

EFFECT OF ZIRCONIUM UPON THE THERMAL CONDUCTIVITY OF COPPER

PAVOL ŠEBO, ŠTEFAN KAVECKÝ, PAVOL ŠTEFÁNIK,
GERHARD GROBOTH, GEORG KORB

Effect of zirconium upon the thermal conductivity of copper-zirconium alloys was studied in the temperature range of 323–873 K. Thermal diffusivity of Cu-Zr alloys containing 0.1, 0.9, and 3.6 at. % zirconium was measured by Nd glass laser flash method. Specific heat of these alloys was measured in differential scanning calorimeter. Thermal conductivity of Cu – 0.1 at. % alloy decreases with temperature, whereas alloys with higher zirconium concentrations have a positive dependence of thermal conductivity on temperature. Thermal conductivity decreases very strongly with zirconium concentration, nevertheless, its decrease is ten times smaller than that in Cu-Ti alloys with titanium concentration. This fact supports the intent of using zirconium as a bonding layer in copper-carbon fibre composites.

VPLYV ZIRKÓNU NA TEPELNÚ VODIVOSŤ MEDI

Študovali sme vplyv zirkónu na tepelnú vodivosť zliatin meď-zirkón v teplotnom intervale 323 – 873 K. Tepelnú difuzivitu Cu-Zr zliatin s obsahom 0,1, 0,9 a 3,6 at. % sme merali metódou ohriatia vzorky Nd skleným laserom. Špecifické teplo sme merali diferenciálnym riadkovacím kalorimetrom. Tepelná vodivosť zliatiny Cu – 0,1 at. % Zr klesá s teplotou, zatiaľ čo tepelná vodivosť zliatin s vyššou koncentráciou zirkónu s teplotou rastie. Tepelná vodivosť klesá veľmi rýchlo s koncentráciou zirkónu, avšak klesá 10-krát pomalšie ako s titánom v zliatinách Cu-Ti. Táto skutočnosť umožňuje používať zirkón ako vrstvu na zlepšenie adhézie uhlíkových vlákien k medi v kompozitoch meď-uhlíkové vlákna.

Key words: copper, zirconium, thermal conductivity, laser flash method

RNDr. P. Šebo, CSc., Ing. Š. Kavecký, CSc., Ing. P. Štefánik, CSc., Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Račianska 75, 838 12 Bratislava 38, Slovak Republic.

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

1. Introduction

For many applications (examples are given later) materials with good mechanical properties (e.g. strength, modulus of elasticity) as well as with required physical properties (e.g. good thermal conductivity, thermal dimensional stability) are needed. Most applications are in electrical engineering industry, in aerospace, in transport, and in some other branches.

Among applications of such material the following examples can be mentioned:

- module frame in standard electronic modules which serve as heat sinks for the attached electronic component,
- electronic packaging,
- short circuiting rings in high performance electric drives (e.g. in high speed trains),
- resistance welding electrodes,
- rotating anodes in X-ray tubes,
- hypersonic vehicle applications, e.g. high conductivity heat exchanger,
- space power system applications, e.g. high conductivity radiator fins for solar or nuclear power systems and others.

Composite materials are able to fulfil the above-mentioned requirements on the properties by the combination of proper materials possessing an individual property.

To obtain these properties a combination of copper and carbon fibres can be used. Copper has very good thermal and electrical conductivities, however, its coefficient of thermal expansion and density are very high. Carbon fibres are available with very broad interval of mechanical as well as physical properties (strength, modulus of elasticity, thermal conductivity) and their density is very low ($1600\text{--}2200\text{ kgm}^{-3}$). Most kinds of carbon fibres reveal negative thermal expansion. The required property within the given range could be chosen by incorporating a proper volume fraction of carbon fibre.

Carbon fibre (CF) - copper matrix composites can be produced either by infiltration of liquid copper into the carbon fibre tows or by diffusion bonding of copper coated carbon fibre [1]. Difficulties, we encounter when using carbon fibre with copper, are in the lack of adhesion between copper and carbon fibres.

Neither liquid copper wets carbon nor chemical reaction occurs at the interface between copper and carbon fibre. This interface is chemically inert with respect to carbon fibres. Several authors (e.g. [2, 3]) studied the influence of some elements added to copper on its wetting of carbon surfaces. They found out that transition metals, whose binary alloys form the miscibility gap in liquid state and have rather small solubility in solid state in copper, are potential candidates for the improvement of carbon fibres wettability by copper. This improvement is attributed to the interface reactions between alloying elements and carbon fibre, which lead to the

reduction of interface tension.

