



# Diamond nucleation and growth on WC-Co inserts with Cr<sub>2</sub>O<sub>3</sub>-Cr interlayer

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## ABSTRACT

Cr<sub>2</sub>O<sub>3</sub>-Cr interlayer was prepared by magnetron sputtering to restrict graphite formation on WC-Co before diamond nucleation. Continuous diamond coatings containing little graphite phase were successfully deposited on single Cr<sub>2</sub>O<sub>3</sub> interlayered WC-Co substrates. For Cr<sub>2</sub>O<sub>3</sub>/Cr duplex interlayer, a low nucleation density was observed at a low CH<sub>4</sub> concentration, but a continuous diamond coating was readily obtained with an increased CH<sub>4</sub> concentration during nucleation stage. X-ray diffraction and X-ray absorption analysis reveal that the Cr top layer was carburized to Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub> after diamond deposition while Cr<sub>2</sub>O<sub>3</sub> layer kept unchanged. In addition, the indentation test shows that the diamond coating has poor adhesion to the substrate with a single Cr<sub>2</sub>O<sub>3</sub> interlayer, while the adhesion was significantly enhanced with the Cr<sub>2</sub>O<sub>3</sub>/Cr duplex interlayer combined with a high CH<sub>4</sub> concentration for nucleation.

## 1. Introduction

Cemented carbide cutting tools are widely used in machining industry due to their high modulus of elasticity, high thermal conductivity, and wide temperature range for operation. However, they are subject to high wear rate when cutting aluminum alloys, green ceramics, and abrasive composites. The fast development of new materials appeals for the research of new cutting tools. Diamond has unique properties such as high hardness, corrosion resistance and chemical inertness [1]. As a result, it is considered as one of the most promising coating materials to improve both the life time and cutting productivity of cemented carbide cutting tools.

The poor adhesion between diamond coatings and cemented carbide cutting tools restricts their wider application. This is caused by several factors. The major factor is the Co, a binder phase inside cemented carbide, diffuses to the surface during diamond deposition to catalyze the formation of graphite before diamond nucleation [2]. The presence of graphite in the interface between diamond and carbide substrate results in deteriorated adhesion. Additionally, the mismatch of thermal expansion coefficient between diamond and carbide substrate would lead to large thermal compressive stress inside diamond coating once the coating is cooled down from high deposition temperature [3], even though the existence of compressive stress may improve the wear resistance of the diamond coatings by suppressing the crack propagation under load [4]. Various methods have been applied to solve the problems. One way is to use chemicals including acid and Murakami's solution to remove the Co from the near surface of WC-Co

substrate [5–7]. However, the lack of Co on the surface may affect the toughness of the inserts [8]. Another way is to apply interlayers to suppress the diffusion of Co. Many interlayers have been tried so far, including CrN, Cr, Ti, Al, W, SiC [9–15]. Our group's previous research has discovered Al is an efficient interlayer material to block the diffusion of Co due to the formation of an aluminum oxide [16,17]. However, Al is soft and easily damaged during diamond seeding pre-treatment in an ultrasonic bath. In this work, Cr<sub>2</sub>O<sub>3</sub> is chosen as an interlayer candidate considering its demonstrated diffusion barrier property. To compare the efficiency of Cr<sub>2</sub>O<sub>3</sub> in suppressing the diffusion of Co, Cr<sub>2</sub>O<sub>3</sub> were deposited on as-polished and Murakami's solution and Caro's acid etched bare WC-Co substrates, respectively. Meanwhile, Cr<sub>2</sub>O<sub>3</sub>/Cr interlayer is designed to illustrate the mechanism of nucleation and growth of diamond coating on Cr<sub>2</sub>O<sub>3</sub> and Cr.

## 2. Experiment methods

Commercial cemented carbide inserts (Grade K68, WC-6%Co) purchased from Kennametal were chosen as the substrates. They were firstly polished by sandpaper and diamond suspension into mirror-like surface, and then cleaned by ethanol. One group of substrates were pre-etched by Murakami's solution (10 g K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 10 g KOH + 100 mL H<sub>2</sub>O) for 10 min and followed by Caro's acid (3 mL H<sub>2</sub>SO<sub>4</sub> (96%) + 88 mL H<sub>2</sub>O<sub>2</sub> (30%)) for 10 s to remove Co from the surface. The interlayers were deposited by magnetron sputtering system manufactured by Plasmonique with RF power of 300 W. The Cr<sub>2</sub>O<sub>3</sub> layer was deposited at the temperature of 300 °C by sputtering 99.95%

