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Analysis of the Properties of a Cu-Al_2O_3 Sintered System based on Ultra Fine and Nanocomposite Powders

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Abstract:

In this paper synthesis of a composite based on Cu-Al_2O_3 by a thermo-chemical method is shown along with a comparative analysis of the properties of the obtained nanocomposite sintered samples, which are characterized by a good combination of electric-mechanical properties, suitable for work at elevated temperatures. Ultra fine and nanocrystal powder Cu-Al_2O_3 is obtained by a chemical method, starting from water solutions of nitrates up to achieving the requested composition with 3 and 5% of Al_2O_3. Synthesis of composite powders has been developed through several stages: drying by spraying, oxidation of the obtained powder of precursor and then reduction by hydrogen until the final composition of nanocomposite powder is achieved. After characterization of the obtained powders, which comprised examination by the Scanning Electronic Microscopy (SEM) method and X-ray-structure analysis (RDA), the powders were compacted with compacting pressure of 500 MPa. Sintering of the obtained samples was performed in the hydrogen atmosphere in isothermal conditions at temperatures of 800 and 900°C for 30, 60, 90 and 120 minutes. Characterization of the obtained Cu-Al_2O_3 of the nanocomposite sintered system comprised examination of microstructure by the Scanning Electronic Microscopy (SEM), as well as examining of electric mechanical properties. The obtained results show a homogenous distribution of dispersoides in the structure, as well as good mechanical and electric properties.

Keywords: *Copper, Alumina, Nnano-composite powders, Sintering, properties.*

Introduction

It is known that by introducing fine dispersed particles into a metal base, significant reinforcing effects are accomplished, which can be kept in the conditions of elevated temperatures. For such reinforcing, ultra fine and nano particles of oxides are suitable, which due to their hardness, stability and insolubility in the metal base also represent obstacles to dislocation motion at elevated temperatures. Maximum effects of reinforcing are achieved by even distribution of oxide particles and at short distance, their fine dispersion in the matrix of the basic metal, respectively [1-3]. Research of materials reinforced by dispersion points to the significance of properties of the starting powders, importance of the starting structure, respectively, which, although suffering certain changes in further processing basically remains in the structure of the final product [4].

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Obtaining of powders by a chemical method where all the materials are in liquid phase is not a new procedure and lately, due to the development of contemporary materials with in advance pre-set properties, interest in this method of obtaining first of all ultra fine and nano powders intensified [1, 2, 4]. According to Jeni and associates [1] synthesis of nanocomposite powders by a chemical method can be carried out in two ways. The first way comprises of adding of a certain quantity of CuO into a solution of aluminium nitrate in distilled water. The obtained gel is annealed at 850°C with the aim of getting a mixture of Cu and Al oxides. The obtained mixture of the oxides is reduced in hydrogen atmosphere in order to achieve the final structure. For other synthesis methods aluminium nitrate and CuO are also mixed in appropriate proportions in distilled water. However, in this case, ammonium hydroxide is added to this gel for hydrolysis of aluminium nitrate to hydroxide. As in the first case, the mixture was annealed at 850°C, and then reduced in hydrogen atmosphere until the final structure was obtained.

Sintering of ultradispersed powders, according to [4-6], happens due to particles sliding through along their borders, then to a dislocative mechanism that is responsible for creation of surplus vacancies. Concentrations of surplus vacancies can reach a value, which corresponds to the concentration of vacancies in the area of temperatures close to the temperatures of material melting. On the basis of that, it can be concluded that diffusion activity during sintering of ultradispersed particles in the area of really low temperatures (0.1-0.3T_t) is conditioned by the presence of unbalancing "recrystallization" vacancies. High recrystallization speeds of ultradispersed particles are a subsequence of the process of recrystallization selfactivation.

Experimental

For synthesis of nanocomposite Cu-Al_2O_3 powder by a thermochemical method, nitrates of copper and aluminium were used $Cu(NO_3)_2 \times 3H_2O$ and $Al(NO_3)_3 \times 9H_2O$ as a transient component. The synthesis process developed in four stages, as follows:

- obtaining 50% of water solution in which $Cu(NO_3)_2$ and $Al(NO_3)_3 \times 9H_2O$ are dissolved up to achieving the requested composition of Cu-Al_2O_3 nanocomposite system with 3 and 5% of alumina,
- drying by spraying, using a modified house sprayer at a temperature of 180^{o}C with the aim of obtaining composite particles of nitrate salts,
- annealing of the obtained loose mixture in air atmosphere at the temperature of 900^{o}C for 1 hour with the aim of forming copper oxide and phase transformation of Al_2O_3 up to thermodynamically stable α-Al_2O_3 phase,
- reduction of thermally treated powders in hydrogen atmosphere at the temperature of 400^{o}C for one hour, whereas copper oxide is transformed into elementary copper, and α-Al_2O_3 remains in unchanged form.

