

Processing and Microstructure of Al₂O₃-Cu Composite Material Interpenetrating Network Type

Katarzyna Pietrzak^{1,2}, Katarzyna Jach¹, Dariusz Kalinski¹, Marcin Chmielewski¹, J. Morgiel³
¹) Institute of Electronic Materials Technology, 133 Wolczynska Str., 01-919 Warsaw, Poland, ²)
Institute of Fundamental Technological Research, Polish Academy of Science,
5B Pawinskiego., 02-106 Warsaw, Poland,
³) Institute of Metallurgy and Materials Science, Polish Academy of Sciences,
25 Reymonta Str. 30-059 Krakow, Poland

ABSTRACT

Alumina/copper composites have been used where high thermal conductivity, high absorption and dissipation of heat, high resistance to thermal fatigue and good frictional wear resistance are required. This kind of composites may be applied in medicine, electronic and automotive industry. Both the physical and mechanical properties of this type of composites are strongly influenced by the properties of its individual constituents and, also, by the properties of interface layer between ceramic and metal. One of the solution, from the point of view of the best properties' achievements (especially thermal, structural and shape stability), is the production of ceramic-metal composites with interpenetrating networks structure. They can be produced using porous alumina performs, which are infiltrated (pressure or pressureless) by molten metal or sintered with metallic powders. The subject of the presented paper is the development of the interpenetrating network Al₂O₃-Cu composites, processed by sintering porous ceramic perform (85 and 90% porosity) with copper powder. The paper presents the new developed technology, results of microstructure investigations, measurements of the selected physical and mechanical properties and the analysis of the influence of the processing conditions on the properties and interface morphology between ceramic and copper.

INTRODUCTION

The progress in many branches of industry requires new multi-phase materials that could operate under exceptionally hard conditions. These new materials should have e.g.: higher mechanical strength, increased Young's modulus, high thermal conductivity, improved resistance to thermal fatigue, frictional wear resistance in conjunction with thermal structural and shape stability. These advanced materials may be applied in medicine, electronics, power and automotive industry. One of the most predisposed kind of materials which can characterise itself by so wide range of the advantages can be ceramic-metal composites with interpenetrating networks structure. Interpenetrating composites of ceramic and metals are designed to take advantage of the best aspects of both phases. High wear resistance is achieved from ceramic/metal microstructures because of the high hardness and high wear resistance of the ceramic part of composite. The metallic part increases the fracture toughness of the composite, which improves its strength and its resistance to thermal shock and impact damage. Interpenetrating composites have an advantage over other types, because the continuous metallic network provides effective crack bridging, while the ceramic network provides dimensional stability at high temperatures. Interpenetrating ceramic/metal composites can be produced by a number of techniques [1,2]: by direct oxidation of the appropriate metal, using porous alumina performs, which are infiltrated (pressure or pressureless) by molten metal or sintered with metallic powders, etc.

Also, a number of fabrication techniques are currently available for producing these porous ceramic materials [1-9], including the firing of ceramic powder compacts with pore-forming fugitive phases, the replication of polymer foams by impregnation, the pyrolysis of pre-ceramic precursors, the gel casting, etc. Each of these methods has its own merits and drawbacks, e.g. the polymer foam replication method can achieve ultrahigh porosity with large interconnections; however, reticulated porous ceramics produced by this technique often have poor mechanical properties because of the defects formed during the pyrolysis of the polymer foam. On account of future application of developed material (necessity of high porosity), the ceramic performs which were used in these investigation were produced following the replication method, which consists on depositing a ceramic slurry on a substrate made of polymeric sponge materials. The method permits producing porous ceramic with the highest possible degree of porosity amounting to 99vol.%. As the final product we obtain a ceramic material with a structure which is a precise copy of the adopted reference structure.

