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M. CHMIELEWSKI*#, K. PIETRZAK*, A. STROJNY-NĘDZA*, D. JARZĄBEK**, S. NOSEWICZ**

INVESTIGATIONS OF INTERFACE PROPERTIES IN COPPER-SILICON CARBIDE COMPOSITES

This paper analyses the technological aspects of the interface formation in the copper-silicon carbide composite and its effect on the material's microstructure and properties. Cu-SiC composites with two different volume content of ceramic reinforcement were fabricated by hot pressing (HP) and spark plasma sintering (SPS) technique. In order to protect SiC surface from its decomposition, the powder was coated with a thin tungsten layer using plasma vapour deposition (PVD) method. Microstructural analyses provided by scanning electron microscopy revealed the significant differences at metal-ceramic interface. Adhesion force and fracture strength of the interface between SiC particles and copper matrix were measured. Thermal conductivity of composites was determined using laser flash method. The obtained results are discussed with reference to changes in the area of metal-ceramic boundary.

Keywords: copper matrix composites, silicon carbide, interface, thermal conductivity, adhesion

1. Introduction

Materials for use in electronic industry should be characterized by the following properties: a high thermal conductivity, thermal expansion coefficient adapted to the properties of semiconductors, good mechanical properties, good workability, the ability to bonding, structural stability during heat cycles, and a low manufacturing cost [1]. Conventional materials hardly ever meet the aforementioned criteria. The literature of the subject is full of examples of materials with a high application potential, e.g. Cu-Mo, Cu-Be, Cu-C (diamond, CNT, graphene), Cu-SiC, Cu-AlN, Al-SiC, Al-AlN [2-3]. Copper with a thermal conductivity of about 400 W/mK is used whenever both high thermal and electric conductivities are required, but the application range of this material is limited because of its unsatisfactory mechanical properties, particularly at elevated temperatures. Moreover, the high thermal expansion coefficient of copper (16.5×10^{-6} 1/K) may result in the induction of considerable residual stresses. Application of silicon carbide can be advantageous due to its low thermal expansion (5.0×10^{-6} 1/K) and high thermal conductivity. It should be noticed that copper decomposes SiC to Si and C at an elevated temperature [4]. As a result of this process, silicon is dissolved into copper, which highly influences the decrease of thermal conductivity of the matrix.

The structure of the interface which depends on a number of different factors may have a major effect on the properties of the composite, comparable to that of the matrix and the reinforcing phase themselves. In case of metal-ceramic composite materials, various types of bonding between these two phases are possible e.g. mechanical, adhesive, diffusive or reactive [5-6]. Each of them, due to their nature, strongly influences the macroscopic properties of bulk materials.

The technological and research tasks were focused on the following objectives: (i) to determine the effect of the process' conditions on the changes within the copper-silicon carbide area, (ii) to evaluate the effect of the metallic layer deposited on SiC powder on the interface's quality, (iii) to examine the mechanical strength of the metal-ceramic bonding, and (iv) to investigate the relation between a type of bonding and the thermal conductivity of composite materials.

2. Materials and methods

In this experiment, copper powder produced by NewMet Koch, with regular shape, grain size of 40 μm, and purity of 99.99%, was used as the matrix starting material. Silicon carbide particles with a mean size of about 80 μm (product of Saint-Gobin) and purity 99.99% was selected as the reinforcement. To protect SiC particles from decomposition silicon carbide particles were covered with tungsten layer using the plasma vapour deposition (PVD) method. The process of spraying was conducted in ULVAC sputtering system. The process was carried out for 12 h at the power of 200 W emitted by the installation's high-frequency generator, which gave a thickness of tungsten coating, $g_W = 0.5$ μm.

Two powders mixtures with different volume fractions of silicon carbide (10.0 and 20.0vol.%) were prepared using

* INSTITUTE OF ELECTRONIC MATERIALS TECHNOLOGY, 133 WÓLCZYŃSKA STR, 01-919 WARSAW, POLAND,
** INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH POLISH ACADEMY OF SCIENCES, 5B PAWINSKIEGO, 02- 106 WARSAW, POLAND
# Corresponding author: marcin.chmielewski@itme.edu.pl

a planetary ball mill (Pulversiette 6, Fritzsch). The mixing process was carried out for 2 h at a rotational speed of 200 rpm in air atmosphere.

