The synthesis of ultrafine and nanocomposite powders based on copper, silver and alumina

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Abstract

Contemporary materials with predetermined properties can be successfully synthesized by utilizing the principles of hydrometallurgy and powder metallurgy. The results of developing a new procedure for the synthesis of ultrafine and nanocomposite powders based on copper, silver and alumina are presented in this paper. A two-component nanocomposite powder, Cu-Al_2O_3, was synthesized by a thermochemical procedure, by deposition from an aqueous solution of soluble metal salts, $Cu(NO_3)_2$ and $Al(NO_3)_3$. A three-component Cu-Ag-Al_2O_3 powder was produced by mechanically alloying nanocomposite Cu-Al_2O_3 powder and Cu-Ag powder, synthesized by the thermochemical procedure. The produced powders were characterized by determining the particle specific area, pouring density and fluidness, differential thermal and thermogravimetric analysis (DTA-TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

K e y w o r d s: copper, alumina, silver, thermochemical processing, nanocomposites

1. Introduction

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. Keeping in mind that the starting structure undergoes certain changes in further processing, but remains basically preserved in the structure of the final product [1], there is an increased necessity for a larger number of methods for producing powders. Although obtaining powders by the thermochemical method is not a new procedure, recently, due to the development of contemporary materials with pre-set properties, there is a renewed intensive interest in this method, especially for nano-powder production [2–7].

Apart from conventional methods of obtaining Cu-Al_2O_3-based composites, an overview of obtaining these composites by the thermochemical method is presented in [3–6], with a comparative analysis of the properties of the sintered samples. According to Jena et al. [3–6], in the first case, the required quantity of CuO powder is added to $Al(NO_3)_3$ solution, and in the second case, aqueous solutions of $Cu(NO_3)_2$ and $Al(NO_3)_3$ were subjected to certain chemical and thermal treatments in order to achieve the required chemical composition, of nanoscale particle size and a homogenous distribution of the dispersoid in a copper matrix.

Considering the exceptional electric and thermal conductivity, low contact resistance and ability of deformation shaping, silver could be an addition to composite materials based on copper and alumina. Research directed towards the synthesis of silver-copper(II) oxide composite powder by spray pyrolysis is presented in [8], whereas the input are aqueous solutions of silver and copper nitrates mixed in the quantities necessary to obtain an adequate ratio of silver and CuO in the final composite powder. Papers [9, 10] present the procedure for the synthesis and characterization of nanocomposite Cu-Ag powders by the mechanical alloying procedure at lower temperatures.

Ultrafine and nanocomposite powders based on copper, silver and alumina can be successfully used to manufacture dispersion-reinforced sintered polycrys-

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talline materials with a submicron, i.e. nanocrystal structure and an excellent combination of electrical and mechanical properties. These materials are widely applied in the field of electronics and electrical engineering as highly conductive materials for operation at elevated temperatures, as electrodes for spot welding, different contact materials, various switches, thermal and electric conductors, microwave tubes, commutators for starting helicopter engines, relays, catalysts with a high degree of conversion, coatings with low porosity and high adhesion, etc.

2. Experimental

Soluble nitrates of copper and aluminium, $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, were used to synthetize a nanocomposite Cu-Al_2O_3 powder by the thermochemical procedure, as a transient component. The synthesis was carried out in four stages (Fig. 1):

– The preparation of 50 wt.% aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. The quantities of salt were set so that the requested composition of a Cu-Al_2O_3 nanocomposite system with 3 and 5 wt.% of alumina could be achieved;

– Spray drying using a modified house sprayer at 180 °C for producing the precursor powder;

– Annealing of the precursor powder in an air atmosphere at 900 °C for 1 hour to form copper oxide and the phase transformation of Al_2O_3 up to the thermodynamically stable α-Al_2O_3 phase;

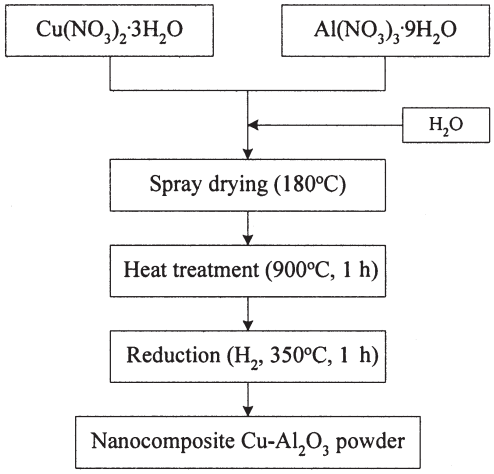

Fig. 1. Schematic presentation of the synthesis of Cu-Al_2O_3 nanocomposite powder by the thermochemical procedure.

