

A R C H I V E S o f

ISSN (1897-3310) Volume 14 Issue 2/2014

 $85 - 90$

F O U N D R Y E N G I N E E R I N G

17/2

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Physical Properties of Copper Based MMC Strengthened with Alumina

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Received 10.03.2014; accepted in revised form 30.03.2014

Abstract

The aim of this work is the development of $Cu-Al₂O₃$ composites of copper $Cu-ETP$ matrix composite materials reinforced by 20 and 30 vol.% Al₂O₃ particles and study of some chosen physical properties. Squeeze casting technique of porous compacts with liquid copper was applied at the pressure of 110 MPa. Introduction of alumina particles into copper matrix affected on the significant increase of hardness and in the case of Cu-30 vol. % of alumina particles to 128 HBW. Electrical resistivity was strongly affected by the ceramic alumina particles and addition of 20 vol. % of particles caused diminishing of electrical conductivity to 20 S/m (34.5% IACS). Thermal conductivity tests were performed applying two methods and it was ascertained that this parameter strongly depends on the ceramic particles content, diminishing it to $100 \text{ Wm}^{-1}\text{K}^{-1}$ for the composite material containing 30 vol.% of ceramic particles comparing to 400 $Wm⁻¹K⁻¹$ for the unreinforced copper. Microstructural analysis was carried out using SEM microscopy and indicates that $AI₂O₃$ particles are homogeneously distributed in the copper matrix. EDS analysis shows remains of silicon on the surface of ceramic particles after binding agent used during preparation of ceramic preforms.

Keywords: Metal matrix composite, Copper, Alumina particles, Squeeze casting, Thermal conductivity, Electrical conductivity

1. Introduction

Aluminum oxides and its hydrates present a variety of useful physical and chemical properties like large hardness, insolubility in solvents and inertness to some chemical compounds [1]. Nowadays many companies offer aluminum oxide in different forms, such as powder in the form of particles, from the nano- to microparticles, fibers like SAFFIL [2, 3] and whiskers. The most common allotropic form of crystalline aluminum oxide is very durable corundum α -Al₂O₃ and in this form it is applied as a reinforcement in presented investigations. Aluminum oxide also exists in other allotropic forms like γ, δ, η, θ, κ, β, and χ polymorphic form.

Copper as a matrix for composite materials has been selected specifically taking into account the excellent electrical and

thermal conductivity and very good corrosion resistance. Copper– alumina composite materials can be widely applied in car technology because they combine the properties of copper, i.e. excellent electrical and thermal conductivities and high hardness and resistance to wear caused by the introduction of hard alumina particles into the matrix [4, 5].

2. Experimental procedure

Physical and chemical properties of the strengthening material are shown at Table 1. The molten pure copper (Cu-ETP - 99,9% purity) with the theoretical density 8.94 g/cm^3 , melting point of 1083°C and hardness of 62 HBW2.5/62.5 was overheated about 100°C above the melting point and infiltrated into alumina preforms under the pressure 110 MPa and held for few minutes to complete solidification.

Table 1.

For the preparation of preforms, portions of components were mixed in silica water solution with an inorganic binder and then dried and fired at the temperature of 1000° C. To improve the flow of liquid copper through the porous preforms during squeeze casting operation, preforms were preheated to the temperature of 800 $^{\circ}$ C, and the tools were preheated as follows: die to 350 $^{\circ}$ C and the punch to 250ºC. Figure 1 shows the microstructure of the composite materials on copper matrix containing 30 vol.% of Al2O³ particles. The manufactured composite materials consisted of the areas of diameter 20-30 µm, filled with copper what is caused by the structure of porous preforms with larger pores randomly arranged and very small pores of diameter 2-5 µm. Quantity of these areas, filled with copper, their size and arrangement depended on the volume fraction of the reinforcing alumina particles.

The SEM investigations of the composite materials with Cu-ETP matrix strengthened with 30 vol. % of Al_2O_3 particles show that the alumina particles are homogeneously distributed in the matrix. (Fig. 2). Black regions between of alumina particles and metal matrix indicate for lack of proper adhesion at these regions. This phenomen is especially seen in the regions of clusters of strengthening alumina particles where liquid copper has no possibility to infiltrate the porous structure.