The densification of the material was carried out using two different techniques. Non-coated and coated SiC particles mixed with cooper were subjected to Hot Pressing and Spark Plasma Sintering. The HP process was carried out using Astro Thermal Technology press with following parameters: sintering temperature = 1050°C, heating rate = 10°C/min, holding time = 30 min and pressure = 30 MPa in protective atmosphere of argon. The SPS densification process was performed in a vacuum chamber (5.0×10^{-5} mbar) under following conditions: sintering temperature = 950°C, heating rate = 100°C/min, holding time = 10 min, and pressure = 50 MPa. In case of mixtures with SiC powder coated by tungsten, the sintering process was carried out using the SPS method under analogous conditions. After preparing metallographic specimens, the materials were subjected to microstructural examination using scanning electron microscopy with special focus on phenomena occurring at the metal-ceramic boundary. The density of the obtained composite materials was investigated by hydrostatic method. The interface's strength was tested with the use of a microtensile tester [7]. Thermal diffusivity of the obtained composites was measured using laser pulse technique and thermal conductivity of obtained materials was calculated. This was done using the LFA 457 device by Netzsch at the temperature of 50°C in argon atmosphere.

3. Results and discussion

The results of density measurements performed for the obtained Cu-SiC composite materials are presented in Table 1. The theoretical density of the composites was defined for the assumed volume contents, using the density of copper ρ_{Cu} = 8.89 g/cm^3 and the density of silicon carbide ρ_{SiC} = 3.2 g/cm^3. Based on this data for Cu-10%SiC and Cu-20%SiC estimated theoretical densities are $\rho_{Cu\text{-}10SiC}$ = 8.33 g/cm^3 and $\rho_{Cu\text{-}20SiC}$ = 7.76 g/cm^3, respectively.

The obtained results point to significant differences in densification of Cu-SiC composites in relation to the applied sintering method. Although the temperature used in the hot pressing method is higher than in the case of SPS process, the relative density is much lower. All the samples sintered by SPS method, both with uncoated and coated SiC particles, have the measured density similar to the theoretical values (it oscillates around 99%). Some explanation of such behavior can be found in the specific character of the spark plasma sintering process. During the heating and holding time at sintering temperature, the electrical current passes through graphite plugs, and additionally across the Cu-SiC compact. Both components (Cu and SiC) are good conductors of heat and electricity, so they can be easily heated (because of the effect of Joule's heating [8]). As a result, a local temperature increase on grain-to-grain contact sites can be observed, hence it influences the rate of the mass transport (evaporation, convection and diffusion), especially in the case of metal-to-metal contacts. The microstructures of Cu-SiC composite structures after HP and SPS process are presented in Fig. 1.

As it can be seen, the thermal conductivity strongly depends on the material's quality. Two main reasons are decisive: (i) total amount of porosity and (ii) the structure of copper-silicon carbide interface. Higher is the amount of pores in the structure, lower is the thermal conductivity. Cu-SiC composites obtained by Hot Pressing have lower values of relative density in comparison to materials subjected to SPS process. Additionally, the decrease of ability of heat transfer is caused by silicon dissolution in copper. EDX analysis, presented in Fig. 2, proves that part of Si has dissolved in the Cu. Due to the phenomenon of contamination carbon linear distribution results should be treated approximately as a supplement to other results.The observed effect of silicon dissolution has been studied and reported in many papers [9-12]. Even such small disadvantageous changes at metal-ceramic boundary result in the decrease of global thermal conductivity, which is visible in case of coated SiC particles. In this case no pores at the interface and no chemical changes in the structure are observed.

Significant diversification of Cu-SiC composite structure with different sintering methods is the most striking observation of this research. Diversity in composite structure is particularly prominent at metal-ceramic boundary. Despite a higher temperature in case of the HP method (1050°C), pores are observed in large numbers, mainly in the copper matrix.

