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# Adhesion enhancement of diamond coating on minor Al-modified copper substrate

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ABSTRACT

We report on the enhanced interfacial adhesion of diamond coating on copper substrate modified by a small fraction of Al. For pure copper substrate, the diamond coating formed tends to crack and delaminate, primarily caused by a slight accumulation of detrimental graphite intermediate layer and thermal stress induced by mismatch of the coefficients of thermal expansion. Additions of 1 and 3 at.% Al to the copper substrate gradually decrease the intermediate graphitic phase. At the higher Al concentration, an aluminium oxide forms at the coating–substrate interface, and graphitic/amorphous carbon is completely inhibited, leading to significantly enhanced interfacial adhesion of diamond coating. The electron structure of copper is not observed to significantly alter on this Cu–Al dilute alloy. The alumina barrier layer preferentially formed on copper surface is believed to play a key role in preventing graphitization and adhesion enhancement.



## 1. Introduction

Diamond possesses many outstanding physical and chemical characteristics including the highest hardness (100 GPa) and thermal conductivity (2000 W $m^{-1}$ $K^{-1}$), exceptional chemical inertness, optical transparency and radiation-resistance, as well as low friction coefficient and superior wear resistance [1]. It is therefore considered a promising material for a wide range of applications as infrared windows, thermal management devices, wear-resistant protective coatings, composite additives and particle detectors. Combining diamond with copper or copper-based substrates, which have large heat capacity, has attracted increasing interest to produce highly efficient heat sinks and heat conductors [2,3]. However, unlike on silicon and refractory metal substrates, diamond coatings directly grown on pure copper substrate tend to delaminate from substrates during cooling stage after deposition [4–9]. To enhance the interfacial bonding strength, different methods like surface pre-treatment and using interlayer have been developed [5,6,9]. The disadvantage of introducing extra interfaces is that this may increase the total thermal resistance, and the adhesion between each interface should be simultaneously secured. Our recent studies have showed that aluminium alloying on Fe-base alloys can significantly promote the formation of adherent diamond films [10–12]. In comparison with Fe, Cu has a different electron configuration and carbon affinity. In this study, diamond deposition on Al-modified Cu substrate will be investigated.

## 2. Experiment

The substrate materials used for diamond deposition were commercial pure Cu and two Cu–Al alloys with an Al fraction of 1 and 3 at.%, respectively. The alloy was prepared by repeated arc-melting appropriate amounts of high-purity metals (99.999%) under a Ti-gettered inert atmosphere using non-consumable tungsten electrodes. The substrates were machined into specimens of 10 mm × 10 mm × 1 mm in size by wire cutting and mechanically polished with SiC sandpapers down to 600 # grid, and ultrasonically cleaned in ethanol for 10 min then dried for use.

Deposition of diamond was carried out in a 2.45 GHz microwave plasma assisted CVD system (Plasmionique) using $H_2$ and $CH_4$ gas mixture. The deposition parameters include a total flow rate of 100 sccm, an input power of 700 W, a working pressure of 30 Torr, and the substrate temperature of about 650 °C.

The morphologies, compositions and structures of the CVD products and coating–substrate interface were characterized by scanning electron microscopy (SEM) and micro-Raman spectroscopy. Synchrotron-based X-ray near-edge fine structure absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) were performed to address the electron configuration changes of copper. Cross-sectional specimens for transmission electron microscopy (TEM) observations were prepared by sequent procedures including cutting, gluing,

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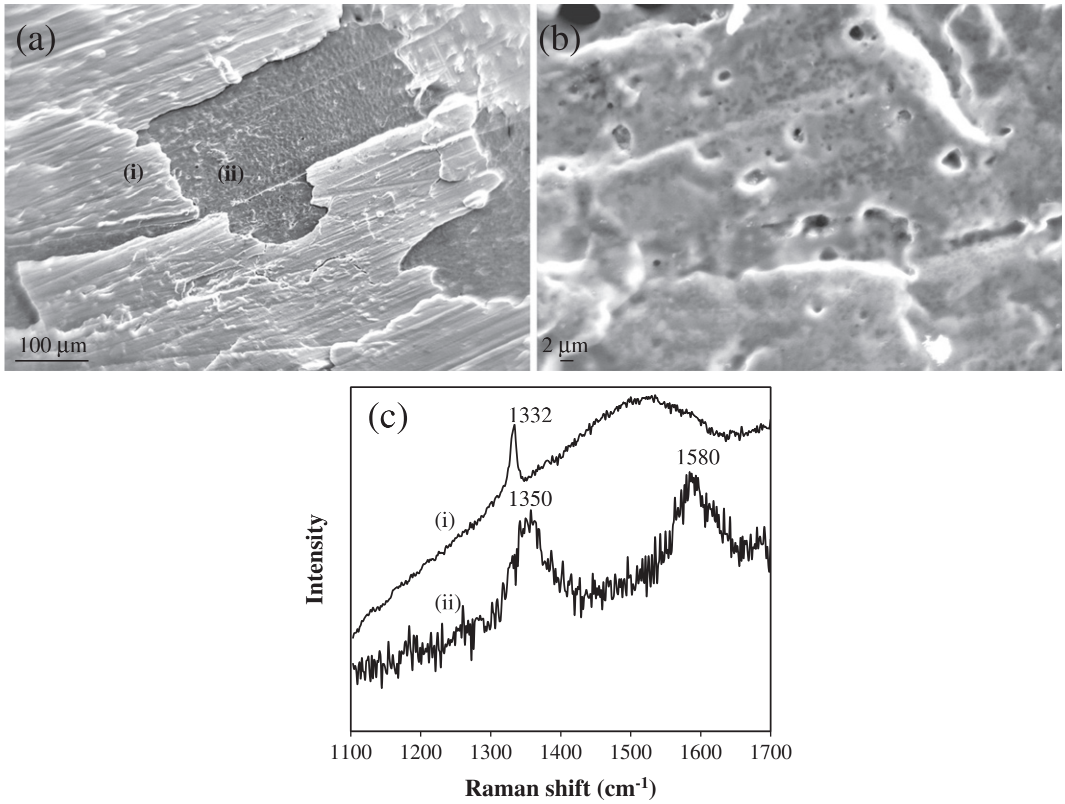


