INFLUENCE OF CARBIDE FORMING ELEMENTS (Ti, Zr) ON THE INTERFACE OF COPPER MATRIX-CARBON FIBRE COMPOSITE

PAVOL ŠEBO, PAVOL ŠTEFÁNIK, ŠTEFAN KAVECKÝ, JOZEF IVAN

Influence of carbide forming (Ti and Zr) elements on the interface structure of copper matrix-carbon fibre (Cu-CF) composite was investigated. Specimens composed of Cu-CF embedded in Cu-(0.7 and 3.6 wt.%)Ti and/or Cu-(0.15; 1.3, and 5.1 wt.%)Zr alloys were prepared by hot isostatic pressing. The structure was studied by light and scanning electron microscopy equipped with X-ray analyser, transmission electron microscopy, and selected area electron diffraction. Titanium from the alloy with higher concentration of Ti diffuses onto the carbon fibres located close to (Cu-CF) border with Cu-Ti alloy and reacts with carbon forming titanium carbide. Zirconium diffuses only to border with Cu-CF composite forming Cu-Zr intermetallics and neither effects Cu-CF composite, nor carbon fibre. Copper oxide was found at the interface between carbon fibre and copper matrix.

Key words: copper matrix, carbon fibre, composite, interface

VPLYV KARBIDOTVORNÝCH PRVKOV (Ti, Zr) NA ROZHRANIE KOMPOZITU MEDENÁ MATRICA-UHLÍKOVÉ VLÁKNO

V práci sme študovali vplyv karbidotvorných (Ti a Zr) prvkov na štruktúru rozhrania kompozitného materiálu medená matrica-uhlíkové vlákno (Cu–CF). Vzorky skladajúce sa z kompozitu Cu-CF umiestneného v zliatinách Cu-(0,7 a 3,6 hm. %)Ti, ako aj Cu-(0,15, 1,3 a 5,1 hm. %)Zr sme pripravili izostatickým lisovaním za tepla. Štruktúru sme študovali svetelnou a riadkovacou elektrónovou mikroskopiou s rtg. analyzátorom, transmisnou elektrónovou mikroskopiou a elektrónovou difrakciou. Titán zo zliatiny s vyššou koncentráciou Ti difunduje k uhlíkovým vláknam lokalizovaným v blízkosti hranice zliatiny Cu-CF a Cu-Ti, reaguje s uhlíkom a vytvára karbid titánu. Zirkónium difunduje iba na hranicu s kompozitom Cu-CF, kde vytvára intermetalidy Cu-Zr a neovplyvňuje kompozit Cu-CF ani uhlíkové vlákna. Na rozhraní medzi vláknom C a medenou matricou sme zistili oxid medi.

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1. Introduction

Many composite materials have been developed as structural materials with improved specific strength, specific modulus of elasticity, and other mechanical properties.

Copper matrix-carbon fibre (Cu-CF) composite possesses mechanical as well as other desirable, utilizable properties like electrical and thermal conductivity, low thermal expansion, and others. This material exploits high electrical and thermal conductivity because of the copper component and negative coefficient of thermal expansion, low density and even high thermal conductivity because of carbon fibres content.

Application of such material can be quite broad. Continuous carbon fibre reinforced copper matrix composites are considered [1] as replacement of monolithic copper frames in standard electronic modules. These composites provide structural support and work as heat sinks for the attached electronics. The increased strength and reduced density of the metal matrix composites allow to decrease the module weight, while their increased stiffness diminishes flexural fatigue of solder joints between chip carriers and circuit boats attached to the module frames. Another area where Cu-CF composites can be used is the space [2]. Significant power usage aboard space craft requires a method of radiating excess heat into space. Space-based radiators fabricated on the Earth need to be both high thermally conductive and as lightweight as possible for launch [3].

One of the method, to prepare continuous carbon fibre-copper matrix composite is diffusion bonding of copper coated carbon fibres [4]. A difficulty in using carbon fibres with copper is the lack of adhesion between copper and carbon fibres. This is manifested at high temperature by spheroidization of copper on carbon fibres [5]. Several experiments have been done to improve this adhesion.

Sun and Zhang [6] studied the interface characteristic and fracture surface of the composites which were prepared by diffusion bonding of copper/nickel and/or copper/iron coated carbon fibres. 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. [7] showed that titanium and chromium bond layers deposited onto carbon fibre prior to copper coating should enhance the adhesion between copper matrix and carbon reinforcement fibres.