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Cr target in the plasma of O<sub>2</sub> and Ar. The flow rates of the O<sub>2</sub> and Ar were 8 sccm and 100 sccm, respectively and the deposition pressure was 5 mTorr. Prior to the deposition of Cr<sub>2</sub>O<sub>3</sub>, a thin layer of Cr was deposited for 5 min to enhance the adhesion. The thickness of Cr<sub>2</sub>O<sub>3</sub> after 3 h deposition is around 250–300 nm measured by Zygo Newview 8000 optical profilometer. Cr layer was deposited by directly sputtering Cr target in an Ar plasma. The deposition pressure was also kept at 5 mTorr. The thickness of the top Cr layer was around 70–75 nm after 15 min deposition. Diamond coating was deposited by microwave plasma enhanced chemical vapor deposition (MPCVD) manufactured by Plasmionique in the gas mixture of H<sub>2</sub> and CH<sub>4</sub>. The pressure was 23 Torr and the methane concentration was 1 vol%. The microwave power was kept at 800 W. The substrate temperature measured by the thermocouple at the back of the substrate was around 670 °C. The thickness of diamond coating after 7 h deposition was around 1.2 μm. To increase the nucleation, the nano-diamond powders with diameter of 3–4 nm were applied to scratch the surface of all the samples in an ultrasonic bath prior to the diamond deposition.

Renishaw 2000 Raman Microscopy with Ar<sup>+</sup> laser (wavelength of 514.5 nm) was used to characterize the bonding state of Cr<sub>2</sub>O<sub>3</sub> interlayer and diamond coatings. Rigaku Ultima IV Grazing Incident X-ray Diffraction (GIXRD) with Cu Kα radiation was employed to identify the phases of as-deposited interlayers. The incident angle is 7°. JEOL JSM-6010 LV SEM was applied to observe the morphology and microstructure of deposited diamond coatings. X-ray diffraction (XRD) with Co Kα radiation was used to identify the phase composition of the samples after diamond deposition. Cr K edge X-ray Absorption Near Edge Structure (XANES) Microscopy with fluorescence mode were employed to observe the chemical state change of interlayers after diamond deposition. The X-ray absorption spectra were measured in Hard X-ray MicroAnalysis (HXMA) beamline of Canadian Light Source. Rockwell C indentation tester manufactured by Instron Wolpert with a load of 1471 N was used to compare the adhesion strength of diamond coatings on the WC-Co inserts. The AXIS SUPRA photoelectron spectrometer manufactured by Kratos Analytical was employed to measure the X-ray photoelectron spectra (XPS) of the imprint areas of the diamond coatings after adhesion testing. The photoelectrons were collected from a circular area with 27 μm diameter. Monochromatic Al Kα excitation was used with the tube voltage set as 15 kV and the emission current set as 25 mA.

### 3. Results and discussion

#### 3.1. Characterization of interlayers

Fig. 1(a) shows the Raman spectrum of the as-deposited Cr<sub>2</sub>O<sub>3</sub>. For Cr<sub>2</sub>O<sub>3</sub>, only two A<sub>1g</sub> and five E<sub>g</sub> vibrational modes are Raman active. The detailed reference table can be found in Mougín and Shim's work [18,19]. In the Raman spectrum of the deposited Cr<sub>2</sub>O<sub>3</sub> layer, it is obvious to see one A<sub>1g</sub> vibration at the peak of 550 cm<sup>-1</sup> and four E<sub>g</sub> vibrations at the peaks of 294 cm<sup>-1</sup>, 350 cm<sup>-1</sup>, 526 cm<sup>-1</sup> and 611 cm<sup>-1</sup>, respectively. The slight shift of the peaks may be affected by the stress inside the coating. The Grazing Incident XRD patterns of the sputtered Cr<sub>2</sub>O<sub>3</sub> interlayer and Cr<sub>2</sub>O<sub>3</sub>/Cr interlayer are shown in Fig. 1(b), confirming that the Cr<sub>2</sub>O<sub>3</sub> interlayer is mainly composed of crystalline Cr<sub>2</sub>O<sub>3</sub>, as all the visible XRD peaks match well with Cr<sub>2</sub>O<sub>3</sub> (PDF#38-1479). In the Cr<sub>2</sub>O<sub>3</sub>/Cr interlayer, the existence of Cr (110) and Cr (200) peaks (PDF#06-0694) confirms the presence of the Cr sublayer, but two small Cr<sub>2</sub>O<sub>3</sub> peaks of (006) and (119) disappear due to the cover of a Cr top layer.