**Fig. 1.** SEM image (a, b), and the corresponding Raman spectra (c) of surface CVD products directly formed on pure copper substrate.

grinding and dimpling to about 15 μm in thickness, then finally ion-milling by $Ar^+$ from both sides until some perforation appeared. A Tecnai $G^2$ F20 transmission electron microscope, equipped with a high-angle angular-dark-field (HAADF) detector and energy-dispersive X-ray spectrometer (EDX) systems, was used at 200 kV for electron diffraction analysis and chemical composition analysis.

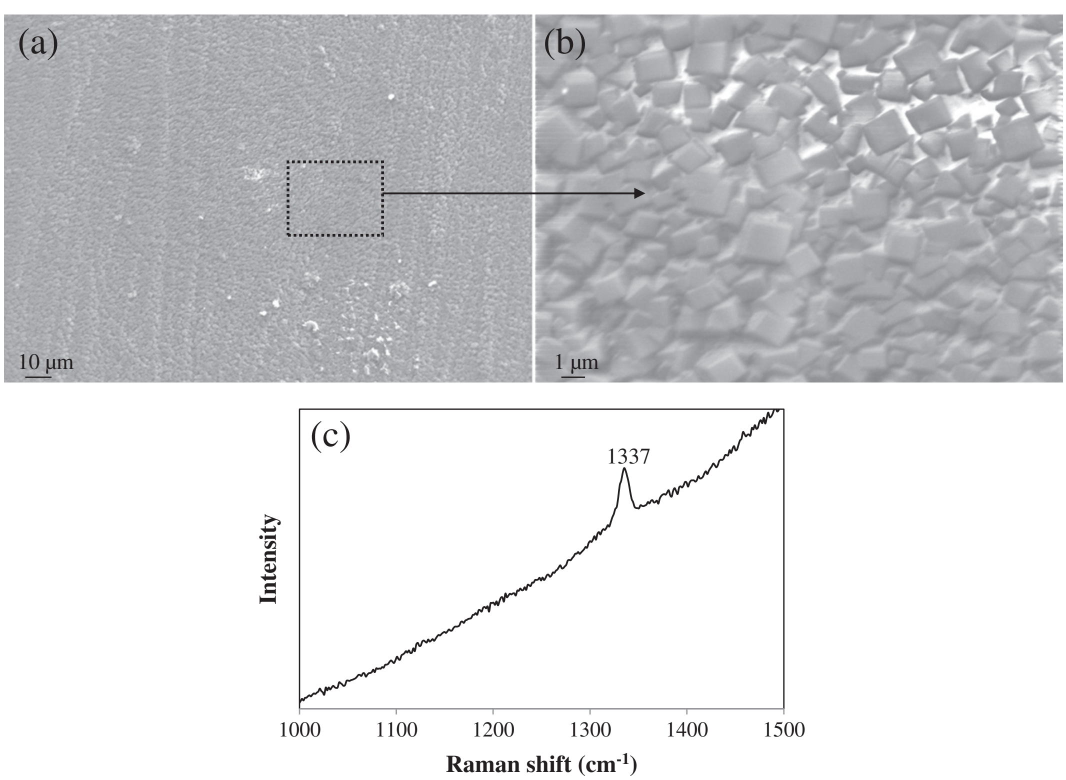


**Fig. 2.** SEM surface images of Cu–3Al substrate coated with continuous microcrystalline diamond film. (a): A general view; (b): a magnified view; (c) the corresponding Raman spectrum.