– The reduction of thermally treated powders in hydrogen atmosphere at 400 °C for one hour, when copper oxide is transformed into elementary copper, and α-Al_2O_3 remains unchanged.

A three-component Cu-Ag-Al_2O_3 system was produced by mechanically alloying the thermochemically synthesized Cu-Al_2O_3 and Cu-Ag powder (Fig. 2). Silver and copper nitrates were used as the starting components in the synthesis of Cu-Ag powder by the ther-

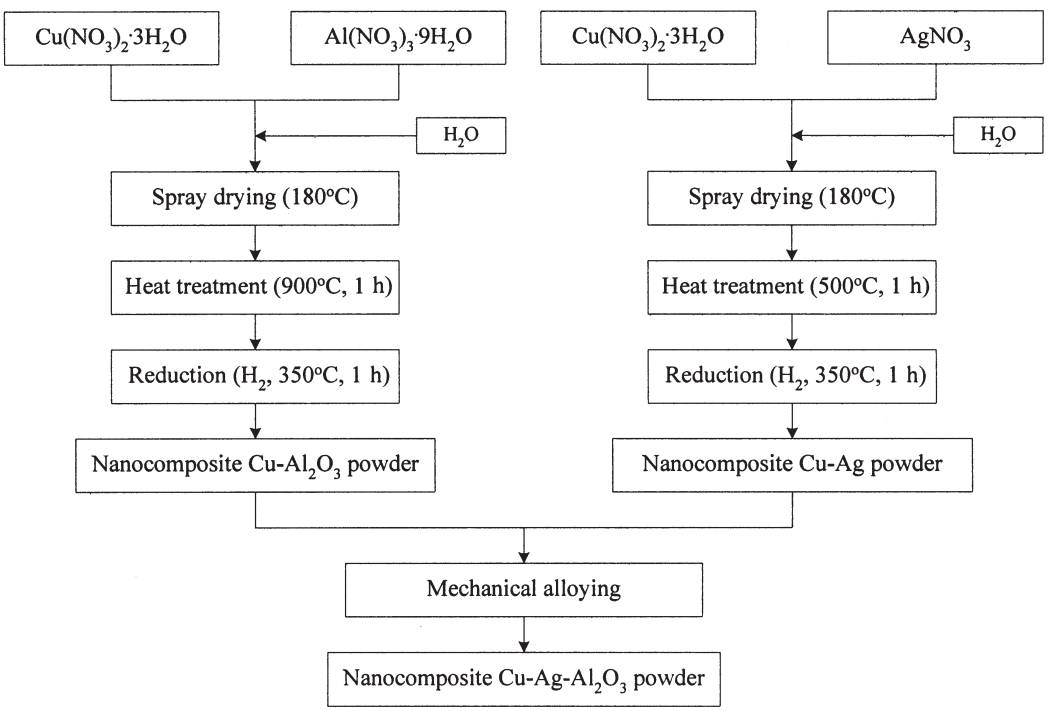

Fig. 2. Schematic presentation of the synthesis of Cu-Ag-Al_2O_3 nanocomposite powder by mechanical alloying.