In this paper, the possibility to develop the interpenetrating network Al_2O_3 -Cu composites, processed by sintering porous ceramic preform with copper powder is discussed. This paper contains descriptions of conditions of sintering porous ceramic preform (85 and 90% porosity) with copper powder, results of microstructure investigations (SEM, TEM, EDAX) and results of measurements of the selected physical and mechanical properties.

EXPERIMENTAL

In the presented investigations, the solid phase used for the preparation of the ceramic slurry was α - Al_2O_3 powder (A16SG; Almatix: average grain size $0.5\mu\text{m}$, specific surface area $8.9\text{ m}^2/\text{g}$, density $3.89\text{g}/\text{cm}^3$ - Fig.2a). Others components of the slurry were: the fluxing component Duramax D-3005 (Rohm&Haas) in an amount of 0.8wt% with respect to the mass of the solid phase and the binders - dispersion of a polymer based on acrylic acid ester and styrene (50% aqueous solution), Mowilith DM765 (Celanese Emulsions GmbH), and poly(vinyl alcohol) Mowiol 40-88. In the next stage, the polymeric sponge/structural foams (Kureta Co. Germany) were saturated with thus prepared the slurry. The samples were then dried at room temperature for 48h, and in the final stage, the samples were subjected to sintering [12]. The program of the sintering operation was chosen based on a thermal analysis of the polymer substrate (the measurement of the mass loss during heating the sample (TG), differential scanning calorimetric examinations (DSC) within the temperature range from 25 to 800°C). The greatest mass loss was observed within the 310 - 440°C range, and the total decomposition occurred at a temperature of 589°C . The sintering process was divided into two stages: 1st included burning the organic substrate, 2nd sintering the ceramic material. The burning was conducted at a rate of $0.8^\circ\text{C}/\text{min}$ to a temperature of 600°C , and then at a rate of $2^\circ\text{C}/\text{min}$ to 1100°C . Sintering was realized at a temperature of 1700°C for 60min. The quality of the ceramic layer deposited on a polymeric sponge strongly depends on the viscosity of the slurry. The suspension prepared with PVA not only has a high viscosity but is also characterized by a high foaming degree. Both these features favor the formation of closed pores in the ceramic preform (Fig.1b), which is very disadvantageous. This can be avoided by selecting appropriately the composition and rheological parameters of the slurry. In fact the close porosity is impossible to remove. The preforms before and after sintering are shown in Fig.1.a

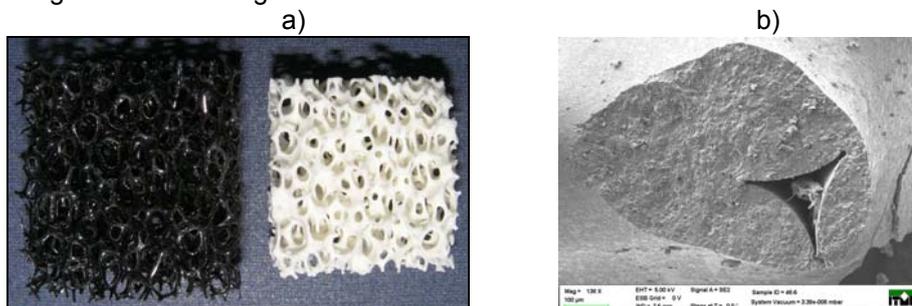


Fig. 1. a) Structural polymeric foam and sintered ceramic preform (open porosity 90), b) microstructure of ceramic preform.

Based on previous experience two types of so prepared ceramic preforms (with 85 and 90% porosity) were produced and used in the study of sintering process conditions. The preforms were fully filled with the copper powder (NewMet Koch, purity 99.5%, particle size D90 - Fig.2b)) and sintered in a hot ASTRO type press in the atmosphere of argon. The sintering tests were made in a graphite pattern. The conditions of the sintering process were in the range of: temperature 1000 - 1050°C , time 15-45 min, pressure 10-24 MPa; the heating speed was $10^\circ\text{C}/\text{min}$, and that of cooling - $5^\circ\text{C}/\text{min}$.

