DEPTH PROFILE OF COPPER, ZIRCONIUM, AND CARBON IN Cu-Zr-C SYSTEM AFTER HEAT TREATMENT

PAVOL ŠEBO, GEORG KORB

The diffusion of zirconium and copper deposited on a flat graphite surface after annealing at 898 K for 1800 s and 1233 K for 300 s was studied by glow discharge optical emission spectrometry. At the temperature of 898 K no mutual diffusion of Zr and Cu appears. At the temperature of 1233 K Zr diffuses into Cu, and a zirconium containing phase at the contact with carbon may occur. The obtained results have a qualitative character and are discussed in connection with the influence of zirconium on the thermal conductivity of the Cu-Zr matrix.

HĹBKOVÝ PROFIL MEDI, ZIRKÓNIA A UHLÍKA V SYSTÉME Cu-Zr-C PO TEPELNOM SPRACOVANÍ

Študovali sme difúziu zirkónia a medi, ktoré sme naniesli na rovinný povrch grafitu po žíhaní pri teplote 898 K počas 1800 s a pri teplote 1233 K počas 300 s optickou emisnou spektroskopiou pomocou tlecieho výboja. Pri teplote 898 K nedochádza k vzájomnej difúzii Zr a Cu. Pri teplote 1233 K Zr difunduje do medi a možno predpokladať vznik fázy obsahujúcej zirkónium v mieste kontaktu s uhlíkom. Získané výsledky majú kvalitatívny charakter a analyzujeme ich z hľadiska vplyvu zirkónia na tepelnú vodivosť matrice Cu-Zr.

1. Introduction

The basic characteristics of the composites required for electric and electronic parts are high thermal and electrical conductivities. Such materials can be applied as a contact material, brush, and substrate for a silicon semiconductor element. Another important application is for rejection of waste heat by radiation to the space environment from the space power system.

By combination of two materials like copper and carbon fibre as composite and utilizing their properties as high thermal and electrical conductivities for copper

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RNDr. P. Šebo, CSc., Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Račianska 75, P. O. Box 95, 830 08 Bratislava 38, Slovak Republic.

Dr. G. Korb, Austrian Research Centre Seibersdorf, A-2444 Seibersdorf, Austria.

and high mechanical properties (strength, elastic modulus), low density, negative coefficient of thermal expansion, high thermal conductivity (some kinds) for carbon fibres, one can tailor the properties of the finished material.

Carbon-fibre-copper-matrix composites can be prepared either by infiltration of liquid copper into the carbon fibre tows or by diffusion bonding of copper coated carbon fibres [1]. A difficulty in using carbon fibres with copper is the lack of adhesion between copper and carbon fibres. This is manifested at high temperatures by spheroidization of copper on carbon fibres [2].

Liquid copper neither wets carbon nor chemical reaction occurs at the interface between copper and carbon fibre. This interface is chemically inert against carbon fibres.

Najdich [3] investigated the wetting of diamond and graphite surfaces by alloying the copper with various metals and found out that Cu alloys with carbide forming elements improve wetting of graphite substrate. Mortimer and Nicholas [4, 5] investigated the wetting of graphite and vitreous carbon by alloying the copper with small amounts of active metals. They found out that at the temperature 1145℃ and pressure of $\sim 7 \times 10^{-3}$ Pa copper required addition of ~ 10 at.% titanium before wetting either vitreous carbon or graphite. Chromium additives to copper as low as 0.15 at.% produced wetting of vitreous carbon. Liu et al. [6] studied also the effect of alloying on the wettability of carbon fibres by copper. They found out that transition metals, whose binary alloys form a miscibility gap in liquid state and have rather small solubility in solid state in copper (Mo, Cr, V, Fe, Co), are potential candidates for the improvement of the wettability of carbon fibres by copper. This improvement of wettability can be attributed mainly to the interface adsorption of alloying elements and to the interface reactions between alloying elements and carbon fibres which lead to the reduction of interface tension.

Sun and Zhang [7] studied interface characteristic and fracture surface of C-‑Cu, C-Cu-Ni and C-Cu-Fe composites, which were prepared by copper coating of carbon fibre in the first case and by duplex coating Cu-Ni and/or Cu-Fe and additional Cu deposition in the last two cases and by diffusion bonding. Interfaces of C-Cu-Fe and C-Cu-Ni composites are strengthened by the reaction between Fe and carbon fibre and dissolution of Cu-Ni solid solution in carbon fibre, respectively. Abel et al. [8] showed that Ti and Cr bond layers deposited onto carbon fibre prior to copper coating should enhance the adhesion between copper matrices and carbon reinforcement fibres. From the thermal conductivity point of view, chromium appears to be the better candidate for actual use as it has a much lower solubility in copper than titanium has.

