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Synthesis and Characterization of Dispersion Reinforced Sintered System Based on Ultra Fine and Nanocomposite Cu-Al_2O_3 Powders

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1. Introduction

The research in nanocrystal materials has intensified in the last years, primarily due to their attractive potential, i.e. properties which are significantly improved compared to large grain materials [Karch, et al., 1987; Milošević, 1999; Ristić, 2003]. Nanostructure materials rank in the group of ultrafine metastable structures which contain a high defect concentration (spotted defects, dislocations, grain boundaries, interphase boundaries, etc). These materials are structurally different from crystal and amorphous forms, due to the fact that grain boundaries and the interphase represent a specific condition of the solid matter, since the atoms on the boundary are subject to a periodical potential field of crystal from both sides of the boundary [Milošević, 1999]. Nanostructural materials can be synthesized in controlled processes by the following methods: highly energetic reactive milling [Ahn, 1996], solution precipitation (sol-gel [Ruys & Mai, 1999], hydrothermal synthesis [Byrappaa & Adschirib, 2007], electrochemical synthesis [Yuana et al., 2007]), internal oxidation [Afshar & Simchi, 2008] etc. The synthesis of nanoparticles is generally performed by the methods of "from the bottom - to the top approach" ("bottom-up approach"), such as the deposition from the gas or liquid phase, thermal decomposition (evaporation-condensation), and the methods based on "from the top - to the bottom approach" ("top-down approach"), wherein mechanical grinding processes are distinctive. When using the bottom-up method, nanoparticles are formed atom by atom or molecule by molecule, whereas when using the top-down approach, large volumes are gradually reduced in proportion to reach the nanometer dimensions [Hosokawa, 2007].

The synthesis of metal and alloy powders represents the starting stage in the production of sintered metal materials. For obtaining sintered products with the required properties, the starting material, powders of metals or alloys, are of decisive importance. Since the starting structure undergoes certain changes in further processing, but, basically, remains preserved in the structure of the final product [Anđić, 2007; Ristić, 2003], there is an increased necessity for a larger number of methods for producing powders. Although obtaining powders by a thermochemical method, where the input materials are in liquid phase, is not a new

procedure, the interest in this method has intensified recently, due to the development of contemporary materials with pre-set properties, especially in terms of nano-powder production [Jena et al., 2001; Lee et al., 2001; Wu et al., 2001].

This paper presents the synthesis and characterization of Cu-Al_2O_3 nanocomposite systems using a combination of procedures suitable for obtaining sintered materials with nanocrystal structure and homogenous distribution of dispersoids in the basic material matrix, characterized by a good combination of electro–mechanical properties. The obtained sintered materials with nanocrystal structure based on Cu-Al_2O_3 nanocomposite powders have a wide application in the field of electronics and electrical engineering. They are used as electrodes for spot welding, different contact materials, various switches, as well as thermal and electric conductors, microwave tubes, commutators for starting helicopter engines, relays, etc. In addition to this, there is a significant possibility of using these systems as coatings with low porosity and high adhesion degree [Anđić et al., 2006, 2007; Korać et al., 2007].

Disperse reinforcement has recently raised great theoretical and practical interest. It is known that the introduction of finely dispersed particles into a metal matrix could have significant reinforcing effects, which can be maintained at elevated temperatures. Consequently, dispersion reinforced materials of this type show good mechanical properties during exploitation at elevated temperatures and during preservation at room temperature after high temperature exposure. The improvement of mechanical properties is achieved without any significant loss in electric and heat conductivity [Naser et al., 1997; Trian et al., 2006; Trojanová et al., 1999]. For such reinforcement, ultra fine particles and nano particles of oxides are suitable, which, due to their hardness, stability and insolubility in a metal matrix present exceptionally good obstacles to dislocation motion at elevated temperatures. Dispersed phases present in metals before deformation, affect the structural design and behaviour of metals when heated. The deformed material structure created in the presence of secondary phases depends on the size and distance of particles. Small finely dispersed particles which are at a smaller distance cause the high density of evenly distributed dislocations. The borders of subgrains and individual subgrains are vaguely expressed, and the curve of the lattice, i.e. the discrepancy in the orientation of adjacent subgrains is too small for them to become the germs of new recrystallised grains, which consequently leads to the reduction in the speed of grain production, i.e. in recrystallisation speed, which may be totally obstructed. Finely dispersed particles at a smaller distance obstruct, i.e. reduce subgrain moveability so that the subgrains which might transform into germs are activated with great difficulty and they are turned into new recrystallised grains. Finely dispersed particles and their homogenous distribution in the base metal matrix cause stabilization of dislocation substructure formed during deformation and create significant reinforcing effects by a complex action of different mechanisms [Lianga et al., 2004; Plascencia & Utigard, 2005]. The third, $Cu_xAl_yO_z$, phase has a considerable influence since it appears in the structure due to the eutectic reaction on Cu-Al contact surfaces [Jena et al., 2001, 2004; Korać et al., 2010]. Accordingly, it has been concluded that binding mechanisms on $Cu/CuAlO_2$, $Cu_2O/CuAlO_2$ and $Al_2O_3/CuAlO_2$ inter-surfaces are considerably stronger compared to those on Cu/Al_2O_3 and Cu_2O/Al_2O_3 contact surfaces, and indicated that the formed third phase influences the stabilization of dislocation substructure and thereupon the improvement of mechanical properties and the achievement of a good combination of

electro - mechanical properties of the sintered systems [Entezarian & Drew, 1996; Lee & Kim, 2004; Yi et al., 1999; Yoshino & Shibata, 1992].

The characteristics of starting powders significantly determine the later-stage processing and sintering properties and eventually determine the microstructure of the composite. Nano-powders give better performance in sintering due to their high surface area and, therefore, can tremendously improve the sintering process. The parts produced from nano-powders will have high density, hardness and fracture toughness [http://www.nanopowders.com/].

Sintering is an extremely complex process with a complex action of multiple mechanisms of material transfer and the distribution and change of particle shapes, which are all processes that are closely connected with the off-balance condition of the crystal lattice and that have a considerable influence on the properties of the obtained metal materials. The driving force of sintering is the free energy of the system, which is off-balance from the thermodynamic point of view. This results from the highly developed free surface of powder particles and the presence of balance (point defects) and off-balance defects (dislocations) [Anđić, 2007; Ristić, 2003]. Sintering of ultradispersed powders occurs due to particles sliding along their borders and a dislocation mechanism that is responsible for the creation of surplus vacancies. Surplus vacancy concentrations can reach a value which corresponds to the vacancy concentration in the area of temperatures close to the temperatures of material melting. On the basis of this, it can be concluded that diffusion activity during sintering of ultra dispersed particles in the area of really low temperatures (0.1-0.3Tm) is conditioned by the presence of unbalancing 'recrystallization' vacancies. High recrystallization speeds of ultradispersed particles are a subsequence of the process of recrystallization self-activation [Lapovok & Novikov, 1983; Mohorov et al., 1977; Ristić, 2003]. A considerable number of studies have examined fundamental issues related to the mechanism and kinetics of sintering [Lapovok & Novikov, 1983; Mohorov et al., 1977; Ristić, 1993, 2003], by using the existing phenomenological equations which have considerably contributed to the theory and technology of sintering and also enabled numerous technological processes in the production of various ceramic and metal-ceramic materials. On the basis of the kinetic analysis of the process of sintering powders from the Cu-Al_2O_3 system, it was concluded that sintering process occurs in two phases. Given that the volume diffusion requires higher activation energy, the results of the kinetic analysis indicate that the surface diffusion and grain- boundary diffusion occur in the first phase, whereas the mass transfer occurs in the second phase during the process of volume diffusion [Ristić, 1993, 2003]. The kinetic analysis results indicate higher values of activation energy due to the exceptionally small sizes of particles of nano-composite Cu-Al_2O_3 powder, i.e. their large surface and an extremely large surface between individual particles created at the very beginning of the process.

