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Influence of Ti and Zr on the bond strength between carbon rod and Cu-Ti and/or Cu-Zr alloys

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Influence of Ti and Zr in Cu matrix on the shear strength between Cu-Ti and Cu-Zr alloys and carbon rod was studied. Cu based specimens containing 0.7 and 3.6 wt.% Ti as well as 0.15; 1.3 and 5.1 wt.% Zr were prepared by hot pressing (HP) and hot isostatic pressing (HIP). In all cases, titanium diffuses to the boundary between carbon rod and Cu-Ti alloys and reacts with oxygen forming titanium oxides. Shear strength is higher for HIP specimens and increases with Ti content. The layer adjacent to carbon rod, in the case of Cu-Zr alloys, is pure copper (except for Cu-5.1 wt.% Zr alloy). The shear strength in this case is close to that of pure copper. For Cu-5.1 wt.% Zr the adjacent copper layer to C rod contains Cu-Zr particles. The shear strength is higher compared to Cu-0.15 and 1.3 wt.% Zr alloys, which can be due to the presence of this complex layer.

1. Introduction

Carbon fibre-copper matrix composite can be used as a contact material, for example as substrate for powerful semiconductor elements or rejection of waste heat by radiation to the space environment, and many others. This material utilises the properties of its components: very high thermal conductivity of copper with high mechanical properties, the negative thermal expansion, and the low density of carbon fibre.

Most composite materials with metallic matrix reinforced by carbon fibres are prepared by liquid matrix infiltration, either by continuous casting or by using the external pressure to infiltrate the fibre preform. Liquid copper neither wets the carbon fibre nor do chemical reactions occur at the interface between copper and carbon fibres. The interface is chemically inert against carbon fibres and may not be strong enough to transfer the applied load between the copper matrix and the carbon fibres.

Sun and Zhang [1] studied the interface characteristics and surface structure of carbon fibre (CF)-copper-nickel and CF-copper-iron composite. They found that interfaces CF-Cu-Ni and CF-Cu-Fe are strengthened by the dissolution of Cu-Ni solid solution in CF and by the reaction between Fe and CF, respectively. Abel *et al*. [2] showed that Ti and Cr bond layers deposited onto CF prior to copper coating should enhance the adhesion between the copper matrix and the carbon reinforcement fibres.

The aim of the present study was to investigate the influence of Ti and Zr contained in Cu-Ti and Cu-Zr alloys on the bond strength, using carbon bar as a model.

2. Experimental

Five various alloys and pure copper were prepared to study the interface between these alloys and carbon rod: pure Cu, Cu-0.7 wt.% Ti, Cu-3.6 wt.% Ti, Cu-0.15 wt.% Zr, Cu-1.3 wt.% Zr and Cu-5.1 wt.% Zr. Two kinds of specimens were prepared:

(a) Cylinder of Cu alloys (diameter $\phi = 12$ mm) were cut to achieve discs of the length of 2 and 5 mm and holes of diameter $\phi = 3.2$ mm were drilled into each disc. A graphite (C) rod of diameter $\phi = 3.2$ mm was inserted into the hole. Each disc with C rod was treated with a graphite die and hot pressed at a temperature of 1123 K (850 °C), at a pressure of 36.6 MPa during 900 s in vacuum ∼1 Pa. Diffusion bonded Cu alloys to carbon rod have been obtained. From the thinner specimens (thickness $h = 2$ mm) samples were cut for scanning electron microscopy (SEM) and energy dispersive system (EDS) analysis. Thicker ($h = 5$ mm) specimens were used to measure the shear strength between Cu alloy and carbon rod by pushing the graphite rod out of the Cu-alloy disc by Instron testing machine measuring the load necessary to push out the rod and the contact surface between alloys and carbon rod.