The improvement of copper adhesion to carbon fibre in composites prepared by diffusion bonding of copper coated carbon fibre was also studied by several authors (e.g. [4, 5]) by adding another layers to copper (Cu-Ni, Cu-Fe). They found that interfaces between coated carbon fibres and copper are strengthened by the reaction between Fe and CF and by dissolution of Cu-Ni solid solution in CF. Abel et al. [5] showed that Ti and Cr bond layers should enhance the adhesion between Cu matrix and CF. However, thermal conductivity of copper decreases with addition of those elements. Especially titanium lowers electrical (and thermal) conductivity very much. In the amount of 0.01 at. % it reduces electrical copper conductivity about 10 % .

Another carbide forming element – zirconium can be also used to improve adhesion of copper which is the subject of another paper. The aim of this paper is to find the effect of zirconium addition to pure copper upon its thermal conductivity.

2. Experimental procedure

Thermal conductivity λ can be defined as the heat flow q passing through a unit area A per second per unit temperature gradient dT/dx ,

$$\lambda = -\frac{q}{A(dT/dx)}. \quad (1)$$

In some methods it is not the thermal conductivity but the thermal diffusivity a which is determined

$$\lambda = aC_p\rho. \quad (2)$$

This quantity represents the rate of heat diffusion per unit time. C_p is the specific heat and ρ is the density.

Determination of thermal conductivity of the specimens consisted of measurements of specific heat, density, and thermal diffusivity.

a) Measurement of specific heat

Specific heat was measured in a differential scanning calorimeter for temperatures 313 K and from 373 to 873 K in 100 K step. Two identical sample holders were heated individually at the heating rate of 20 K/min in argon atmosphere in such a way that their temperatures remain equal. The material was placed in one of the sample holders in order to establish thermal equilibrium. Then, additional heat, equivalent to the heat capacity, was required. This was determined by measuring a reference sample and the baseline of the instrument.

b) Measurement of density

Density of each specimen was determined by measuring the dimensions of the specimen and calculating its volume and its weighing.

c) Measurement of thermal diffusivity

Thermal diffusivity was measured by laser flash method. The flash energy source is a high energy and Nd glass laser which has a pulse duration of 0.5 ms. The disc-like sample of 10 mm diameter with thickness of 3 mm of copper-zirconium alloys containing 0.15 (0.10), 1.3 (0.91), and 5.1 (3.61) wt. % (at. %) of zirconium was heated up to the test temperatures (313, 373–873 K in 100 K step) by resistance heater. Then, the front of their surface was additionally heated by a laser flash. The absorbed energy causes an increase of the sample temperature which is detected on the rear surface of the specimen as a function of time. The sample temperature is measured by a Ni-NiCr thermocouple, the temperature increase on the back side of the sample is monitored with the aid of an IR detector. Thermal diffusivity is calculated using the formula

$$a = \frac{0.139 \cdot l^2}{t_{1/2}}, \quad (3)$$

where a is the thermal diffusivity, l is the thickness of the sample disc, and $t_{1/2}$ is the time until half of the maximum temperature increase is reached.

To avoid heat loss, the sample was supported in a horizontal position on three thin insulating ceramic tubes, specimen chamber was evacuated, and radiation shields were installed. A stainless steel standard was measured before and after each series of measurements for calibration.

3. Results and discussion

Measured values of specific heat and thermal diffusivity for all the three Cu-Zr alloys in the temperature interval of 323–873 K are given in Tables 1 and 2. For comparison specific heats of pure copper and zirconium taken from [6] are given in Table 1, as well.

Specific heat of pure zirconium is smaller than the one of copper, and thus, decrease of specific heat of Cu-Zr alloys with increasing amount of Zr can be expected.

