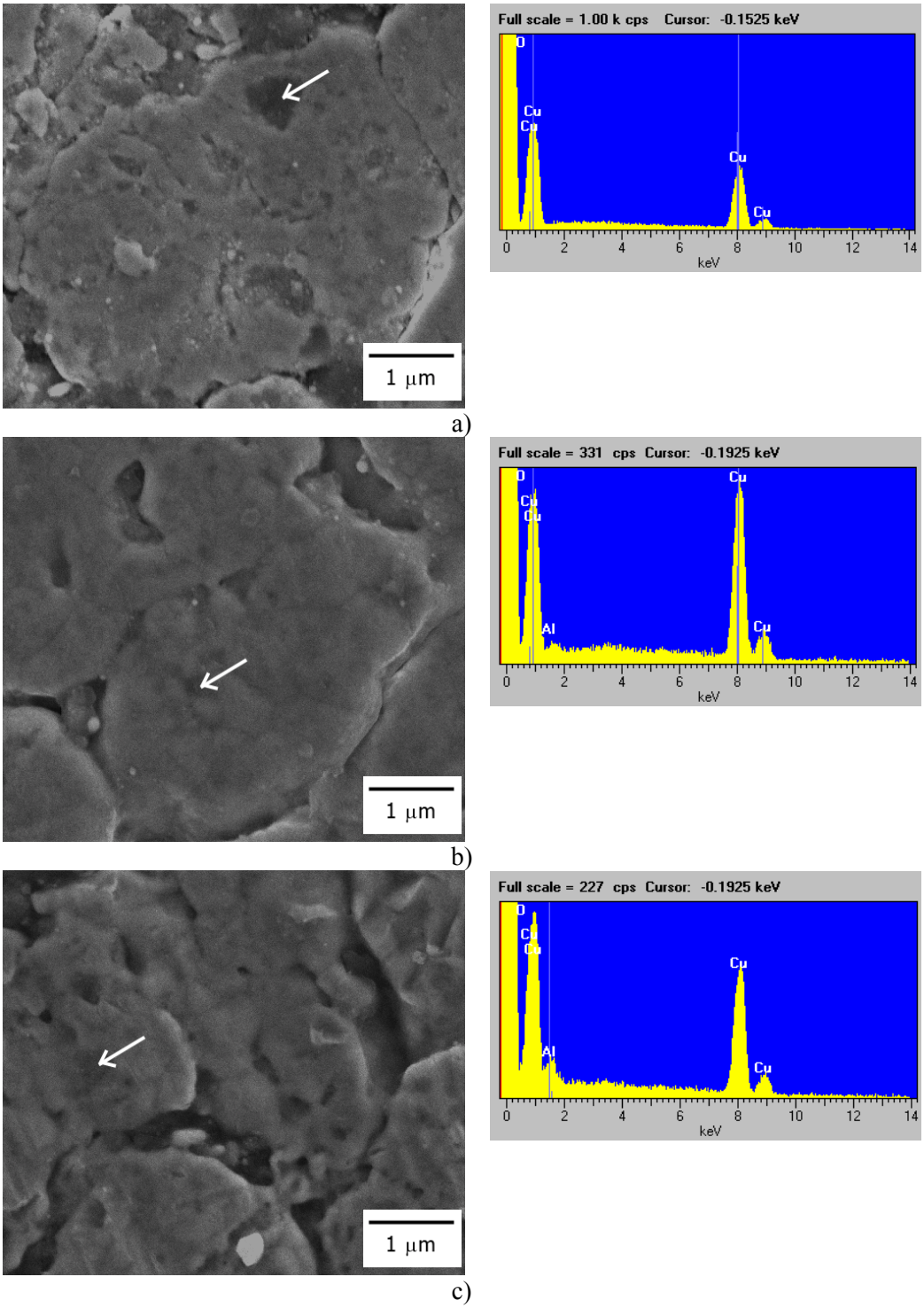


**Fig. 5** EDS analysis of marked spots in SEM micrographs of Cu-$Al_2O_3$ composite with a) 1; b) 1.5 and c) 2wt.% $Al_2O_3$

These results are also confirmed by measurements of hardness and electrical conductivity as presented in the following Tabs and Figs.