Characterizations of the obtained powders comprised examinations by the X-ray-structural analysis (RDA) and Scanning Electronic Microscopy (SEM) method. After characterization of the obtained powders, compacting by the action of a pressing force was performed from both sides in tooling with dimensions 8×32mm at a height h=2mm, with a compacting pressure of 500 MPa. Sintering of the obtained samples was performed in hydrogen atmosphere in isothermal conditions at temperatures of 800 and 900^{o}C for 30, 60, 90 and 120 minutes. Characterization of the obtained nanocomposite Cu-Al_2O_3 sintered system comprised of microstructure examinations by Scanning Electronic Microscopy, examination of electric and mechanical properties, as well as examinations of density and relative volume changes.

Results and Discussion

Characterization of the obtained Cu-Al_2O_3 nanocomposite powder, obtained by thermochemical method comprised examinations by RDA and SEM methods.

In Fig. 1 RDA analysis is shown of the powder precursor obtained by drying with spraying of a water solution of copper and aluminium nitrates. In accordance with the experimental set-up only the peaks in the structure corresponding to copper and aluminium nitrates were registered.

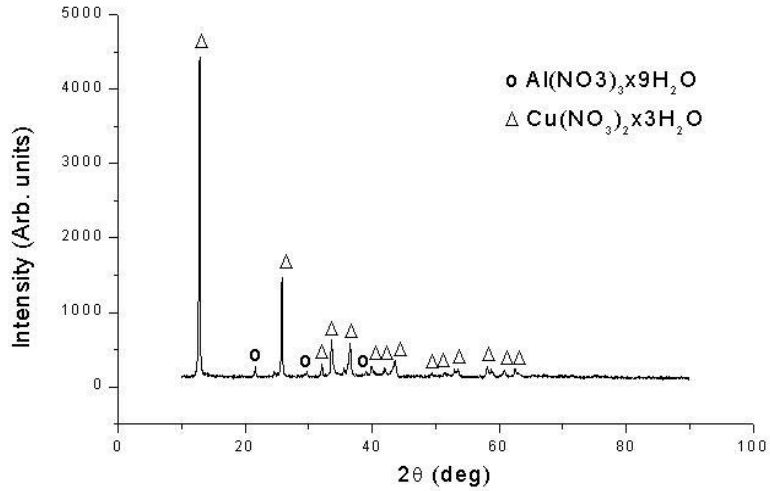

Fig. 1 RDA of Cu+3%Al_2O_3 powder after drying with spraying

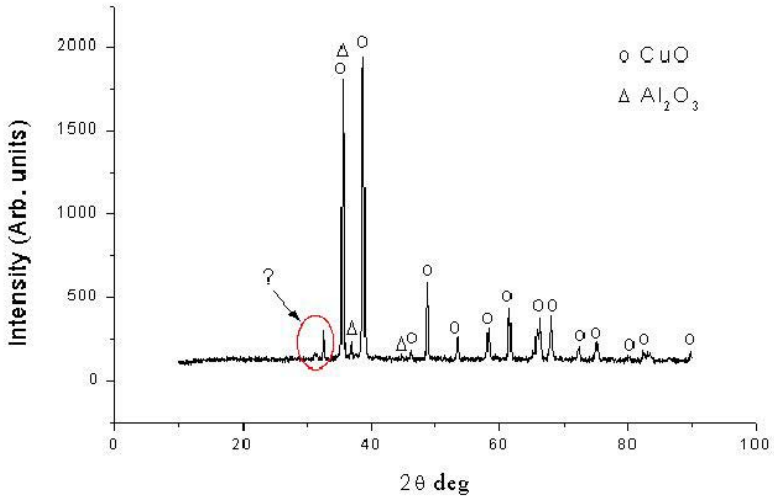

Fig. 2 RDA of the dried Cu+3%Al_2O_3 powder after thermal treatment

The RDA of the dried powder after thermal treatment is shown in Fig. 2. Detected peaks correspond to CuO and Al_2O_3. Also, a peak was detected, which most probably, in accordance with [7-9], corresponds to the third stage, $Cu_xAl_yO_z$ that appears in the structure because of the eutectic reaction of copper and aluminium, and the forming of which on Cu-Al