As noted, disperse phases present in the material prior to deformation influence structure designing, whereas uniform dispersion of nanoparticles of Al_2O_3 in a copper matrix provides completely new, improved, even unexpected properties. However, these unique properties essentially depend on the microstructure, which is a direct consequence of the synthesis procedure of Cu-Al_2O_3 nanocomposites. By hydrometallurgy and powder metallurgy along with prognosis of physical-chemical properties, a synthesis of new improved materials can be successfully performed with pre-set properties which are conditioned by the quality of starting powders i.e. by the improvement of their structure. In

addition to the conventional methods of obtaining composites based on Cu-Al_2O_3, the paper shows the synthesis of these composites in a chemical way by liquid phase deposition, with a comparative analysis of the properties of the obtained nano-composite sintered samples characterized by a good ratio of electro - mechanical properties, suitable for operations at high temperatures.

2. The synthesis and characterization of ultrafine and nanocomposite Cu-Al_2O_3 powder

2.1 The synthesis of ultrafine and nanocomposite Cu-Al_2O_3 powder

Soluble 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, were used for the synthesis of nanocomposite Cu-Al_2O_3 powder by a thermochemical method. The synthesis process developed in five stages (Fig. 1), as follows:

- obtaining 50% of water solution in which $Cu(NO_3)_2 \times 3H_2O$ 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 5wt.% of alumina,
- drying by spraying, using a modified house sprayer at a temperature of 180°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°C for one hour with the aim of forming copper oxide and phase transformation of Al_2O_3 up to a thermodynamically stable α-Al_2O_3 phase,
- 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 -Al_2O_3 remains unchanged,
- homogenisation in a jar mill, type HM1, milling chamber dimensions with an internal diameter of 180mm, height of 160mm and volume of 4L.

2.2 The characterization of ultrafine and nanocomposite Cu-Al_2O_3 powder

The characterization of the produced powders consisted of determining the particle specific area, the pouring density and fluidness by the differential thermal and thermogravimetric analysis (DT-TGA), X-ray diffraction (XRD) and analytical electron microscopy (AEM) coupled with energy dispersive spectroscopy (EDS).

The fluidness and pouring density were determined by the standard method, using a Hall apparatus, and in accordance with the appropriate standards (ASTM B13 and ASTM B212). The specific area of the particles was determined by the gas absorption method (BET).

DTA-TGA was performed using a NETZCH STA model 409EP up to 1100°C. A Pt-Pt-Rd alloy S-type thermocouple was utilized. α-Al_2O_3 was used as the reference material.

The quantitative X-ray diffraction analysis of the powder was performed using a Siemens D500 PC difractometer, CuK_α radiation, in the range $2\theta = 0\text{-}100^o$ with a step of (2θ) 0.02^o.

The analytical electron microscopy (AEM) coupled with energy dispersive spectroscopy (EDS) was carried out on a JEOL 200CX microscope on powders spread on conductive carbon tape.

The results of the determination of fluidness, pouring density and specific area of the nanocomposite Cu-Al_2O_3 powder particles, with different dispersoid contents, obtained by

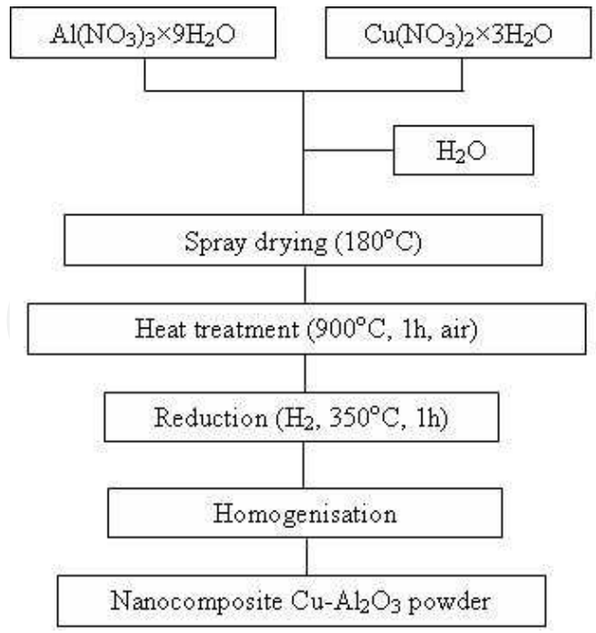


Fig. 1. Schematic presentation of the synthesis of Cu-Al_2O_3 nanocomposite powder by the thermochemical procedure

the thermochemical procedure are presented in Table 1. The results of the determination of fluidness, pour¬ing density and specific area of the obtained nano-structured composites with different amounts of Al_2O_3 dispersed in a copper matrix show that all investigated powders are not fluid and that mean values of pouring density and specific area are the same for different contents of Al_2O_3 (1.04 g/cm3 and 0.75 m^2/g, respectively).

Al_2O_3 (wt.%)	Fluidness	Pouring density (g/cm^3)	Specific area (m^2/g)
3	not fluid	1.04	0.75
5	not fluid	1.04	0.75

Table 1. Fluidness, pouring density and specific area of particles of the nanocomposite Cu-Al_2O_3 powder obtained by the thermochemical procedure (mean values)

The DTA-TGA curves of the nanocomposite Cu-Al_2O_3 powder with 5wt.% Al_2O_3, obtained by the thermochemical procedure are shown in Fig. 2. Two endothermic peaks may be observed on the DTA curve at approximately 150°C and 250°C, and they correspond to the evaporation and dehydratation of residual moisture, respectively. The exothermic peak at 324°C was accompanied by a mass increment of 5.88% and represents the beginning of fine copper powder oxidation. An intensive mass increase on the TG curve was recorded up to approximately 550°C, after which the TG curve levelled off, showing an insignificant mass increase of only a few percent. The overall mass increment during heating was 28.43%. Several exothermic peaks were observed at 684, 820, 885 and 938°C due to the phase transformations of Al_2O_3.

The XRD analysis of the spray-dried Cu-Al_2O_3 powder with 3wt.% of dispersoid is shown in Fig. 3. In accordance with the experimental set-up, only the peaks which correspond to copper and aluminium nitrates were registered in the structure.