Results of HRF hardness measurements are presented in Tab. I.

**Tab. I** HRF hardness of sintered Cu-$Al_2O_3$ composites

| T, °C / t, min | 725 | 775 | 825 | 875 | 925 |
|---|---|---|---|---|---|
| 1 wt.% $Al_2O_3$ | | | | | |
| 15 | 52 | 49 | 50 | 52 | 42 |
| 30 | 52 | 54 | 50 | 50 | 52 |
| 60 | 53 | 46 | 48 | 50 | 46 |
| 90 | 48 | 52 | 44 | 45 | 40 |
| 120 | 47 | 46 | 46 | 52 | 44 |
| 1.5 wt.% $Al_2O_3$ | | | | | |
| 15 | 42 | 42 | 40 | 42 | 40 |
| 30 | 48 | 44 | 40 | 46 | 38 |
| 60 | 44 | 44 | 42 | 40 | 42 |
| 90 | 42 | 43 | 39 | 42 | 38 |
| 120 | 44 | 39 | 40 | 39 | 43 |
| 2 wt.% $Al_2O_3$ | | | | | |
| 15 | 42 | 29 | 22 | 26 | 19 |
| 30 | 26 | 27 | 12 | 20 | 19 |
| 60 | 30 | 24 | 22 | 26 | 20 |
| 90 | 24 | 26 | 15 | 20 | 16 |
| 120 | 30 | 26 | 13 | 23 | 22 |

Results show that with increase of temperature and time of sintering HRF values slightly and unevenly decrease. Increase of $Al_2O_3$ content has a significant effect on hardness. It was expected that the increase of $Al_2O_3$ content in the structure would result in an increase of hardness, but the results show an opposite trend. With increase of $Al_2O_3$ from 1 to 1.5 wt.% there is a slight decrease in HRF values, while an increase up to 2 wt.% $Al_2O_3$ provokes a rather significant decrease in HRF.

Possible reasons for this behavior is ascribed to a positive effect on dispersion strengthening of the copper matrix which occurred when the amount of $Al_2O_3$ dispersoids is up to 1 wt.%, whereas further increase of $Al_2O_3$ content has a negative effect on hardness as previously postulated by EDS analysis (Fig. 4). This problem supposedly may be solved using the hot extrusion process.

Fig. 6 illustrates the influence of composition and duration of sintering on hardness values of composite materials for a selected temperature of 875°C.

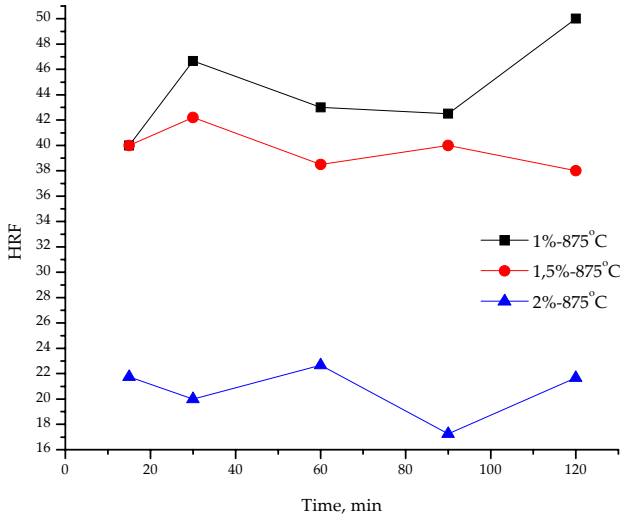


**Fig. 6.** HRF hardness of sintered Cu-$Al_2O_3$ composites with different $Al_2O_3$ content at 875°C

Electrical conductivity measurements of composites with different $Al_2O_3$ content at various sintering conditions are presented in Tab. II.

