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Growth of β-SiC interlayers on WC–Co substrates with varying hydrogen/tetramethylsilane flow ratio for adhesion enhancement of diamond coatings

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ABSTRACT

Cubic silicon carbide (β-SiC) thin films were synthesized on cemented carbide (WC–Co) substrates as an interlayer for modifying the adhesion of diamond coatings. The influence of varying the hydrogen (H_2)/tetramethylsilane (TMS) flow ratios on the microstructure, phase composition and adhesion of the β-SiC films was investigated. It was found that with the increase of the H_2/TMS flow ratios, the SiC crystallite size increases from 6.5 nm to 22.2 nm. When the flow ratio was 40:5, the film was formed of loose cauliflower-like agglomerates, containing SiC granular particles. With the flow ratio increased from 40:5 to 120:5, the films became more uniform and denser, resulting in adhesion enhancement. However, when the ratio increased from 160:5 to 200:5, clusters composed of faceted particles replaced the agglomerates, and the adhesion reduced. The β-SiC film deposited with a H_2/TMS flow ratio of 120:5 possessed a more uniform and denser structure, as well as better adhesion than the others. After subsequent diamond deposition, homogeneous nanocrystalline diamond coatings were realized on the β-SiC interlayered substrates. Compared with the results on the well-known two-step chemically etched substrates, the diamond coatings deposited on the substrates with the β-SiC interlayer possess excellent adhesion. It was also validated in this research that the β-SiC interlayer deposited with a H_2/TMS flow ratio of 120:5 was effective in enhancing the adhesion of diamond coatings prepared on WC–Co substrates.

1. Introduction

Chemical vapor deposition (CVD) diamond-coated cemented carbide (WC–Co) tools are considered as one of the most promising candidates for cutters in machining applications [1]. However, several limitations exist for this class of tools related to the poor adhesion of diamond coating [2]. The major reason for this poor adhesion is the detrimental catalytic effect of the binder phase cobalt (Co) in the WC–Co substrates. It has been generally determined that Co preferentially suppresses the nucleation process of diamond and promotes the formation of a graphitic intermediate layer, resulting in poor adhesion of the diamond coatings [3–5].

Researchers have studied this adhesion issue for several decades and developed several pretreatment approaches to attempt to mitigate the problem. These approaches can be categorized by two types. One is the removal of cobalt from the outermost layers of WC–Co substrate by aqueous solutions of either strong acids or with a high power diode laser [6]. Among these pretreatments, the most well-known approach is two-step wet chemical etching pretreatment, employing Murakami's reagent ($KOH:K_3[Fe(CN)_6]:H_2O = 1:1:10$) and Caro's acid ($H_2SO_4:H_2O_2 = 1:10$) [7]. However, this approach sometimes results in micro-gaps on the surface, which results in decreasing the toughness and embrittling the tools [8]. The other is the introduction of an interlayer between substrate and diamond coating, which can suppress the deleterious effects of Co without these drawbacks.

Among the interlayer materials, the effectiveness of cubic silicon carbide (β-SiC) interlayer has been recently confirmed [9]. The β-SiC interlayer is expected to reduce the residual stresses in the coatings by adjusting the mismatch of thermal expansion coefficients between WC–Co and diamond [10]. Gil Cabral and his coworkers [11] have confirmed that the SiC interlayered diamond coated inserts exhibited the longest tool lives compared with those of diamond coated inserts pre-treated by two-step chemical etching and commercial sintered diamond (PCD) tools. And they also found that SiC interlayer can react with Co to form carbon and cobalt silicide (i.e. CoSi and Co_2Si) during the early stages of deposition, which do not affect the performance of diamond coatings. In our previous studies, β-SiC interlayer can enhance the adhesion of diamond coatings without deteriorating the fracture resistance of the tools [12].

In fact, the structure and adhesive performance of the interlayer is demonstrated to be crucial in determining the adhesion of diamond

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coatings [13]. V.V.S.S. Srikanth et al. have successfully synthesized diamond/β-SiC nanocomposite interlayers on W, Mo, and WC–Co substrates by microwave plasma chemical vapor deposition for enhancing the adhesion of diamond coatings; the interlayers were controlled by adjusting gas concentrations [14–17].

In this paper, we report on the evolution of β-SiC films as a function of hydrogen (H_2)/tetramethylsilane (TMS) flow ratio. Subsequently, a well-adhered and effective β-SiC film was used as an interlayer for diamond deposition. Finally, we compared our findings with the results obtained from diamond coatings deposited on the two-step chemically etched substrates.

2. Experimental detail

2.1. Preparation of β-SiC films

Commercial cemented carbide (WC–6%Co) inserts of dimensions 10 mm × 5 mm × 10 mm were used as substrates for the depositions. Both the deposition of β-SiC films and the subsequent growth of diamond coatings were performed using a high current-extended DC arc plasma CVD apparatus, which has been described in earlier works [18,19].

Prior to the deposition of β-SiC films, the substrates were polished using 40-μm diamond powders followed by ultrasonic bath in ethanol to remove contaminants from the surface. Argon (Ar, purity of 99.99%), H_2 (purity of 99.999%) and TMS ($Si(CH_3)_4$, purity of 99.9%) were chosen as the gaseous precursors for β-SiC deposition. The total pressure was maintained at 0.5 kPa, as measured by a piezoresistive diaphragm manometer. The flow rates of Ar and TMS were 1800 sccm (standard $cm^3\ min^{-1}$) and 5 sccm, respectively. The H_2/TMS flow ratio was varied from 40:5 to 200:5. The substrate temperature was determined by an optical pyrometer. The β-SiC deposition processes lasted for 3 h. The detailed parameters of the β-SiC deposition processes are summarized in Table 1.