The aim of this project is to investigate the influence of carbide forming elements (Ti and Zr) on the structure of Cu-CF composite and on the interface in composite between the carbon fibre and copper embedded in Cu-Ti and/or Cu-Zr alloys as a source of carbide forming elements after hot isostatic pressing.

2. Experimental procedure

The source of carbide forming element for its interaction with carbon fibre as well as with copper matrix in Cu-CF composite can be either a thin layer of this element deposited on carbon fibre followed by copper coating and diffusion bonding or a Cu alloy containing carbide forming element in which copper matrix-carbon fibre composite is embedded, which was our way.

Cu-Ti (containing 0.7 and 3.6 wt.% Ti) and Cu-Zr (containing 0.15, 1.3 and 5.1 wt.% Zr) in the form of cylinder with diameter 12 mm and $\approx$ 50 mm length were prepared. Holes of diameter 3.2 mm were drilled into the cylinders as well as into an identical cylinder of pure copper. The holes were filled with copper coated carbon fibres. Carbon fibres (Torayca T 300) were chemically and galvanically coated with copper of thickness about 1 μm. All the filled Cu, Cu-Ti, and Cu--Zr cylinders were inserted into a container, evacuated and isostatically pressed at temperature 1223 K, with a pressure of 100 MPa, during 1 hour. After isostatic pressing the cylinders were cut and specimens were metallographically prepared for studying of the structure by optical and scanning electron microscopy using the energy dispersive X-ray analysis.

Optical micrographs were obtained to recognize the border between Cu-CF composite and Cu-Ti and/or Cu-Zr alloys hollow cylinder.

Scanning electron microscopy (SEM) analysis was performed to investigate the reaction layer. Energy dispersive X-ray analysis was used to measure the linear concentration profile across the boundary between both parts of the specimen, i.e. Cu-CF composite and Cu-Ti or Cu-Zr alloy, as well as to identify the presence or absence of carbide forming element around the carbon fibre.

A transmission electron microscopy (TEM) investigation of the carbon fibre//copper matrix interface was conducted on Cu-CF – Cu-3.7 Ti and Cu-CF – Cu--5.1 Zr. Specimens were prepared by sectioning the cylinder upright to the fiber axis. Discs were mechanically grinded and ion-beam etched until the perforation of the foil by the rapid etching system 010. The reaction layer was studied and identified using a combination of imaging and selected area electron diffraction (SAED) methods.

3. Results

Fig. 1 shows, as an example, the arrangement of both parts of specimen, carbon fibre reinforced copper matrix composite embedded in Cu-5.1wt.%Zr alloy after hot isostatic pressing at 1223 K, 100 MPa and 1 h. Similar arrangement was used for all studied samples. Because of the reaction products from Cu-Ti and Cu-Zr alloys are different, the respective results will be given separately.

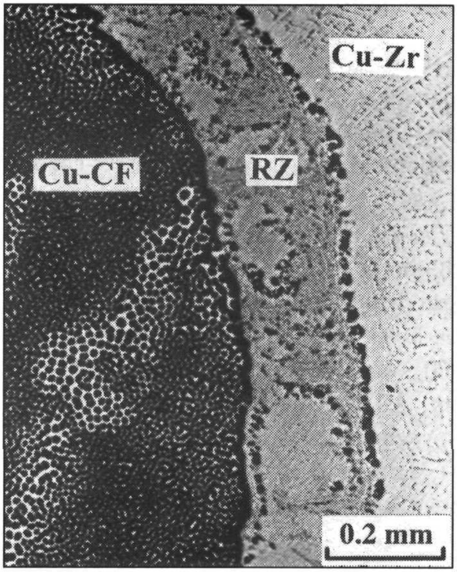


Fig. 1. Arrangement of copper-coated carbon fibres composite (Cu-CF) embedded in Cu-5.1wt.%Zr alloy (Cu-Zr) cylinder after hot isostatic press, RZ – reaction zone.

