

SYNTHESIS AND SINTERING OF Cu-Al₂O₃ NANOCOMPOSITE POWDERS PRODUCED BY A THERMOCHEMICAL ROUTE

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ABSTRACT

By hydrometallurgy and powder metallurgy along with prognosis of physical-chemical properties, a synthesis of new improved materials can be successfully performed with in advance pre-set properties which is conditioned by a quality of starting powders i.e. by improving their structure. In accordance with that, this paper presents synthesis of the nanocomposite Cu-Al₂O₃ powder by thermochemical method and sintering with a comparative analysis of the mechanical and electrical properties of obtained solid samples. Nanocrystalline Cu-Al₂O₃ powders were produced by thermochemical method through following stages: spray-drying, oxidation of precursor powder, reduction by hydrogen and homogenisation. Characterization of powders included differential-thermal and thermo-gravimetric analysis (DTA-TGA), X-ray-diffraction (XRD) and analytical electron microscopy (AEM) coupled with energetic dispersive spectroscopy (EDS). Size of produced powders was 20-50nm with noticeable presence of agglomerates. Composite powders are characterized with Al₂O₃ homogenous distribution in copper matrix. Powders were cold pressed with pressure of 500 MPa and sintered. Sintering of the obtained samples was performed in the hydrogen atmosphere in isothermal conditions at temperature range from 800 to 900°C and time up to 120 minutes. Characterization of Cu-Al₂O₃ sintered system included examination of density, relative volume change, electrical and mechanical properties, examination of microstructure by SEM analysis, as well as by EDS. The obtained nanocomposite, which structure is with certain changes preserved in final structure, has provided sintered material with homogenous distribution of dispersoids in copper matrix, with exceptional effects of reinforcing and excellent combination of mechanical and electrical properties.

Key words: copper, alumina, powder, nanocomposite, sintering

INTRODUCTION

Research of nanocrystal materials in recent years has been intensified, primarily, due to their attractive potential, i. e. properties which are significantly improved compared to the conventional grain materials [1-3]. Nanostructure materials rank into the group of ultrafine, metastable structures which contain a high concentration of defects (point defects, dislocations) and boundaries (grain boundaries, interphase boundaries and etc). These materials are structurally different from crystals and amorphous forms,

because of the fact that grain boundaries and interphases represent a specific state of the solid matter, since the atoms on the boundaries are subjected to periodical potential field of crystal from the both sides of the boundary [2]. Obtaining powders of metals and alloys represents a starting stage in production of sintered metal materials. For obtaining sintered products with the demanded properties, the starting material, powder of metal or alloy, has a decisive importance. Having in mind that the starting structure, although suffering certain changes in further processing, basically is preserved in the structure of the final product [3], a necessity of working out greater number of methods for production of powders is imposed. Nanostructural materials can be synthesized in a controlled processes by the following methods: condensation from the gas stage, by synthesis in vacuum, highly energetic reactive milling, by precipitation from solution (sol-gel, hydrothermal synthesis, electrochemical synthesis, reactions in aerosol-reactive spraying, sublimated drying) [2, 4].

Although obtaining powders by the thermochemical method by depositing metal salts is not a new procedure, in the last time, due to development of contemporary materials with in advance pre-set properties, it has come to an intensive interest in this method of obtaining of, first of all nano powders. Obtaining of powders by a thermochemical method, where input materials are in liquid state, is not a new procedure and recently, due to development of contemporary materials with on advanced set of properties, it came to an intensive interest in this method for production of ultra fine and nano powders [4-6]. According to Jena et al. [5, 7] the synthesis of nanocomposite powders by a chemical method is possible in two ways. The first method comprises adding of a certain quantity of CuO into solution of aluminium nitrate. For other synthesis method aluminium nitrate and CuO are also mixed in appropriate proportion in distilled water. However, in this case, ammonium hydroxide is added to form gel for hydrolysis of aluminium nitrate up to hydroxide. In both cases mixture was annealed at 850°C, then reduced in hydrogen atmosphere at 975°C for 2h until the final structure was obtained.

Nanopowders give better performance in sintering due to their high surface area, and therefore, can tremendously improve the sintering process. The part produced with nanopowders will have high density, hardness and fracture toughness [8].