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

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

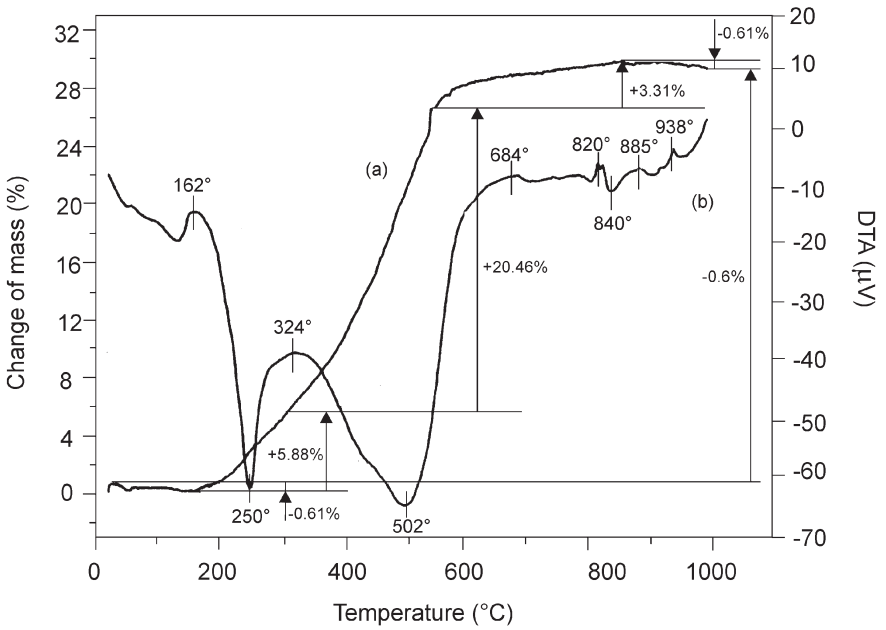

Fig. 3. DTA-TGA curves of the Cu-5wt.%Al_2O_3 powder obtained by the thermochemical procedure.

mochemical procedure. The synthesis of this powder also involves spray drying at 180 ℃, as in the case of Cu-Al_2O_3 synthesis, but the annealing temperature was set at 500 ℃. At this temperature copper nitrate is transformed into copper oxide, while silver is directly transformed into an elementary form. In order to achieve the final form of the composite material, the powder was reduced at 35 ℃ for 1 h to transform copper oxide into an elementary form. The Cu-Ag powder was then mixed with the previously synthesized Cu-Al_2O_3 nanocomposite powder in a ceramic ball mill, type TMF HM1, with the following milling chamber dimensions: internal diameter 180 mm, height = 160 mm and volume 4 l. The milling media were pure alumina ($\geq$ 99 % Al_2O_3) cylinders of $\varnothing$ = 18 mm × h = 20 mm and balls of d = 30 mm. Milling was performed for 1 hour at 300 min^{-1} by the wet method in ethanol (99.8 % C_2H_5OH) in order to intensify the milling process. The powder ratio was set, so the final structure contained 25 wt.% Ag and 5 wt.% Al_2O_3.

The characterization of the produced powders consisted of determining the particle specific area, the pouring density and fluidness, differential thermal and thermogravimetric analysis (DTA-TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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 adsorption method (BET).

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

Qualitative X-ray diffraction analysis of the powders was performed using a Siemens D500 PC diffractometer, CuK_α radiation, in the range $2\theta = 0$–100° with a step of (2θ) 0.02°.

SEM analysis was used to quantitatively analyse the size and shape of the samples and it was performed on a JEOL JSM-T20 instrument with a magnification interval of 35 to 75 000×.

3. Results and discussion

The results of the determination of the fluidness, pouring density and specific area of the nanocomposite Cu-Al_2O_3 powder particles, with different contents of dispersoid, obtained by the thermochemical procedure are presented in Table 1.

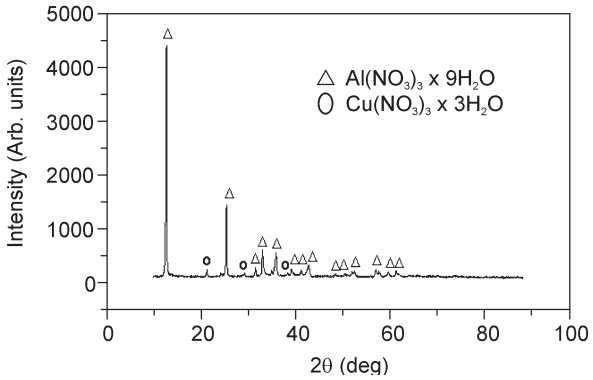

Fig. 4. XRD of the Cu+3wt.%Al_2O_3 powder after spray--drying.