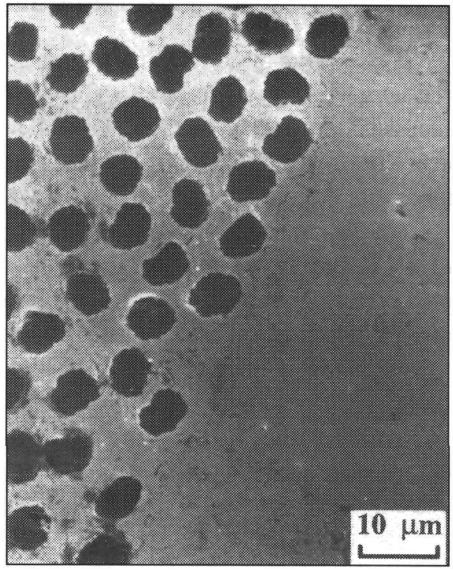
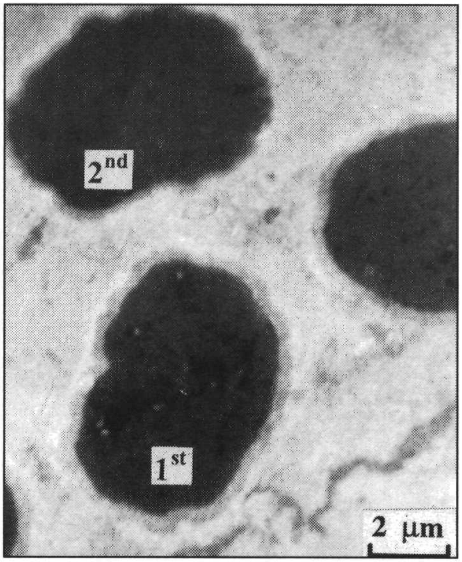


Fig. 2. Copper-coated carbon fibres embedded in Cu-0.7wt.%Ti alloy cylinder.

3.1 Cu-Ti alloys

Fig. 2 shows the cross section of Cu-0.7Ti-(Cu-CF composite) after hot pressing. The SEM with energy dispersive system (EDS) analysis revealed an increased concentration of titanium at the interface between composite material and Cu-Ti alloy. No titanium was detected in the copper matrix itself as well as around the carbon fibres. Another picture appears in the specimen with higher titanium concentration (Cu-3.6wt.%Ti) (Fig. 3). Titanium diffuses into Cu-CF composite forming a reaction zone around the carbon fibres. This one is the thicker the closer the carbon fibre is located to the boundary between composite and Cu-Ti alloy. The thickness of reaction zone for the most outer fibres (the closest to the alloy) is about 0.5 μm and decreases for the fibres with increasing distance from the boundary. For given parameters of sample production, titanium diffuses up to the fourth "layer" of carbon fibres from the boundary between the composite and Cu-Ti alloy (two of them can be seen in Fig. 3). Transmission electron microscopy from the foil made of (Cu--CF composite)-Cu-3.6Ti alloy sample reveals that the reaction zone around the carbon fibre is titanium carbide (Figs. 4a,b).

Fig. 3. Two "layers" (1^{st}, 2^{nd}) of carbon fibres located closest to the border between Cu-3.6wt.%Ti alloy and Cu-CF composite.



