Modification of wetting of copper (Cu) on carbon (C) by plasma treatment and molybdenum (Mo) interlayers

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Available online 20 January 2006

Abstract

Manipulating wetting and adhesion between the chemically immiscible elements Cu and C is of high interest for the production of C-fiber reinforced Cu–C metal matrix composites (MMC’s) which are potential materials for high performance heat sinks.

This work presents two approaches to adhesion manipulation: (i) the activation of the C-surface by a treatment in nitrogen (N2) radio frequency (RF) plasma and (ii) the deposition of a Mo-interlayer on the C-surface.

Both approaches yield a significant increase in adhesion for Cu-coatings deposited immediately after pre treatment. Heat treatment (30 min, 800 °C, high vacuum furnace) leads to a drastic loss in adhesion for the plasma treated samples while the samples containing the Mo-interlayer retain excellent adhesion values.

Results of thermal cycling experiments (RT—500 °C) combined with in situ X-ray diffraction (XRD) measurements show a similar picture. The Cu-coating on the plasma treated sample delaminates after one cycle. The sample with the Mo-interlayer can go through several cycles and is able to sustain thermally induced stresses.

The difference in the response of the two sample types to post deposition thermal treatment can be tracked back to the de-wetting behavior of Cu on the different substrates. Void formation is observed at the Cu–C interface in the case of plasma treatment but not for samples with a Mo-interlayer.

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PACS: 68.08.Bc; 68.35.Np; 68.55.–a; 81.15.Cd; 81.20.Ev; 07.10.Lw; 61.10.Nz

Keywords: Carbon; Copper; Metal matrix composite; Plasma treatment; Molybdenum interlayer; De-wetting

1. Introduction

Metal matrix composites (MMC’s) represent a material class with mechanical and thermal properties tuneable by the ratio of the constituents. They find applications in environments where the matching of thermomechanical characteristics is crucial. Carbon-fiber reinforced copper carbon MMC’s are potential materials for heat sinks in high performance electronic components or fusion reactor components. These applications require a reliable joining of the two components, Cu and C. A promising route to produce Cu–C MMC’s is coating short C-fibers (approximately 0.5 mm length, 7–10 μm diameter) with copper and then consolidating the material by unidirectional hot pressing [1,2]. Copper may be deposited by electrochemical methods [3–5] or by magnetron sputtering [6,7] which has the advantage of either allowing a plasma-pre-treatment of the C-surface or the deposition of adhesion promoting interlayers. Both, plasma-pre-treatment by a radio frequency nitrogen (RF-N2) discharge as well as the deposition of a 100 nm Mo interlayer on a C surface have a beneficial effect on the adhesion of Cu-coatings in the as-deposited state. If the samples are heat treated there is a drastic adhesion loss in the case of the plasma treated samples while heat treatment increases the adhesion promoting effect of the Mo interlayer [6]. It is the intention of this paper to further investigate the influence of heat treatment on the adhesion of Cu on modified C
surfaces by X-ray methods as well as by atomic force microscopy (AFM).

2. Experimental

All investigations presented in this work were performed on plane substrates to facilitate the sample characterization but their results are, as the authors have observed, also valid for Cu on C fibers [6]. All samples consisted of Cu-coatings of 1.5 μm thickness which were deposited on glassy carbon substrates (SIGRADUR G, [8,9]) with an area of 10 mm × 20 mm and a thickness of 2 mm. SIGRADUR G was chosen because its atomic bulk- and surface structure is based on turbostratic graphitic planes and therefore can be compared to the bulk/surface structure of various C-fiber types. The substrates were degreased and dried [6,7] and then stored at 100 °C until insertion into the deposition chamber via a load-lock system. After a base pressure of 10⁻⁴ Pa was reached the C-substrates were subjected either to a N₂ plasma-pre-treatment in a hollow cathode (50 mm diameter, 150 mm length) operated with a RF-discharge at a pressure of 4 Pa and a RF-Power of 50 W for 1 min or coated with 100 nm Mo at room temperature (RT) with a deposition rate of 0.5 nm/s. Immediately afterwards 1.5 μm thick Cu-coatings were deposited. Further data concerning the deposition equipment and deposition parameters are given in [6]. After deposition selected samples were subjected to a thermal annealing step of 60 min under high vacuum at 800 °C which mimicks the thermal load which is exerted on the fiber during uniaxial hot pressing.

To determine the macroscopic adhesion of the Cu-coating to the modified C surface a destructive pull-off adhesion test [10] was used. The surface morphology of samples before and after heat treatment was investigated by a TOPOMETRIX Explorer AFM in contact mode with a Si₃N₄-Tip with 50° opening angle. Tensions within the Cu-coating which are induced by the thermal treatment were investigated in situ with a SEIFERT PTS3000 four circle diffractometer using Co Kα radiation. A special heating attachment (Domed Hot Stage (DHS) 900) allowed the achievement of temperatures in a range from room temperature to 500 °C under N₂ protection gas atmosphere [11,12]. The calculation of the in-plane stresses within the polycrystalline Cu-coating was performed following the procedure described in Ref. [13].