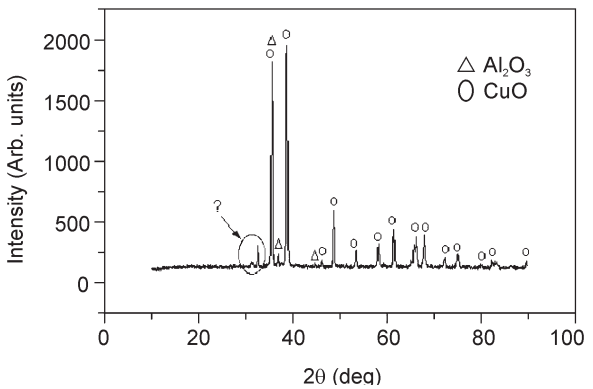

Fig. 5. XRD of the dried Cu+3wt.%Al_2O_3 powder after thermal treatment.

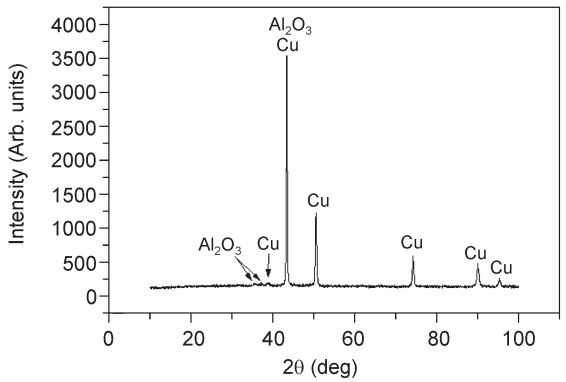

Fig. 6. XRD pattern of the Cu+3wt.%Al_2O_3 powder after reduction.

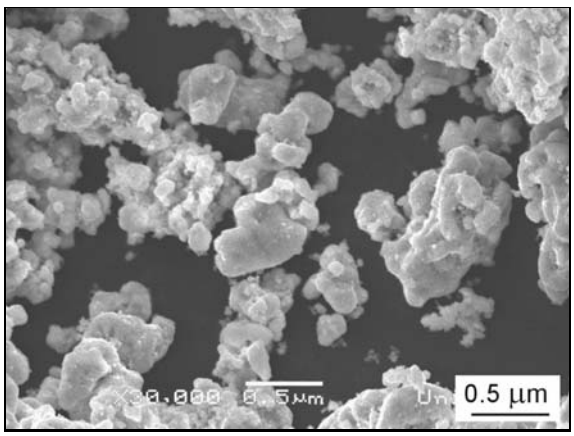

Fig. 7. SEM micrograph of the nanocomposite Cu+3wt.%-Al_2O_3 powder.

The DTA-TGA curves of the nanocomposite Cu--Al_2O_3 powder with 5 wt.% Al_2O_3, obtained by the thermochemical procedure are shown in Fig. 3. Two endothermic peaks may be observed on the DTA curve at approximately 150 ℃ and 250 ℃, which correspond to the evaporation and dehydration of residual moisture, respectively. The exothermic peak at 324 ℃ 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 ℃, 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 ℃ due to the phase transformations of Al_2O_3.

The XRD analysis of the spray-dried Cu-Al_2O_3 powder with 3 wt.% of dispersoid is shown in Fig. 4. In accordance with the experimental set-up, only the peaks which correspond to copper and aluminium nitrates were registered in the structure.

The X-ray diffraction analysis after annealing of the dried powder is shown in Fig. 5. The detected peaks correspond to CuO and Al_2O_3. An unidentified peak was also detected. In accordance with the literature [5, 11, 12], 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 possible at Cu-Al contact surfaces.

During the eutectic joining of copper and Al_2O_3, the eutecticum formed by heating 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 inter-surface. The formed third phase influences the nature of the dislocative structure and, therefore, the improvement of the mechanical properties and achievement of a good combination of mechanical and electrical properties of the sintered systems.

