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Full length article

Wetting and solidification of silver alloys in the presence of tungsten carbide

Nachiketa Ray*, Ludo Froyen, Kim Vanmeensel, Jef Vleugels

KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg, 44, B-3001 Heverlee, Belgium

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ABSTRACT

The wettability of pure Ag and Ag alloys (with Ni and Cu) on WC was investigated as a function of temperature by means of sessile drop experiments. Ni was found to preferentially segregate at the Ag/WC interface resulting in a decreased contact angle as compared to Cu. The influence of the Ni content and WC particle size on the solidification behavior of Ag in infiltrated Ag-WC-Ni (40 wt% WC and 0.07/5 wt% Ni) composites was assessed, revealing the pushing of WC particles by the solidification front, especially in the materials with a finer WC particle size. Addition of Ni decreased the grain size of the Ag phase by promoting heterogeneous nucleation. Complete coherency between the Ag and Ni phases was confirmed by electron backscattered diffraction analysis.

1. Introduction

The use of a metallic binder in brittle ceramics has been of considerable interest in order to find a balance between toughness and hardness. Refractory metal carbide rich composites, commonly known as cemented carbides, are popular in the cutting tool industry whereas conductive metal rich composites are used as electrical contact materials. Silver based refractory metal/metal carbides are known for their excellent resistance to electric arcs and are established to operate at medium (10–100 A) or high currents (1–100 kA) [1,2]. Although the electrical and thermal properties of these materials are of major relevance for the electrical industry [3], the science behind the processing of these materials appeals to a broader readership. The manufacturing process involves combining two or more compounds which have negligible solubility in both the solid and liquid phase [4]. Although it is a desired feature for the application, as the individual properties of each phase are retained, the fabrication of these materials presents serious challenges.

Ag-WC/W composites consisting of WC/W particles in a Ag matrix are mainly prepared by powder metallurgical routes which involves powder compaction followed by densification. Although researchers have managed over time to densify these materials up to 99% of the theoretical density, a stable porosity-free production of these composites has been a challenge. The traditional densification step involves ‘cold press-sinter-infiltration’ at temperatures above the melting point of silver. Therefore, two physical aspects of the process have been investigated in this work. The first one is the wetting behavior of silver and tungsten carbide, which would determine the likelihood of the silver to adhere to the WC above its melting point. Sessile drop experiments have been regarded as one of the most popular methods to measure the contact angle, allowing to estimate the interfacial energy by solving the Young's equation. Although the contact angle of silver at its melting point on tungsten [5,6] and tungsten carbide [7] substrates has been measured before, it has been pointed out that the contact angle strongly depends on factors like, temperature [6,8], substrate roughness [9–11], drop size [10] and oxidation of substrate [11]. In this work, a *wettable flat* substrate as defined by Nakae et al. to have a surface roughness in-between 0.01-0.5 μm [9] and a low oxygen content have been used. The effect of temperature and alloying elements like Ni and Cu were investigated. The second part of this work is focused on the solidification behavior of silver in the vicinity of WC. Solidification of metal-matrix particulate composites has been extensively studied in terms of the chemistry and mechanics of wetting, the influence of particles on nucleation, the growth of the solid metal with stationary/mobile reinforcements and chemical reactions at the liquid/solid interfaces [12,13]. Since Ag and WC show no evident chemical reaction or phase solubility, this study is mainly focused on the growth of the silver grains and their preferred orientation.

* Corresponding author.
E-mail address: nachiketa.ray.1014@gmail.com (N. Ray).

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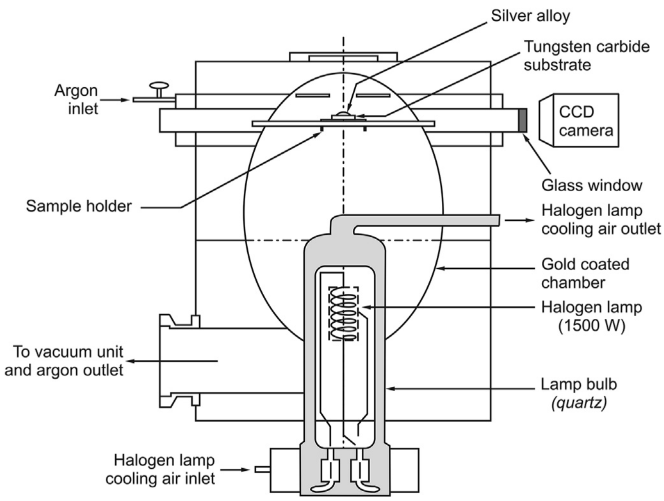

Fig. 1. Schematic showing the construction of the SVF17SP heating system used for contact angle measurements.