The paper presents the results of study the diffusion of zirconium as a carbide forming element and copper deposited on graphite flat surface as a model at various temperatures from the point of view of the possible influence of zirconium on the thermal conductivity of the Cu-Zr matrix when either using the zirconium for coating of carbon fibres or using the zirconium as addition to copper alloy to improve the adhesion of copper to carbon fibres.

2. Experimental procedure

Flat graphite was used as a substrate for the analysis of diffusion between zirconium and copper deposited on it and carbon. Zirconium was deposited on graphite by evaporation in the vacuum evaporation equipment at the vacuum of the order of 10^{-3} Pa. After deposition of zirconium a copper layer was deposited on zirconium coated graphite at the same conditions. Simultaneously, zirconium as well as copper were deposited on pure glass to be able to measure the thicknesses of both deposits. Thickness of Zr and Cu layers was measured by profilometer Talystep as well as by optical interferometry. The results from both methods are practically the same. Thickness of zirconium was 35 nm and that of copper 60 nm.

To determine the benefits of the bond coatings, substrates with deposited layers were annealed at 898 K (625 °C) for 1800 s and at 1233 K (960 °C) for 300 s in flowing nitrogen to reduce film sublimation during annealing. To measure the distribution and depth profile of the relevant elements, the glow discharge optical emission spectrometry was used. Glow discharge optical emission spectrometry (GDOES) presents the combination of sputtering and atomic emission. In a glow discharge lamp cathode which is made of analyzed sample and anode are separated in a glass vacuum chamber and a carrier gas (argon) is introduced and voltage is applied between the electrodes. Argon in the cathode dark space is ionized and these argon ions bombard the cathode (sample) surface causing sputtering. Sputtered material enters the negative glow region where it glows brightly by atomic emission. The emission lines are then detected and recorded by the photomultipliers in the spectrometer attached to the glow discharge lamp to analyze the material being sputtered from the sample. By this method the depth profile of copper, zirconium, and carbon elements for as-deposited Cu and Zr on graphite as well as for annealed samples were obtained. The sample composition and annealing conditions are summarized in Tab. 1.

Table 1. Annealing conditions of Cu-Zr-C specimens

Sample	Structure	Annealing temperature [K]	Annealing time [s]
Zr 1	Cu-Zr-C	RT	
Zr 2	Cu-Zr-C	898	1800
Zr 3	Cu-Zr-C	1243	300

3. Results

Figures 1a,b,c show glow-discharge-optical-emission-spectrometry depth profile of copper, zirconium, and carbon from the as-deposited as well as annealed copper and zirconium deposited on graphite substrate. GDOES depth profile, which displays the emission intensity (which is proportional to the elements concentration) vs. sputtering time (expressing the depth of the sputtered material) of the as-deposited Cu and Zr on C substrate, shows the expected two-layer structure for copper and zirconium interlayers (Fig. 1a). As it can be seen from this spectrum, zirconium and copper, due to the porosity of graphite, penetrate into the graphite up to the depth corresponding to ~ 120 s of sputtering time. Porosity of the graphite causes that the emission intensity from copper as well as from zirconium does not decrease fast after sputtering the zirconium layer off, but emission intensity is slowly decreasing with the sputtering time (i.e. depth) showing that the copper as well as zirconium are found in pores of the graphite to some depth. After annealing at 898 K for 1800 s (Fig. 1b), both zirconium and copper diffuse deeper into graphite – to the depth corresponding to ~ 170 s of sputtering time