(b) Cylinders of Cu alloys ($\phi = 12$ mm) were cut to a length of 50 mm, holes of diameter 3.2 mm were drilled into each cylinder and a graphite rod was inserted into Cu alloy cylinders. These cylinders with C rod were placed into a steel tube, evacuated, sealed and hot isostatically pressed. The pressing parameters were as follows: temperature 1223 K (950 °C), pressure 100 MPa, time 1 h. After pressing, the samples were cut to 2 and 5 mm lengths, as in the case (a). Thinner specimens were used for SEM and EDS analyses, and thicker ones were used for shear strength measurement.

Scanning electron microscopy analyses were performed on metallographic specimens to investigate the reaction layers. Energy dispersive system analysis was used to measure the linear concentration profile and area distribution of the elements across the boundary between carbon rod and Cu alloys as well as to measure the chemical composition of individual phases. The Instron testing machine was used to measure the shear strength between carbon rod and Cu alloys by pushing the carbon rod from Cu alloy disc.

3. Results

3.1. Specimens prepared by hot pressing

The shear strength (average from three measurements) between copper, copper-titanium and copper-zirconium alloys and carbon rod and standard deviations are given in Table I.

The interface between C rod and Cu-0.7 wt.% Ti alloy contains a zone of increased concentration of titanium which is about 0.2 μm thick.

Fig. 1a,b show the microstructure and X-ray line profile of the interface between carbon rod and Cu-3.6 wt.% Ti after etching of a specimen. Titanium diffuses close to the carbon and forms a continuous Ti-rich zone about 0.8 μm thick. Titanium concentration decreases across this zone in the direction to the original Cu-Ti alloy at a distance of up to about 5 μm (Fig. 1b).

The interfaces between carbon rod and Cu-0.15 wt.% Zr and Cu-1.3 wt.% Zr alloys are formed only by the contact of pure copper with carbon. The reaction zone in Cu-5.1 wt.% Zr alloy-C rod specimen is ~10 μm wide. Except for pure copper, which is adjacent to carbon rod, it consists of a phase (A) containing 49 at.% copper, 19 at.% zirconium and 32 at.% oxygen (Fig. 2).

3.2. Specimens prepared by hot isostatic pressing

Table II gives the shear strength with standard deviations between Cu-Ti and Cu-Zr alloys and carbon rod. The reaction zone between carbon and Cu-0.7 wt.% Ti is about 10 μm thick and contains individual particles of three compositions: 1. Titanium 17.0; copper 43.1 and oxygen 39.9 at.%, 2. Titanium 26.8; copper 23.2 and oxygen 50.0 at.%, and 3. Titanium 34.0 and oxygen 66.0 at.% in Cu matrix.

TABLE I Shear strength of Cu, Cu-Ti and Cu-Zr alloys and carbon rod (hot pressed)

Alloy (wt.%)	Shear strength (MPa)	Standard deviation (MPa)	Alloy (wt.%)	Shear strength (MPa)	Standard deviation (MPa)
Cu	5.0	±0.9	Cu 0.15 Zr	5.0	±1.2
Cu-0.7 Ti	5.5	±0.5	Cu-1.3 Zr	2.5	±1.5
Cu-3.6 Ti	8.1	±1.2	Cu-5.1 Zr	4.0	±1.1

