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CVD deposition of nanocrystalline diamond coatings on implant alloy materials with CrN/Al interlayer

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ABSTRACT

Integration of smooth nanocrystalline diamond coatings on biomedical implant substrates (CoCr, SS316) for enhanced biomedical performances has great application potentials due to their extraordinary wear/corrosion resistance and biocompatibility. However, chemical vapor deposition (CVD) of adherent diamond coatings on such substrates encounters a major technical barrier of weak interface bonding strength. In this study, single CrN interlayer of different thickness and duplex CrN/Al interlayer have been prepared on CoCr alloy and SS316 steel substrates to improve the adhesion of diamond coatings. The diamond coating produced with a single CrN interlayer up to 1 μm thick still shows insufficient adhesion ability to the substrates. A combination of CrN and Al, with a total thickness of 0.45 μm, significantly enhances the diamond coating/substrate bonding strength. The fundamental mechanism of enhanced interfacial adhesion is discussed in terms of the individual role the two kinds of interlayer materials play.

1. Introduction

CoCr ally and SS316L steel have been commonly used as implantable biomaterials owing to their decent biocompatibility, superior mechanical properties and relatively low cost. During their service in aggressive human being environment, the implant surface can be damaged by corrosion and wear, and the released wear debris and metal ions also cause unexpected health problems [1]. Polycrystalline diamond and amorphous diamond like carbon (DLC) are characterized by their high hardness, low friction coefficient, superior chemical inertness and good bio-compatibility. Therefore, modifying the implant surface by diamond and related coating materials has attracted increasing attention to reduce the disadvantages of metallic biomaterials [2–6]. However, a major technological barrier exists in the insufficient interfacial bonding strength between the diamond-related coatings and the substrates. For DLC coatings, huge residual stress accumulated within the coatings readily causes coating cracking and delamination. Especially, diamond deposition is performed at much higher temperatures, and the coating properties are strongly affected by more complex factors such as the huge thermal stress due to the mismatch of thermal expansion coefficients, competitive nucleation and growth between graphite and diamond, and interaction of the substrate with the reaction atmosphere [7].

To enhance the interface strength, an intermediate layer applied on the substrate surface is usually required. The interlayer should be properly selected such that it can act as a diffusion barrier to prevent a direct contact of the base metal to the reaction atmosphere. Furthermore, the interlayer should adhere well both to the top coating and to the underlying substrates, as well as provide an intermediate coefficient of thermal expansion to minimize the residual stress. So far various interlayer materials from metals to ceramics have been extensively developed to enhance the properties of diamond coatings deposited on special heterogeneous substrates [8–14]. Among these interlayers, CrN and Al have received special attention, and their respective efficiency on diamond deposition behaviors has been demonstrated [15–18]. However, a thick CrN interlayer is usually needed in order to provide a complete diffusion barrier effect [19,20]. On the one hand, a thick CrN buffer layer is beneficial to compromise the thermal stress in the diamond coatings. On the other hand, a thick interlayer will negatively deteriorate the accurate geometry of small implant components. Element Al is very reactive to oxygen and readily forms a dense alumina layer, and a very thin Al layer can perform perfect diffusion barrier function. However, an Al interlayer itself is not good enough as a buffer layer to accommodate the thermal stress. In the current study, we have examined the effectiveness of CrN/Al dual layer on diamond deposition on the conventional CoCr and SS316 steel substrates.

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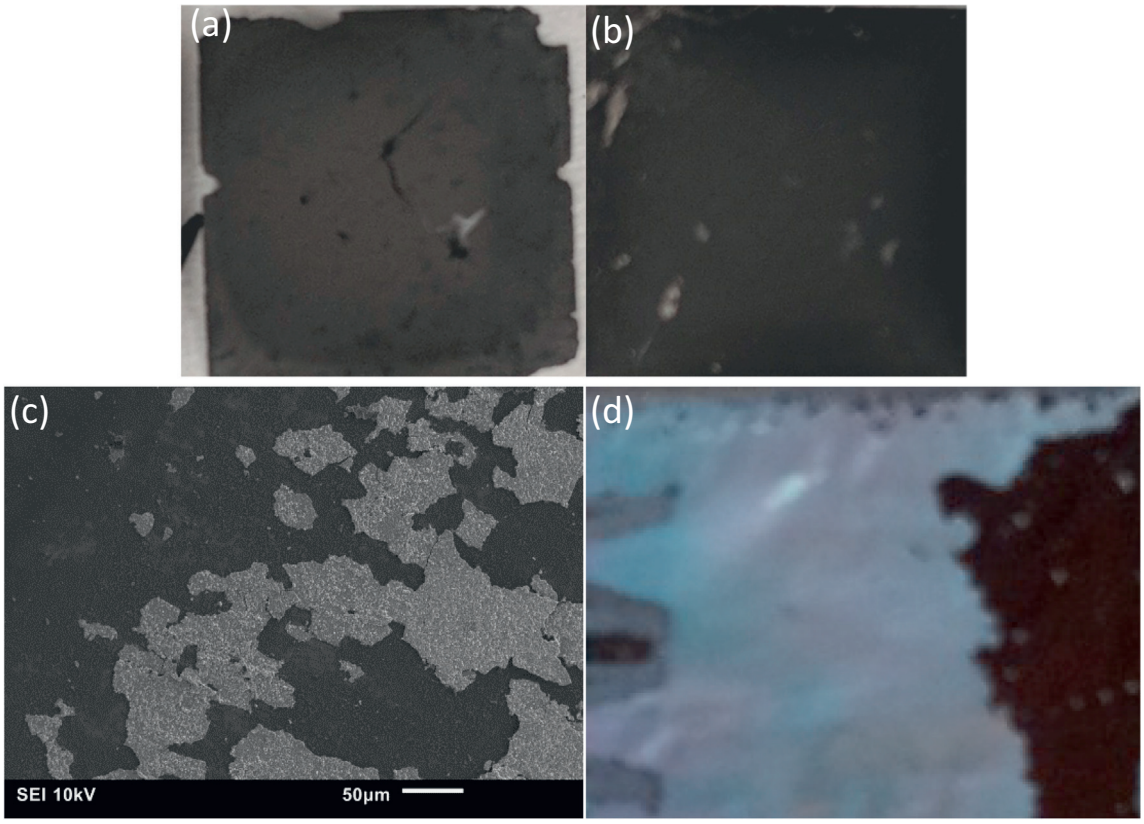