Fine dispersed particles introduction into the metal matrix, have significant reinforcing effects, which can be kept at elevated temperatures. For such reinforcement, ultra fine and nano particles of oxides are suitable, which, due to their hardness, stability and insolubility in the base metal also represent obstacles to moving of dislocations at the elevated temperatures. Maximum effects of reinforcing are achieved by even distribution of oxide particles and short distance, their fine dispersion in the matrix of base metal, respectively [9]. Research of dispersion reinforced materials, points out the significance of properties of the starting powders, importance of the starting structure, respectively, which, although suffer certain changes in further processing, basically remains preserved in the structure of the final product [3, 10]. Also very important aspect of dispersion strengthening is introduction of as less as possible amount of dispersed particles into volume of base material.

The above characteristics significantly determine the later-stage processing and sintering properties and eventually determine the microstructure of the composite. Uniform powder shape and narrow size distribution provide reduced microstructural defects in the sintered composites by enhancing powder flow and packing efficiency during slip casting and cold isostatic pressing (CIP) [11].

Sintering of ultradispersed powders occurs due to sliding of the particles along their borders [3], then to a dislocative mechanism which is responsible for creation of surplus vacancies. Concentration of surplus vacancies can reach a value which corresponds to the concentration of vacancies in the area of temperatures near to the materials melting temperature. On this basis, it could be concluded that diffusion activity during sintering of ultradispersed particles in the area of really low temperatures (0.1-0.3T_m) is conditioned by presence of unbalancing "recrystallization" vacancies. High recrystallization rate of ultradispersed particles are a consequence of the selfactivated recrystallization process.

EXPERIMENTAL

Previous papers related to similar topic [12, 13] show that for thermochemical synthesis of nanocomposite Cu-Al₂O₃ powder, as a transient component, soluble nitrates of copper and aluminium, Cu(NO₃)₂·3H₂O and Al(NO₃)₃·9H₂O, could be used. The synthesis process, in this work, followed four stages:

- obtaining 50wt.% water solution of Cu(NO₃)₂ and Al(NO₃)₃·9H₂O; quantities of salts were set so the requested composition of Cu-Al₂O₃ nanocomposite system with 3 and 5wt.% of alumina could be achieved,
- spray drying using modified house sprayer at temperature 180°C for producing precursor powder,
- annealing of precursor powder in air atmosphere at 900°C for 1 hour for forming copper oxide and phase transformation of Al₂O₃ up to thermodynamically stable phase α-Al₂O₃,
- reduction of thermally treated powders in hydrogen atmosphere at the temperature of 400°C for one hour, whereas copper oxide is transformed into elementary copper, and α-Al₂O₃ remains in the unchanged form,
- homogenisation in jar mill, type TMF HM1, milling chamber dimensions were internal diameter 180mm, height=160mm and volume 4L.

Characterization of the synthesised powders included DTA-TGA (NTZCH STA model 49EP), XRD (Siemens D500 PC, CuKα, 2θ=1-100°, pace (2θ) 0.02°) and AEM (JEOL 200CX).

After characterization of powders, cold pressing by action of pressing force was performed from the both sides in appropriate tool, 8×32×2mm by compacting pressure of 500 MPa. For pressing laboratory hydraulic power press "Zim", Russia was used. Sintering of the obtained samples was in hydrogen atmosphere in isothermic conditions at two different temperatures, 800 and 900°C, for 30, 60, 90 and 120 minutes. Sintering was performed in laboratory electroresistance tube furnace, power 3kW with thermoregulation ±1°C. Internal diameter of furnace is 45mm and length 100cm. Maximum temperature in working area (55cm) is 1300±1°C.

Characterization of sintered system of nanocomposite Cu-Al₂O₃ included examination of density, relative volume change, electrical and mechanical properties and examination of microstructure by SEM, as well as EDS analysis.