Although this phase was identified by XRD analysis, it was not identified by SEM with EDS analysis (Oxford Instruments, UK type QX2000). Peaks of elementary copper and Al_2O_3 were detected in the XRD pattern of the Cu-3wt.%Al_2O_3 powder after reduction, Fig. 6. Additionally, the peak corresponding to

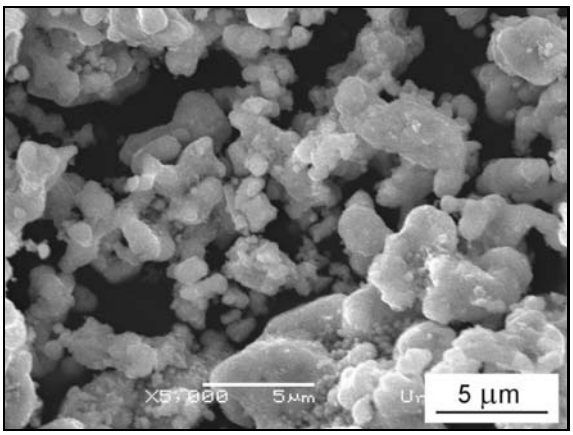

Fig. 8. SEM micrograph of the nanocomposite Cu+5wt.% -Al_2O_3 powder.

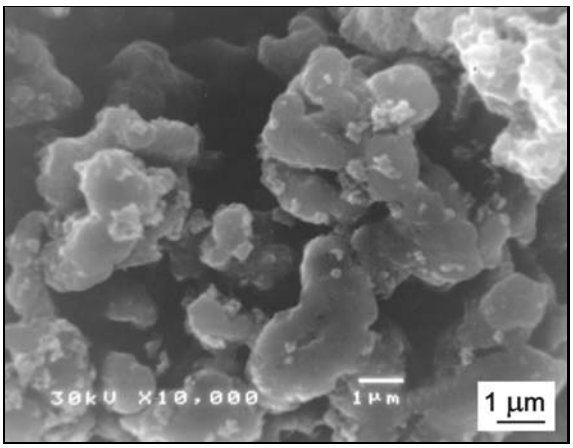

Fig. 9. SEM micrograph of the nanocomposite Cu-Ag- -Al_2O_3 powder.

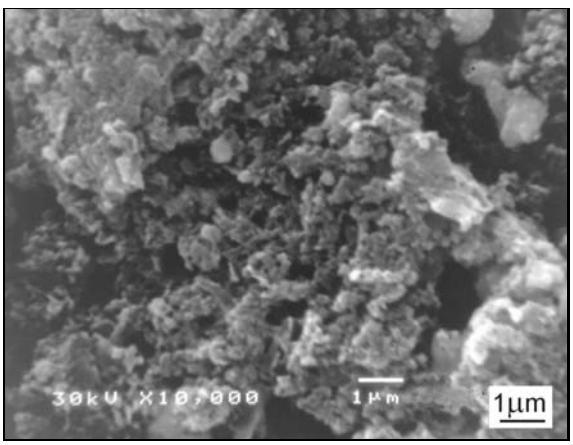

Fig. 10. SEM micrograph of the nanocomposite Cu-Ag- -Al_2O_3 powder.

CuO was detected. CuO appears in the final structure due to incomplete reduction, i.e. it is necessary to perform two-stage reduction in order to achieve the desired structure without oxides.

Nanocomposite Cu-Al_2O_3 powders, produced by the thermochemical method, were also examined by scanning electron microscopy (SEM), as presented in Figs. 7 and 8. The shape of the powder particles was determined in accordance with ISO Standard 3252.

Microstructural analysis of the powders confirmed the possibility of Cu-Al_2O_3 nanocomposite synthesis by the thermochemical procedure, starting from aqueous solutions of $Cu(NO_3)_2$ and $Al(NO_3)_3$. Particle sizes of 100–200 nm are clearly visible, as are individual particles of less than 100 nm. The shape of the particles is irregular with the presence of individual nodular-shaped particles. The surface morphology is rough.

Agglomerates of size 2–5 μm were also registered. The agglomerates are sponge-shaped. Namely, the agglomeration of finer particles is the consequence of their large surface, high surface energy, and an effect of the bonding forces between them. At the contact surfaces, due to the atomic connections at the interface, attracting strains are created, the magnitude of which depends directly on the surface energy of the particles that are in contact. Taking into consideration the appearance of the agglomerates, particular attention will be paid in future research to the production of non-agglomerated powders, where surfactants will be used to deagglomerize the particles. The application of polyethylene glycol [2] and ultrasonification [13, 14] are under consideration.

The results of the fluidness, pouring density and specific area of the Cu-Ag-Al_2O_3 nanocomposite powder particles are presented in Table 2.

SEM microphotographs of the Cu-Ag-Al_2O_3 nanocomposite powder are shown in Figs. 9 and 10. It may be noticed in the microphotographs that the particle size of the obtained powder is 100–300 nm. Apart from the individual particles, the presence of agglomerates of the size < 5 μm was registered.