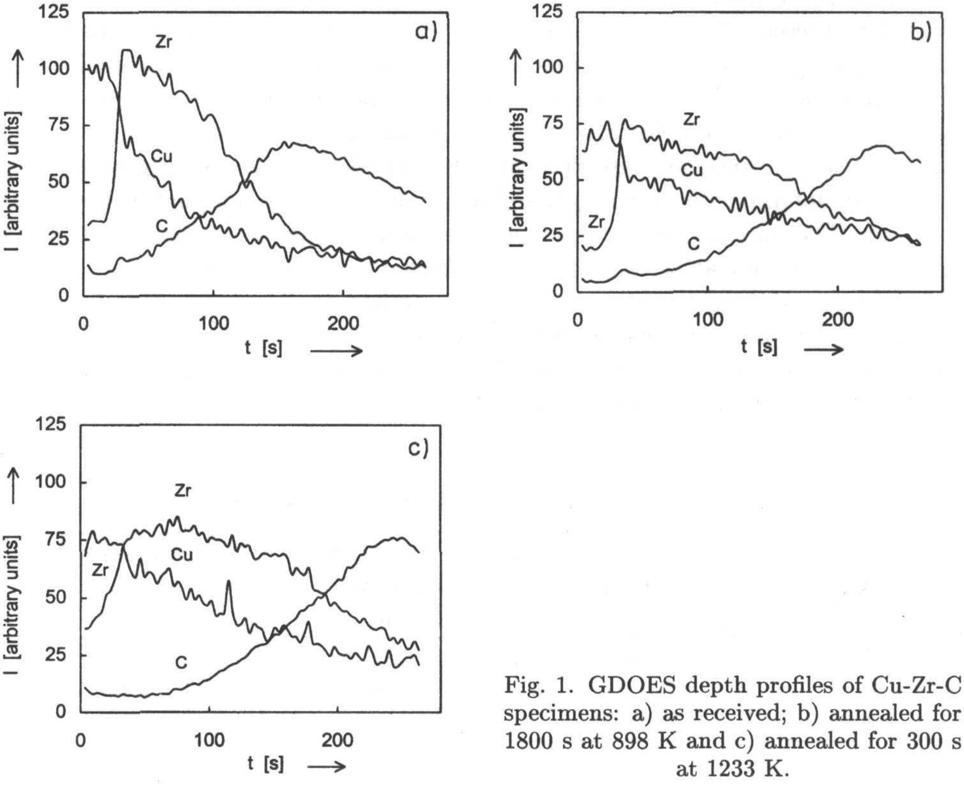

Fig. 1. GDOES depth profiles of Cu-Zr-C specimens: a) as received; b) annealed for 1800 s at 898 K and c) annealed for 300 s at 1233 K.

(copper and zirconium reveal smaller gradient of their concentrations) – than to as-deposited sample. Temperature 898 K is approximately the temperature of diffusion bonding of copper-coated carbon fibres producing the Cu-C fibre composite. From the spectrum (Fig. 1b) one can see that zirconium (at this temperature and time) does not diffuse into copper which is important from the point of view of thermal conductivity of the matrix. In both of these cases (Fig. 1a,b) the emission intensity of zirconium is increasing sharply just after sputtering the copper off.

After the thermal treatment at 1233 K and 300 s (Fig. 1c) zirconium began to diffuse into the copper forming thus the gradient of zirconium concentration in the copper layer. Emission intensity from zirconium does not increase sharply and zirconium is found in the copper layer. Close to this copper layer (with Zr concentration gradient) a relatively thick zirconium layer arises which could suggest forming a phase containing zirconium.

4. Discussion

The object of this work is to study the diffusion of zirconium and copper deposited on graphite from the point of view of the possible influence of zirconium in copper on the thermal conductivity of the matrix, having in mind the use of zirconium as a carbide forming element for improving the adhesion of the copper matrix to carbon fibre in Cu-C fibre composite.

As it was mentioned in introduction, one of the directions of using composite material with carbon-fibre-copper matrix is utilization of its thermal conductivity which should approach to that of copper or even be greater. It is generally known that even low concentration of alloying element can significantly reduce copper electrical conductivity (e.g. addition of 0.01 at.% Ti in Cu reduces its electrical conductivity by 10% [8]), which is found to be proportional to its thermal conductivity. From this point of view, an area of concern of these materials is the diffusion of bond layer material into the copper matrix with the resulting loss of high matrix thermal conductivity.

In the case of Cu-Zr alloy, the obtained results (which have a qualitative character because the relation between the intensity of emission and atomic concentration of the elements has not been determined) show that zirconium appears to be a promising bond layer material. Solid solubility of zirconium in copper is very low (0.11 wt.%). GDOES depth profiles show no mutual diffusion of copper and zirconium metals at the temperature of 898 K after 1800 s (which are the parameters of Cu-C fibre composite production). This fact can have a positive effect on the thermal conductivity of the Cu matrix which is not influenced by zirconium. Another question is the real improvement of adhesion of copper containing zirconium matrix to the carbon fibres which is the subject of another study. At the temperature of 1233 K after 300 s zirconium diffuses into copper layer which certainly would reduce the thermal conductivity of the Cu-Zr matrix. At the contact of zirconium with carbon one can expect arising of zirconium containing phase.

5. Conclusions

The depth-profile concentrations of copper, zirconium, and carbon were measured on the specimens prepared by vacuum evaporation of zirconium on flat graphite surface followed by the deposition (again by vacuum evaporation) of copper on this zirconium coated graphite. Measurements were done for as-deposited sample as well as for other two samples annealed at two temperatures (898 K for 1800 s and 1233 K for 300 s) by the GDOES method. The results obtained by investigation of diffusion of copper and zirconium deposited on graphite flat specimens can be summarized as follows:

GDOES depth profile of Cu-Zr-C specimen annealed at 898 K for 1800 s shows that zirconium does not diffuse into the copper what should have a positive effect on the thermal conductivity of the Cu matrix as it is not influenced by zirconium. Copper and zirconium diffuse deeper into the carbon. At the temperature 1233 K after 300 s, zirconium diffuses into the copper layer which certainly would reduce the thermal conductivity of the Cu-Zr matrix. Close to this Cu layer a relatively thick zirconium layer arises which suggests the possibility of forming a phase containing zirconium.

Zirconium thus seems to be promising as a bond layer in copper-carbon fibre composite at least from the point of view of not influencing the thermal conductivity of the Cu matrix at the temperature corresponding to the Cu-C composite material production.

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