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Quantitative determination of the adhesive fracture toughness of CVD diamond to WC–Co cemented carbide

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Abstract

Well-separated diamond particles were nucleated and grown by hot filament chemical vapor deposition (HFCVD) onto WC–Co cemented carbide pretreated by Murakami's reagent and $H_2O_2 + H_2SO_4$ solution. The adhesive strength of diamond particles to WC–Co cemented carbide was quantitatively determined in terms of interface toughness by directly applying an external load to the CVD diamond particles. From the measurement of the maximum load required to scratch off the particles, we determined that the adhesive toughness was 14 J/m^2. This value is more than twice as high as that of CVD diamond on smooth silicon substrate and comparable to the cleavage fracture energy of diamond. The newly developed procedure will allow to check the effectiveness of substrate surface pretreatments for further improving the adhesion level of diamond films on WC–Co.

Keywords: Chemical vapor deposition; Interface/interfacial; Mechanical properties; Pretreated substrate

1. Introduction

Since chemical vapor deposition (CVD) methods have been developed, synthetic polycrystalline diamond films attract more and more attention. Unfortunately, the application of CVD diamond films is still limited due to their weak adhesive strength to the substrates. As a matter of fact, the evaluation of adhesive strength is of great importance to ensure the integrity of diamond coatings under severe conditions. For example, adhesive strength is a critical problem for wear-resistant coatings of diamond on superhard materials such as WC–Co cemented carbide used as cutting tools and wear parts [1,2]. A number of researches can be found where adhesive properties of CVD diamond on WC–Co substrates are examined. Huang et al. [3] presented the effect of surface roughness of substrates on the interface crack extension resistance, while Taher et al. [4] tried to find the optimum total wear resistant performance including adhesion with respect to the methane concentration in CVD process. For the enhancement of adhesion, the effect of metallic interlayers were also surveyed by Lopez et al. [5]. However, quantitative evaluation of adhesion is quite difficult for the case of hard coatings [6]. Several techniques are commonly known [7,8], such as scratching and indentation methods which were employed also in the literature mentioned above. But the parameters evaluated by these methods have little physical meanings, and even lead to contradictory results among different methods [9]. Moreover, no quantitative physically meaningful value has ever been obtained for CVD diamond on cemented carbides, which could allow comparison of the interface strength of different coating/substrate systems.

Under these circumstances, a new method of evaluation for adhesive toughness of CVD diamond has been

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recently developed [10]. The method allows for the suitable characterization of the mechanical strength of brittle interfaces in terms of adhesive toughness, which represents the macroscopic energy required to extend a unit area of interface crack. In this paper, we first present a quantitative measurement of the adhesive toughness for CVD diamond deposited on WC–Co cemented carbide substrates. Prior to diamond deposition, the substrate surface was subjected to an adhesion-enhancement pretreatment previously described [11]. The obtained result is quantitatively compared to the data already obtained for the case of smooth silicon surface [10].

2. Experimental details

$10 \times 10 \times 3$ mm WC–Co cemented carbide (WC–5.8 wt.% Co) substrates were sintered using WC with an average grain size of 1 μm (ISO grade, K10, by F.I.L.M.S. SpA). The as-sintered samples were ground and then rinsed with acetone and de-ionized water in an ultrasonic bath. Prior to diamond deposition, the substrates were etched by Murakami's reagent (10 g $K_3[Fe(CN)_6]$ + 10 g KOH + 100 ml water) for 20 min in an ultrasonic vessel in order to obtain a rough surface. Then the surface Co was removed by 10 s etching in an acid solution hydrogen peroxide (3 ml 96 wt.% H_2SO_4 + 88 ml 40% m/v H_2O_2). Following each wet pretreatment, the substrates were rinsed with deionized water. The average roughness (R_a) of the pretreated substrates was measured using Taylor-Hobson Form Talysurf-120 equipment.

Diamond depositions were performed in a conventional hot-filament chemical vapor deposition (HFCVD) chamber [12]. The deposition conditions are listed in Table 1. According to a previous study [13], the process conditions here employed ensure the formation of well-separated diamond particles at the substrate surface. The samples were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Prior to deposition, the substrates were also analyzed by X-ray photoelectron spectroscopy (XPS).