**Tab. II** Electrical conductivity of sintered Cu-$Al_2O_3$ composites, %IACS

| T, °C / t, min | 725 | 775 | 825 | 875 | 925 |
|---|---|---|---|---|---|
| 1 wt.% $Al_2O_3$ | | | | | |
| 15 | 54.88 | 59.90 | 56.83 | 55.05 | 55.19 |
| 30 | 53.94 | 55.39 | 56.48 | 57.16 | 56.06 |
| 60 | 55.44 | 54.61 | 56.28 | 56.69 | 55.51 |
| 90 | 58.00 | 55.13 | 54.54 | 55.25 | 54.81 |
| 120 | 56.37 | 54.24 | 55.15 | 56.43 | 55.87 |
| 1.5 wt.% $Al_2O_3$ | | | | | |
| 15 | 42.76 | 42.49 | 43.51 | 43.86 | 43.81 |
| 30 | 45.07 | 42.52 | 42.51 | 44.02 | 47.81 |
| 60 | 40.94 | 43.27 | 45.48 | 49.59 | 49.88 |
| 90 | 39.86 | 41.87 | 42.63 | 46.72 | 48.08 |
| 120 | 43.19 | 39.11 | 42.76 | 45.80 | 48.80 |
| 2 wt.% $Al_2O_3$ | | | | | |
| 15 | 32.66 | 32.54 | 30.71 | 30.35 | 31.25 |
| 30 | 29.25 | 31.27 | 29.92 | 31.13 | 40.70 |
| 60 | 31.93 | 30.89 | 31.72 | 36.94 | 39.99 |
| 90 | 31.35 | 31.72 | 31.76 | 37.61 | 39.35 |
| 120 | 30.53 | 31.66 | 31.66 | 33.43 | 41.21 |

Influence of the $Al_2O_3$ content on electrical conductivity for sintering temperature of 875°C is illustrated in Fig. 7. With increase of $Al_2O_3$ content in composite materials the values of electrical conductivity decrease.

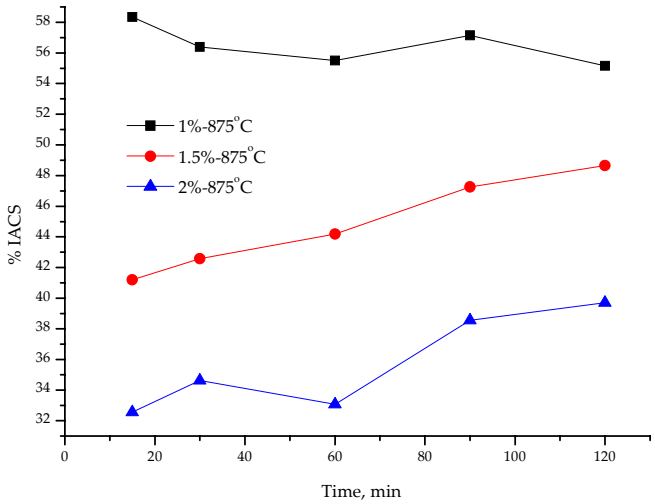


**Fig. 7.** Electrical conductivity of sintered Cu-$Al_2O_3$ composites

Values of electrical conductivity are over 55% IACS for compacts with 1wt% $Al_2O_3$, which corresponds to dispersion strengthened copper alloys intended for application at elevated temperatures. The limitation value for application is 50% IACS [25].

## Conclusion

From the presented results it can be concluded that nano-composite powders based on copper with different $Al_2O_3$ content could be successfully produced by the novel method of synthesis, i.e. by a combination of a thermo-chemical route and mechanical alloying. The produced powders were characterized by an average individual particle size of 30nm, with the presence of a small number of aggregates with a size of 150nm.

After compaction and sintering compacts with 1wt% $Al_2O_3$ show the best results corresponding to oxide dispersion strengthened copper, i.e. hardness combined with electrical conductivity suiTab. for exploitation at elevated temperatures. With increase of $Al_2O_3$ content the properties of composites decreased and this problem could be solved using the hot extrusion process. Also, with increase of $Al_2O_3$ content aluminum-rich regions are formed, contributing to decrease of mechanical and electrical properties.

Further treatment of compacts, mechanical processing and heat treatment is expected to additionally increase properties of compacts from composite powders synthesized by the novel method with 1wt.% of $Al_2O_3$.

## Acknowledgement

The authors wish to thank the Ministry of Science and Technological Development of the Republic of Serbia for financial support, project 19032.

## References

1. J-H. Ahn, I-H. Song, Y-D. Hahn, Mater. Trans. JIM, 37 (1996) 733.
2. A.J. Ruys, Y-W. Mai, Mater. Sci. Eng. A, 265 (1999) 202.