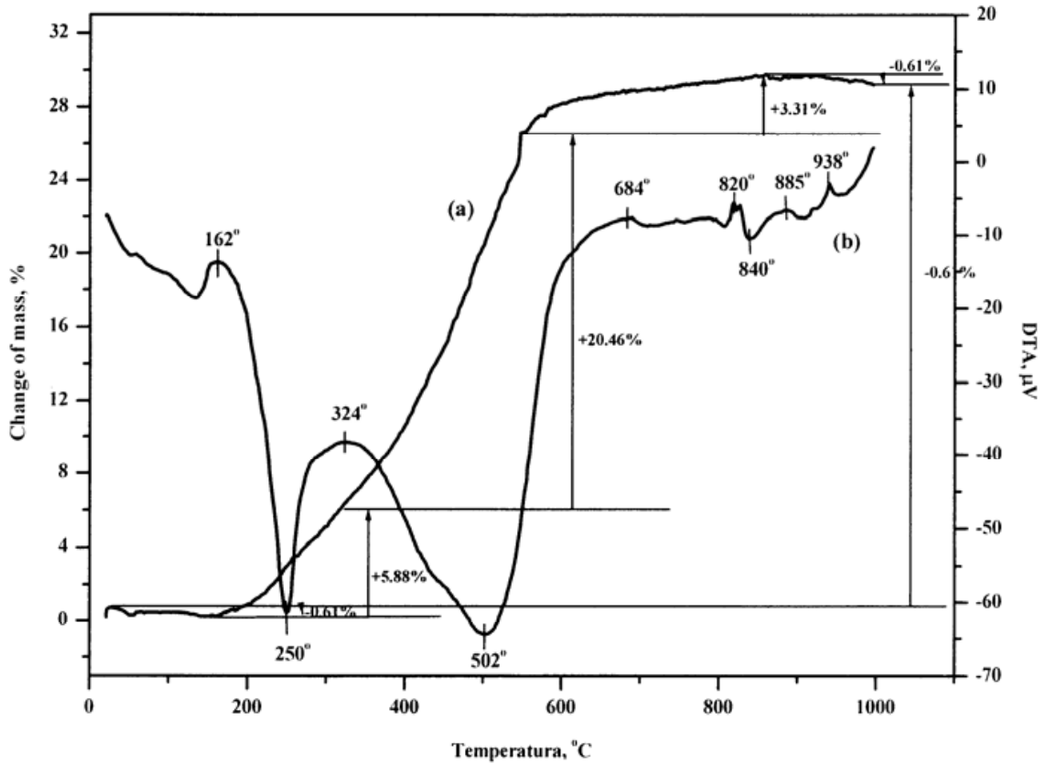


Fig. 2. DT-TGA curves of the Cu-5wt.%Al_2O_3 powder obtained by the thermochemical procedure

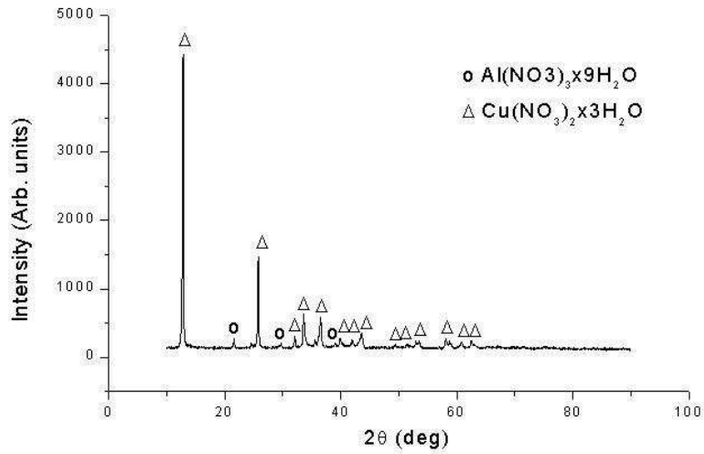


Fig. 3. XRD of the Cu-3wt.%Al_2O_3 powder after spray-drying

The X-ray diffraction analysis after annealing the dried powder is shown in Fig 4. The detected peaks correspond to CuO and Al_2O_3. An unidentified peak was also detected. According to previous studies, [Entezarian & Drew, 1996; Jena et al., 2001, 2004], this peak

corresponds to the third phase, $Cu_xAl_yO_z$, which appears in the structure due to the eutectic reaction of (Cu+Cu_2O) with Al_2O_3. The formation of this phase is thermodynamically posible on Cu-Al contact surfaces. During the 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 forming $Cu_xAl_yO_z$, which is compatible with both phases on the intersurface. The formed third phase influences the nature of the dislocation structure and also the improvement of the mechanical properties and the creation of a good combination of mechanical and electrical properties of the sintered systems.

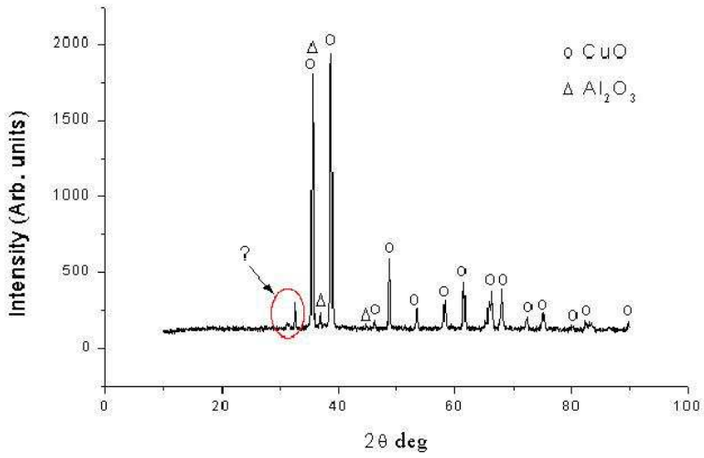


Fig. 4. XRD of the dried Cu-3wt.%Al_2O_3 powder after thermal treatment

XRD of powder after the reduction (Fig. 5) shows the presence of peaks which correspond to the elementary copper and Al_2O_3.

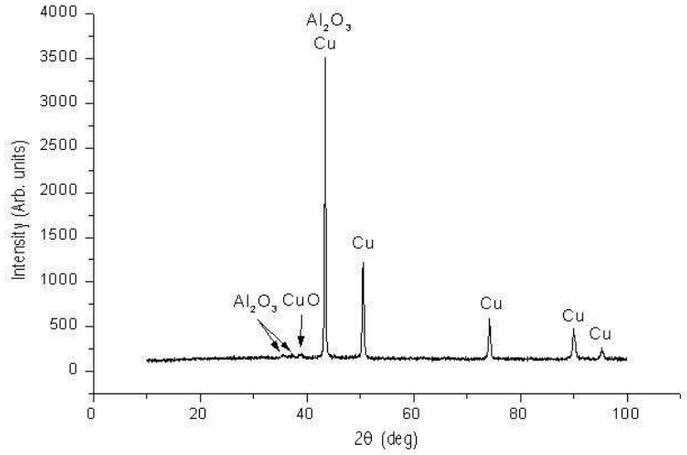


Fig. 5. XRD pattern of the Cu-3wt.%Al_2O_3 powder after reduction

The obtained powders were analyzed at the National Center for Electron Microscopy, University of California, Berkeley, by Analytical Electron Microscopy (AEM) with a suitable EDX (at the marked spot), as presented in Figure 6.