Table 2 gives the thermal diffusivity for three Cu-Zr alloys. Thermal diffusivity is related to thermal conductivity through specific heat and density. These quantities decrease either with temperature and amount of zirconium in copper (specific heat) or with the amount of zirconium in copper (density). (Density of copper is 8900 kg/m³ and that of zirconium 6400 kg/m³.) As the thermal diffusivity of Cu

Table 1. Measured specific heat C_p [J/gK] of Cu-Zr alloys for various temperatures and for pure Cu and Zr taken from [6]

Temperature [K]	Cu	Cu – 0.1 at. % Zr	Cu – 0.9 at. % Zr	Cu – 3.6 at. % Zr	Zr
323	0.385	0.397	0.372	0.365	0.285
373	0.393	0.397	0.396	0.388	0.306
473	0.414	0.409	0.407	0.398	0.322
573	0.423	0.418	0.415	0.403	0.333
673	0.431	0.424	0.421	0.412	0.341
773	0.444	0.433	0.426	0.418	0.348
873	0.456	0.442	0.431	0.425	0.355

Table 2. Thermal diffusivity a [m²/s] of Cu-Zr alloys for various temperatures

Temperature [K]	Cu – 0.1 at. % Zr $a \times 10^6$	Cu – 0.9 at. % Zr $a \times 10^6$	Cu – 3.6 at. % Zr $a \times 10^6$
313	101.61	49.13	36.84
373	98.79	50.46	37.55
473	94.91	54.49	41.02
573	91.54	56.69	41.82
673	84.53	57.40	42.62
773	83.06	57.92	43.28
873	81.02	62.50	45.33

Table 3. Linear regression constants A and B expressing the temperature dependence of thermal conductivity of Cu-Zr alloys

Alloy	A	B
Cu – 0.1 at. % Zr	374.2	-0.07071
Cu – 0.9 at. % Zr	139.8	0.10751
Cu – 3.6 at. % Zr	103.0	0.07326

– 0.1 at. % Zr decreases with temperature and for other two Cu-Zr alloys (with 0.9 and 3.6 at. % Zr) it increases, the same tendency will be valid for thermal conductivities of all the alloys.

Temperature dependence of the thermal conductivity of all the studied Cu-Zr alloys is linear and can be expressed as

$$k = A + BT, \quad (4)$$

where A and B are linear regression constants, T is temperature [K]. The constants A and B for the three studied alloys are in Table 3.

Thermal conductivity of the lowest alloyed copper (Cu – 0.1 at. % Zr) decreases with temperature similarly as the conductivity of pure copper. For higher zirconium concentrations the thermal conductivity of Cu-Zr alloys increases with temperature. This can be due to the decreasing amount of primary copper in an eutectic alloy with increasing zirconium concentration, taking into account the existence of Cu-ZrCu₃ eutectics at 9.1 at. % and 1237 K in Cu-Zr system. Thus, ZrCu₃

contributes to the temperature dependence of thermal conductivity changing the slope of its plot from negative (for pure copper and low zirconium concentration) to positive (for higher Zr concentrations).

Fig. 1 shows the dependence of thermal conductivity on the amount of zirconium in copper at room temperature (for 300 K it was obtained by linear regression) and at 773 K.

The decrease (at room temperature) of thermal conductivity (and through the Lorenz number also electrical conductivity) for 0.1 at. % of zirconium is almost 12 % which is approximately the same as for 0.01 at. % of

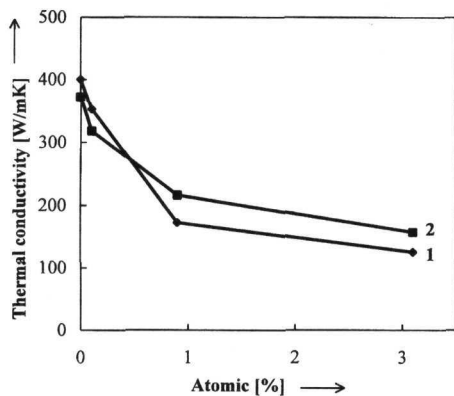


Fig. 1. Plot of thermal conductivity of Cu-Zr alloys vs. concentration of Zr for temperatures 300 K – 1 and 773 K – 2.

titanium in Cu-Ti alloys. Thus, zirconium has about 10 times lower effect upon the thermal conductivity in Cu-Zr alloys than titanium has in Cu-Ti ones.

4. Conclusions

Thermal conductivity of three Cu-Zr alloys containing 0.1, 0.9 and 3.6 at. % Zr was calculated from the measured values of their specific heat, density, and thermal diffusivity. These quantities were measured in the temperature interval of 323–873 K. Thermal conductivity of Cu-Zr alloys decreases with zirconium. This rate is about ten times smaller than that for titanium in Cu-Ti alloys. The use of zirconium as a bond layer in copper-carbon fibre composites has to be considered carefully; control of zirconium amount in copper is necessary in order not to decrease the thermal conductivity of Cu-C composites very much.

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