The reason of such differences could be a higher pressure that assists sintering in SPS method. An external pressure raises the driving force, which results in a faster densification of materials. It is significantly important in the final stage of sintering, when the diffusional creep controls final pore elimination and copper grains can be easily deformed. The distribution of the

TABLE 1

Density results of Cu-SiC composite materials

Chemical composition (vol.%)	Material type and sintering method	Measured density (g/cm^3)	Relative density (%)	Thermal conductivity (W/mK)
Cu-10%SiC	uncoated SiC, HP	7.50	90.0	267.4
	uncoated SiC, SPS	8.22	98.7	323.9
	W coated SiC, SPS	8.24	99.0	336.0
Cu-20%SiC	uncoated SiC, HP	6.81	87.7	234.8
	uncoated SiC, SPS	7.71	99.3	283.4
	W coated SiC, SPS	7.73	99.6	302.0

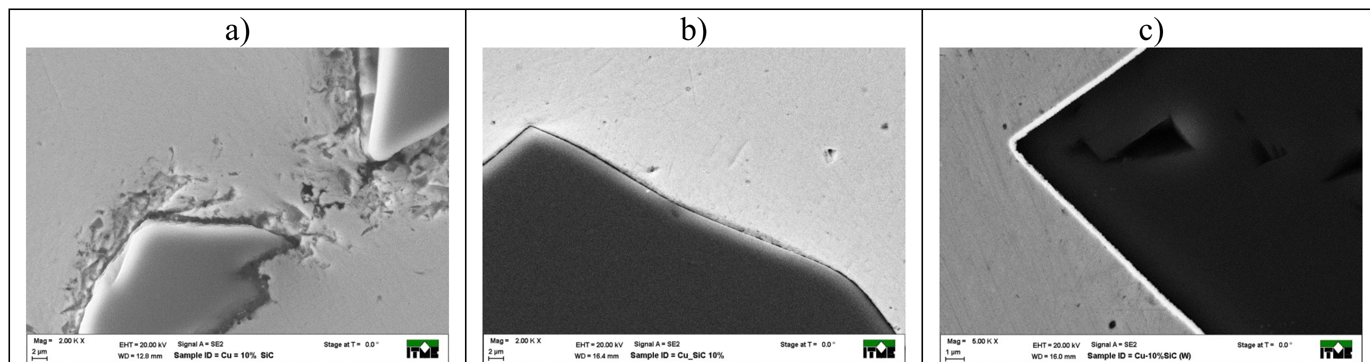

Fig. 1. SEM images of Cu-10%SiC composite structure obtained by: a) HP (uncoated SiC), b) SPS (uncoated SiC) and c) SPS (tungsten coated SiC)

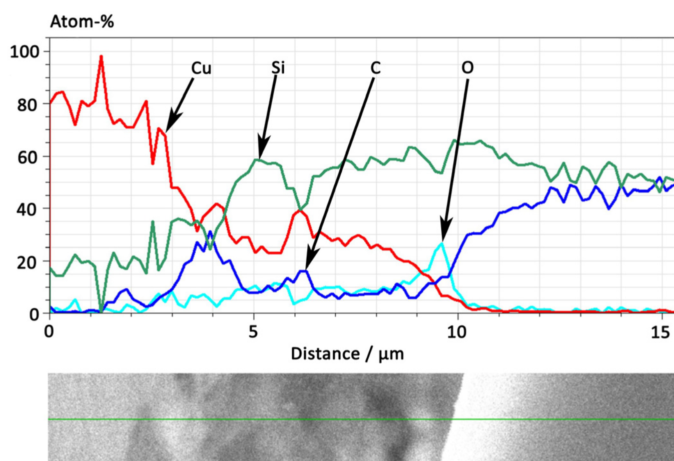

Fig. 2. Linear distribution of elements (Cu, Si, C, O) across the metal-ceramic interface in Cu-SiC composite obtained by HP

copper phase in the composite is alike in both cases, regardless of the employed sintering method. Particular grains are well separated from one another and no SiC aggregates can be found. The material's exposure time at an elevated temperature plays a significant role in the effects occurring within the interface. Indeed, temperature and time have an impact on changes at the copper-silicon carbide boundary. As it can be observed in Fig.1a, the area of structural damage within the interface reaches up to a couple of micrometres. Visible aggregation of pores in combination with the dissolution of silicon in copper significantly affects the mechanical and thermal properties of the composite material. Changes at metal-ceramic bonding after sintering by SPS method are far more limited (up to 200 nm), but will also affect the quality (properties) of the material. Composites sintered by SPS method are characterised by a more gentle course of changes at the metal-ceramic boundary, yet for this case the decomposition of SiC has also been confirmed. Therefore, it seems purposeful to protect silicon carbide with a metallic layer separating SiC from any contact with copper. The observations of microstructure testifies the lack of contact between copper and silicon carbide which prevents the layer from decomposition. The employed material (tungsten) provides a good cover of all layer of the ceramic phase, preventing the possibility of adverse reactions between the components of the composite material.