contact surfaces is possible from the thermodynamic aspect. During eutectic joining of copper and Al_2O_3, the eutecticum formed by heating up to the eutectic temperature expands and reacts with Al_2O_3 also creating $Cu_xAl_yO_z$, which is compatible from both stages on the inter-surface. The formed third stage has an influence on the nature of the dislocative structure, and therefore on improvement of mechanical properties.

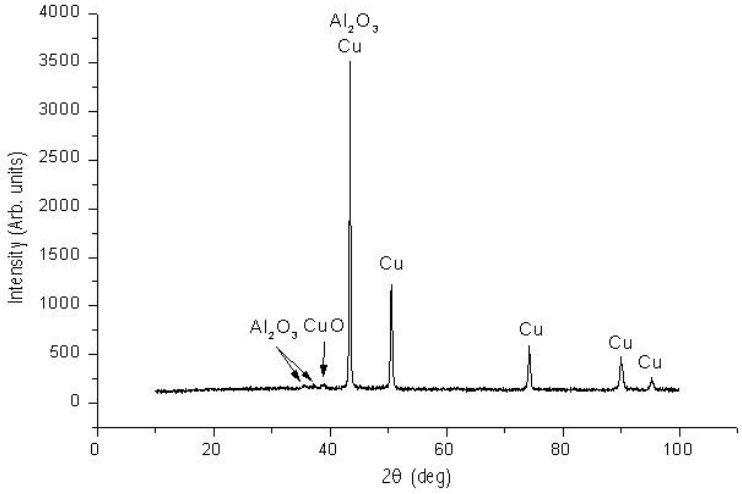

Fig. 3 RDA of Cu+3%Al_2O_3 powder after the reduction process

In Fig. 3 the RDA diagram is shown of Cu+3%Al_2O_3 powder after the reduction process, whereas the peaks of elementary copper and Al_2O_3 are detected. Apart from that, a peak is detected which corresponds to CuO. The reason of CuO appearance in the final structure is an incomplete reduction, i.e. it is necessary to perform a two-degree reduction with the aim of achieving the desired structure without oxygen surplus.

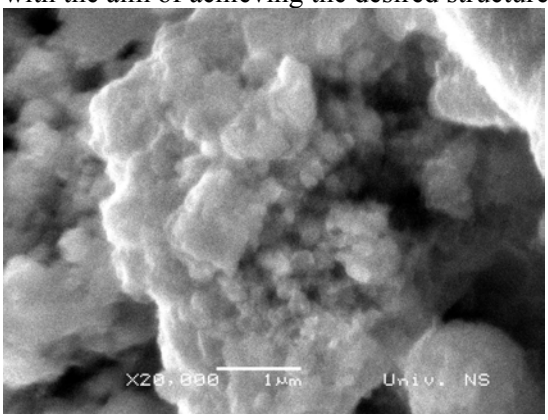

Fig. 4 SEM microphotograph of a Cu+3% Al_2O_3 powder composite, magnification ×20 000

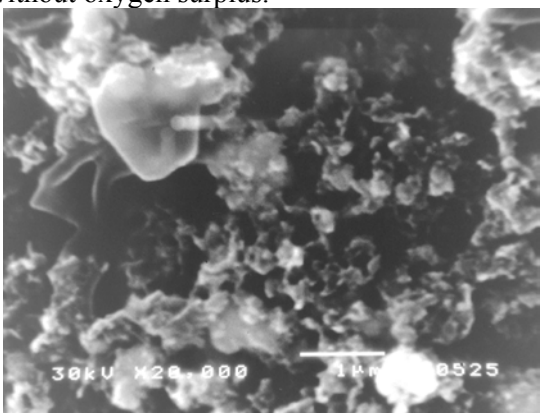

Fig. 5 SEM microphotograph of a Cu+5% Al_2O_3 powder composite magnification ×20 000

The obtained Cu-Al_2O_3 powders were characterized by Scanning Electronic Microscopy (SEM) at different magnifications (Fig. 4 and 5). The microstructure analysis of the obtained powder shows that the obtained particles of powders are of ≤500 nm size, which points to a possibility of synthesis of a nanocomposite Cu-Al_2O_3 system by a thermochemical method, starting from water solutions $Cu(NO_3)_2$ and $Al(NO_3)_3$. In the microphotographies the presence of agglomerates can be seen. The size of the obtained agglomerates is below 1μm.

