

Letter to the Editor

Influence of chromium in copper alloys on wetting of some refractory metals

P. Štefánik*, N. Beronská, P. Šebo

*Institute of Materials and Machine Mechanics, Slovak Academy of Sciences,
Račianska 75, 831 02 Bratislava, Slovak Republic*

Received 26 May 2009, received in revised form 11 August 2009, accepted 11 August 2009

Abstract

The aim of this work is to identify the wetting of refractory metals with copper alloys. We investigated the effect of chromium (0; 0.12; 0.24; 0.61 and 1.22 at.%) in Cu-Cr alloys and Cu-Cr-Zr (0.85 at.% Cr, 0.20 at.% Zr, balance Cu) on wetting of pure molybdenum, molybdenum alloy (1.0 at.% Ti, 0.08 at.% Zr – TZM) and tungsten. Only the binary alloys with the lowest Cr concentration (0.12–0.61 at.%) effectively wet refractory substrates.

Key words: wetting, copper alloys, refractory metals, microstructure

1. Introduction

Metal matrix composites (MMCs) with tailorable anisotropy can be prepared from both continuous and discontinuous fibres [1–5]. However, the highest mechanical and thermal properties of unidirectional composites are only in direction parallel to the fibre orientation. The properties of composites perpendicular to fibre orientation are markedly lower. To eliminate these effects the combination of fibre orientation or combination of fibres with various properties can be used.

In many cases, it is necessary to use material with stable structure at the temperatures up to 700 °C with the highest possible thermal conductivity and to have the possibility to control thermal expansion. One type of such materials is copper matrix continuous fibre composite. Tungsten fibres have coefficient of thermal expansion (CTE) about $4 \times 10^{-6} \text{ K}^{-1}$. To decrease expansion of MMCs to lower values the carbon fibres can be used. CTE of these fibres in direction parallel to fibre axis is even negative. Combination of refractory metal fibres and plates and carbon fibres gives the material with very low thermal expansion and relatively high thermal conductivity. However, the carbon materials are not wetted by copper or some copper al-

loys [6, 7]. Even relatively high pressure in autoclave is not sufficient to infiltrate carbon fibres by copper in whole volume. Improving wetting can be reached by adding the carbide-forming element to the copper, e.g. Cr, Zr. However, addition of such metal to copper lowers its thermal conductivity. The optimum amount of carbide forming element that improves wetting of carbon fibres is not established. In some papers [8–11] it was discussed that copper with low concentration of chromium (about 1.0 at.%) wetted the vitreous carbon. Composites prepared from pitch-based carbon fibres have better mechanical and thermal properties even if 0.3 wt.% of Cr was used in copper matrix [12, 13].

The aim of this contribution is to recognize the influence of concentration of chromium in Cu-Cr and/or Cu-Cr-Zr alloys on the wetting of pure molybdenum, molybdenum alloy TZM and tungsten substrate and potential creation of new phases at the boundary between these constituents.

2. Experiment

Copper-chromium alloys with 0.12; 0.24; 0.61 and 1.22 at.% Cr prepared in induction furnace and Cu-

*Corresponding author: tel.: +421 2 49268218; fax: +421 2 44253301; e-mail address: ummsstef@savba.sk