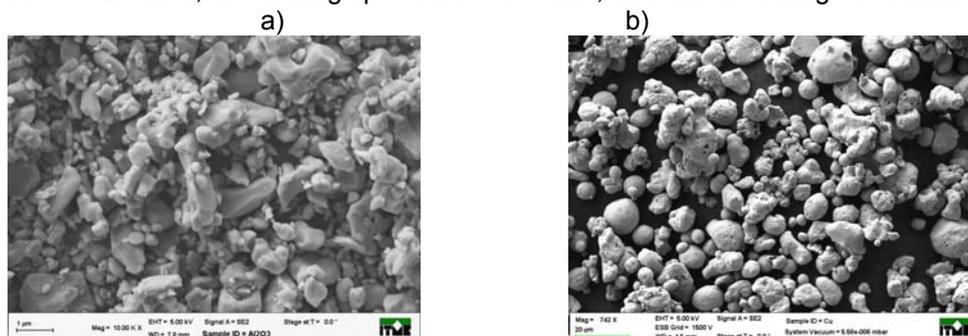


Fig. 2. The Al_2O_3 (a) and Cu (b) powders.

The microstructure of produced composite materials on the base of Al_2O_3 containing 85 and 90% of copper were investigated using scanning eXL30 and transmission TECNAI Super TWIN FEG (200kV) electron microscopes with integrated EDAX microanalysis system. Thin foils were cut using Quanta 3D focused ion beam equipped with Omni probe lift-out attachment.

The density of the $\text{Cu-Al}_2\text{O}_3$ composites was measured according to the Archimedes method. The hardness (HV5) was tested with a Vickers diamond indenter using a load of 49N with loading time of 10 s. Each indentation was placed at least 10 diagonal lengths away from adjacent indentation. The hardness results were averaged over 10 indentations per specimens.

The bending strength was examined in a ZWICK 1446 strength machine at a support spacing of 25 mm and a head travel speed of 1.0 mm/min. The samples intended for the bending strength tests were sized at 5x5x30 mm, and the head load was 10 kN.

Thermal conductivity. Laser flash method was applied for thermal properties measurement of obtained Al_2O_3 -Cu composite materials. The entire set of experimental data was fitted by Cape-Lehman theoretical model with the pulse correction, which takes into consideration radiative heat loss [13]. In this method, a pulse of energy is absorbed instantaneously on the front face of specimen and the subsequent temperature change on the rear face is measured. Only the shape of the time-temperature curve is used in further analysis. The thermal diffusivity can be directly calculated from the curve and the sample thickness. The thermal diffusivity was measured within temperature range of 50-600°C by laser flash method (Netzsch LFA 457) in the argon atmosphere. Before conducting the experiments, the surfaces of samples were covered by thin layer of graphite. The conditions of measurements for both type of materials were: size of samples: 10x10x3mm, laser voltage 1730 V, amplifier gain 200, laser filter 100%.

RESULTS and DISCUSSION

The selected results of obtained materials investigations (microstructure, physical and mechanical properties) are presented below.

Microstructure examinations (SEM, TEM, EDAX)