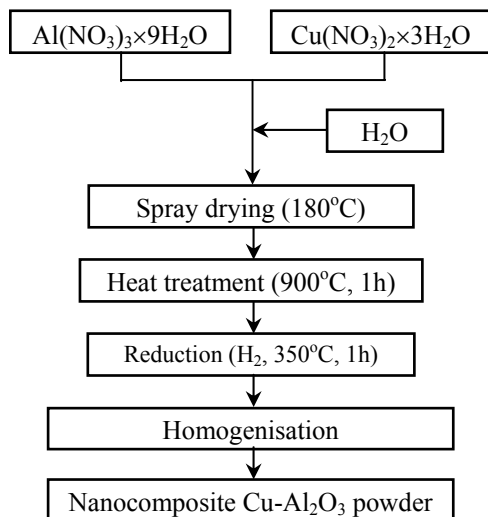


Fig. 1. Schematic presentation of the synthesis of Cu-Al₂O₃ nanocomposite powder by the thermochemical procedure

RESULTS AND DISCUSSION

Characterization of Cu-Al₂O₃ powders. DTA-TGA analysis of nanocomposite Cu-Al₂O₃ powder with 5 wt.%Al₂O₃, obtained by the thermochemical procedure show two endothermic peaks, at approximately 150°C and 250°C, which are related to evaporation and dehydration of the residual moisture. Exothermic peak at 324°C is accompanied by mass increment of 5,88%, which represents the beginning of the oxidation process of the present fine copper powder. Intensive mass increase at the TG curve is recorded at the temperature approximately 550°C, after which the TG curve is stabilized, showing insignificant mass increase of some percents only, whereas the overall mass increment during heating is 28,43%. Further increase of temperature indicates existence of four peaks of exothermic character at 684, 820, 885 and 938°C, which correspond to the phase transformations of Al₂O₃, occurring in this system.

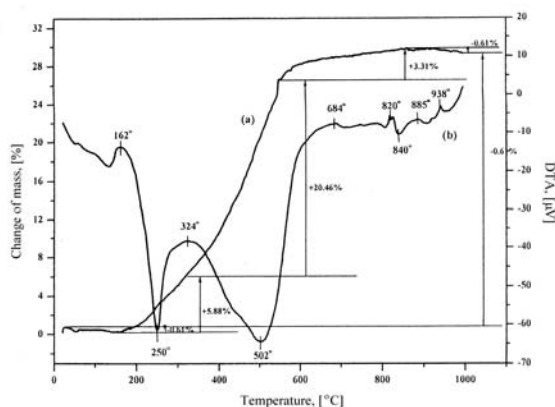


Fig. 2. DTA-TGA curves of the Cu-5 wt.%Al₂O₃ powder obtained by the thermochemical procedure

XRD of precursor powder produced by spray drying of copper and aluminium nitrates water solution, only the peaks corresponding to nitrates of copper and aluminium are identified in the structure which is in accordance with the experiment set-up [14].

In the X-ray differential analysis after annealing of dried powder detected peaks correspond to CuO and Al₂O₃. Also unidentified peak was detected. In accordance with literature [6] this peak corresponds to the third phase, Cu_xAl_yO_z which appears in the structure due to eutectic reaction of (Cu+Cu₂O) with Al₂O₃. Forming of this phase is thermodynamically possible on Cu-Al contact surfaces. During eutectic joining of copper and Al₂O₃, the eutecticum formed by heating up to eutectic temperature expands and reacts with Al₂O₃ creating Cu_xAl_yO_z, which is compatible from the both phases on inter-surface.

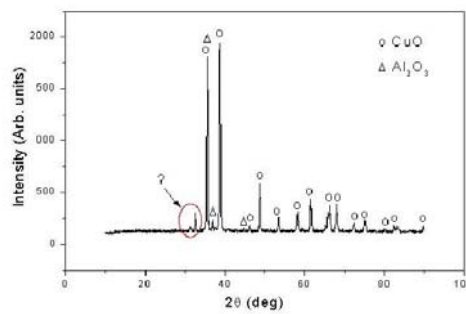


Fig. 3. XRD of the dried Cu+3 wt.%Al₂O₃ powder after thermal treatment

XRD of powder after the reduction show presence of peaks which correspond to the elementary copper and Al₂O₃ [14].

Characterization of the nanocomposite Cu-Al₂O₃ powder, obtained by the thermochemical procedure, has also included examinations by the AEM, which is shown in Fig. 4.