Fig. 1. General view of diamond coating delaminated from bare SS316 (a) and exposed substrate surface (b); diamond coating deposited on SS316 substrate with a 0.4 μm CrN interlayer (c), and with 1 μm CrN interlayer (d).

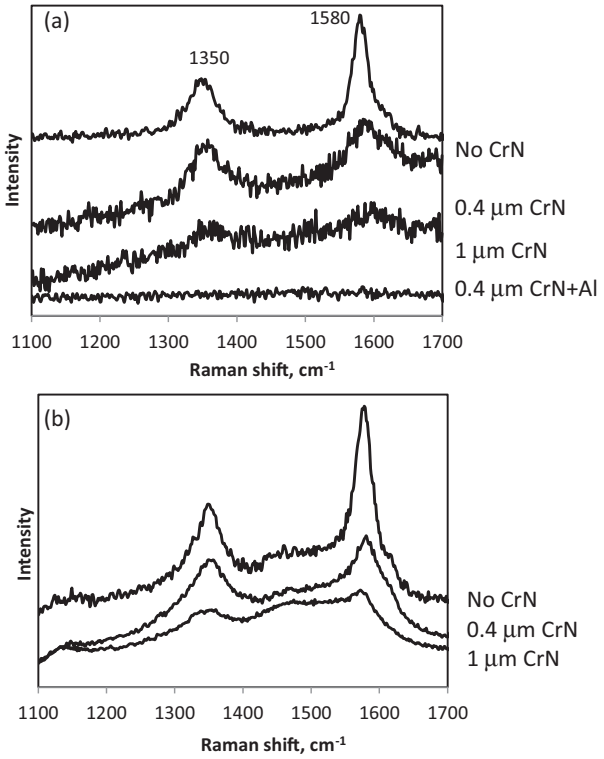

Fig. 2. Raman spectra measured from (a): exposed SS316 surface after deposition and removal of top diamond films, and from (b): the backside of the delaminated diamond films (b) without or with different interlayers.

2. Experimental

Commercial CoCrMO alloy (Co base, 28.0% Cr, 6.5% Mo) and medical class SS316 (Fe base, 17.5%Cr, 13%Ni, 2.5%Mo, all in wt%) were used as substrates for diamond deposition. The specimens were polished into mirror-like surface by sandpapers and diamond suspensions successively, then cleaned in ethanol, with a final surface roughness about 0.087 μm. The CrN and Al interlayers were prepared by a magnetron sputtering system made by Plasmionique Inc., using Ar/N_2 mixture (ratio 2:1) and pure Ar, respectively. The thickness of CrN single layer varies from 0.4–1 μm, while the thickness of CrN and Al in the CrN/Al interlayer was 0.4 and 0.05 μm, respectively, as measured by an optical profilometer manufactured by Zygo. The base pressure is 2×10^{-6} Torr and the deposition pressure was 1.3 mTorr and at room temperature. The Al interlayer was deposited using pure Ar (99.99%), and CrN was deposited by sputtering Cr target in an Ar and N_2 gas mixture.

Prior to diamond deposition, the substrates coated with interlayer were ultrasonically scratched for 20 s by diamond suspension in ethanol, rinsed in acetone and dried by flowing N_2 for use. Diamond deposition was carried out in a 2.45 GHz microwave plasma enhanced chemical vapor deposition (MPCVD) system. The input microwave power was 800 W, and the substrate surface temperature was approximately 700 °C as measured by a thermocouple mounted underneath the stainless steel substrate holder. The system was pumped to a base pressure of 1×10^{-6} Torr then a gas mixture of CH_4/H_2 was introduced to the chamber at a total flow rate of 100 sccm with 5 vol% CH_4. The deposition pressure was maintained at 23 Torr and the diamond coating deposition period was 12 h.

The morphologies, compositions and microstructures of the substrates, interlayer and the top deposits were characterized by Raman spectroscopy (Renishaw 2000, Ar laser 514 nm wavelength), X-ray