3. Results and discussion

Fig. 1 shows the adhesion values of several sample types resulting from pull-off tests. For each sample type 3 pull-off tests were performed. The light grey regions in the columns represent the mean square deviation of the measurement results. It is clearly visible that before heat treatment, the substrates subjected to the N₂ plasma-RF hollow cathode discharge exhibit the highest adhesion values while the introduction of the 100 nm Mo interlayer does not have an equally pronounced (although measurable) adhesion improving effect. Heat treatment results in an almost complete loss in adhesion for the plasma treated samples while adhesion is significantly increased for the systems containing Mo interlayers. A probable reason for this behavior becomes apparent in

![Fig. 1. Adhesion strengths of 1.5 μm thick copper coatings before heat treatment: on untreated C-substrates (1st column), on N₂-plasma treated C-substrates (2nd column) and on C-substrates with a 100 nm Mo layer (3rd column); after heat treatment at 800 °C under high vacuum for 60 min: on N₂-plasma treated C-substrates (4th column) and on C-substrates with a 100 nm Mo layer (5th column).](image)

![Fig. 2. Contact mode topographic AFM scans of a 1.5 μm thick Cu-coating on modified C-substrates. (a) Before heat treatment; (b) on N₂-plasma treated C-substrates after heat treatment; (c) on C-substrates with a 100 nm Mo layer after heat treatment. Bright regions correspond to elevated sample positions.](image)
Fig. 2. Fig. 2a shows an AFM micrograph of the initial surface morphology of the 1.5 μm thick Cu-coating of all sample types. The surface is extremely smooth. The only distinct morphological features visible in Fig. 2a are contaminations on the sample surface. After heat treatment this changes significantly. In the case of the plasma treated system (Fig. 2b) two effects are observable: (i) the formation of crystallites in the Cu-coating (which is not evident in the present topograph but can definitely be observed in an AFM sensor image) and (ii) the formation of distinctly visible, equally spaced elevated regions (represented by bright grey scales). For the sample containing the Mo-interlayer recrystallization is also observed, but the crystallites remain extremely flat and the mean crystallite size is larger. Since the Cu-coatings could easily be removed from the plasma treated C surfaces after heat treatment it was possible to investigate the reverse side of the Cu-coating, i.e. the former Cu/C interface.

According to Srolovitz and Goldiner [14], stresses may be involved in the de-wetting process of a film from the substrate. Therefore in situ XRD measurements in the temperature range from RT to 500 °C (heating rate: 10 °C/min) were performed for both, plasma treated samples and samples containing Mo interlayers. The results of these measurements are shown in Fig. 5 (plasma treated sample) and Fig. 6 (Mo interlayer). Both figures display two heating (full symbols) and cooling cycles (open symbols). For plasma treated samples in the first heating cycle (Fig. 5) compressive stresses build within the range from RT to approximately 150 °C due to the different coefficients of thermal expansion (CTEs) of Cu (16 ppm/K) and SIGRADUR G (2.6 ppm/K). Upon further heating the compressive stresses are reduced due to the onset of recrystallization, annealing of defects and plastic deformation in the film. Within the first cooling cycle tensile stresses build up gradually. At RT in-plane tensile stresses remain which significantly differ from the magnitude of stresses in the as deposited sample. They are thermal stresses built up during the cooling of the layer caused by the thermal expansion mismatch. Stresses may also act as a driving force of surface diffusion fluxes at all involved interfaces (Cu/C, grain boundaries in Cu and Cu/ambient). These diffusion fluxes facilitate void formation at the Cu/C interface and are an essential part of the de wetting process [14]. In the second heating cycle, the tensile stresses decrease rapidly to the stress free state between RT and 150 °C and then remain
constant. This is a sign of delamination which was also macroscopically observed when the sample was removed from the heating stage. In the second cooling cycle, the sample remains at the stress free state until approximately 150 °C. At lower temperatures slight tensile stresses are observed, but remain significantly below the values reached in the first heating cycle.

For the sample containing the Mo interlayer (Fig. 6) the same phenomena as described above are observed in the first heating cycle. Slightly lower levels of compressive stress are reached in the low temperature regime which might be attributed to the Mo layer acting as a compliant layer with its coefficient of thermal expansion of 5.2 ppm/K lying between that of SIGRADUR G and Cu. The significant difference to the plasma treated sample is the second heating cycle. It is basically identical to the first cycle except for the different magnitude of tensile stress at RT and the slightly lower compressive stress values which may be attributed to the absence of significant recrystallization events during heating. The emergence of tensile stress during cooling is identical to the first cycle. These data suggest that no delamination occurs and that the system is capable of (at least limited) thermal cyclability. In addition the introduction of intermediate layers are a powerful tool to influence the wetting behavior of liquid Cu on C. The suppression of de-wetting by Mo interlayers will be the starting point of further work in which the influence of Mo on the wetting behavior of liquid Cu on C will be investigated.

Acknowledgements

This work is supported by the Austrian Science Fund (FWF) under grant Nr. P-14534 and by the country of Styria within the project “Multimethodenanalytik Nanoteilchen und Nanoteilchenverbunde”.

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