The state of material at the boundary of the composite's components plays an extremely important role in shaping its global properties. The performed strength tests of the interface confirm our hypothesis.

The force of adhesion between ceramic particle and metal matrix was measured by the precise microtensile tester described in details in [7]. After the tensile test, SEM images of the top of both parts of the broken microwire were taken, the contact area was determined and the interface strength s was calculated.

The particle and the contact area are clearly seen (Fig. 3). In the case of composites with uncoated SiC particles the failure occurs at metal-ceramic boundary. Looking at the particle of silicon carbide surface after debonding, the SiC decomposition has been confirmed. For composites with tungsten coated silicon carbide

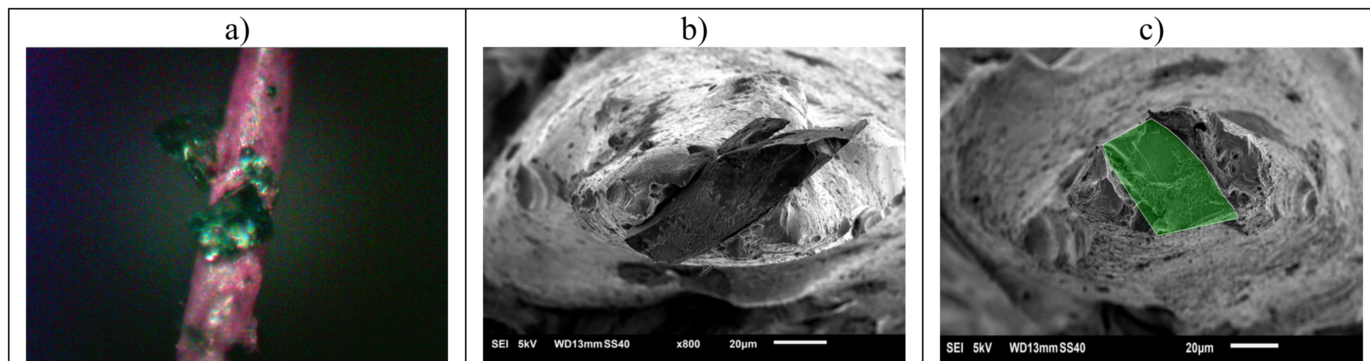

Fig. 3. The microwire of copper with a SiC ceramic particle before (a) and after the test (b and c)

particles, the rupture has a more irregular shape. In all examined cases the debonding surface run across copper-tungsten boundary, some amount of copper on the tungsten layer can be seen.

The interface strength is the highest for samples with particles covered with tungsten (69 ±8 MPa). The strength of interface with uncoated samples produced by means of HP and SPS were 41 ±4 MPa and 54 ±5 MPa, respectively. Note that the value of the interface strength is the average determined from 5 measurements for each sample and the measurement error is determined from a standard deviation of the experiment's results and the inaccuracy of contact area evaluation.

4. Conclusions

The paper analyses the effect of metal-ceramic bonding structure on the properties of composite material. Given a high reactivity of the Cu-SiC system at an elevated temperature, it seems purposeful to cover the SiC powder with a metallic layer for protection. Based on a series of experiments, the following conclusions can be drawn:

(1) during the process of sintering of Cu-SiC composites, silicon carbide is decomposed, which results in the dissolution of silicon copper and the formation of a free layer of carbon,
(2) the range of changes within the interface is highly dependent on the heating time during sintering and ranges from a couple of hundreds of nanometres to a couple of micrometres,
(3) the use of a thin layer of tungsten prevents silicon carbide from decomposing, Cu/W and W/SiC boundary contact points are not ruptured,
(4) the strength of Cu-SiC bonding in case of coated powders is higher by 25% compared to uncoated ones and obtained in the course of an analogous process,
(5) thermal conductivity of the manufactured composite materials is dependent on the interface's structural condition, and even small changes in the copper matrix at contact points with silicon carbide cause this parameter to drop.

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