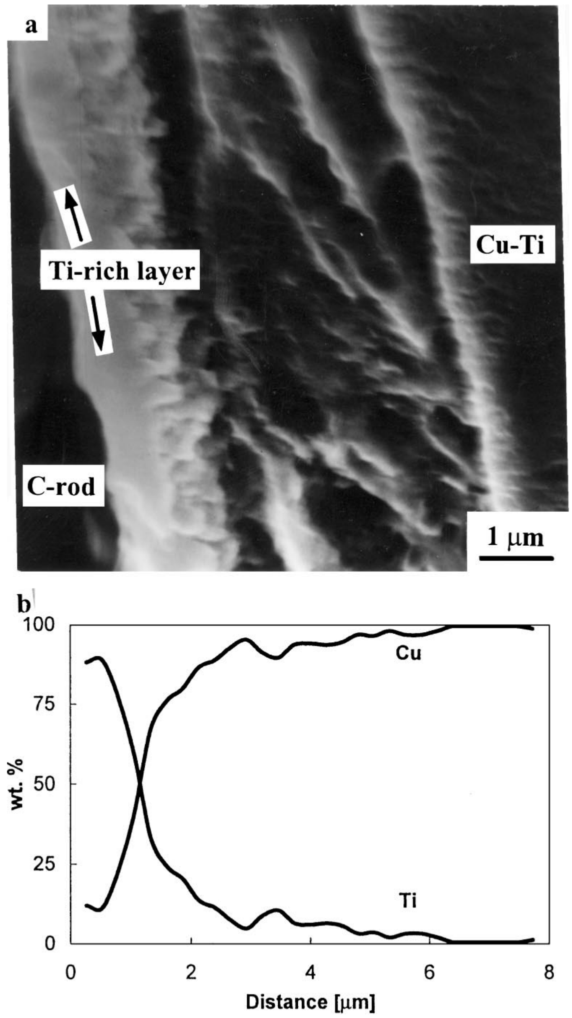

Figure 1 Interface between carbon rod and Cu-3.6 wt.% Ti alloy after hot pressing at 1123 K, 36.6 MPa during 900 s: (a) SEM, (b) concentration profile of Ti and Cu across the interface starting at the border between carbon rod and reaction zone.

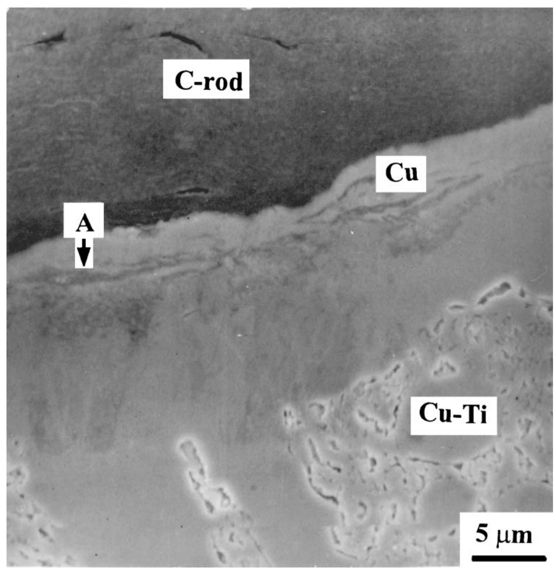

Figure 2 Reaction zone between carbon rod and Cu-5.1 wt.% Zr alloy after hot pressing at 1123 K, 36.6 MPa and 900 s.

Fig. 3a,b show the microstructure and X-ray image analysis of Cu and Ti of the reaction zone between carbon and the Cu-3.6 wt.% Ti alloy after hot isostatic pressing. The total thickness of the zone is about 10 μm.

TABLE II Shear strength of Cu-Ti and Cu-Zr alloys and carbon rod (hot isostatic pressed)

Alloy (wt.%)	Shear strength (MPa)	Standard deviation (MPa)	Alloy (wt.%)	Shear strength (MPa)	Standard deviation (MPa)
Cu-0.7 Ti	11.7	±0.9	Cu-0.15 Zr	7.9	±1.9
Cu-3.6 Ti	27.7	±1.1	Cu-1.3 Zr	9.0	±1.4
			Cu-5.1 Zr	16.5	±1.7