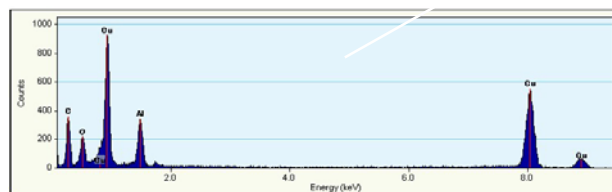
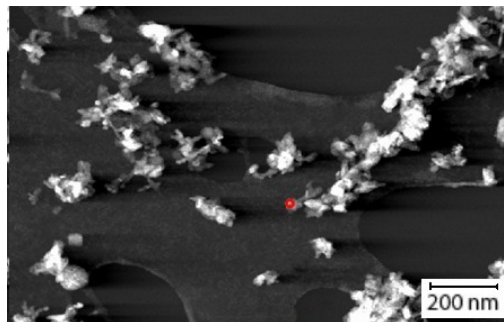


Fig. 4. AEM analysis of Cu-Al₂O₃ powder with 5wt% of Al₂O₃

Typical microstructural analysis of powders show possibility of synthesis of the nanocomposite Cu-Al₂O₃ system by the thermochemical procedure, starting from nitrates water solutions. Particles, size 20-50nm, are clearly noticeable, as well as presence of agglomerates >100nm. Particles are irregularly shaped with presence of nodular individual particles with rough surface morphology.

Agglomeration of finer particles is a consequence of their large surface, i.e. high surface energy and an effect of bonding forces between them, due to contacts between particles, interatomic bonds were introduced. The magnitude of those bonds depends directly on surface energy of particles. Taking into account appearance of agglomerates, a particular attention will be paid in future reaserach to production of non-agglomerated powders, where the surface active agents will be used for deagglomeration. Nowadays, applications of polyethyleneglycol [15] and ultrasonification [16-18] are under consideration.

Sintering. In Table 1, the results of density examination, relative volume change, specific electric resistance and hardness are given.

Table 1. Average density, $\Delta V/V_0$, specific electric resistance and hardness for sintered samples of Cu-Al₂O₃ with different alumina content

Temperature, °C	Time, min	Density \bar{d}_s , g/cm ³	$\Delta V/V_0$ (average)	Specific electric resistance $\bar{\rho}$, 10 ⁻⁶ Ωm	Hardness HRB 10/40 (average)
Cu+3wt.%Al₂O₃					
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+5wt.%Al₂O₃					
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

At temperatures higher than 900°C, e.g. 1000°C sintered plates were distorted with presence of molten phase. Due to small size of Cu-Al₂O₃ nanopowders, their maximum temperature of sintering is 900°C, which is lower than for conventional powders [10].

Results given in Table 1. show that the density of the sintered samples for the same sintering temperature and time decrease with Al₂O₃ content increasing. However, with temperature increasing, density of the sintered samples increases. In the higher

temperature range, where diffusion mobility of atoms is high enough, a complex diffusion mechanism of mass transport is occurring, which is responsible for the sintering process. With sintering temperature increasing, acting of complex mechanism is more intens, which directly affects formation of contacts between particles, growth of contact surface, formation of closed pores and grain growth. Therefore with temperature increase, during time it comes to increase of the sintered density.

Change of relative volume, as a measure of the system activity, is increased with sintering temperature increasing. Values of the relative volume change, at same temperature and sintering time, are decreased with Al₂O₃ content increasing. Starting from general kinetic equations, and with the aim of sintering kinetics analysis, the obtained results are in accordance with other results of the research and certainly confirm earlier investigations of the possibility to use existing phenomenological equations of sintering [3].

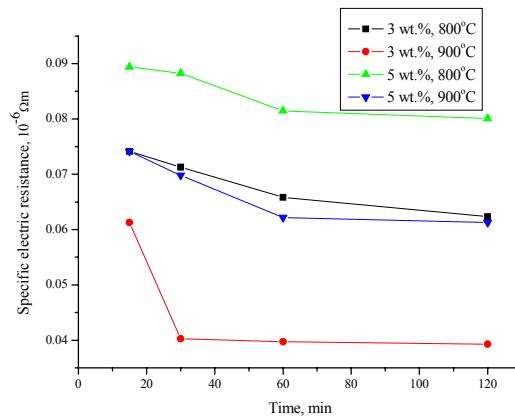


Fig. 5. Dependence of specific electric resistance on sintering time at different temperatures and alumina content

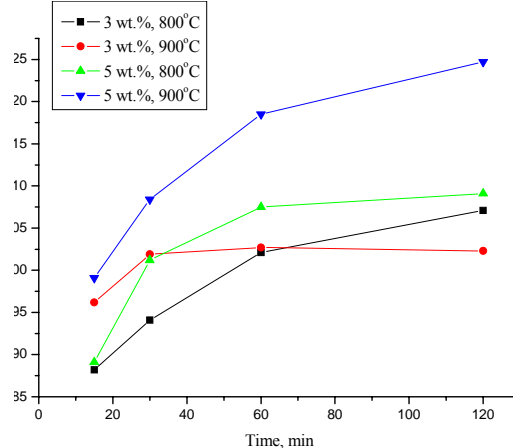


Fig. 6. Dependence of hardness on sintering time at different temperatures and alumina content

In Figs. 5. & 6. dependance of specific electric resistance and hardness, respectively, from temperature and time of sintering and alumina content are presented.