Fig. 1. Microstructure of the composite material Cu-30 vol.% Al_2O_3

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Fig. 2. Microstructure of copper based composite material strengthened with 30 vol. % Al_2O_3 particles (SEM)

Observations of fracture surface of Cu-30 vol. % Al_2O_3 with the scanning electron microscope show the relatively good bonding between reinforcement and the copper matrix (Fig. 3). Particles after braking of the composite materials are undamaged and fracture surfaces occur at the interface ceramic particlescopper matrix.

Fig. 3. Fracture surface of composite materials Cu-30 vol. % of $Al_2O_3(SEM)$

The analysis of the chemical composition of the cross-section of composite materials containing 30 % vol. of alumina particles show that around alumina particles small amounts of silicon or it oxides are present, which probably are remains after binding material applied during forming of porous preforms (Fig. 4). The silicon occurrence is visible at mapping analysis as well as for the presence of silicon indicated the linear EDS analysis. Analyzing the fracture surface of composite material Cu-30 vol. % of Al_2O_3 (Fig. 3), it can be concluded that the liquid copper wets ceramic alumina particles.

composite materials on copper matrix with 30 vol. % of Al_2O_3 particles: a) microstructure (SEM), b) distribution of copper, aluminum, oxygen and silicon, c) the linear EDS analysis

Taking into account the fact that the wettability of alumina by copper is relatively good and solidification process is very fast, the bonding between alumina particles and copper matrix is good. However, the linear EDS analysis shows that Cu oxides may be formed.

3. Discussion

The density of the composite materials was calculated theoretically and then measured by Archimedes method examining the weight of composite materials in toluene (density 0.87 g/cm³). Results are shown in Fig. 5. The value of porosity of composite materials is about 2%.

Fig. 5. Theoretical and measured density of composite materials Cu-alumina particles

Fig. 6. Hardness HBW of composite Cu-based materials and hardness of copper at the not strengthened area

Hardness of composite materials was measured applying the Brinell Hardness Tester with the ball of diameter of 2.5 mm and load of 625 N (Fig. 6). Hardness examinations HB have shown significant reinforcement effect and composite materials exhibit about 2 times higher hardness in relation to pure Cu-casting.

Thermal conductivity (κ) measurements were performed by two methods. First method was based on the axial stationary heat flow in the temperature interval -200 to $+25^{\circ}$ C, namely from the temperature of liquid nitrogen to room temperature. Second applied method of measurements in the temperature range +50 to +600 °C, was based on indirect measurements at 50, 100, 200, 400 and 600°C, where thermal diffusivity on the nonlinear mathematical Cape-Lehman model was calculated, taking into account radiation losses, an atmosphere of protective gas-argon and the covering of samples with graphite on both sides. Experimental results of measurements of thermal conductivity for Cu-ETP used for squeeze casting process and Cu cut from the outside of the infiltration area and for composite materials containing 20 vol.% and 30 vol.% of alumina particles are shown at Fig. 7.

Fig. 7. Thermal conductivity of composite materials vs. temperature (temperature range -200 to +25°C)

The values of thermal conductivity for pure Cu-ETP copper are almost the same as for the copper of non-strengthened part after squeeze casting. The addition of 20 vol. % Al_2O_3 particles results in the lowering of thermal conductivity by about 40%, and for 30 vol.% of Al_2O_3 particles in the copper matrix by about 55% The values of thermal conductivity measured at the range +50 to +600 °C, basing on the second method are presented at Fig. 8.

Fig. 8. Thermal conductivity vs. temperature of composite materials (temperature range $+50$ to $+600$ °C)

The measurements tests were performed on Cu – ETP matrix and Cu with 30 vol. % Al_2O_3 particles The addition of 30 vol.% of Al_2O_3 particles effects on the lowering of thermal conductivity about 40%.

