Wettability and joining of cobalt sintered tungsten carbide by liquid copper

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Abstract

The contact angle of pure liquid copper (Cu) on cobalt sintered tungsten carbide (WC-Co) substrate was found to vary from about 0° for the freshly polished surface to above 90° for the as-received, oxidised surface. Liquid Cu was found to be a perfect joining agent for polished WC substrates.

\textit{Keywords:} Tungsten carbide, liquid copper, contact angle, joining, oxide layer

1. Introduction

Wettability of ceramic substrates by liquid metals is one of the key parameters in processing and joining ceramic materials. The cobalt-sintered tungsten carbide (WC-Co) substrates present a special interest due to their excellent properties.

Tungsten carbide (sintered by cobalt) was found wetted very well by liquid copper by the majority of investigations carried out so far. The contact angle was found to be 20° by Gurland and Norton [1], 20° by Ramquist [2], 17° by Mortimer and Nicholas (17°) [3],

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between 0° and 28° (as function of the Co-content) by Verhoturov et al [4], 20° by Warren [5] and about 0° (with no Co-content) by our recent investigation [6]. Good wettability of WC by liquid copper is also confirmed in reviews by Naidich [7] and Eustathopoulos et al [8].

However, in the paper of Samsonov et al. [9] the contact angle in the WC/Cu system was found to be 120°. In our previous paper [10] a hypothesis has been suggested that this contradiction might be due to the presence of a thin oxide layer on WC substrate. The goal of the present paper was to show experimentally the role of the oxide layer on WC-Co substrate on its wettability by liquid copper, and also on the possibility to join WC-Co ceramic parts by liquid copper.

2. Materials and experimental procedure

In the present paper Co-sintered WC substrates with 8 w% of Co content were used in the ‘as-received’ form, and also after polishing them by a 1 μm diamond paste. The ‘as-received’ samples had a dark colour, indicating a slight oxidation of their surface, while substrates after polishing were metal-bright. Substrates had a thickness of 2 mm, and a shape of a trapezium (9 mm * 6 mm * 6 mm * 4.9 mm). Pure copper with maximum 0.01 % of total impurity level was used for the experiments.

All experiments were conducted in a horizontal tube furnace, under high vacuum, at 10⁻⁸ bar of residual argon pressure (the details of the experimental equipment were described elsewhere [11]).

In the first round of experiments a sessile drop method was applied, with about 0.055 g Cu, situated on a surface of a single WC-Co substrate. Photographs were taken right after melting and also later by a CCD camera.
The second round of experiments was planned to simulate joining of WC-Co substrates by liquid Cu. Three small copper samples, each with weight between 0.015-0.02 g were carefully situated between two identical WC-Co substrates. The amount of Cu was calculated such that in case of total spreading of liquid copper between the two plates, the gap of 150 µm thickness could be fully filled by the liquid metal. The system was heated in vacuum till 1,100 °C, kept at this temperature for 5 minutes, and then naturally cooled down. Photographs were taken after the experiments.

3. Results and discussion

In Fig.1. the photographs of the liquid copper drops taken right after their melting are given for the ‘as-received’ and for the polished samples. As one can see from Fig.1.a, copper does not wet the ‘as-received’ WC-Co sample. The contact angle gradually decreased from the initial 106° to the final 95° after 29 minutes of contact time. However, liquid copper immediately spread over the polished surface of WC-Co after melting, and contact angle could be hardly determined from photo 1.b. From the shape of the spread and solidified copper droplet after the experiment the contact angle was estimated being between 0° and 20°.

Perfect wettability in inert systems, such as WC-Co/Cu, by high surface tension liquid metals, such as Cu, is possible only due to metal-metal interactions through the phase boundary. This type of interaction is due to partly metallic character of both phases WC and Co of the WC-Co substrate. The difference in the observed contact angles between Fig-s 1.a-b is obviously due to the presence of the thin oxide layer on the ‘as-received’ sample, preventing the formation of the metallic bonds through the solid/liquid interface. Although this phenomenon is well established for wettability of solid metals by liquid metals [7, 8], its
role is not so widely documented for the wettability of metal-like ceramic compounds by liquid metals.

![Image](image.png)

**Fig. 1.** Liquid copper droplet right after its melting on the surface of the ‘as-received’ (a) and polished (b) surface of WC-Co substrate
(size of the grid is 0.5 mm)

In Figs. 2-3 the results of experiments planned to simulate joining of WC-Co ceramic substrates by liquid copper are shown. As one can see from Fig. 2, between the ‘as-received’ WC-Co substrates the three small copper droplets remained separated and did not effectively join the substrates. In fact, the two WC-Co substrates could easily separated after the experiment by hand. The gap between the two WC-Co substrates remained 720 \( \mu m \), instead of the planned 150 \( \mu m \).

On the other hand, as shown by Fig. 3, the three, initially separated copper droplets spread and joined together between the two polished WC-Co substrates and also effectively joined the two WC-Co substrates. As one can see in photos of Fig. 3, probably due to asymmetric melting of the copper droplets, the upper WC-Co substrate was even turned by almost 90°, and the two WC-Co substrates were pulled together by liquid copper so much,
that in fact the majority of its flew out of the gap. The final gap between the two WC-Co samples was found to be less than 150 µm, instead of the planned 150 µm. The joined in this way WC-Co substrates have a very high adhesion.

Consequently, the effect of the oxide layer observed in the wetting experiments also remained in the experiments simulating the joining of WC-Co substrates. Hence, joining of WC-Co substrates by pure liquid copper can be performed only, if their surfaces are effectively cleaned from the oxide layer.

Fig.2. Photographs of the two ‘as-received’ WC-Co substrates joined by originally separated three Cu-droplets (largest length of the substrate is 9 mm)

Fig.3. Photographs of the two polished WC-Co substrates joined by originally separated three Cu-droplets (largest length of substrate is 9 mm)
4. Conclusions

The oxide layer, covering the surface of the ‘as-received’ WC-Co substrates prevents the formation of the metallic interfacial bonds with liquid copper, and thus the system seems to be non-wettable, and as a consequence, joining of WC-Co substrates by liquid Cu seems to be impossible. However, if the oxide layer from the WC-Co substrate is removed for example by polishing it with fine diamond paste (or by any other chemical way), copper is found to wet the WC-Co substrate with contact angle close to $0^\circ$ right after its melting. Pure, liquid copper can also be considered as a perfect joining metal for cobalt sintered tungsten carbide parts, if the oxide layer from the surfaces to be joined is removed prior to the joining process.
References