Adhesive toughness was measured by applying an external load in a scanning electron microscope to diamond crystallites in order to scratch them off from the substrate [10]. The experimental set up is schematically illustrated in Fig. 1. The samples, i.e. substrates on which diamond particles were nucleated and grown, were set on the stage of the microscope. A diamond needle with an apex angle of 90° and 0.2 μm tip radius was fixed in the center of observation area at an angle of 45° with respect to the substrate surface. The diamond needle was supported by a beam which was fixed to the specimen chamber. The applied load could be measured by the strain gauges shown in Fig. 1. By moving the diamond particles horizontally, they were loaded by the diamond needle in the direction parallel to the substrate surface. This process of loading could be observed on the monitor screen. After the needle touched a particle, the load simply increased until the particle was suddenly scratched off at the maximum load. The particle disappeared away and the load unstably dropped to zero. This maximum load was obtained for some dozens of particles as the load required to scratch them off.

Table 1
Diamond deposition conditions

CH_4/H_2 volume ratio	0.5%
Total gas pressure	4.8 kPa
Filament–substrate distance	8 mm
Filament temperature	2440 K
Substrate temperature	1220 K
Deposition time	4.5 h

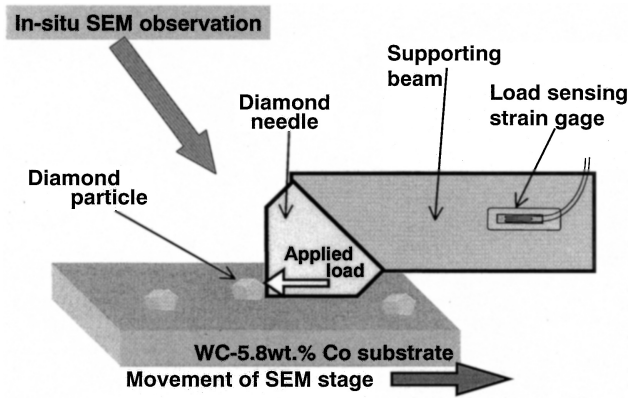

Fig. 1. Schematic illustration of the experimental set-up.

3. Results and discussion

In Fig. 2 the SEM micrograph of a pretreated subs-

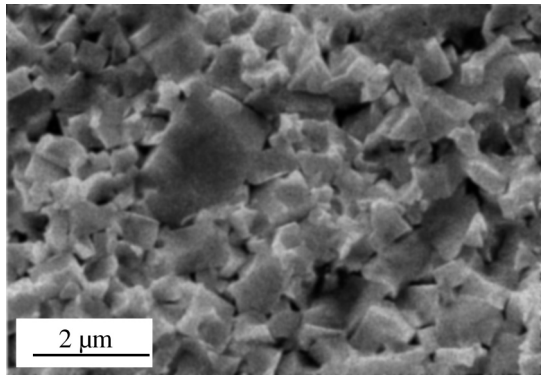

Fig. 2. SEM micrograph of the pretreated WC–5.8 wt.% Co substrate (R_a = 0.14 μm).

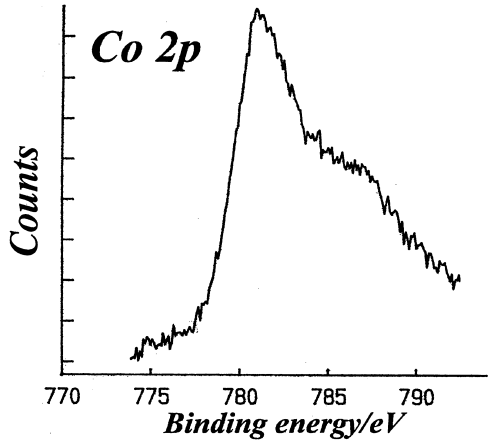

Fig. 3. XPS spectrum of *Co 2p* on WC–5.8 wt.% Co substrate after the etching pretreatments.

trate is reported. The effects of the chemical etching are clearly visible. In fact, one can observe that the pretreatment led to the surface roughening of the substrate due to the chemical attack of WC performed by the Murakami's reagent. Co-etching was in turn achieved by the acid solution of H_2O_2 and no Co peaks could be detected in the EDS spectrum. The resulting average roughness (R_a) was 0.14 μm.

In Fig. 3, a typical XPS spectrum of *Co 2p* core level on pretreated WC–5.8 wt.% Co substrates is reported. The lower binding energy contribution is due to elemental Co, whereas the higher binding energy contribution should be assigned to a cobalt oxide. This occurrence indicates that a thin layer of slightly oxidized Co was still retained at the substrate surface, even after the cobalt removal treatment.