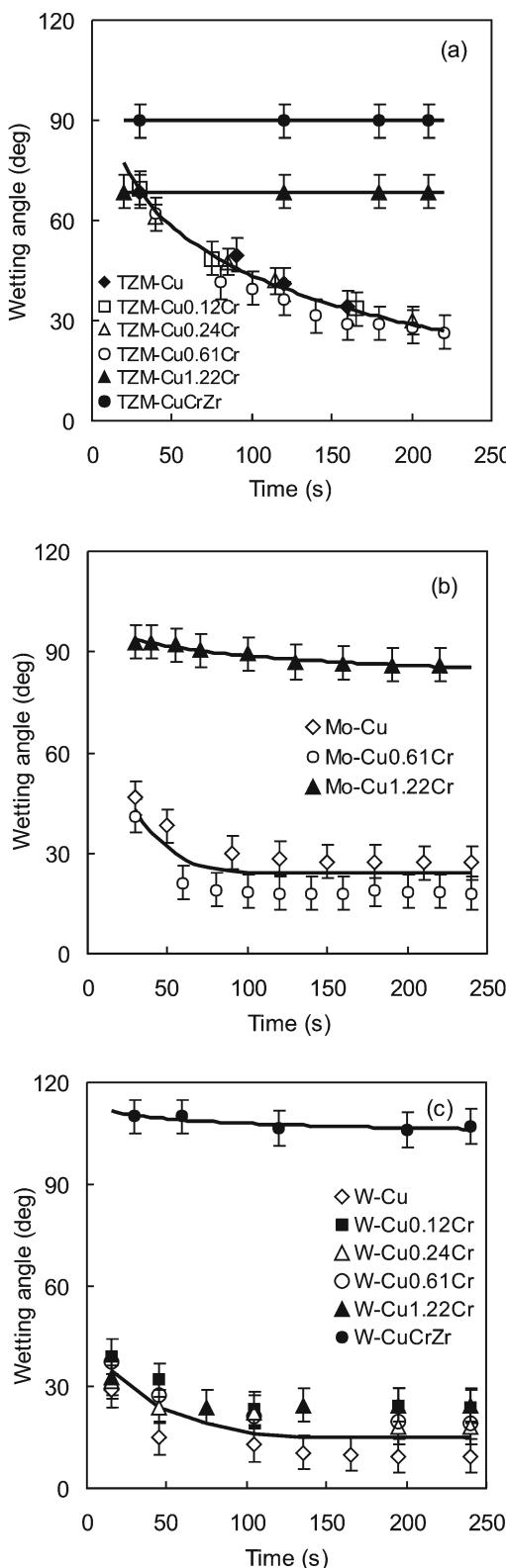


Fig. 1. Time dependence of wetting angle of TZM (a) molybdenum (b) and tungsten (c) with Cu-Cr and Cu-Cr-Zr alloys for 1150°C.

Cr-Zr alloy were used. Substrates from molybdenum, TZM and tungsten of diameter 15 mm and thickness

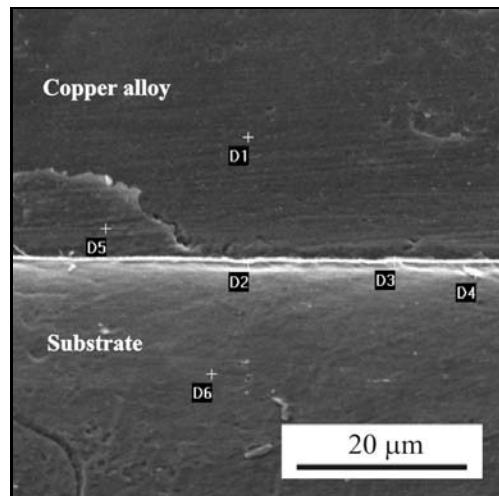


Fig. 2. Boundary between TZM substrate and drop of Cu-1.22 at.-% Cr alloy.

of 2 mm were cleaned in ultrasound using acetone. Cu alloy in the form of cylinder with 6 mm diameter and 4 mm tall was inserted on substrate into the furnace, which was a part of apparatus for wetting angle measurement – sessile drop method. After melting an alloy in vacuum the drop was photographed during 240 s at 1150°C. Wetting angles were measured from the photography and time dependence of wetting angle was made. After solidifying the specimen was cut perpendicularly to the plane of substrate and after metallographic treatment the structure of the interface between drop and substrate was studied to identify the effect of chromium on the creation of new phase at the interface. Electron microscopy equipped with X-ray analyser (EDAX) was used.

3. Results and discussion

The results of time dependence of wetting of molybdenum, TZM and tungsten by Cu-Cr-Zr and/or Cu-Cr alloys with various amount of chromium at 1150°C are given in Fig. 1a–c. The wetting of molybdenum, TZM and tungsten with pure copper and alloy with low amount of chromium (up to 1.22 at.-%) is very good and decreases with time to the value of 30°. Alloy containing Cr and Zr even does not wet substrate made of molybdenum, TZM and tungsten. Poor wetting or even not wetting of studied refractory metals by CuCrZr alloy may be due to the presence of thin oxide layer on the surface of an alloy. Zirconium is extremely sensitive to oxidation, but detecting of this layer is difficult.

Figures 2 and 3 show the interface between TZM and/or W substrates and the drops of Cu-1.22 at.-% Cr alloy. No interlayer between substrate and the drop

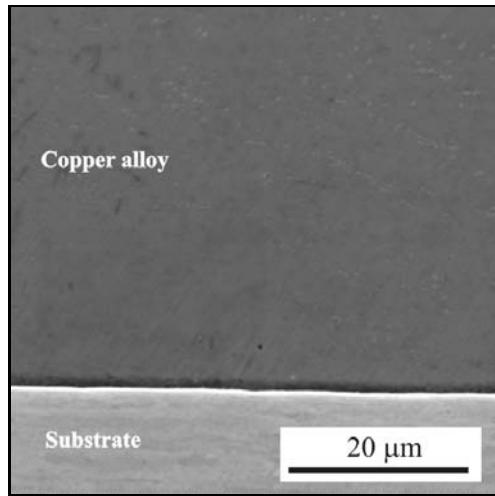


Fig. 3. Boundary between W substrate and drop of Cu-1.22at.%Cr alloy.

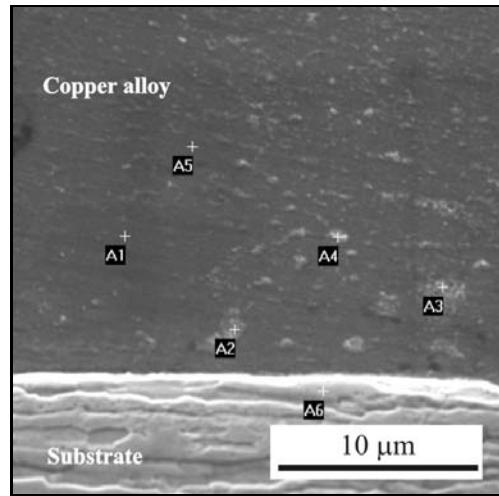


Fig. 5. Boundary between W substrate and drop of Cu-Cr-Zr alloy.