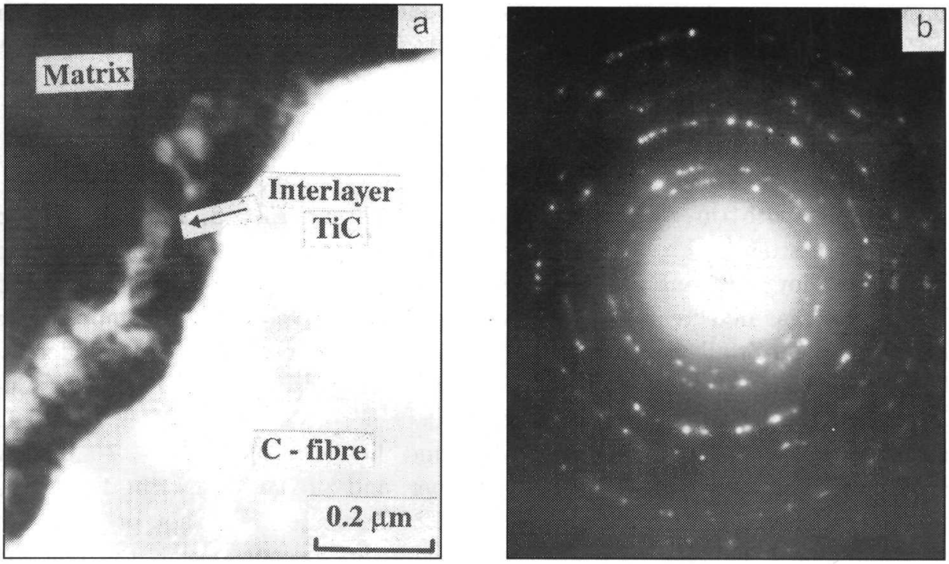


Fig. 4. Sample Cu-3.6wt.%.Ti alloy and Cu-CF composite. (a) Transmission electron microscopy of the reaction zone around the carbon fibre in Cu-CF composite and (b) electron diffraction pattern from the reaction zone.

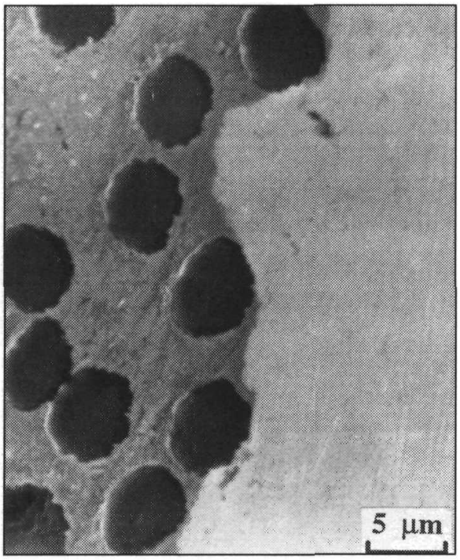


Fig. 5. SEM of the boundary between Cu--0.15wt.%Zr alloy and Cu-CF composite after hot isostatic pressing (1223 K, 100 MPa, 1 h).

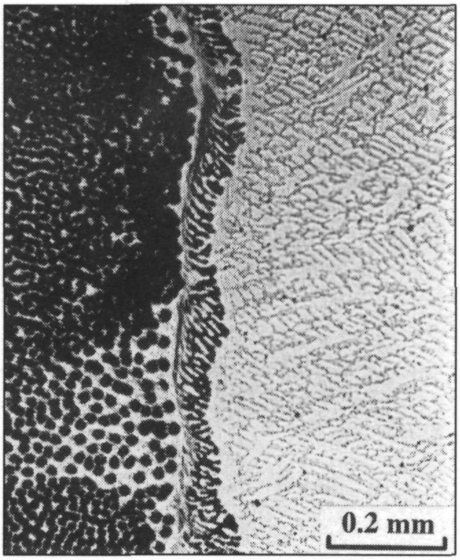


Fig. 6. Reaction zone around Cu-CF composite located in Cu-1.3wt.%Zr alloy after hot isostatic pressing (1223 K, 100 MPa, 1 h).

3.2 Cu-Zr alloys

Samples with three concentrations of zirconium 0.15, 1.3, and 5.1 wt.% in copper were studied. Fig. 5 shows the boundary between Cu-CF composite and Cu-0.15Zr alloy. No diffusion of zirconium to the border between the composite and Cu-Zr alloy was detected. Similarly, no zirconium was detected in composite. In another two Cu-Zr alloys (3.1 and 5.1%Zr) the behaviour of zirconium is different. Around all composite a "ring" of Cu-Zr intermetallics appears (Fig. 6 for Cu--1.3Zr and Fig.1 for Cu-5.1Zr). Zirconium does not diffuse out of this zone, i.e., neither into the Cu-CF composite, nor around the carbon fibre. Figs. 7 a,b show SEM picture and EDS map of carbon, copper, and zirconium distribution in the boundary between Cu-CF composite and Cu-5.1Zr alloy after hot pressing. No diffusion zone is evident. Transmission electron microscopy reveals the reaction zone (thickness $\approx$ 0.1 μm) around each carbon fibre (Fig. 8). Selected electron diffraction from this zone (Fig. 9 in dark field) gives copper oxide Cu_2O (Fig. 10).