Typical appearance of diamond particles on the substrate is presented in Fig. 4. The average load required to scratch off these diamond particles from the surface of substrate was obtained to be 46 mN. Fig. 5 shows the finite element model of a diamond particle for the

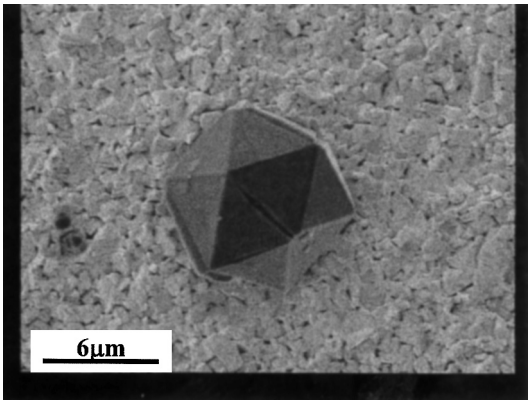

Fig. 4. SEM micrograph of the diamond crystallite nucleated and grown at the surface of the pretreated substrates after 4.5 h of deposition.

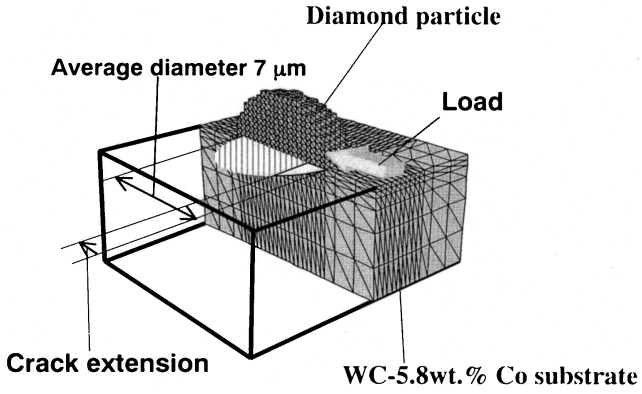

Fig. 5. Finite element model for the simulation of crack extension.

simulation of interface crack extension. Interface crack would be supposed to initiate just beneath the loading point and extend in the direction of loading. The crack front was assumed to remain straight and perpendicular to the loading throughout the extension. The energy released when the crack extends by a unit area, i.e. the energy release rate, could be calculated by using this model. By assuming the energy release rate to be a constant while crack extends, which should be the toughness of interface, the load required to extend the interface crack could be obtained as a function of crack extension length. The simulated load was plotted in Fig. 6 against the length of crack extension. Note that the load should experience its maximum in the midway. Therefore unstable fracture should be expected in the actual experiment just after passing the maximum load, which corresponds to the load to scratch off the particles in the microscope. In the correspondence of simulated maximum load and experimentally obtained load, the energy release rate should be 14 J/m^2 as shown in Fig. 6, which gives the toughness of adhesion.

Compared to the value (5 J/m^2) measured by the same technique for the case of diamond on mirror-polished silicon surface deposited with the same methane concentration in the source gas [10], the adhe-

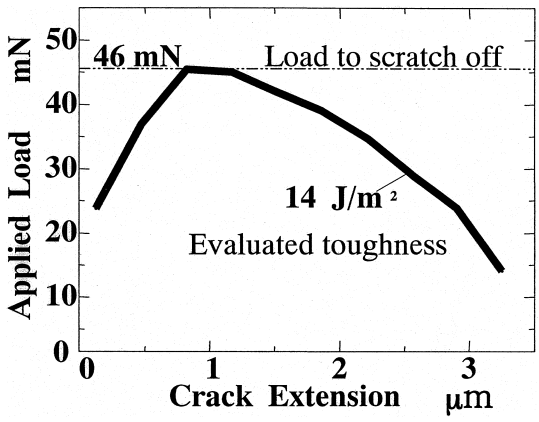

Fig. 6. Simulated load-crack extension diagram.

sive toughness of CVD diamond on pretreated cemented carbide was more than two times higher. Moreover, the measured value is comparable to the cleavage fracture energy of diamond which is in the 10–18 J/m^2 range, depending on the crystal planes [14]. Therefore, surface roughness created by the Murakami treatment led to a large macroscopic adhesive toughness of diamond on hardmetal substrates, despite of the presence of still remaining cobalt at the substrate surface after the binder etching treatment.

By using the new methodology here presented for the evaluation of the adhesion strength of diamond, comprehensive studies should be performed in order to investigate the effects of both the geometrical roughness and the surface chemical composition of the substrate, whose control may lead to a significant improvement of the adhesion of CVD diamond coatings on cemented carbide cutting tools.

4. Conclusions

For the first time a new methodology has been utilized to measure the adhesive toughness of diamond deposited on cemented carbide substrates. The fact that a fundamental physical parameter of adhesion can be evaluated implies that quantitative investigations can be performed in order to understand the effects of both topography and chemical composition of the substrate surface on the adhesive strength of diamond films. Therefore, the new adhesion measurement methodology will help diamond coaters in the selection of proper pretreatments and deposition conditions, thus ensuring the development of diamond-coated tools with superior cutting performance.

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