Particles of 20-50nm in size are clearly noticeable. The shape of particles is irregular, with the presence of individual particles of nodular shape. The surface morphology is rough. The agglomerates of the size >100nm, formed by the individual particles of the stated size are also observed. The agglomerates are of a spongy shape. Since the powders with exceptionally fine particles are obtained by the previously described procedure, the basic "condition" for the appearance of agglomerates is fulfilled. Namely, agglomeration of finer particles is a consequence of their large surface and high surface energy, respectively, and of the effect of attracting forces acting between them. The creation of attracting strains, the magnitude of which depends directly on the surface energy of the particles which are in contact, occurs on contact surfaces due to the atomic connections in the interface.

With the EDS composition of nanocomposite Cu-5wt.% Al_2O_3 powder is determined as shown in Figure 6. The EDS analysis of the spot marked in Figure 6. shows that the identified peaks correspond to Cu, Al and O. The intensity of peaks corresponds to the required composition of the examined systems. Therefore, the peak corresponding to copper is considerably higher than the peaks corresponding to aluminum and oxygen. The obtained results of the examinations are statistically processed and shown in Table 2.

The characterization of the obtained powder indicates a possibility of the synthesis of a nanocomposite Cu-Al_2O_3 system by a thermochemical method, starting from water solutions $Cu(NO_3)_2$ and $Al(NO_3)_3$.

Element	Weight%	Atom. %	Measurement discrepancy	Detection correction	k - factor	Absorption correction
O	6,087	20,191	0.189	0.376	2,702	1,000
Al	1,224	2,408	0.047	0.952	1,044	1,000
Cu	92,687	77,399	0.502	0.996	1,743	1,000

Table 2. Statistical data for the EDS analysis

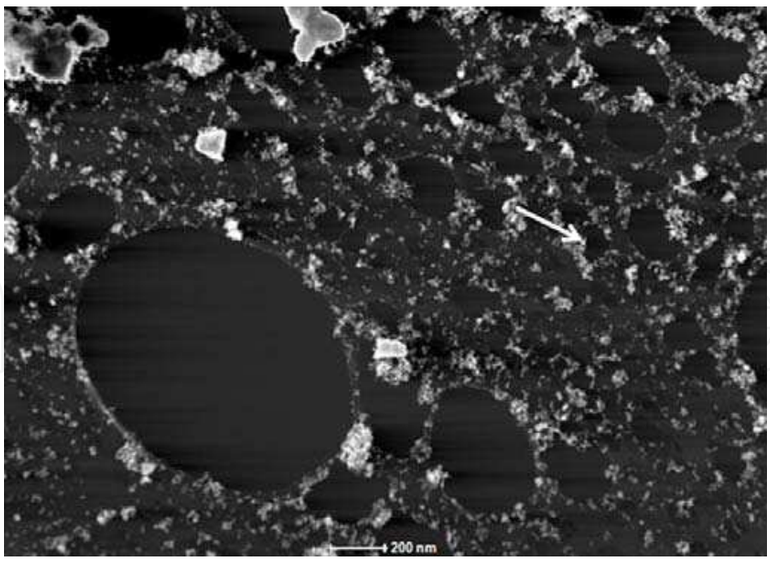
3. Dispersion reinforced sintered system based on ultra fine and nanocomposite Cu-Al_2O_3 powders

After the characterization of powders, cold pressing by pressing force was performed from both sides with an apropriate tool with the dimensions of 8×32×2mm under compaction pressure of 500MPa. The hydraulic lab power press "ZIM", Russia, was used for pressing.

Sintering of the obtained samples was carried out in hydrogen atmosphere in isothermal conditions at two different temperatures, 800 and 900°C, for 30, 60, 90 and 120 minutes. Sintering was performed in a laboratory electric resistance tube furnace, with the power of 3kW and thermoregulation of ±1°C. The internal diameter of the furnace was 45mm and length 100cm. The maximum temperature in the working area (55cm) was 1,300±1°C.

The characterization of the Cu-Al_2O_3 sintered system included examinations of density, relative volume change, electrical and mechanical properties, examination of microstructure by the scanning electronic microscopy (SEM), the energetic dispersion spectroscopy (EDS), the transmission electron microscopy (TEM) and the high-resolution transmission electron microscopy (HRTEM), examinations by the focused ion beam (FIB) method and examinations of the selected area diffraction pattern (SADP).

The values of density, relative volume change, hardness and specific electrical resistence were determined by the standard methods in the above-mentioned examinations. The



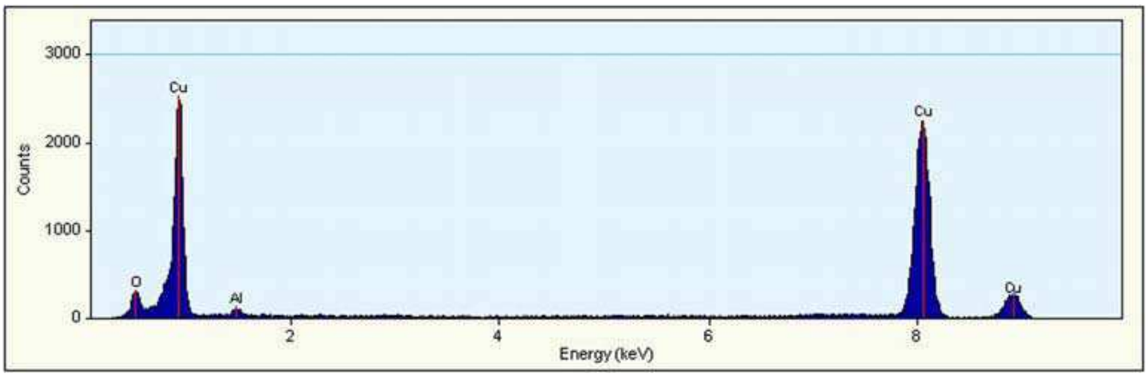


Fig. 6. AEM analysis of Cu-Al_2O_3 powder with 5wt.% of Al_2O_3

scanning electron microscopes, types JEOL JSM-T20 and JEOL 5300, as well as the analytical electron microscope (AEM), type JEOL 200CX with the ability to work in TEM and STEM modes between 80 and 200kV, were used for the examination of the microstructure of sintered systems. The contents of the examined systems were determined qualitatively by the energy dispersive spectroscopy (EDS – JEOL Superprobe 733, 20kV). HRTEM analysis was performed using Philips CM200/FEG.

The results of density examination, relative volume change, specific electric resistance and hardness are shown in Table 3..

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

Temperature, °C	Time, min	Density $\bar{d}_s$, g/cm^3	$\Delta V/V_o$ (average)	Specific electric resistance ρ, $10^{-6}\Omega m$	Hardness HRB 10/40 (average)
Cu-3wt.%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 wt.%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

Table 3. Average density, $\Delta V/V_0$, specific electric resistance and hardness for sintered samples of Cu-Al_2O_3 with different alumina content

The relative volume change, as a measure of the system activity increases with the growth of the sintering temperature. The values of the relative volume change, at a certain temperature and sintering time, decrease with the increase in 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 [Ristić, 2003].