2.2. Preparation of diamond coatings

In order to evaluate the effect of the interlayer, the well-adhered β-SiC film, Sample III, was chosen as an interlayer for diamond deposition. Before the diamond deposition, the samples were first ultrasonically abraded in a 0–500 nm diamond powder ethanol suspension (concentration: 50 ct/l, purity of ethanol: 99.7%) for 30 min. This treatment, referred to as "seeding", was used to enhance the diamond nucleation density. The samples were subsequently cleaned with ethanol in an ultrasonic bath for 5 min. The gaseous precursor chosen for diamond deposition was a gas mixture of Ar, H_2 and methane (CH_4, purity of 99.995%). The deposition pressure was maintained at approximately 0.5 kPa. The flow rates of Ar, H_2, and CH_4 were 1800 sccm, 100 sccm and 10 sccm, respectively. The substrate temperature was approximately 875 °C. The diamond coatings were grown for 6 h under these conditions.

For the sake of comparison, the diamond coatings were also deposited on the two-step chemically etched substrates. That is, the substrates were dipped in the Murakami solution for 10 min followed by etching with Caro's acid for 1 min before the diamond deposition.

Table 1
Deposition parameters of SiC films.

Sample no.	I	II	III	IV	V
Pressure (Pa)	500	500	500	500	500
Ar flow rate (sccm)	1800	1800	1800	1800	1800
H_2:TMS flow ratio (sccm)	40:5	80:5	120:5	160:5	200:5
Substrate temperature (°C)	825 ± 20	840 ± 20	850 ± 20	865 ± 20	870 ± 20
Deposition time (h)	3	3	3	3	3

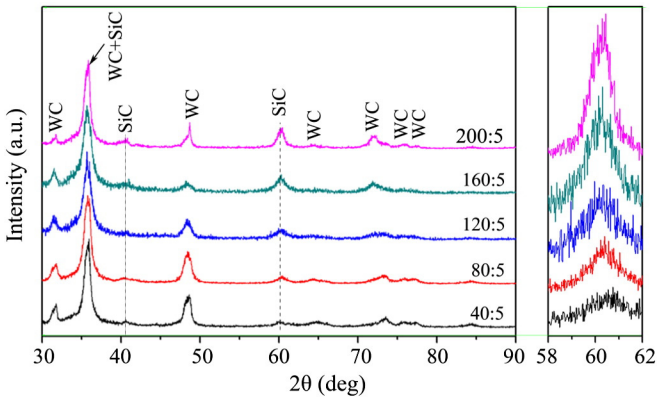

Fig. 1. XRD patterns of the deposited β-SiC films as a function of the H_2/TMS flow ratios. Closeup of the broadening of the β-SiC (220) peak is shown right.

Afterwards, the substrates were also ultrasonically seeded for 30 min. The chemically etched substrates were submitted to the identical diamond deposition conditions.

2.3. Characterization of the β-SiC films and diamond coatings

A field emission scanning electron microscope (FESEM, ZEISS Augriga Focus Ion Beam/Field-Emission Scanning Electron Microscope dual-cross system) was used to characterize the surface and cross-sectional morphologies of the β-SiC films and the diamond coatings. An energy dispersive X-ray spectrometer (EDS) was utilized to perform microanalysis of the selected areas of the samples.

Both the β-SiC films and the diamond coatings were analyzed with an X-ray diffraction (XRD, Bruker D8 Advance) apparatus at a grazing angle of 2° (scan step size: 0.02°). The bonding structure of the diamond coatings was determined by a Raman spectrometer (Renishaw RM2000) at an Ar + laser wavelength of 514.5 nm and a laser power of 100 mW.

The adhesion of the β-SiC films was evaluated by a WS-2005 scratching tester, under a maximum load of 120 N, a loading speed of 100 N/min and a total length of 1 mm. After the scratching test, the samples were observed by FESEM. The adhesion of the diamond coatings was evaluated by the Rockwell C indentation tests using an HBRV-187.5 hardness tester with a load of 1500 N.

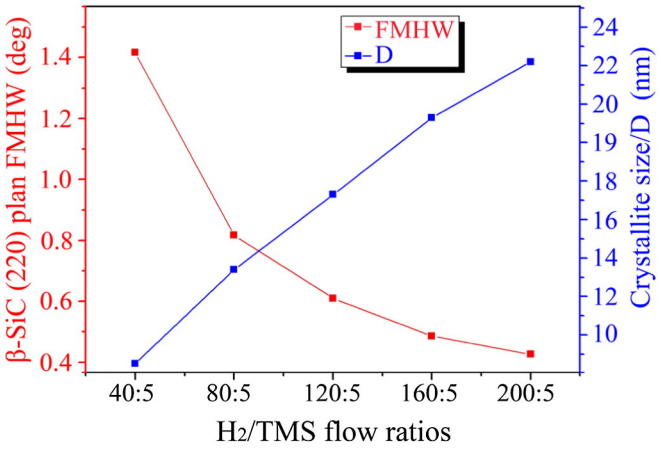

Fig. 2. FWHM and crystallite size of the deposited β-SiC films as a function of the H_2/TMS flow ratios.