The theoretical value of thermal conductivity for the room temperature was calculated using the Hasselman and Johnson model given by the expression (1) and they introduced the concept of boundary conductance [6].

$$
k = k_m \left(\frac{2\left(\frac{k_T}{k_m} - \frac{k_T}{\Delta k_c} - 1\right) V_d + \frac{k_T}{k_m} + \frac{2k_T}{\Delta k_c} + 2}{\left(1 - \frac{k_T}{k_m} - \frac{k_T}{\Delta k_c}\right) V_d + \frac{k_T}{k_m} + \frac{2k_T}{\Delta k_c} + 2} \right) \tag{1}
$$

where:

 \bf{k}_{m} - thermal conductivity of the matrix (in this case copper)

kr - thermal conductivity of the reinforcement

Vd - volume fraction of reinforcement

hc - boundary conductance

a - radius of the spherical reinforcement

The value of thermal conductivity of copper at room temperature is 400 $\text{Wm}^{-1}\text{K}^{-1}$, and of alumina is 20 $\text{Wm}^{-1}\text{K}^{-1}$. The boundary conductance of Cu-Al₂O₃ at room temperature is 0.23 GW m⁻² K⁻¹ [7] (Fig. 9).

Thermal conductivity is dependent on the boundary conductance between matrix and reinforcement, so theoretical value of thermal conductivity was calculated from the surface particle average diameter [8, 9].

Thermal conductivity decreases proportionally with the increase of alumina particles volume content (Fig. 10). The measured value for Cu-matrix is approximately equal the theoretical, but the measured values of thermal conductivity for composite materials are smaller from the theoretical values by about 15%.

Electrical conductivity measurements were made applying the Sigmatest 2.069 (Foerster Instruments Inc. TM). The results are given in the two units (Table 2); MS/m and commonly used % IACS (International Annealed Copper Standard) for metals and alloys relative to a standard annealed copper conductor; an IACS value of 100% refers to the conductivity of 58×10^6 Siemens per meter (58.0 MS/m) and they are shown at the Table 2.

Fig. 10. The comparison of theoretical and measured values of thermal conductivity at the ambient temperature

Table 2.

The electrical conductivity and volume resistivity at ambient temperature of composite materials Cu-alumina particles

Materials	σ [S/m]	ρ [Ω ·mm ² /m]	[% IACS]
$Cu - ETP$	58.35	0.01714	100.6
Cu - matrix	58.20	0.01718	100.3
$Cu + 20\%$ Al ₂ O ₃	33.20	0.03012	57.2
$Cu + 30\%$ Al ₂ O ₃	20.70	0.04831	35.7

Comparison of the electrical conductivity value of Cu-ETP used for the squeeze casting process and copper cut from the nonreinforced area after squeeze casting, indicates for the same values. The addition of 20 vol.% of the alumina particles reduced the electric conductivity by about 45% and the addition of 30 vol.% of ceramic particles by 65% (Fig. 11).

Fig. 11. The electrical conductivity at room temperature of copper and composite materials Cu-alumina particles

On the slight lowering of electrical conductivity probably affect the eduction of oxides at copper grain boundaries as shown at Fig. 12.

Fig. 12. Microstructure of the composite material: Cu-20 vol.% of $Al₂O₃$ particles (etched with the Mi18Cu reagent)

4. Summary

- 1. Composite materials composed of alumina particles and pure copper manufactured by squeeze casting technology are characterized by homogeneously distribution of reinforcement and low residual porosity.
- 2. Reinforcing by Al_2O_3 particles of Cu matrix applying the squeeze casting method makes possible manufacturing of composite Cu-based materials characterized by large hardness.
- 3. Thermal and electrical conductivity decrease with increasing volume content of reinforcing alumina particles, but these materials are still good electrical and thermal conductors and they are promising materials in industries where high thermal and electrical conductivity is desired.

4. High hardness and assumed large resistance to wear combined with the good electrical and thermal conductivities make these materials useful in electrical power applications.

Acknowledgments

The experiments were executed within the Research Project POIG.01.03.02-14-013/08-00 "KomCerMet" "*Ceramic Metal Composites and Nanocomposites for the Aerospace and Car Industry*" funded by the Polish Ministry of Science and Higher Education, Warsaw, Poland in the framework of the Innovative Economy Operational Programme (POIG) 2007-2013.

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