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Copper wettability on tungsten carbide surfaces

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Abstract

The wetting behavior of copper on tungsten carbide surfaces was investigated through the sessile drop method, at 1080 °C, in vacuum atmosphere. Tests were performed on three different types of substrates: (i) commercial sample of WC–Co with 3.5 wt% of cobalt; (ii) WC thin film sputter-deposited on the aforementioned commercial WC–Co sample and (iii) WC sample processed by hot pressing. The lowest final contact angle was achieved on the WC–Co surface (6°), followed by those of WC thin film (13°) and WC (25°). The contact angle values were inversely correlated with the wetting behavior, i.e. the highest wettability was found for the WC–Co and the lowest for the WC surfaces. Structural, microstructural and elemental characterizations of the interface region between the molten copper and the substrate were performed, using low angle X-ray diffraction and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). The wettability behavior was discussed taking into consideration the effect of minor phases, such as cobalt.

Keywords: Wettability; Copper; Tungsten carbide; Hardmetal

1. Introduction

Composites of tungsten carbide (WC) and cobalt, Co, known as hardmetals, have been the preferred material choice in arduous applications, covering a large range of industries such as cutting tools, mining and oil/gas extraction, among others. The search for alternative binders with improved features, namely increased corrosion/oxidation resistance, lower toxicity and stable quotation, is currently one of the research guidelines [1–4]. In order to attain an efficient binder selection, some criteria for successful consolidation using liquid phase sintering (LPS) should be achieved, as high solubility for the WC phase in the liquid phase, good wetting of the solid grains and high temperature difference between the WC melting point and the eutectic temperature [5]. For such a purpose, the prior knowledge of the wettability behavior of selected metals on the tungsten carbide surface is of large importance. Furthermore, the wettability analysis must reproduce the thermal consolidation conditions, i.e., high temperature and reduced atmosphere [6]. A few studies concerning the wetting and spreading of cobalt and nickel, the usual hardmetal binders, on tungsten carbide, in reduced atmospheres are available in the open literature [7–9]. The increased interest on copper matrix composites for wear and cutting resistant applications has been encouraging the investigation of the wetting behavior of ceramics by copper [10–12]. Moreover, the wettability of brazing copper alloys on WC based cemented carbide surfaces was investigated by Mirski et al. [12] to improve the brazing process. The surface wettability enhancement by selective electrolytic etching the WC phase was reported [12], with a wetting angle decrease from 120° to 30° at 1100 °C and 70° to 4° at 1180 °C in nitrogen atmosphere. However, the available information about the wettability and interfacial chemistry of metals or metal alloys on WC surfaces at high temperatures is limited to a few species [9–11] and specific experimental conditions and more studies are needed to enlarge the knowledge and, therefore, the application of those findings.

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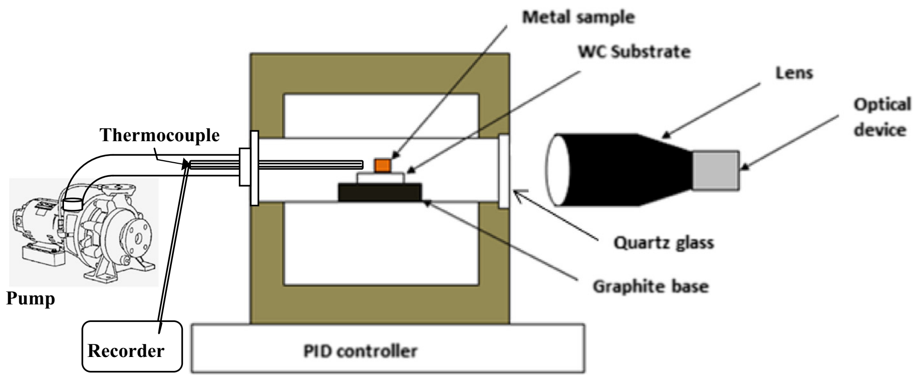

Fig. 1. Schematic representation of vacuum furnace coupled with acquisition image system.