As by the previously described procedure the powders with exceptionally fine particles are obtained, therefore the basic "condition" for the appearance of agglomerates is fulfilled. Namely, agglomeration of finer particles is a consequence of their large surface, of high surface energy, respectively and an effect of attracting forces between them. At the contact surfaces due to atomic connections in attracting strains are active on the interface, whose magnitude depends directly on the surface energy of particles, which are in contact. Taking into consideration the appearance of agglomerates, during future research, particular attention will be paid to obtaining of non-agglomerated powders, whereas active agents will be used for disagglomeration that cause corresponding rejecting forces between the particles and enable obtaining of a system with finely dispersed particles or ultrasound.

Such obtained powders were compacted with a compacting pressure of 500 MPa. Sintering of the compacted samples was performed in hydrogen atmosphere in isothermal conditions at temperatures of 800 and 900^{o}C for 30, 60, 90 and 120 minutes.

In Tab. I, the results of density examination, relative volume change, specific electric resistance and hardness are shown.

The results of research show that the density of the sintered samples at certain temperatures and times decrease with increasing Al_2O_3 content. However, with temperature increasing, density of the sintered samples increases. In the area of higher temperatures, when diffusion mobility of atoms is high enough, complex action of all diffusion mechanisms of mass transport is going on and they are responsible for the sintering process. With sintering temperature increase, the action of these mechanisms is more intensive, which directly affects formation of contacts between certain particles, growth of contact surfaces, formation of closed pores and grain growth. From this it follows that with temperature increase, after a certain time the sintered density increases.

Tab. I Average density, $\Delta V/V_o$, specific electric resistance and hardness for sintered samples of Cu-Al_2O_3 with different alumina content

Temperature °C	Time, min	Density $\bar{d}_s$, g/cm^3	$\Delta V/V_o$ (average)	Specific electric resistance $\bar{\rho}$, $10^{-6}\Omega$m	Hardness HRB 10/40 (average)
Cu+3%Al_2O_3					
800	15	5.58	0.1042	0.07413	88.2
	30	5.62	0.1194	0.07128	94.1
	60	5.70	0.1442	0.06581	102.1
	120	5.68	0.1448	0.06232	107.1
900	15	5.84	0.1821	0.06127	96.2
	30	6.14	0.1932	0.04027	101.9
	60	6.42	0.1933	0.03971	102.7
	120	6.44	0.1929	0.03927	102.3
Cu+5%Al_2O_3					
800	15	5.28	0.0612	0.08941	89.1
	30	5.34	0.0982	0.08827	101.2
	60	5.52	0.1191	0.08146	107.5
	120	5.58	0.1332	0.08007	109.1
900	15	5.94	0.1763	0.07413	99.1
	30	5.98	0.1824	0.06981	108.4
	60	6.14	0.1894	0.06218	118.5
	120	6.20	0.1888	0.06127	124.7

Relative volume change, as a measure of the system activity increases with the growth of the sintering temperature. Values of the relative volume change, at a certain temperature and sintering time, decrease with the increase of the Al_2O_3 content. Starting from

general kinetic equations, and with the aim of an analysis of the sintering kinetics, the obtained results are in accordance with other research results and certainly confirm earlier investigations of the possibility of the use of existing phenomenological equations of sintering [4].

Results of the examination of hardness of the sintered samples, as a measure of reinforcement of the highly conducting copper matrix, show that the growth of hardness value is a function of the decrease of specific electric resistance, i.e. of structural stabilization of the system. The results also point to the growth of hardness with Al_2O_3 content increasing, at a certain temperature and sintering time. The obtained results of hardness examination are the consequence of a relatively even distribution of Al_2O_3 dispersoides in the copper matrix. The relatively even distribution of alumina in the nanocomposite system, achieved during synthesis of powder by depositing from a liquid phase, causes stabilization if the dislocative structure and achievement of significant reinforcing effects by complex action of several mechanisms. Thereby, reinforcement of the material with a small-grain structure can be caused by reinforcing of the grain boundaries, dissolving reinforcement and by Orowan's mechanism.

