Improved adhesion of polycrystalline diamond films on copper/carbon composite surfaces due to in situ formation of mechanical gripping sites

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ABSTRACT

Diamond coatings are investigated for thermal management, wear protection and corrosion resistance in harsh environments. In power electronic industries, copper (Cu), which shows high thermal conductivity, is considered as a promising substrate for diamond based heat-spread materials. However, the coefficient of thermal expansion (CTE) mismatch between diamond and Cu induces thermo-mechanical stresses that affect the integrity of the diamond-Cu assembly. In fact, diamond films deposited on Cu substrates tend to peel-off upon cooling due to the compressive stresses present at the diamond-Cu interface. This investigation is focused on the growth of polycrystalline diamond thin films onto Cu/carbon fibers (CFs) composite materials, using combustion flame chemical vapor deposition (CVD). It has been found that increased CF content in the Cu/CF materials leads to a reduced CTE improving, hence, the adhesion between the diamond film and the Cu/CF substrate and reduces Cu/CF-diamond interfacial residual thermal stresses. At a CF content of 40% in volume, the residual thermal stress of the diamond film deposited on the Cu/CF composite is lower than that on bare Cu and adapted with CVD diamond growth. Naturally engineered composite surfaces have enhanced the adhesion of the diamond film on the composite substrate via mechanical interlocking.

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1. Introduction

Diamond exhibits exceptional properties that make it a suitable material for various applications such as coatings for cutting and drilling tools and thermal dissipation. Combustion flame chemical vapor deposition is being used to produce polycrystalline diamond films [1–3]. Its flexibility allows operating in open air and at a low cost, which results in high growth rates.

Diamond depositions have been conducted on several non-diamond substrates showing mainly two issues, low growth rate and poor adhesion. While the growth rate is related to nucleation density [4], the adhesion is compromised because of the internal residual stresses in the deposited diamond films [5]. These stresses are divided in two parts, thermal stress which is provoked by the coefficient of thermal expansion (CTE) mismatch between the diamond film and the substrate, and intrinsic stress which is related to the grain boundary formation and impurity content during diamond growth. As diamond is

characterized by a very low CTE, it is often incompatible with conventional non-diamond substrates, such as metals. The thermal stresses in these cases are often compressive and result in the diamond film cracking and eventually peeling off [6–10].

The substantial differences in thermo-mechanical properties of the non-carbon substrates and diamond, makes it difficult to obtain adherent diamond films. Several techniques, such as heat treatments, and chemical and physical etching [11], have been applied to reduce the amounts of residual stresses and therefore prevent delamination. Ali et al. have opted for a carbide-forming chromium interlayer to chemically modify the surface and use covalent bonding to make diamond adherent on copper [12]. While a number of studies on the modification of the surfaces either by insertion of carbide forming interlayers [12–13] or by heat treatments and etching have been carried out, there is still very few information on diamond growth on copper surfaces.

The purpose of this work is to investigate diamond deposition on copper/carbon composite materials using combustion flame CVD in open air. Depositions were carried out on a number of composites of different volume fractions of CFs. Different volume fractions resulted in different surfaces in terms of carbon content and allowed natural surface engineering to occur. Additionally, theoretical and experimental CTEs have also been investigated. Adherent diamond films were characterized using scanning electron microscopy (SEM) to investigate the

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surface and cross-sectional morphologies of the films. Raman spectroscopy investigations were carried out to evaluate the phase purity and residual stresses of the diamond films. The SEM micrographs have allowed suggesting a growth mechanism of diamond films on copper-based composites. The Raman analyses have shown the dependence of phase purity and residual stresses on the film thickness. It was found that composites containing sufficient amounts of CFs were suitable substrates for adherent diamond films.

2. Experimental details

2.1. Copper-based composites

The composite materials consist of a copper matrix and short CF reinforcements. The CFs (K223HM, CTN DIALEAD/BOBBINS, Sumitomo Corporation Europe) are pre-grinded to an average length of 200 μm. Dendritic copper powders (Eckart Granulate Velden GmbH) (d_{50} close to 35 μm) were used as the matrix material.

The sintering of the composite materials has been carried out using a Termolab press. The powders were mixed and compacted in a steel mould heated by an induction system. The powders were pressed at 650 °C under 40 MPa for 30 min. The temperature is controlled with the use of a thermocouple which is inserted in the steel mould. The chamber is put under vacuum (10^{-2} mbar range) to prevent the oxidation of the copper matrix during heating and/or cooling. Composites with 10%, 20%, 30%, 40%, and 50% volume fractions of CFs were densified. The final porosities observed are inferior to 4% for 10 to 40% CF and 7% for 50%. Furthermore, the CFs show no specific degradation. The final outcome is pellets of 40 mm of diameter and 2 mm in thickness. The pellets of the composites, up to 40% volume fraction of CFs, were then cut in $6 \times 6 \times 2$ mm^3 pieces using an ISOMet 1000 precision saw. The optical micrographs of the Cu/CF composite materials show a strong anisotropic structure (Fig. 1), with the orientation of the CFs perpendicular to the compaction direction. This anisotropy is caused by strains and stresses imposed by the processing-induced deformations and geometry, and will be reflected in the anisotropic thermal (k) and thermomechanical (CTE) properties of the composite materials.