In the present work, high temperature measurements of the contact angle of melted Cu, on different WC based surfaces were performed in low vacuum atmosphere. Cu was chosen as a potentially interesting WC binder for cemented carbide composites, due to its excellent thermal conductivity, high ductility and good toughness.

The methodology used to measure the contact angle was the sessile drop method [7]. Several factors may influence the wetting behavior determined by this method (or equivalent ones), such as substrate roughness, surface heterogeneities and adsorbed species, reaction between solid and liquid, atmosphere, time and temperature, hindering the comparison among experimental values [10,11,13]. In this study, the effect of chemical and morphological characteristics of WC based surfaces, namely the influence of the presence of cobalt at the surface of the substrate, were investigated and correlated with the copper wetting behavior and surface reactivity.

2. Experimental

Three types of tungsten carbide based surfaces were selected as substrates: (i) a commercial hardmetal sample with 3.5 wt% of cobalt, the composition available in the market with lowest Co amount; (ii) a thin film of WC sputter-deposited on the surface of the aforementioned WC-3.5 wt% Co commercial sample and (iii) a WC sample consolidated by hot pressing (HP) WC powders. These substrates will be designated hereafter as (i) WC–Co, (ii) WC thin film and (iii) WC, respectively, and details of their characteristics are presented in following.

The WC–Co commercial substrate (i) was acquired to DURIT, Hartmetall (ref. BH03), had a parallelepipedic shape with $2.0 \times 2.0 \times 0.2\ cm^3$ and a fine grain size of 0.8 µm. The WC thin film in (ii) was sputter-deposited from a WC target ($\phi = 100$ mm, 99.5% purity, CERAC) on the WC–Co commercial substrate using an Edwards E306A sputtering equipment, with the following deposition parameters: sputtering pressure of 0.5 Pa; magnetron power of 500 W; substrate polarization of 50 V and deposition time of 20 min. The WC coating was also sputtered on glass substrate, using the same deposition parameters aforementioned, and detached for an easier complementary morphological characterization. Finally, in (iii), a WC sample with a cylindrical geometry (20 mm of diameter and 5 mm of thickness) was produced by hot pressing WC powders (H.C. Starck, HCST-Germany) with 99% purity and 2.5 µm of average particle size. For such purpose, a graphite die, heating/cooling rates of 15 °C/min, maximum temperature of 1650 °C, during 2 h, and 20 MPa of applied pressure were used.

The substrates were polished until diamond paste of 1 µm. The surface roughness (Ra) was evaluated with a rugosimeter (Hommel Tester T 1000) and the structural characterization was carried out with X-ray diffraction, XRD (Philips, XPert MPD).

For the wettability measurements, near cubic pieces were cut from a copper foil (99.9% purity) with 5 mm side. The Cu cubes were roughly polished to remove chips and some oxide layers eventually formed. The wettability studies were performed in a vacuum furnace coupled with an acquisition image system (Canon EDS 1100D, Zoom Lens EF 75–300 mm), Fig. 1, using thermal cycles with a heating rate of 8 °C/min until a maximum temperature of 1080 °C, during 30 min, in low vacuum atmosphere (20 Pa). The temperature control was performed with a thermocouple type R (Pt–Pt 13%Rh) placed near the sample (see Fig. 1) and the vacuum was achieved with a primary vacuum pump. The images were captured each 10 s, from the beginning of the Cu melting. The wetting angles were measured trough image analysis using Image J software (NIH, USA).

Cross-sections of the molten Cu on the WC surfaces were polished with SiC abrasive papers and diamond paste of 6 and 1 µm. The structure of the interface between the molten copper and the WC based surface was carried out by low angle XRD (Philips, XPert MPD). Scanning electron microscopy (SEM, Hitachi-SU70) coupled with energy dispersive spectroscopy (EDS, detector Rontec) was applied for microstructural and chemical characterization.

3. Results and discussion

The morphology and structure of the three WC based substrates used in this work and designated as WC–Co, WC thin film and WC were characterized. The XRD spectrum of the commercial WC–Co sample presents Co and WC phases,