With Al_2O_3 content increasing, duration of the sintering process is increased. However, with increasing sintering temperature for same time, the value of specific electric resistance 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 it has not come to structural stabilization of the system, i.e. the structural stabilization process is not completed. Also, with the sintering temperature increasing, duration of the sintering process is shortened (Fig. 2). Based on the value of specific electric resistance for the system with 3% of Al_2O_3 during sintering at 800°C , the sintering lasts for entire 120 minutes, while for the same system during sintering at 900°C the sintering process lasts for 30 minutes.

Values of hardness of the sintered samples are in agreement with values of specific electric resistance, i.e. of structural stabilization of the system. These results also show increase of hardness with Al_2O_3 content increasing, for the same temperature and sintering time. The obtained results of hardness examination are a consequence of a relatively even distribution of Al_2O_3 dispersoids in the copper matrix. Relatively even distribution of alumina in the nanocomposite system, achieved during synthesis of powder during depositing from liquid phase, leads to stabilisation of dislocation structure and achieving of significant reinforcing effects by a complex acting of more mechanisms. Thereby, reinforcement of the small-grain material structure can be caused by reinforcing of the grain boundaries, dissolving reinforcement and by the Orowan's mechanism. Also dislocations can disappear in the grain boundaries or stop to multiply, since the Frenk-Read's sources of dislocations cannot be activated in small-grain multi-phase materials, which represent an additional mechanism of reinforcement [19].

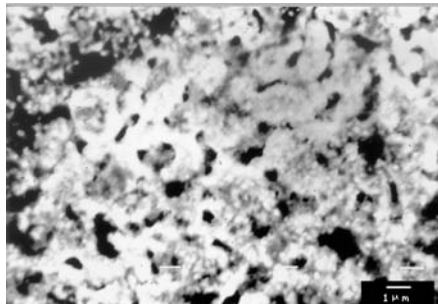


Fig. 7. SEM of the sintered $\text{Cu}+3\%\text{Al}_2\text{O}_3$ system (800°C , 30 min), magnification $\times 3000$

Analysis of the microstructure of corresponding sintered samples confirms assumptions. In Fig. 7 microstructure of the sample sintered at 800°C for 30 minutes is given, 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 stadium of sintering, and also, in certain areas, for achieving contacts between certain particles, typical for the beginning stadium of sintering. Fig. 8 and 9 presents the microstructure of the samples sintered at 900°C for 15 and 30 minutes. The shown microstructures are characteristic of medium (Fig. 8) and final stadium (Fig. 9) of sintering, confirming the analysis of system structural stabilization based on values of

specific electric resistance of the sintered samples. Apart from this, relatively even distribution of pores can be seen in the examined samples, which, among other, significantly contributes to reinforcement of highly-conductive copper matrix.

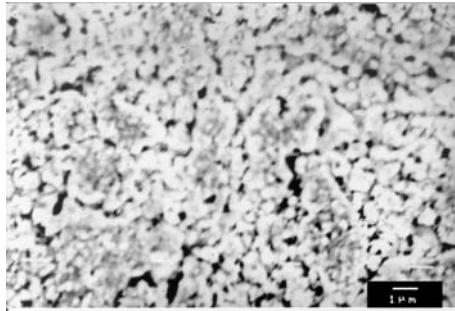


Fig. 8. SEM of the sintered Cu+3%Al₂O₃ system (900°C, 15 min), magnification $\times 3000$

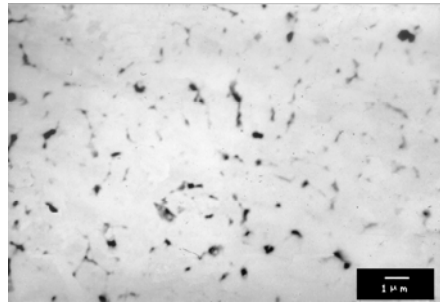


Fig. 9. SEM of the sintered Cu+3%Al₂O₃ system (900°C, 30 min), magnification $\times 3000$

For determination of distribution of elements in the structure, sample surface analysis has been done by EDS. SEM of the examined sample with the marked surface on which surface scanning has been performed is shown in the Fig. 10, and the results of examining sample of sintered Cu-3 wt.% Al₂O₃ system by EDS are given in Figure 11.