4. Discussion

The bond layer application is relied on the diffusion kinetics of titanium and

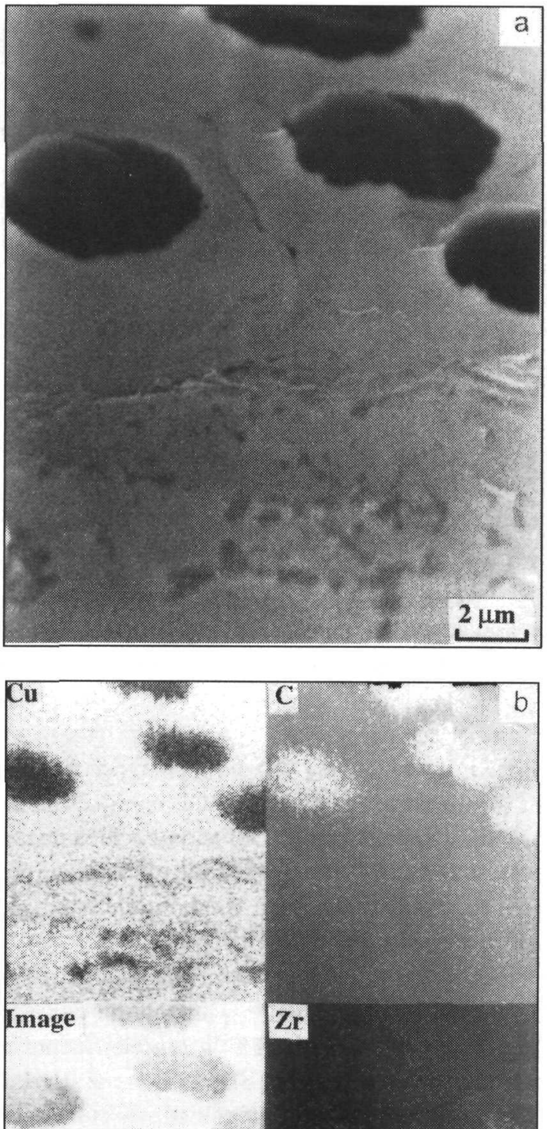


Fig. 7. SEM picture showing (a) the boundary between Cu-CF composite and Cu-5.1wt.%Zr alloy after hot pressing; (b) X-ray map of Cu, Zr, and C distribution.

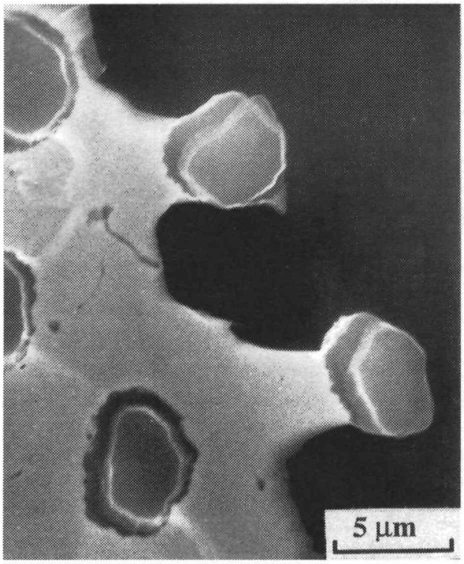


Fig. 8. SEM picture showing part of Cu--CF composite in the form of foil prepared for TEM.

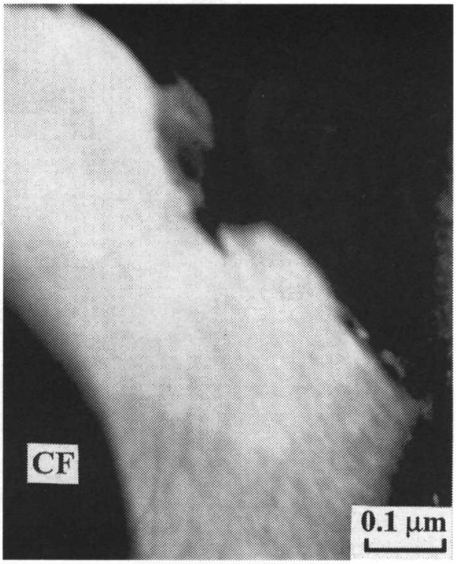


Fig. 9. Reaction zone around carbon fibre (CF) in dark field (white area) in TEM.

zirconium in copper forming the matrix of Cu-CF composite reaching the interface between carbon fibre and copper matrix. Diffusion coefficient of titanium in copper for T = 1223K is $D = 3.1 \times 10^{-13}$ m^{2}s^{-1} [8]. For given conditions (1223 K, 1 h) titanium diffuses to the distance from the boundary between Cu-Ti alloy and Cu-CF composite of about 30 μm, which corresponds to the calculated diffusion distance $x = \sqrt{Dt} = 33.4$ μm, where t is time of diffusion.