The dependence of hardness and specific electric resistance on the temperature, time of sintering and alumina content are presented in Figs. 7 and 8, respectively.

The 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 dispersoids 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 of the dislocation structure and achievement of significant reinforcing effects by a complex action of several mechanisms. Thereby, reinforcement of the material with a small-grain

structure can be caused by the reinforcement of the grain boundaries, dissolving reinforcement and by Orowan´s mechanism. Additionally, dislocations can disappear in the grain boundaries or cease to multiply, since the Frenk-Read source of dislocations cannot be activated in small-grained multi-phase materials, which represents an additional mechanism of reinforcement [Morris, D.G. & Morris M.A., 1992].

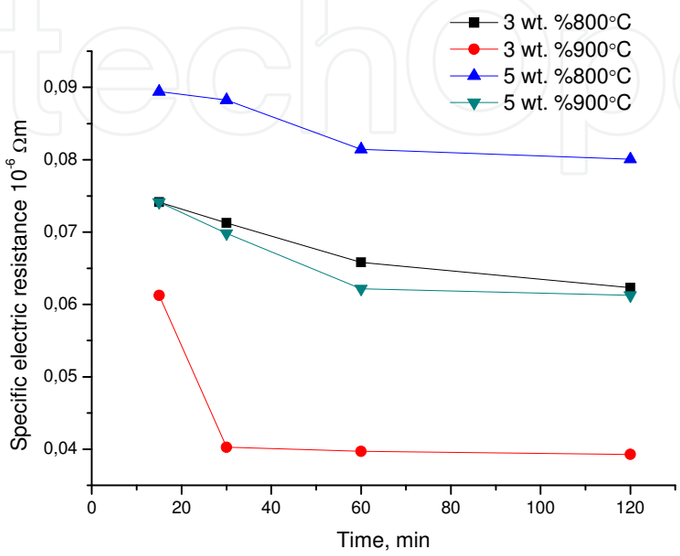


Fig. 7. Dependence of hardness on the sintering time at different temperatures and different alumina contents

With Al_2O_3 content increasing, the duration of the sintering process is increased. However, with increasing of the sintering temperature for a period of 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 the 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. 8). Based on the value of specific electric resistance, as a measure of structural stabilization, for the system with 3wt.% Al_2O_3 during sintering at 800°C, sintering lasts 120 minutes, whereas for the same system during sintering at 900°C the sintering process lasts 30 minutes.

The analysis of the mechanical and electrical properties of Cu-Al_2O_3 sintered systems showed that for the system with 3wt.%Al_2O_3 structural stabilization had finished after 30 min of sintering at 900°C, with significant reinforcment effects. For the other systems, structural stabilization was not completed even after 120 min. The optimal solution for the production of dispersed reinforced Cu-Al_2O_3 is the process conducted at 900°C for 30 min with 3wt.%Al_2O_3, which was confirmed by microstructural analysis, presented in Figs. 9-11.

Considering the fact that the structure takes a central place in the complex of the materials science as a parameter through which the connection between the properties and synthesis of new materials is expressed i.e. since it directly determines mechanical as well as electrical

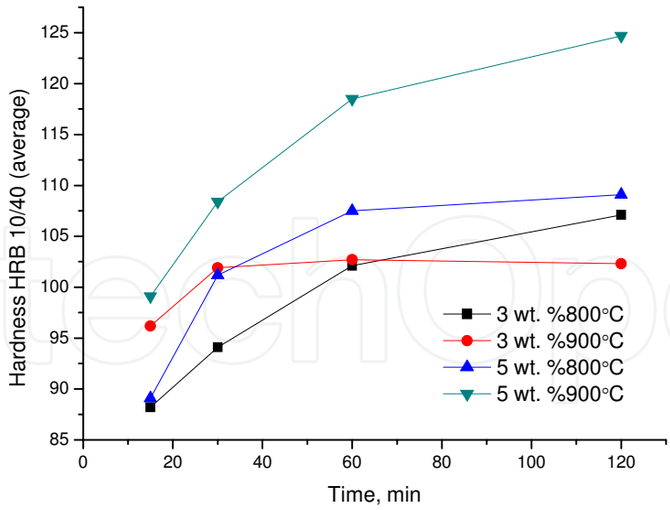


Fig. 8. Dependence of specific electric resistance on sintering time at different temperatures and different alumina contents

properties, the following development of microstructural constituents through all individual stages of the technological process is of an exceptional importance. The analysis of the microstructure of the corresponding sintered samples confirms the stated stipulations. In Fig. 9 a microstructure survey of the sample sintered at 800°C for 30 minutes is given, and it is clearly seen that the structural stabilization process is not completed. The microstructure is characterized by the formation of closed pores, which is typical of a medium stage of sintering, and also, in certain areas, by achieving contacts between certain particles, which is typical of the starting sintering stage. In Figs. 10 and 11. a survey of the microstructure of samples sintered at 900o°C for 15 and 30 minutes is given. The shown microstructures are characteristic of the medium (Fig. 10), i.e. final stages (Fig. 11) of sintering, which is confirmed by the analysis of the 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 other things, significantly contributes to the reinforcement of the highly conductive copper matrix.

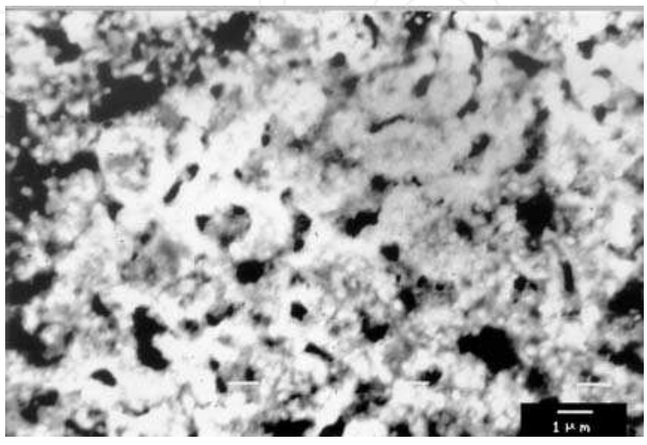


Fig. 9. SEM of the sintered Cu-3wt.%Al_2O_3 system (800°C, 30 min)

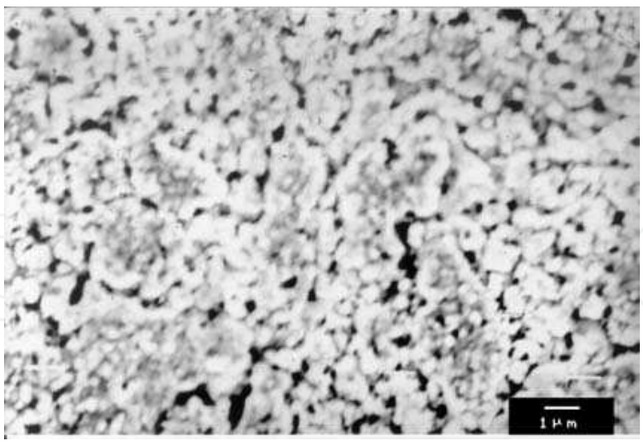


Fig. 10. SEM of the sintered Cu-3wt.%Al_2O_3 system (900°C, 15 min)