4. Conclusion

Ultrafine and nanocomposite powders based on copper, silver and alumina were successfully synthesized by the procedures of hydrometallurgy and powder metallurgy. Cu-Al_2O_3 nanocomposite powder was synthesized by the thermochemical procedure, by deposition from aqueous solutions of metal salts, $Cu(NO_3)_2$ and $Al(NO_3)_3$. The microstructure of the obtained powder clearly indicated particles of 100–200 nm size, as well as individual particles of less than 100 nm. The shape of the particles was irregular with the presence of nodular-shaped particles. A three-component Cu-Ag-Al_2O_3 powder was obtained by mechanically alloying Cu-Al_2O_3 nanocomposite

Table 2. Fluidness, pouring density and specific area of the particles of the nanocomposite Cu-Ag-Al_2O_3 powder particles produced by mechanical alloying (mean values)

Cu (%)	Ag (%)	Al_2O_3 (%)	Fluidness	Pouring density (g/cm^3)	Specific area (m^2/g)
70	25	5	not fluid	1.18	0.46

powder and Cu-Ag powder synthesized by the thermochemical procedure. The size of the particles of the obtained Cu-Ag-Al_2O_3 powder was 100–300 nm and their shape was irregular.

A relatively even distribution of the alumina in the nanocomposite system was achieved during the synthesis of the powder by depositing metals from solutions of metal salts. This strategy caused stabilization of the dislocative structure and accomplished significant reinforcing effects, i.e. the manufacture of sintered materials with a combination of electrical and mechanical properties that makes them superior to conventional materials.

References

[1] RISTIC, M. M.: Fundamental Problems of the Science of Materials. Cacak, TF Cacak and Serbian Academy of Science and Arts 2003.
[2] WU, Y.-Q.—ZHANG, Y.-F.—HUANG, X.-X.—GUO, J.-K.: Ceramics International, *27*, 2001, p. 265.
[3] JENA, P. K.—BROCCHI, E. A.—MOTTA, M. S.: Materials Science and Engineering, *A313*, 2001, p. 180.
[4] LEE, D. W.—HA, G. H.—KIM, B. K.: Scripta Mater., *44*, 2001, p. 2137.
[5] JENA, P. K.—BROCCHI, E. A.—SOLÓRZANO, I. G.—MOTTA, M. S.: Materials Science and Engineering, *A317*, 2004, p. 72.
[6] SKOUFADIS, C.—PANIAS, D.—PASPALIARIS, I.: Hydrometallurgy, *68*, 2003, p. 57.
[7] KAMBEROVIĆ, Ž.—KORAĆ, M.—ANĐIĆ, Z.—TASIĆ, M.: In: Proc. of the II International Symposium Light Metals and Composite Materials 2004. Ed.: Talijan, N. Belgrade, Institute of Chemistry, Technology and Metallurgy 2004, p. 61.
[8] MAJUMDAR, D.—GLICKSMAN, H. D.—KODAS, T. T.: Powder Technology, *110*, 2000, p. 76.
[9] ZGHAL, S.—HŸTCH, M. J.—CHEVALIER, J.-P.—TWESTEN, R.—WU, F.—BELLON, P.: Acta Materialia, *50*, 2002, p. 4695.
[10] ZGHAL, S.—TWESTEN, R.—WU, F.—BELLON, P.: Acta Materialia, *50*, 2002, p. 4711.
[11] JENA, P. K.—BROCCHI, E. A.—MOTTA, M. S.: Mater. Sci. Eng., *C15*, 2001, p. 175.
[12] ENTEZARIAN, M.—DREW, R. A.: Mater. Sci. Eng., *A212*, 1996, p. 206.
[13] JOHNSON, D. W., Jr.—NITTI, D. J.—BERRIN, L.: Bull. Amer. Ceram. Soc., *51*, 1972, p. 896.
[14] HSU, W. C.: Ultrasonic treatments of aluminum and aluminum-zirconium (ZTA) hydroxides for the preparation of ultrafine aluminum and aluminum-zirconium (ZTA) oxide powders. [M.Sc. Thesis]. Tainan, Taiwan, National Cheng Kung University 1997.