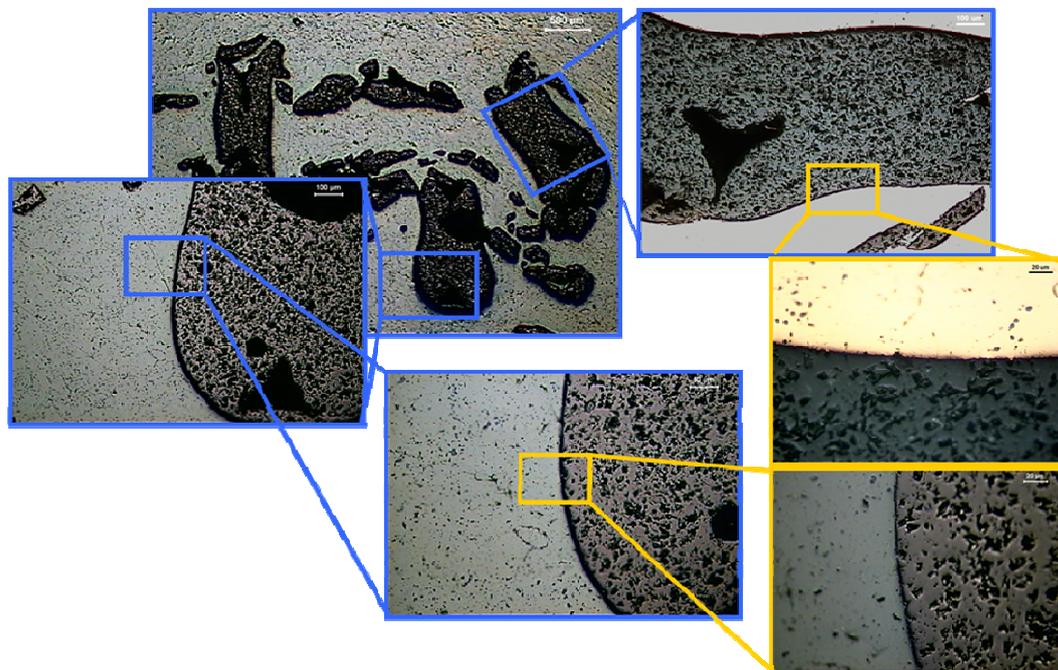


Fig. 3. The microstructure of Al_2O_3 -90%Cu interpenetrating composite, obtained by: $T=1050^\circ\text{C}$, $t=30$ min, $p=24$ MPa.

As you can observe the applying of high value of pressure (24 MPa) caused the crushing of ceramic bridges during the sintering process. It should be noticed that the structure of ceramics is additionally weakened by the presence of closed porosity inside the ceramic perform.

The next experiments were conducted by lower value of the pressure.

Since the properties of obtained composite materials, in large measure, depend on the morphology and character of the interface between Al_2O_3 and Cu, the next stage of the microstructure examinations was the observations of the ceramic/metal boundary. Fig. 4. shows the surface distribution of the elements on the ceramic-metal boundary for the composite obtained by $T=1050^\circ\text{C}$, $t=30$ min, $p=10$ MPa.

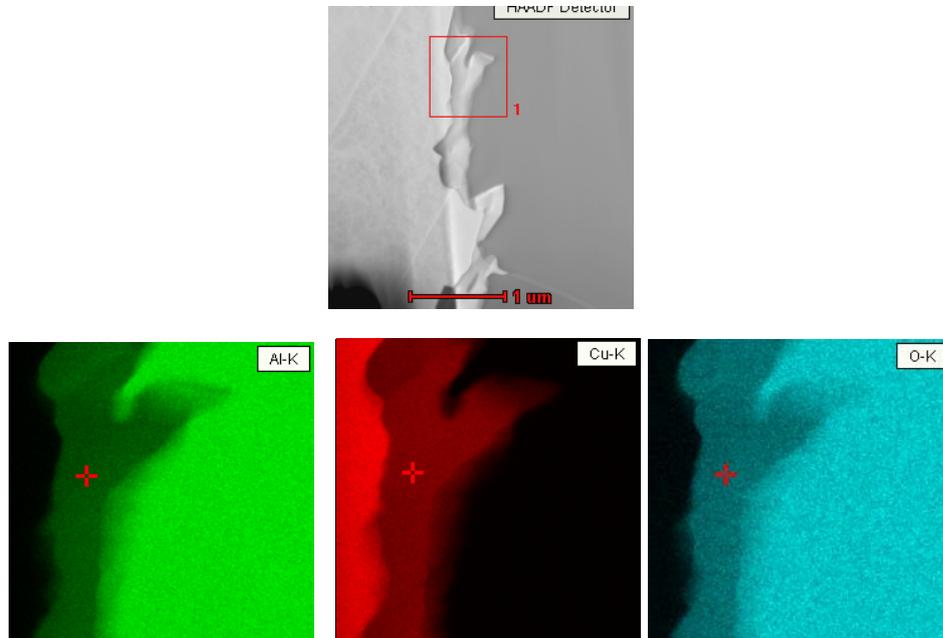


Fig. 4. The microstructure and surface distribution of elements on the boundary $\text{Al}_2\text{O}_3/\text{Cu}$