With Al_2O_3 content increasing, the duration of the sintering process is increased. However, with increasing of the sintering temperature for a certain time, the value of specific electric resistance after sintering is decreased. In accordance with the stated and having in mind that the change of specific electric resistance represents a measure of structural stabilization of the system, it can be ascertained that at certain temperatures structural stabilization of the system has not occurred, i.e. the structural stabilization process is not completed. Also, with the sintering temperature increasing, the duration of the sintering process is shortened (Fig. 6). Based on the value of specific electric resistance, as a measure of structural stabilization, for the system with 3% of Al_2O_3 during sintering at 800°C, the sintering lasts 120 minutes, while for the same system during sintering at 900°C the sintering process lasts 30 minutes.

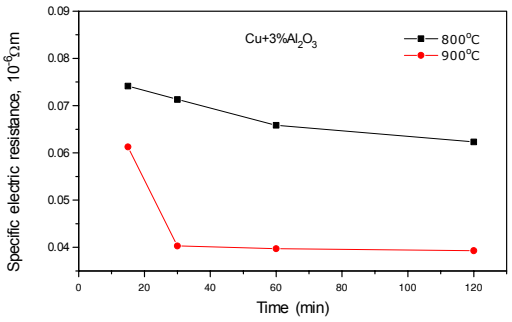

Fig. 6 Dependence of specific electric resistance on sintering time at different temperatures

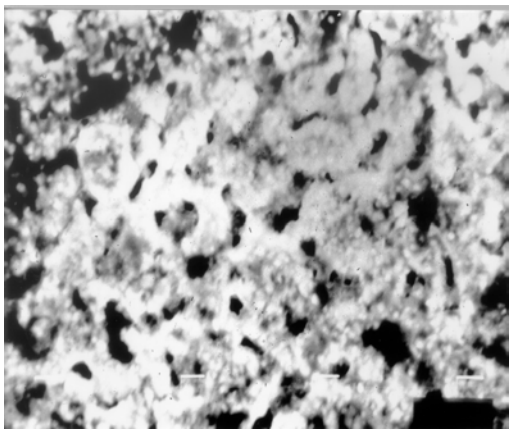

Fig. 7 SEM of the sintered Cu+3%Al_2O_3 system (800°C, 30 min), magnification ×3000

Analysis of the microstructure of corresponding sintered samples confirms the stated stipulations. In Fig. 7 a microstructure survey is given of the sample sintered at 800°C for 30 minutes, whereas it is clearly seen that the structural stabilization process is not completed. The microstructure is characterized by formation of closed pores, which is typical for a medium stage of sintering, and also, in certain areas, for achieving contacts between certain particles, typical for the starting sintering stage. In Fig. 8 and 9 a survey is given of the microstructure of samples sintered at 900°C for 15 and 30 minutes.

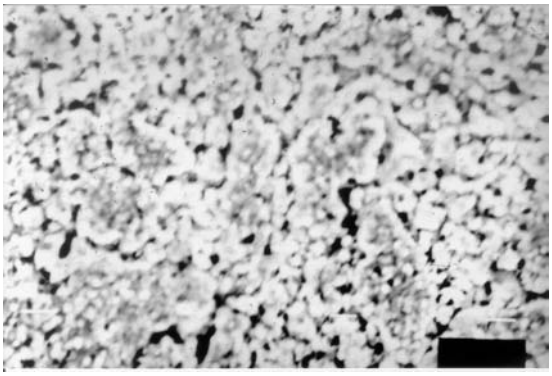

Fig. 8 SEM s of the sintered Cu+3% Al_2O_3 system (900°C, 15 min), magnification ×300

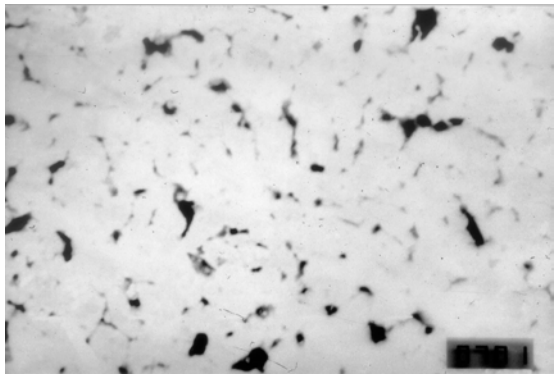

Fig. 9 SEM of the sintered Cu+3%Al_2O system (900°C, 30 min), magnification ×3000

The shown microstructures are characteristic for medium (Fig. 8), i.e. final stages (Fig. 9) of sintering, which is confirmed by analysis of structural stabilization of the system based on the value of specific electric resistance of the sintered samples. Apart from that, a relatively even distribution of pores can be seen in the examined samples, which, among others, significantly contributes to reinforcement of the highly conductive copper matrix.