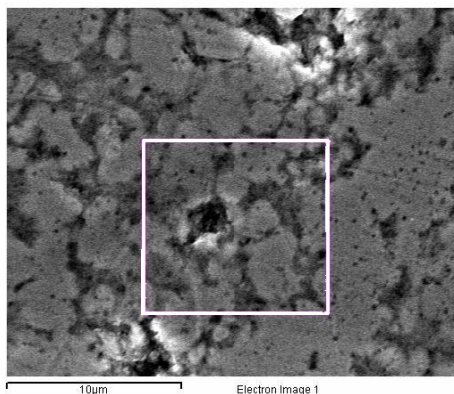


Fig. 10. SEM micrograph of sintered Cu-3 wt.% Al₂O₃ sample with the marked surface scanning area

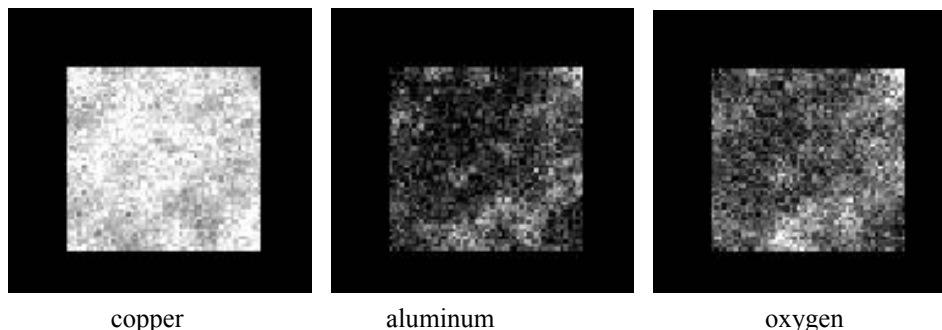


Fig. 11. Surface scanning of sintered Cu-3wt.% Al₂O₃ sample by EDS

Results of surface scanning show homogenous distribution of elements in the structure. From Fig. 11 it can be seen that copper covers almost entire surface of the sample. Results of scanning surface on aluminium and oxygen show that these two elements are less present in the structure of sintered sample and the surfaces they occupy are inter-lapping, which corresponds to existing of Al₂O₃ dispersoids in the structure. Except for aluminium and oxygen, also inter-lapping of all the three elements is noticeable, which leads to assumption on presence of Cu_xAl_yO_z phase [7]. Finally, for a detailed characterization of the third Cu_xAl_yO_z phase, an apparatus of exceptionally high resolution is necessary.

CONCLUSION

Detailed characterization of the obtained powder which comprised DT/TGA, XRD and AEM, points out possibility of synthesis of nanocomposite Cu-Al₂O₃ system by a thermochemical method, by deposition from aqueous solutions of metal salts, Cu(NO₃)₂ and Al(NO₃)₃. The microstructure of the obtained powder clearly indicated particles of 20-50nm size.

Such obtained nanocomposite powders, with structure preserved in the structure of the final product, has provided production of the sintered system with exceptional effects of reinforcement and a good combination of mechanical and electrical properties. Thereby, the results of the hardness examination of the sintered samples show that the growth of the hardness value is in function of decreasing specific electric resistance, i.e. structural stabilization of the system, which was confirmed by the microstructural research. The achieved significant effects of reinforcement are consequence of relatively even distribution of Al₂O₃ in the copper metal matrix, already achieved in the process of powder synthesis by depositing from the liquid phase, which is also confirmed by the results of the sample surface analysis by EDS.

Identification of Cu_xAl_yO_z phase in structure and studying its influence to stabilization of dislocative structure, and thereby to improvement of mechanical properties and accomplishing of a better combination of mechanical and electrical properties of the sintered systems is an essential aspect of this research and will be continued.

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