On the basis of the analysis of these results it was stated, that the interface which was formed on this boundary, comprises the new compound – aluminum/copper/oxygen spinel type, and, that the thickness of the interface increases together with value of the sintering pressure. The formed spinel should have advantages regarding the mechanical properties of the composite due to good strength of the bond. However, the interface may affect the thermo-physical properties.



Fig. 5. TEM image of alumina-copper grain boundary.

Fig. 5 presents an image of a layer of $\text{Al}_x\text{Cu}_y\text{O}_z$ spinel crystallites formed at the $\text{Cu}/\text{Al}_2\text{O}_3$ crystallite interface. The arrangement of the slightly elongated rod-like precipitates, i.e. ends penetrating metal matrix as well as corundum indicates that after nucleation they grow into both materials.

Physical and mechanical properties

The properties obtained by physical and mechanical characterization are presented in table 1. These results (especially with respect to density) are not satisfying and have to be optimised in order to achieve an improved bending strength. But you have to bear in mind that the results of

measurements of density especially of these kind of composites depend on the place of cut out and size of the samples and on the close porosity.

Table 1. The properties of Cu-Al₂O₃ composite materials.

Materials composition (in vol.%)	Measured density (g/cm ³)	Hardness HV5 (GPa)	Bending strength (MPa)
90Cu-10Al ₂ O ₃	6.40	55.9	82.5
85Cu-15 Al ₂ O ₃	5.67	62.3	41.4

These results (especially with respect to density) are not satisfying and have to be optimised in order to achieve an improved bending strength. But you have to bear in mind that the results of measurements of density especially of these kind of composites depend on the place of cut out and size of the samples and on the close porosity.

Thermal conductivity

The experimental results of thermal diffusivity and values of specific heat (determined from the rule of mixture) were used to estimate the thermal conductivity λ [13]. It can be determined from the relation (1):

$$\lambda = \rho(T)c_p(T)D(T) \quad (1)$$

where:

λ [W/m K] – thermal conductivity, $\rho(T)$ [kg/m³] – material density, $c_p(T)$ [J/kg x K] – specific heat, $D(T)$ [m²/s] – thermal diffusivity.

Coefficient of thermal expansion (CTE) in the range of temperature 20-600°C were: for Al₂O₃-85%Cu – $15.52 \times 10^{-6} \text{ K}^{-1}$ and for Al₂O₃-90%Cu – $15.13 \times 10^{-6} \text{ K}^{-1}$, the specific heat (in the same range of temperature) - 0.59 and 0.53 J/gK respectively. The Fig.6 comprises the results of these investigations.