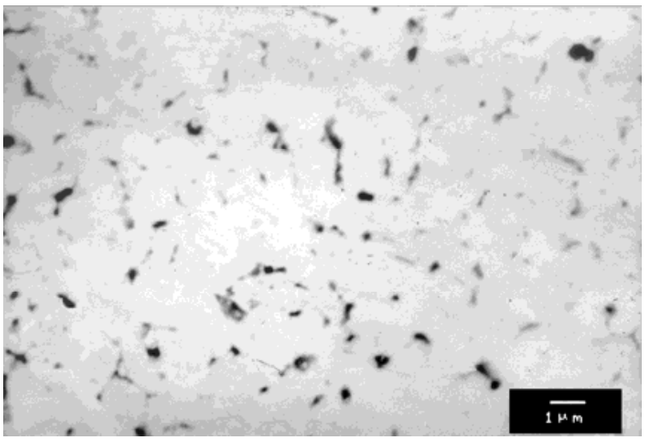


Fig. 11. SEM of the sintered Cu-3wt.%Al_2O_3 system (900°C, 30 min)

In order to determine the distribution of elements in the structure, the surface analysis of the sample was performed by EDS. The SEM microphotograph of the examined sample with the surface on which the surface scanning was performed is shown in Fig. 12, and the results of the examination of the sample of the sintered Cu-3wt.%Al_2O_3 system by EDS are given in Fig. 13.

The results of surface scanning show a homogeneous distribution of elements in the structure. In Fig. 13.a it can be seen that copper covers almost the entire surface of the sample. The results of surface scanning of aluminium (Fig. 13.b) and oxygen (Fig. 13.c) show that these two elements are present less in the structure of the sintered sample and that the surfaces they occupy are inter-lapping, which corresponds to the existence of an Al_2O_3 dispersoid in the structure. Beside aluminium and oxygen, an inter-lapping of all three elements is also noticeable, which leads to the assumption of the presence of a $Cu_xAl_yO_z$ phase [Jena, et al., 2004]. Finally, an apparatus with an exceptionally high resolution is necessary for the detailed characterization of the third. $Cu_xAl_yO_z$ phase.

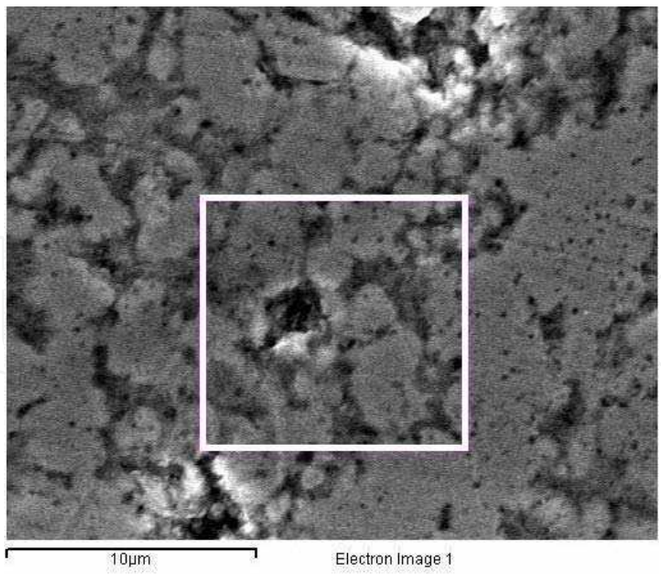
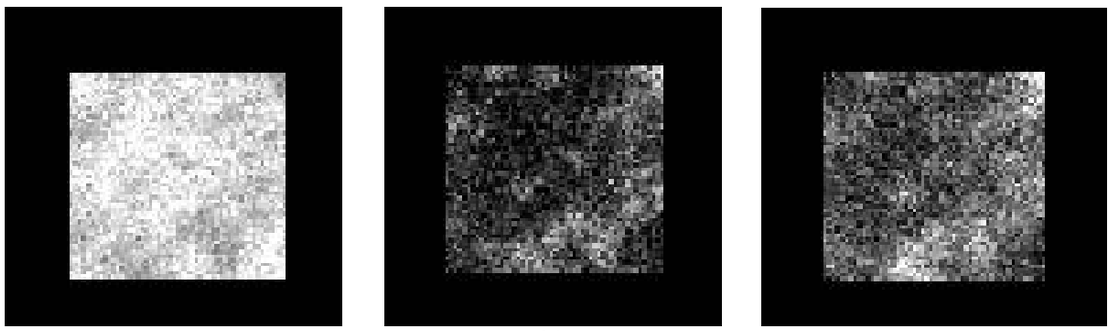


Fig. 12. SEM of the sintered Cu-3wt.%Al_2O_3 sample with the surface scanning area marked



a) b) c)

Fig. 13. Surface scanning of the sintered Cu-3wt.%Al_2O_3 sample by EDS for: a) copper, b) aluminium, c) oxygen

The characterization of the Cu-Al_2O_3 sintered systems based on the powders obtained by the thermochemical procedure, apart from the stated examination, has included examinations by the Focused Ion Beam (FIB), examinations with Transmission Electronic Microscopy (TEM), examinations of selected diffractive fields (SADP) and High Resalution Transmission Electronic Microscopy Examinations (HRTEM), which were carried out at the National Center for Electronic Microscopy, University of California, Berkeley (USA).

The FIB analysis of the sintered Cu-Al_2O_3 system based on the powders obtained by the thermochemical procedure at different magnifications (Fig. 14) did not indicate, even at considerably higher magnifications, the existence of a phase rich in alumina. In accordance with [Jena et al., 2001], bright fields are identified, i.e. a phase rich in copper, as well as gray fields, which lead us to the possibility of the existence of the third, $Cu_xAl_yO_z$ phase. In addition to this, the stated examinations by Scanning Electronic Microscopy [Jena, et al., 2001] are in accordance with the results of the surface EDS analysis showing that the peaks are identified and correspond to copper, aluminum and oxygen, and finally, having in mind that their intensity corresponds to the demanded composition, this additionally points to the