The proper knowledge of the diffusion phenomena can result into forming a reaction zone around each carbon fibre. These reaction zones consist of titanium carbide as it was verified by TEM and SAED. It is generally known that even low concentration of alloying constituents can significantly reduce the thermal conductivity of copper. Titanium causes a significant decrease of conductivity with its percentage. No titanium was detected by EDS analysis in copper matrix of Cu--CF composite in the studied specimens. All titanium which diffused from Cu-Ti alloy into the composite was used for titanium carbide formation around carbon fibres located close to the boundary between Cu-CF composite and Cu-Ti alloy. Titanium carbide layers may lower the thermal conductivity of the composite as a whole. The thermal conductivity of titanium carbide at room temperature is λ_{TiC} = 31.8 W/m.K compared to copper λ_{Cu} = 401 W/m.K at the same temperature [9, 10]. On the other hand, one can assume that titanium carbide at the fiber-matrix interface will enhance the fiber-matrix adherence which is important in controlling the thermal expansion especially at elevated temperatures, where the absence of a chemical bond at the fiber-matrix interface can lead to debonding.

Use of zirconium in copper alloys is quite different than of titanium. Zirconium from the Cu-Zr alloy diffuses only to the boundary between alloy and composite material forming Cu-Zr intermetallics. Because zirconium does not diffuse to the composite at all, neither influence of it on the CF-copper matrix adhesion nor on thermal conductivity of Cu-CF composite can be observed. Transmission electron microscopy from the interface between carbon fibre and copper matrix, however, reveals the existence of Cu_2O around the carbon fibre. Oxygen can be released from the carbon fibre and reacts with copper, forming Cu_2O. The existence of Cu_2O could have also an effect on thermal conductivity (heat transportation across the interface) in carbon fibre – pure copper matrix composites.

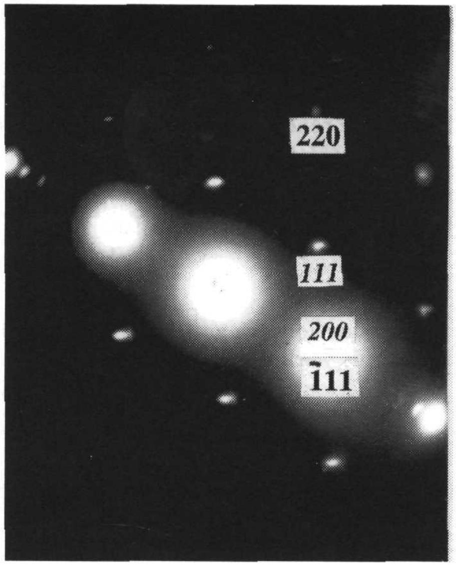


Fig. 10. Selected electron diffraction area from white area of Fig. 9 (hkl – Cu, *hkl* – Cu_2O).

5. Conclusions

The influence of titanium and zirconium in Cu-Ti and/or Cu-Zr alloys on the interface between carbon fibre and copper matrix composite embedded in these alloys was investigated. Titanium diffuses to the carbon fibre, forming a reaction zone around the carbon fibres located close to the boundary between composite and Cu alloy. TEM and SAED methods proved that these reaction zones consist of titanium carbide.

The titanium carbide reduces the mutual diffusion of the copper matrix with titanium. Equable diffusion of titanium to each carbon fibre or coating of carbon fibre by titanium followed by copper coating and titanium carbide forming at the carbon fibre-copper matrix interface may give rise to the material with improved adhesion and not deteriorated thermal conductivity of the copper matrix.

Zirconium diffuses only to the border between Cu-Zr alloy and Cu-CF composite. No influence of zirconium on carbon fibre-copper matrix interface in composite was observed. TEM and SAED from the specimen Cu-CF composite embedded in Cu-5.1Zr, however, showed the presence of copper oxide (Cu_2O) at the interface between carbon fibre and copper matrix in the composite. Copper oxide appears due to the reaction with oxygen which could have been adsorbed during removing the sizing from the carbon fibre prior to the copper coating process. The presence of copper oxide around the carbon fibres can have an effect on the thermal conductivity of Cu-CF composite.

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