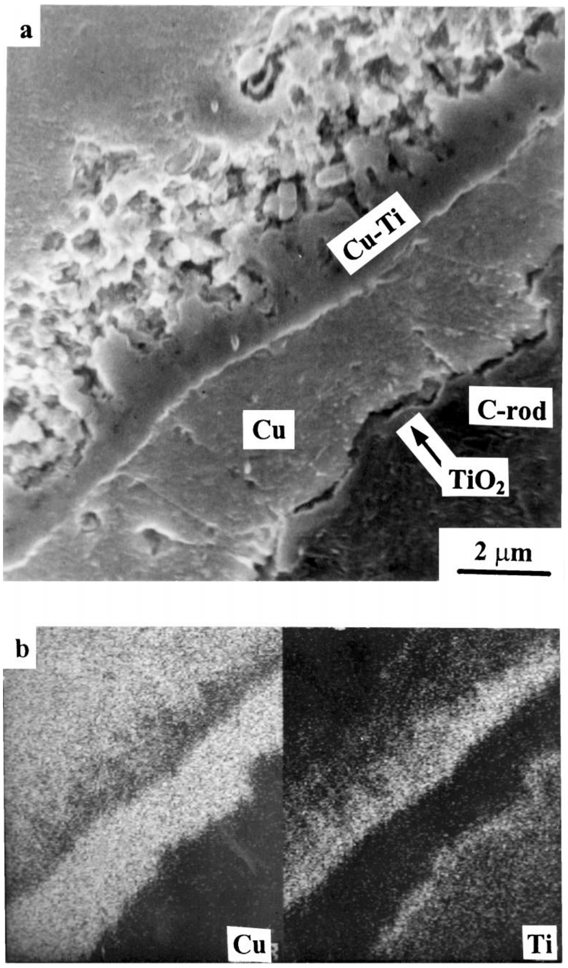

Figure 3 Reaction zone between carbon rod and Cu-3.6 wt.% Ti alloy after hot isostatic pressing at 1223 K, 100 MPa and 1 h: (a) SEM, (b) Cu and Ti X-ray dot maps.

The reaction zone consists of several layers. The reaction layer (thickness about 0.5 μm) adjacent to the carbon forms a continuous layer around the carbon rod. Composition of this layer corresponds to TiO_2. Reaction layer (Cu) (thickness ~5 μm) beside the titanium oxide contains copper and ~1 wt.% titanium. The interface zone (Cu-Ti) (thickness 1.5 μm) next to this copper layer corresponds to eutectic composition (57 at.% Ti). The Kirkendal porous layer is immediately adjacent to the matrix.

The reaction zone in the specimens with low zirconium content (0.15 and 1.3 wt.%) in Cu-Zr alloys prepared by hot isostatic pressing contains a layer of copper (thickness ~3 μm for Cu-1.3 wt.% Zr) adjacent to C rod. Beside the copper layer there is a discontinuous layer (B) which mostly consists of particles of composition 38 at.% Cu and 62 at.% Zr and individual particles (C) of the composition 75 at.% Cu and 25 at.% Zr (Fig. 4).

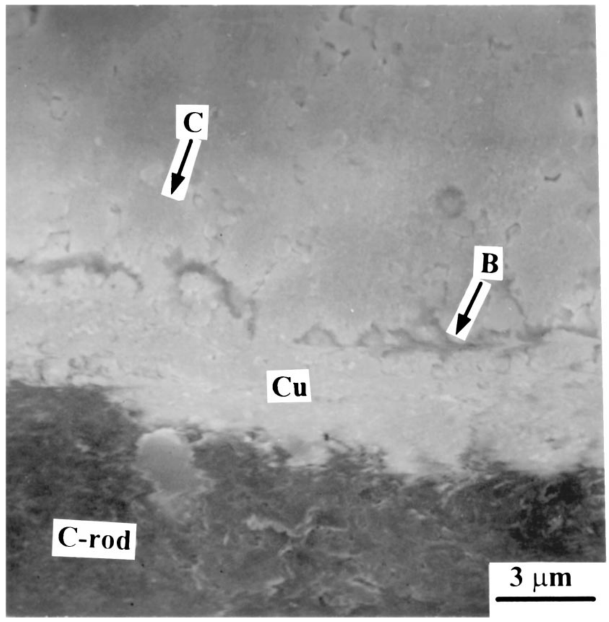

Figure 4 Interface between carbon rod and Cu-1.3 wt. % Zr alloy prepared by hot isostatic pressing at 1223 K, 100 MPa during 1 h.