Conclusion

Characterization of the obtained powder which comprised RDA and SEM, points to a possibility of synthesis of a nanocomposite Cu-Al_2O_3 system by a chemical method, depositing from a liquid phase, starting from $Cu(NO_3)_2$ and $Al(NO_3)_3$ water solutions.

Such obtained nanocomposite powders, whose structure is, with certain changes, preserved in the structure of the final product, has enabled obtaining of a sintered system with exceptional effects of reinforcement and a good combination of mechanical properties-electric properties. Thereby, the results of the hardness examination of sintered samples, as a measure of reinforcement of the highly conducting copper matrix, show growth of the hardness value as a function of decreasing specific electric resistance, i.e. structural stabilization of the system, confirmed by the microstructural research. The achieved significant effects of reinforcement are the consequence of a relatively even distribution of Al_2O_3 in the nanocomposite system, already achieved in the process of powder synthesis by depositing from a liquid phase.

Further research should be directed, first of all, towards identification of the $Cu_xAl_yO_z$ phase and studying its influence on stabilization of the dislocative structure, and thereby on improvement of mechanical properties and accomplishing of a good combination of mechanical-electric properties of the sintered systems.

References

1. P. K. Jena, E. A. Brocchi, M. S. Motta, Mater. Sci. Eng. A313, (2001), 180.
2. D. W. Lee, G. H. Ha, B. K. Kim, Scripta mater. 44, (2001), 2137.
3. Z. Anđić, M. Tasić, M. Korać, B. Jordović, A. Maričić, Materials and Technology, 38 (2004) 245.

4. M. M. Ristic, Fundamental Problems of the Science on Materials, TF Cacak and Serbian Academy of Science and Arts, Cacak, 2003 (in Serbian).
5. I.D. Marohov, L.I. Trusov, S.P. Chiszhnik, Ultrdispersnoe metallicheskie sredoe, Atomizdat, Moskva, 1977 (in Russian).
6. V.N. Lapovok, V.I. Novikov, Fizika tverdogo tela, 25, (1983), 1848 (in Russian).
7. P. K. Jena, E. A. Brocchi, I. G. Solórzano, M. S. Motta, Mat. Sci. Eng. A317, (2004), 72.
8. P. K. Jena, E. A. Brocchi, M. S. Motta, Mater. Sci. Eng. C 15, (2001), 175.
9. M. Entezarian, R. A. Drew, Mater. Sci. Eng. A212, (1996), 206.

Садржај:. *У раду је приказана синтеза композита на бази Cu-Al_2O_3 термохемијским путем уз упоредну анализу својстава добијених нанокомпозитних синтерованих узорака, које карактерише добра комбинација електрична-механичка својства, погодних за рад на повишеним температурама. Ултра фини и нанокристални прах Cu-Al_2O_3 добијен је хемијским путем полазећи од водених раствора нитрата до постизања захтеваног састава са 3 и 5% Al_2O_3. Синтеза композитних прахова се одвијала кроз неколико фаза: сушење распршивањем, оксидација добијеног праха прекурсора и затим редукција водоником до постизање коначног састава нанокомпозитног праха.Након карактеризације добијених прахова, која је обухватила испитивања методом сканирајуће електронске микроскопије (СЕМ) и рендгеноструктурне анализе (РДА), вршено је пресовање прахова притиском пресовања од 500 МРа. Синтеровање добијених узорака вршено је у атмосфери водоника у изотермским условима на температурама 800 и 900^o С у току 30, 60, 90 и 120 минута. Карактеризација добијеног Cu-Al_2O_3 нанокомпозитног синтерованог система је обухватила испитивања микроструктуре сканирајућом електронском микроскопијом, као и испитивања електричних и механичких својстава. Добијени резултати показују хомогену расподелу дисперзоида у структури, као и добре механичке и електричне особине.*

Кључне речи*: бакар, глиница, нанокомпозитни прахови, синтеровање.*