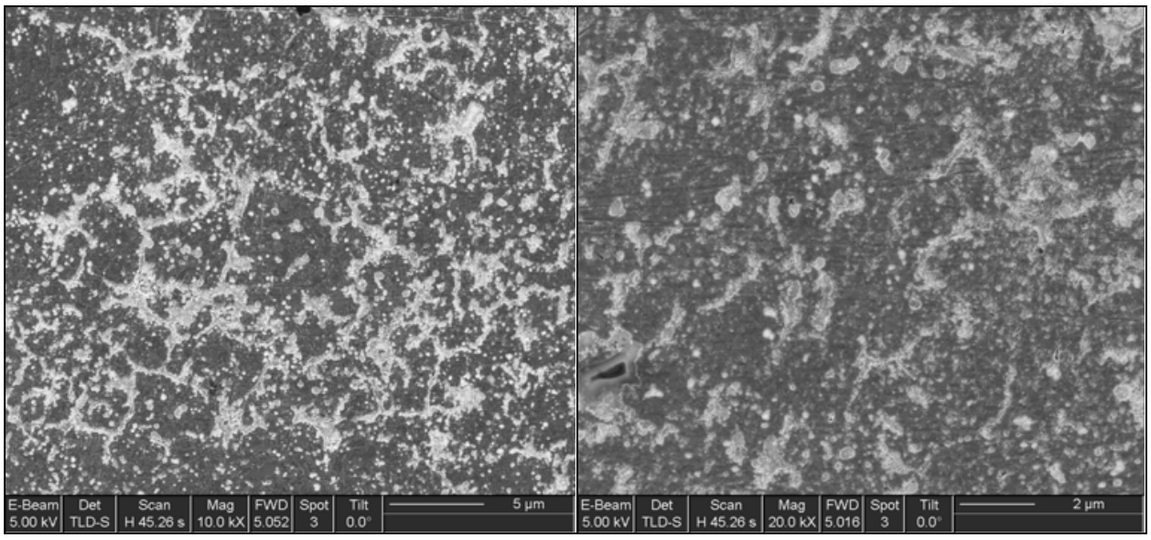


Fig. 14. FIB of the sintered Cu-5wt.% Al_2O_3 system (900°C, 120 nm)

possibility of the existence of the third, $Cu_xAl_yO_z$ phase. The formation of this phase is thermodynamically possible on Cu-Al contact surfaces. During the 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 creating $Cu_xAl_yO_z$, which is compatible with both phases on the inter-surface. In accordance with [Entezarian & Drew, 1996; Jena et al., 2001], the process of formation of the third phase is developed through the following reactions: $CuO + H_2O \rightarrow Cu_2O + H_2O$, $Cu_2O + Al_2O_3 \rightarrow 2CuAlO_2$ and/or $CuO + Al_2O_3 \rightarrow CuAl_2O_4$, whereas Misra and Chaklader [Misra & Chaklader, 1963] have published that CuAlO2 is stable in the air with the temperature range from 800°C to 1000°C, whereas $CuAl_2O_4$ is transformed into $CuAlO_2$ at the temperature of app. 1,000 °C.

Additionally, from microphotographs of the examined samples, homogenous distribution of the present phase is clearly noticeable as well as the size of microstructural constituents in the range of 50 – 250nm (Fig. 14).

As noted, finely dispersed particles and their homogenous distribution in the base metal matrix cause stabilization of dislocation substructure formed during deformation and the achievement of significant reinforcing effects by A complex action of different mechanisms [Lianga et al., 2004; Plascencia & Utigard, 2005]. The third, $Cu_xAl_yO_z$ phase has a considerable influence since it appears in the structure due to the eutectic reaction on Cu-Al contact surfaces [Jena et al., 2001, 2004; Korać et al., 2010]. Consequently, it has been concluded that the binding mechanisms on $Cu/CuAlO_2$, $Cu_2O/CuAlO_2$ and $Al_2O_3/CuAlO_2$ inter-surfaces are considerably stronger compared to Cu/Al_2O_3 and Cu_2O/Al_2O_3 contact surfaces, indicating that the formed third phase has an influence on the stabilization of dislocation substructure and thereupon the improvement of mechanical properties and achievement of a good combination of electro - mechanical properties of the sintered systems [Entezarian & Drew, 1996; Lee & Kim, 2004; Yi et al., 1999; Yoshino & Shibata, 1992].

A typical TEM pair bright field (BF) – the centered dark field (CDF) of nanocomposite Cu-5wt.%Al_2O_3 sintered system based on powders synthesized by the thermochemical procedure are shown in Figure 15 (a and b).

The TEM characterization of nanocomposite Cu-5wt.%Al_2O_3 sintered system based on powders synthesized by the thermochemical procedure reveals a microstructure with several interesting characteristics. In Fig. 15a and 15b, a typical TEM pair bright field (BF) – centered dark field (CDF) of nanocomposite Cu-5wt.% Al_2O_3 sintered system is shown, with the well developed crystals of copper of 100 nm size exposed to twinning despite their small size. The conditions for twinning are achieved when a great number of obstacles are created in the crystal, which hamper the moving of dislocations, dislocation plaits or already present twins. Since dislocations are piled up at the obstacles, internal tension is increased in the local regions, and this, along with external tension, causes the creation of twins. Having in mind that the decrease in dislocations mobility represents a condition for creating a twin embryo, the clearly noticeable presence of twins in Fig. 15a and 15b, indicates a decreased mobility of dislocations, i.e. stabilization of dislocation substructure, which is an elementary precondition for improving mechanical properties. i.e. for the reinforcement of metal materials. Additionally, when the deformed metal material is heated up to the sufficiently high temperature, recrystallization and grain growth occur, whereas in the stated processes and especially for the grain growth, grain boundaries movement is a basic mechanism which causes a relieved formation of twins.

Typical models of selected diffractive fields (SADP) of the examined nanocomposite Cu-5wt.% Al_2O_3 sintered systems based on the powders synthesized by the thermochemical procedure are shown in Figure 15c - at the point (marked by arrow in Fig. 15a) and Fig. 15d - from the overall area.

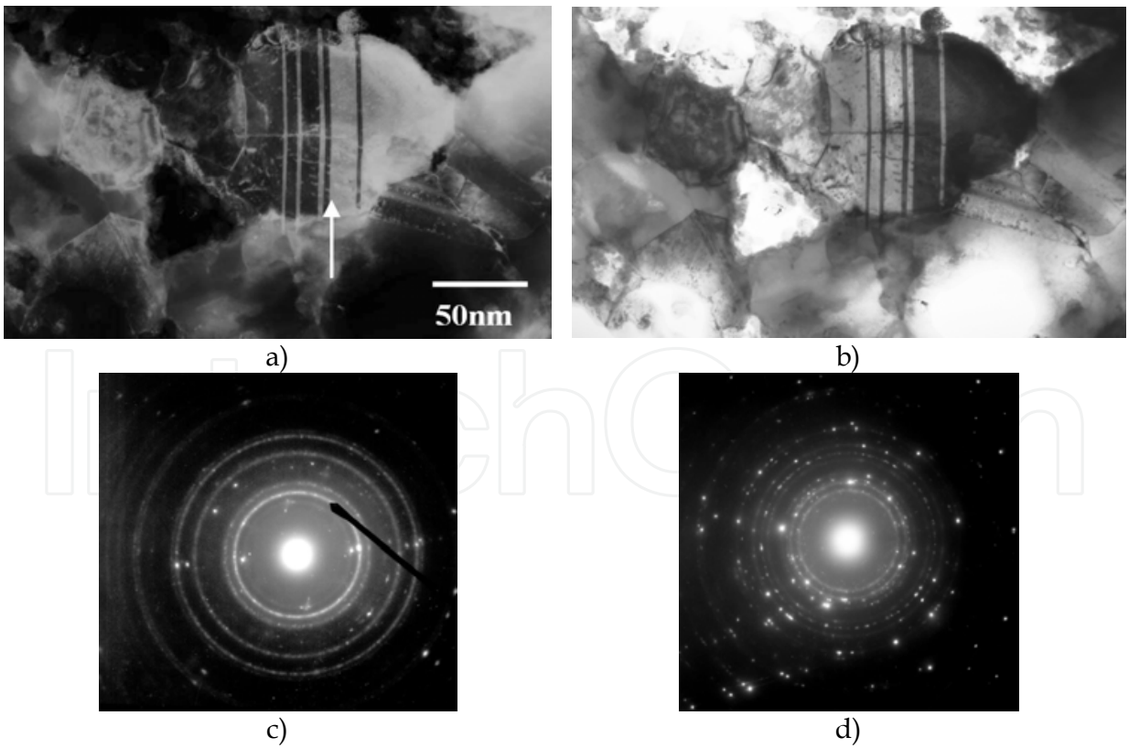


Fig. 15. (a and b) TEM BF – CDF pair of the nanocomposite Cu-5wt.%Al_2O_3 sintered system, (c) SADP centered at the point (marked by arrow in Fig. 15a), (d) SADP taken from the overall area