2. Experimental procedure

2.1. Contact angle measurement

A Ø 30 mm disc of WC was densified from WC powder (d_{50} = 0.8 μm) to 99.9% theoretical density by spark plasma sintering at 1900 °C and 65 MPa for 5 min. The dense block was machined into thin plates of 6 mm × 6 mm × 0.4 mm using electrical discharge machining and ground on all surfaces to generate plane-parallel surfaces. The top surface of the ground substrates was further polished using 3 μm and 1 μm diamond suspension (Kemet) on a polishing cloth (TOUCHLAM® 2TS3, LAM PLAN). The surface roughness of the substrates was measured using a profilometer (Surtronic 3+, Taylor-Hobson), having a resolution of 0.01 μm. Five measurements on five identical WC substrates were measured over a length of 1.25 mm.

Pure silver and $AgNi_{0.15}$, $AgCu_{0.2}$, $AgCu_1$ and $AgCu_{0.2}Ni_{0.15}$ (all values in wt.%) alloys, as extruded in wire form, were used in this investigation. Identical volumes (2 mm^3) of each alloy were carefully placed on top of the WC substrate. This configuration was placed on an alumina hot stage connected to a B-type thermocouple. The SVF17SP heating system was an attachment of a Confocal Scanning Laser Microscope (1LM21-SVF17SP, Lasertec), which was not used in this work. The heating system is basically a small furnace which consists of a 1500 W halogen lamp ideally placed at one of the foci of a reflective ellipsoidal chamber (gold plated), which reflects the light to the other focal point of the ellipsoid, where the sample was strategically positioned. The thermocouple is connected to a PID controller which enables to achieve precise and rapid heating and cooling rates. A glass window (10 SCS 1 DIN, SVAR welding glass, Severosklo) is foreseen at the same height of the sample holder which allows to capture images of the side view of the sample by means of a CCD camera. A detailed schematic of the furnace is shown in Fig. 1. The furnace temperature was calibrated using pure silver and pure copper at their respective melting points and the difference between real and measured temperature was observed to be almost similar at 961.8 °C and 1085 °C with a variation of 0–5 °C. The heating profile consisted of a steep ramp of 200 °C/min up to 900 °C followed by a gradual increase (5 °C/min) in temperature up to 1150 °C, during which the molten metal and substrate configuration was captured by a CCD camera. The cooling cycle was not recorded in order to evade supercooling effects. The camera captured images at 1 frame/s having an image size of 225 kB/frame. Purified argon (argon gas flowing through a Mg powder bed at 500 °C) was used as ambient gas for all experiments at a flow rate of 10 l/hr. After the ellipsoidal chamber was sealed, it was evacuated using a turbomolecular pump, followed by flushing the chamber with purified Ar. This cycle was repeated 3 times in order to ensure minimum oxygen contamination.

The captured images were analyzed by image processing software (ImageJ) using a Java plugin (Drop analysis, LB-ADSA [14]) to measure the contact angle made by the silver alloy on the tungsten carbide substrate as a function of temperature. The interface between the silver alloy and tungsten carbide after the test was investigated using Electron probe micro-analysis (EPMA, JXA-8530F, JEOL).

2.2. Solidification studies

The melting and solidification temperatures of the five silver alloys were characterized using differential scanning calorimetry (DSC, Q600 SDT, TA Instruments). The alloys were first placed in an alumina pan and heated to 1000 °C and cooled down in order to melt and make a thorough contact with the crucible. Then the alloys were re-heated and cooled at 2 °C/min and 10 °C/min respectively for heat flow measurement as a function of temperature and time.

Pressureless molten metal infiltration of porous sintered pellets was carried out in order to investigate the solidification behavior of silver in the vicinity of WC particles. The porous sintered pellets (Ø 7 mm) were prepared by liquid phase sintering of uniaxially pressed Ag, WC and Ni powder mixture discs at 970 °C for 30 min. Three material types with varying WC particle size and Ni content were prepared for the current investigation as summarized in Table 1. The median particle size (d_{50}) of Ag and Ni was 5 μm and 7 μm respectively. The sintered pellets were infiltrated by silver on a graphite crucible at 1070 °C for 30 min (video, supplementary material) which allowed the composite to achieve near theoretical density (>99%) as measured using Archimedes' principle (Table 1). Both sintering and infiltration were carried out in a reducing H_2:N_2 (3:1) atmosphere in order to prevent oxidation of the tungsten carbide. Since the infiltrated pellets were only in contact with the graphite crucible (heat sink) at the bottom, it can be assumed that during cooling (furnace cooling), heat was mainly lost through the bottom of the infiltrated pellets thus resulting in directional solidification.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.actamat.2017.11.012.

Table 1
Materials investigated in this work, tabulating WC particle size, starting powder composition, final composition after infiltration (balance WC) and relative theoretical density.

Material	WC d_{50} (μm)	Powder composition		Final composition		Density (g·cm^{-3})	Relative TD (%)
		Ag (wt.%)	Ni (wt.%)	Ag (wt.%)	Ni (wt.%)		
WC08Ni007	0.8	40	0.1	60	0.07	11.99	99.30%
WC40Ni007	4.0	40	0.1	60	0.07	12.03	99.64%
WC08Ni500	0.8	46	6.0	55	5	11.83	98.94%