The SEM surface images of Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/Cr interlayers before and after seeding are shown in Fig. 2. It can be seen that a lot of scratches were created after diamond seeding for 5 min on both interlayers (Fig. 2c and d). Compared with single Cr<sub>2</sub>O<sub>3</sub> interlayer (Fig. 2e and f), more defects were created on Cr<sub>2</sub>O<sub>3</sub>/Cr interlayer and more diamond agglomerates were embedded onto Cr sublayer since Cr is much

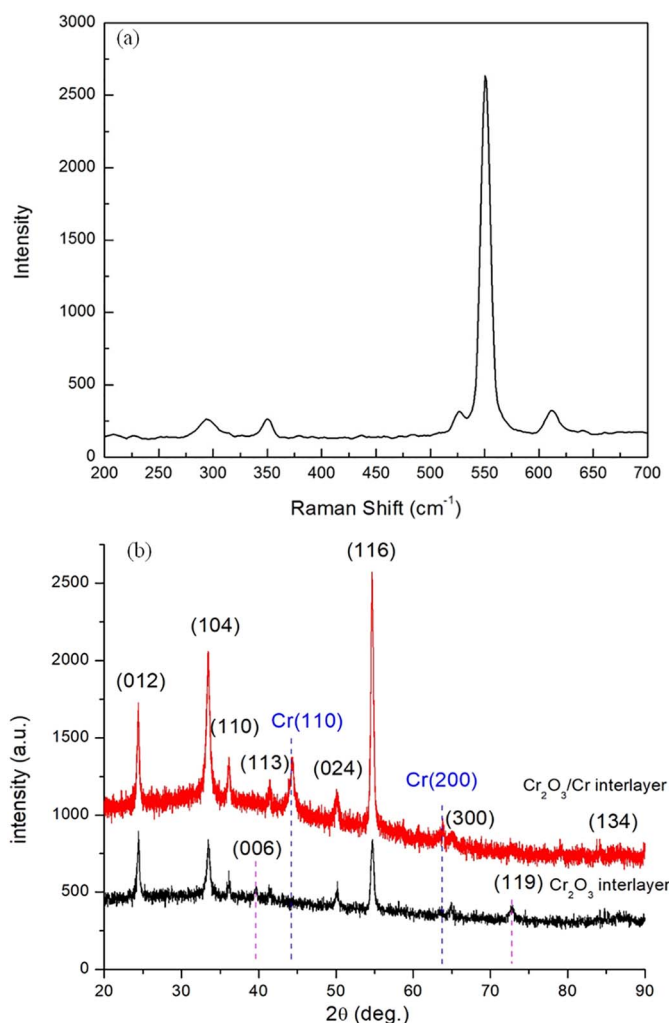


Fig. 1. (a) Raman Spectrum and (b) Grazing Incident XRD patterns of Cr<sub>2</sub>O<sub>3</sub> interlayer and Cr<sub>2</sub>O<sub>3</sub>/Cr interlayer.

softer than Cr<sub>2</sub>O<sub>3</sub>.

#### 3.2. Characterization of diamond coatings

Raman spectra of diamond coatings are shown in Fig. 3. The diamond peak of 1337 cm<sup>-1</sup> can be observed in the samples with Cr<sub>2</sub>O<sub>3</sub> interlayer and etched surface with Cr<sub>2</sub>O<sub>3</sub> interlayer. A broad peak around 1500 cm<sup>-1</sup> is found in the pre-etched sample with Cr<sub>2</sub>O<sub>3</sub> interlayer, which is usually ascribed to the sp<sup>2</sup> amorphous carbon inside the coating [20]. In the sample with a single Cr<sub>2</sub>O<sub>3</sub> interlayer, another broad peak located around 1600 cm<sup>-1</sup> appears, which is attributed to graphite phase [21]. Considering the Raman sensitivity (for Ar<sup>+</sup> laser with a wavelength of 514.5 nm) of the π-bonded amorphous carbon and graphite phase is 50 times higher than sp<sup>3</sup> bonded diamond phase, the diamond phase dominates the coating [22]. On the sample with Cr<sub>2</sub>O<sub>3</sub>/Cr duplex interlayer, the Raman peaks are more complicated, indicating various carbon phases are mixed inside the diamond coating. Besides the diamond peak located at 1334 cm<sup>-1</sup> and the microcrystalline graphite peak at 1574 cm<sup>-1</sup> [23], some other peaks can be observed as well. The origin of the peak at approximately 1240 cm<sup>-1</sup> could be attributed to the peak in the phonon density of states (PDOS) of diamond or transpolyacetylene [24]. The shoulder around 1300 cm<sup>-1</sup> could be ascribed to the sp<sup>3</sup> bonded amorphous carbon [25]. The small broad peaks from 1400 to 1470 cm<sup>-1</sup> might be due to the existence of transpolyacetylene [24]. The shoulder at around 1615 cm<sup>-1</sup> is attributed to the D' band of microcrystalline graphite or disordered carbon

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