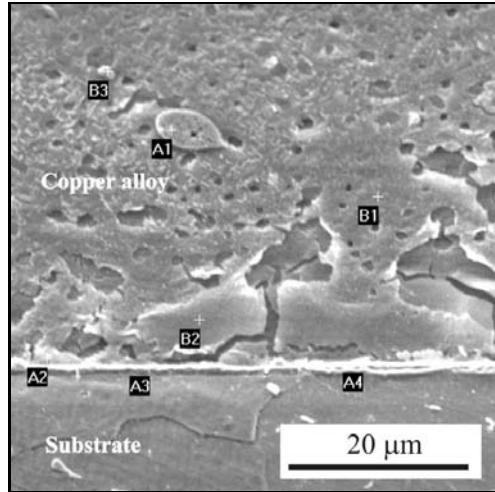


Fig. 4. Boundary between TZM substrate and drop of Cu-Cr-Zr alloy.

detectable using SEM was observed. Neither particles containing chromium were observed in the drop. Chemical composition of some points of Cu-Cr-Zr drop and/or boundary between TZM substrate was also studied (Fig. 4). The relatively high concentration of Zr (17.2 at.%) in particle (point A1) indicates to formation of Cu₅Zr phase. The higher concentration of Cr (9.8 at.% at point A2) near the TZM substrate indicates the formation of Cr_{0.3}Mo_{0.7} alloy. In all other measured points practically the pure copper was detected. Similar chemical compounds (Cu₅Zr, ZrW₂) may be formed at the interface between Cu-Cr-Zr alloy and W substrate. Zirconium (10.2 at.%) and tungsten (16.9 at.%) were found in point A6 (Fig. 5). But exact determinations of phase formation have to be

established by proper method.

4. Conclusion

The obtained results can be summarized as follows:

- Cu alloys with low concentration of chromium (0.12–0.61 at.%) wet molybdenum, TZM and tungsten.

- The wetting angle of tungsten by Cu-Cr alloy is lower than 30°C for Cr concentration up to 1.22 at.%.

- The highest used concentration of chromium in a Cu-Cr alloy increases the wetting angles of melted drops on substrates from molybdenum or molybdenum alloy.

- Cu-Cr-Zr alloy does not wet studied refractory substrates; near the interface with refractory metal increased concentration of Zr was detected indicating formation of Cu₅Zr phase.

- Wetting experiments have shown which Cu alloys can be used for preparing composites reinforced with refractory metals in various form (wire, thin plate) and/or hybrid composites with carbon fibres by infiltration method.

Acknowledgements

The authors gratefully acknowledge the financial support of the Slovak Grant Agency for Science under the contract VEGA 2/7173/27.

References

- [1] LLOYD, J. C.—CLEGG, W. J.: Adv. Mater. Res., 59, 2009, p. 148.

- [2] DUTTA, I.: *Acta Mater.*, **48**, 2008, p. 1055.
- [3] KÚDELA, S. Jr.—RUDAJEVOVÁ, A.—KÚDELA, S.: *Mater. Sci. Eng.*, **A462**, 2007, p. 239.
- [4] RUDAJEVOVÁ, A.—LUKÁČ, P.: *Kovove Mater.*, **46**, 2008, p. 145.
- [5] RUDAJEVOVÁ, A.—KRÁL, R.—LUKÁČ, P.: *Kovove Mater.*, **46**, 2008, p. 179.
- [6] NAIDICH, Y.: In: *Progress in Surface and Membrane Science*. Eds.: Cadenhead, D. A., Danielli, J. F. New York, Academic Press 1981, p. 353.
- [7] MORTIMER, M.—NICHOLAS, N.: *J. Mater. Sci.*, **5**, 1970, p. 149.
- [8] De VINCENT, S. M.—MICHAL, G. M.: *J. Mater. Eng. Perform.*, **2**, 1993, p. 323.
- [9] EUSTATHOPOULOS, N.: *Acta Mater.*, **46**, 1998, p. 2319.
- [10] VOITOVITCH, R.—MORTENSEN, A.—HODAJ, F.—EUSTATHOPOULOS, N.: *Acta Mater.*, **47**, 1999, p. 1117.
- [11] De VINCENT, S. M.: *Interfacial effects on the thermal and mechanical properties of graphite/copper composites*. [Ph.D. Thesis]. Cleveland, Case Western Reserve University 1994.
- [12] IŽDINSKÝ, K.—SIMANČÍK, F.—KORÁB, J.—KRAMER, I.—ŠTEFÁNIK, P.—KAVECKÝ, S.—ŠRÁMKOVÁ, T.—CSUBA, A.—ZEMÁNKOVÁ, M.: *Kovove Mater.*, **44**, 2006, p. 327.
- [13] BERONSKÁ, N.—IŽDINSKÝ, K.—ŠTEFÁNIK, P.—SIMANČÍK, F.—ZEMÁNKOVÁ, M.—DVORÁK, T.: *Kovove Mater.*, **47**, 2009, p. 175.