3. K. Byrappaa, T. Adschirib, Prog. Cryst. Growth Charact. Mater., 53 (2007) 117.
4. G-Q. Yuana, H-F. Jiang, C. Lina, S-J. Liaoa, J. Cryst. Growth, 303 (2007) 400.
5. Afshar., A. Simchi, Scr. Mater., 58 (2008) 966.
6. J. Naser, H. Ferkel, W. Riehemann, Mater. Sci. Eng. A, 234-236 (1997) 470.
7. Z. Trojanová, H. Ferkel, P. Luká, J. Naser, W. Riehemann, Scr. Mater., 40 (1999) 1063.
8. B. Tian, P. Liua, K. Songa, Y. Lia, Y. Liua, F. Rena, J. Sua, Mater. Sci. Eng. A, 435-436 (2006) 705.
9. M.S. Motta, E.A. Brocchi, I.G. Solórzano, P.K. Jena, Multidisciplinary Microscopy Research and Education, FORMATEX, 2004, p. 215-223.
10. M.M. Ristić, S.Đ. Milošević, Science of Sintering, 38 (2006) 7
11. D.W. Lee, B.K. Kim, Mater. Lett., 58 (2004) 378.
12. G. Plascencia, T.A. Utigard, Corros. Sci., 47 (2005) 1149.
13. S. Lianga, Z. Fana, L. Xua, L. Fangb, Composites Part A, 35 (2004) 1441.
14. P.K. Jena, E.A. Brocchi, I.G. Solórzano, M.S. Motta, Mater. Sci. Eng. A, 371 (2004) 72.
15. E.A. Brocchi, M.S. Motta, I.G. Solorzano, P.K. Jena, F.J. Moura, Mater. Sci. Eng. B, 112 (2004) 200.
16. Ž. Kamberović, M. Korać, Z. Anđić, M. Tasić, in: ”36th International October Conference on Mining and Metallurgy”, Ed. Z. Marković, Technical Faculty Bor-University of Belgrade, Bor, 2004, p. 519-524.
17. Z. Anđić, M. Korać, M. Tasić, K. Raić, Ž. Kamberović, Kovove Mater., 44 (2006) 145.
18. Z. Anđić, M. Korać, Ž. Kamberović, A. Vujović, M. Tasić, Science of Sintering, 39 (2007) 145.
19. K. Okuyama, I.W. Lenggoro, Chem. Eng. Sci., 58 (2003) 537.
20. M.Korać, Ž. Kamberović, M.Filipović, Metalurgija, 15 (2009) 129.
21. Y. Yoshino, T. Shibata, J. Am. Ceram. Soc., 75 (1992) 2756.
22. P. K. Jena, E. A. Brocchi, M. S. Motta, Mater. Sci. Eng. C, 15 (2001) 175.
23. S. Yi, K.P. Trumble, D.R. Gaskell, Acta Mater., 47 (1999) 3221.
24. Reimanis, K. Trumble, K. Rogers, B. Dalglrish, J. Am. Ceram. Soc., 80 (1997) 424.
25. J.N. Grant, A. Lee and M. Lou, in: ”High Conductivity Copper and Aluminium Alloys”, Eds. E. Ling and P.W. Taubenblat, The Metallurgical Society of AIME, California, 1984, p. 103–111.

***Садржај:*** *У овом раду је представљена производња синтерованих материјала из нано композита добијених новом методом синтезе, која представља комбинацију термохемијске синтезе и механичког легирања. Произведени прахови се карактеришу средњом величином појединачних честица од 30nm, са малим присуством агломерата средње величине од 150nm. Позитивни ефекти дисперзног ојачавања се постижу додатком до 1 теж.% $Al_2O_3$, где се са даљим порастом садржаја $Al_2O_3$ уочавају негативни ефекти на тврдоћу материјала. Нова метода синтезе је погодна за производњу материјала који максимално садрже 1 теж.% $Al_2O_3$. Овом методом синтезе је могуће произвести композите са добром комбинацијом тврдоће и електричне проводљивости.*

***Кључне речи:*** *Бакар, глиница, нано-композитни прахови, синтеровање, дисперзно ојачавање*