SADP clearly shows spots and rings, where spots refer to the individual crystals of copper, and sharp circles (rings) originate from nanocrystals of alumina dispersed in the copper matrix. Except for copper and alumina, diffractive fields are not identified, which is typical of some other phenomena (e.g. appearance of the third phase). The reason for that could be the common limitations of the technique, i.e. the determined critical value below which the phases cannot be identified. The presence of nano twins within the crystals of copper is partially confirmed by the selected diffractive fields taken from the overall surface (Figure 15d). Finally, apart from the stated, the obtained results of the examinations confirm the crystal nature of copper and dispersed alumina.

The high resolution transmission electron microscopy (HRTEM) of nano composite Cu-5wt.% Al_2O_3 sintered system based on powders synthesised by the thermochemical method is shown in Figure 16.

The HRTEM photos of sintered samples indictae a change in the lattice parameter on the grain boundary, where'raster' and 'fingerprint' variations can be detected. This leads to the conclusion that, due to the presence of alumina, the eutectic reaction ($Cu+Cu_2O$) with Al_2O_3 occurred and the third, $Cu_xAl_yO_z$ phase was formed, which is possible on Cu-Al contact surfaces from the thermodynamic point of view.

Bearing in mind the results of all of the above-mentioned examinations, the reinforcement of the copper matric occurs due to the to mechanisms: dispersion and reinforcement due to the dispersion of the fine particles of Al_2O_3 in the matrix, and the reinforcement of grain boundaries due to the appearance of the third phase.

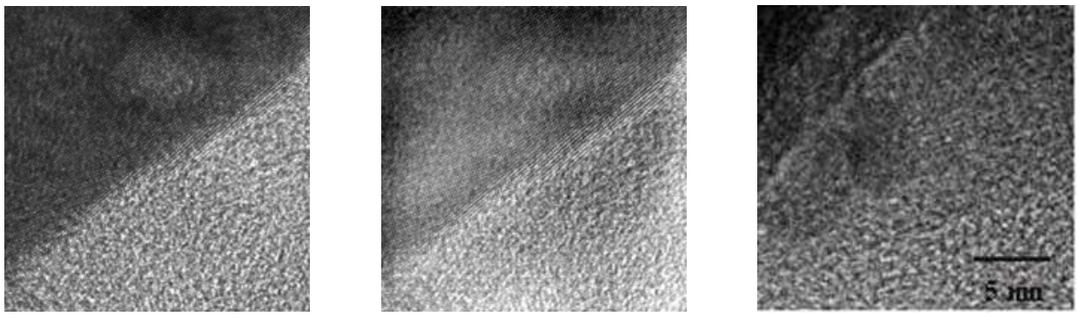


Fig. 16. HRTEM of nanocomposite Cu-5wt.% Al_2O_3 sintered system

4. Conclusion

Characterization of the obtained powder indicates a possibility of the synthesis of nanocomposite Cu-Al_2O_3 system by the thermochemical procedure, starting from water solutions $Cu(NO_3)_2$ and $Al(NO_3)_3$. AEM analysis indicates the presence of individual particles of 20-50 nm size. The shape of particles is irregular, with the presence of individual particles of nodular shape. The surface morphology is rough. Apart from that, the presence of an agglomerate with the magnitude of >100nm and of a sponge shape is noticeable. The obtained nanocomposite powders, with the structure basically preserved together with the final product, provided a significant reinforcement effect in the obtained sintered system. This is a consequence of the homogenous distribution of the elements in the structure, accomplished during the synthesis of powder and presence of the third phase which causes stabilization of dislocation substructure and achieves the relevant reinforcing effect.

The analysis of the mechanical and electric properties of the sintered Cu-Al_2O_3 systems based on powders obtained by the thermochemical method shows that in the system with 3wt.%Al_2O_3, sintered at 900°C, structural stabilisation occurs only after 30 minutes with considerable reinforcement effects. Since in other systems, the structural stabilisation process was not completed even after 120 minutes, the system with 3wt.% of dispersoids sintered at 900°C for 30 minutes seems to be the optimum solution for the production of dispersively reinforced Cu-Al_2O_3 systems. This statement is confirmed by the corresponding analysis of the microstructure.

In accordance with the previous statements, the EDS analysis of the sintered systems surface as well as FIB analysis show a homogenous distribution of elements, i.e. present phases. FIB analysis also indicates the size of microstructural constituents within the range of 50-250nm. TEM analysis of the sintered systems reveals the presence of copper crystals of 100 nm in size exposed to twinning, thus pointing to stabilization of the dislocation substructure. SADP of the examined nanocomposite Cu–Al_2O_3 sintered system shows spots and rings, where spots refer to the individual crystals of copper, and sharp circles (rings) originate from nanocrystals of alumina dispersed in the copper matrix. HRTEM analysis indicates the changes in the lattice parameter, which leads to the conclusion that the eutectic reaction occurred and the third, $Cu_xAl_yO_z$ phase was formed on the grain boundary, which will be the subject of future studies based on a more precise approach to physical chemistry of system surfaces and of thermodynamic examinations of the influences of finely dispersed Al_2O_3 on the formation of the third phase and the increase in the system surface energy.

In the end, all the above-mentioned examinations show that the reinforcement of Cu-Al_2O_3 system occurs via two mechanisms, which are: dispersion and reinforcement mechanism due to the homogenous dispersion of fine particles of Al_2O_3 in the matrix, and the mechanism of grain boundary reinforcement due to the appearance of the third phase.

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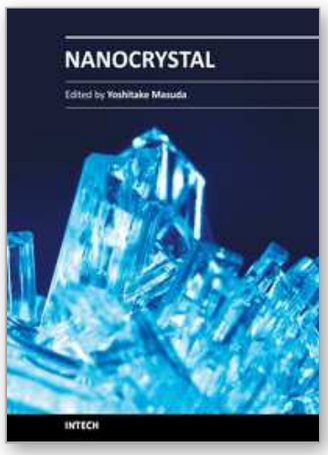

Nanocrystal

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We focused on cutting-edge science and technology of Nanocrystals in this book. â€œNanocrystalâ€ is expected to lead to the creation of new materials with revolutionary properties and functions. It will open up fresh possibilities for the solution to the environmental problems and energy problems. We wish that this book contributes to bequeath a beautiful environment and valuable resources to subsequent generations.

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