The reaction zone between carbon rod and Cu-5.1 wt.% Zr is more complex. It consists of several layers. A layer (A) (thickness ~4 μm) is adjacent to carbon rod and contains Cu-Zr particles (with content of 25 at.% Zr) and copper. A second layer (thickness ~40 μm) consists of copper, Cu-Zr particles with 40 at.% Zr (see X-ray dot maps, Fig. 5b) and particles (B) adjacent to the matrix containing 20 at.% Cu, 35 at.% Zr and 45 at.% oxygen (Fig. 5).

4. Discussion

4.1. Specimens prepared by hot pressing

Titanium in both Cu-Ti alloys after hot pressing diffuses to the boundary with C rod. Ti-rich layers are very thin in both cases and one can suppose on the basis of thermodynamics that titanium reacts with oxygen forming titanium oxide.

The change of free energy associated with all reactions of titanium oxides (TiO, Ti_2O_3, Ti_3O_5 and TiO_2) with carbon are positive [3] and thus titanium oxides are stable with regard to carbon. The reaction of titanium with oxygen is much more probable than the reaction of titanium with carbon. The change of free energy of the reactions at 1123 K is as follows:

$$Ti + 2O \rightarrow TiO_2 \qquad \Delta G = -740\,\text{kJ} \qquad (1)$$

$$Ti + C \rightarrow TiC \qquad \Delta G = -172\,\text{kJ} \qquad (2)$$

Shear strength between carbon rod and Cu-0.7 wt.% Ti alloy is about the same as that for pure copper. A thin Ti-rich layer (~0.2 μm) has only a small influence on the shear strength. In the case of Cu-3.6 wt.% Ti alloy at the interface a much thicker phase arises (~0.8 μm) at the boundary with C rod containing titanium, where after the thermodynamic calculation of free energy change the reaction after Equation 1 can

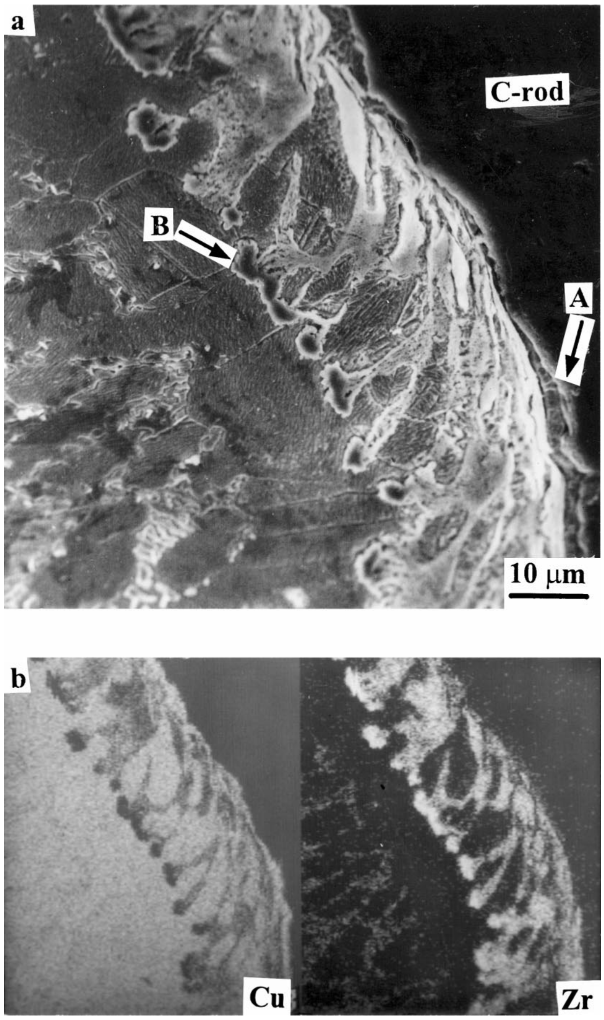

Figure 5 Reaction zone between carbon rod and Cu-5.1 wt.% Zr alloy prepared by hot isostatic pressing at 1223 K, 100 MPa during 1 h: (a) SEM, (b) Cu and Zr X-ray dot maps.