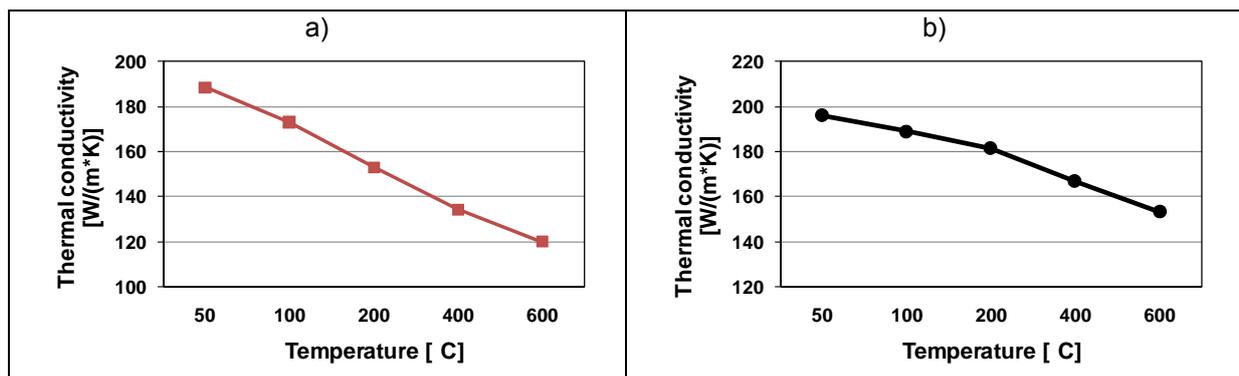


Fig. 6. Thermal conductivity of a) Al₂O₃-85%Cu and b) Al₂O₃-90%Cu as a function of temperature.

The results of thermal conductivity investigations show that the properties depend on the content of copper in composite. The unsatisfying value of thermal conductivity is caused mainly by the presence of porosity in the structure of the composite material. The decrease of λ with increase test temperature is typical for copper matrix composites. The next step in the experimental work will be focused on the development of process parameters to improve the density of obtained materials.

CONCLUSIONS

On the basis of the presented results following conclusion can be drawn:

- i. It's possible to obtain $\text{Al}_2\text{O}_3/\text{Cu}$ composite material interpenetrating type using sintering of appropriate ceramic perform with copper powder
- ii. The layer of new compound - $\text{Al}_x\text{Cu}_y\text{O}_z$ spinel crystallites - formed on the $\text{Al}_2\text{O}_3/\text{Cu}$ boundary; the thickness of this layers depend on the process parameters as the applied pressure,
- iii. Through the appropriate selection of the sintering conditions it's possible to design the interface layer and optimize the properties of the composite.

ACKNOWLEDGMENT

The results presented in this paper have been obtained within the project "KomCerMet" (contract no. POIG.01.03.01-14-013/08-00 with the Polish Ministry of Science and Higher Education) in the framework of the Operational Programme Innovative Economy 2007-2013.

REFERENCES

- [1] M. Newkirk, A. Urquhart, H. Zwicker, E. Brewal, *J. Mat. Res.*, 1(1986) 81-89.
- [2] F.Lange, B. Velamakanni, A.Evans, *J. Am. Cer. Soc.* 73,(1990) 388-393.
- [3] K. Ishizaki, S. Komarneni, M. Nauko, *Porous Materials Process Technology and Applications*, Kluwer, London, (1998).
- [4] L.J.Gibson M.F. Ashby, *Cellular Solids, Structure and Properties*, 2nd edition, Cambridge, (1999).
- [5] N.Q. Minh, *J. Am. Cer. Soc.*, 18 (1998) 563-588.
- [6] F.S. Ortega, F.A.Valenzuela, C.H. Scuracchio, V.C. Pandolfelli, *J. Eur. Ceram. Soc.*, 23 (2003) 75–80.
- [7] P. Colombo, M. Griffoni, M. Modesti, *Journal of Sol-Gel Science and Technology* 13, (1998) 195–199.
- [8] Yoshio Sakka, Fengqiu Tang, Hiroshi Fudouzi, Tetsuo Uchikoshi, *Science and Technology of Advanced Materials*, 6 (2005) 915–920.
- [9] P. Colombo, J. R. Hellmann, *Mat. Res. Innovat.* 6 (2002) 260–272.
- [10] O. Lyckfeldt, J.M.F. Ferreira, *J. Eur. Ceram. Soc.*, 18, (1998) 131-140.
- [11] A. Travitzky, *Journal of Materials Science* 36 (2001) 4459 – 4463.
- [12] K.Jach, K. Pietrzak, D. Kalinski, M. Chmielewski: *Advances in Science and Technology*, vol. 65, (2010), 164-169,
- [13] S. Min, J. Blumm, A. Lindermann: *Thermochemica Acta*, 455 (2007) 46-49