2.2. Combustion flame CVD

The diamond deposition setup consists of a combustion system. The combustion torch, with a diameter of 1.5 mm, delivers a gas mixture of acetylene (C_2H_2, 99.999%), ethylene (C_2H_4, 99.6%) and oxygen (O_2, 99.996%) with a volume ratio of 1:1:2 respectively. The distance between the inner flame cone and the top of the substrate was maintained at 1.5 mm. The substrates were positioned using an X-Y-Z moving stage. A cooling system below the stage is used to regulate the deposition temperature. Unlike diamond depositions on Si and WC substrates [8], the temperature was kept between 710 and 740 °C. The substrate temperature was monitored using an infrared pyrometer (OS3752, Omega Engineering, Inc.).

2.3. Diamond film characterization

The microstructure and cross-section of the deposited diamond films have been evaluated using scanning electron microscopy (XL-30, Philips Electronics). The cross-sections were polished using Argon ion milling (Gatan Model 693, Ilion+) for 4 h under 5 kV. Raman spectroscopic analyses have been carried out using a micro-Raman spectrometer (Renishaw inVia H18415) with a 514.5 nm laser excitation.

2.4. CTE measurements and simulations

Thermo-mechanical simulations were also carried out to evaluate the impact of the diamond film on the surface of a Cu/CF composite, on heat dissipation through the substrate. A volume fraction of 40 vol% of CFs was selected for the simulations. Two geometries were used: one that the several heat sources (simulated silicon chips) are placed on the surface of the Cu/CF composite and one that the heat sources are placed on a diamond film-Cu/CF assembly. The Cu/CF substrate and diamond film thickness are set as 2 mm and 100 μm, respectively.

Thermal expansion coefficients along the fibers direction were measured on all samples of the same dimensions using a horizontal Netzsch dilatometer DIL402C. The device was calibrated using an alumina sample.

The COMSOL software makes it possible to predict the thermo-mechanical behavior of an electronic assembly. The temperature distribution used for the thermomechanical analyses is directly available from the COMSOL heat transfer module. The model developed for these simulations consists of a copper matrix composite reinforced with anisotropic CFs. The aspect ratio of the CFs (diameter/length = 10/200 = 0.05) is respected and different volume fractions of CFs were analyzed: 10%, 20%, 30%, 40% and 50%. A parametric study was done with a parameter angle ranging from 0 to 90°. An average value of the displacement of the composite for all the angles was taken for the CTE calculations. In order to add anisotropic properties to the CFs, according to the different angles, a second rotated coordinate system is added. This rotated system is also parameterized with the parameter angle.

The governing equations consist of the Fourier heat transfer equation. The stationary state heat transfer equation is [6]

$$-\nabla \cdot (k\nabla T) = Q, \tag{1}$$

where T is the temperature, k the thermal conductivity and Q the heat source. The boundary conditions for heat flux are defined as follows:

$$n \cdot (k\nabla T) = h(T_{ext} - T), \tag{2}$$

where n is the normal vector to the boundary, h is the heat transfer coefficient and T_{ext} the external (ambient) temperature. The elastic equation including the thermal expansion of materials is represented in the
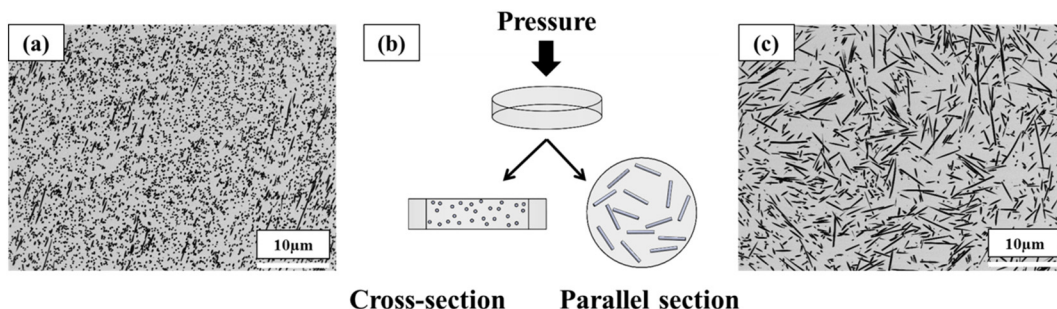

Fig. 1. Optical micrographs of the composite material (40 vol% of CFs) in (a) cross and (c) parallel section after densification and (b) schematic of the CF orientation.