occur and TiO_2 may be formed (Fig. 1a). From the experimental value of shear strength (8.1 MPa) one can suppose that the presence of a thicker titanium-rich layer contributes to the increase in bond strength between the C rod and the Cu-Ti alloy.

In the specimens of C rod and Cu-Zr alloys for all concentrations of zirconium the layer adjacent to the C rod is pure copper. Due to the lack of zirconium close to carbon there is no possibility for zirconium oxide or carbide to form at the interface with the C rod. These are probably the reasons why the shear strength between C rod and Cu-Zr alloys is practically the same as for pure copper, taking the standard deviations into account.

4.2. Specimens prepared by hot isostatic pressing

The shear strength between Cu-Ti alloys and carbon rod increases with titanium concentration. In the layer adjacent to carbon rod there is titanium oxide, in the first case (Cu-0.7 wt.% Ti) as individual oxide particles, and in the second case (Cu-3.6 wt.% Ti) as a continuous oxide layer. Titanium diffuses close to carbon rod and reacts with oxygen that is present in copper oxide form in the inner surface of the specimen before inserting carbon rod into this cylinder. The existence of copper oxide (Cu_2O) was proven by transmission electron microscopy and electron diffraction on similar samples where copper coated carbon fibres were present instead of carbon rod [4].

From the thermodynamic point of view the reaction leading to TiO_2 forming has much lower ΔG than the one leading to TiC forming also at 1223 K.

The interface between carbon and Cu-Zr (0.15 and 1.3 wt.% Zr) alloys in specimens prepared by hot isostatic pressing is similar to those prepared by hot pressing. No particles of oxide, nor diffusion of zirconium were observed by scanning electron microscopy (SEM) and energy dispersive system (EDS) analysis at the interface between carbon rod and Cu-Zr alloy. The layer adjacent to the C rod is in this case only pure copper.

Shear strength between C rod and Cu-0.15 (1.3) wt.% Zr alloy is 7.9 (9.0) MPa, which is higher than that for C rod and Cu specimen prepared by hot pressing. This can be due to higher (temperature, pressure and time) pressing parameters.

Shear strength between C rod and Cu-5.1 wt.% Zr alloy is twice that of Cu-0.15 wt.% Zr alloy. Increase of the shear strength can be due to the presence of copper layer adjacent to the carbon rod containing Cu-Zr particles.

5. Conclusions

The obtained results can be summarized as follows:

- Shear strength between C rod and Cu-Ti alloys in specimens prepared by hot pressing (HP), as well as by hot isostatic pressing (HIP) depends on the amount of titanium in Cu alloy.
- Titanium diffuses in all cases to the border with C rod where titanium oxide may arise which promotes the shear strength.
- Shear strength between C rod and Cu-Zr alloys in the specimens prepared by HP is close to that of pure copper. For low Zr concentrations (0.15 and 1.3 wt.%) specimens prepared by HIP the shear strength is about twice that of specimens prepared by HP. This increase can be due to higher pressing parameters.
- Adjacent layer to C rod in Cu-low concentration Zr alloys is pure copper.
- Shear strength between C rod and Cu 5.1 wt.% Zr alloy in specimens prepared by HIP is about twice that of the lowest Zr concentration prepared by HIP. The copper layer adjacent to the C rod consists of Cu-Zr particles in copper. The presence of such layer can be responsible for the increase of shear strength.
- By the choice of proper amount of titanium and zirconium in Cu-Ti and Cu-Zr alloys and by the knowledge of the structure, the interface between carbon (rod or fibre) and these alloys one can control the bond strength between them.

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