Int. Journal of Refractory Metals and Hard Materials 49 (2015) 307–313

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Growth of diamond coatings on functionally graded cemented carbides

Yong Liu [a,*], Meng Du [a], Mingyang Zhang [a], Qiuping Wei [b], Zhiming Yu [b], Xiaofeng Li [a]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China
[b] School of Materials Science and Engineering, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:
Received 12 March 2014
Received in revised form 28 November 2014
Accepted 30 November 2014
Available online 2 December 2014

Keywords:
Diamond coating
Functionally graded cemented carbide
Growth behavior
Wear resistance

ABSTRACT

Cemented carbides with diamond coatings have been widely used for cutting tools. However, the reaction of Co with the diamond coating during the deposition leads to the deterioration of the coating structure and the bonding strength. In this work, functionally graded cemented carbides (FGCCs), with a WC-rich surface, Co-rich intermediate layer and η phase-containing central part, were prepared. Diamond coatings were prepared on the FGCC by the hot filament chemical vapor deposition (HFCVD), a method of catalytic decomposition of methane and hydrogen mixtures at a heated filament. The crystal growth and the bonding behavior of diamonds to different layers in FGCCs were investigated. Results indicated that the different regions of FGCCs show apparently different grain sizes and morphologies of diamond coatings. The Co-poor layer has a high crystallinity and purity of diamond, and the η phase-containing region is beneficial for the formation of fine diamond grains. The Co-rich layer has a diamond coating of low bonding strength due to the formation of graphite and porosity, while the η phase-containing region has a high bonding strength. By the combined effects of the three different layers, FGCC shows generally a high bonding strength, and is promising for using as a substrate for the diamond coating.

1. Introduction

With the progress of modern machinery industries, the cutting efficiency has been increased very quickly. Under many conditions, high speed, high precision and very wear-resistant cutting tools are required. WC–Co cemented carbides are one of the mostly used cutting tools for steels and other conventional materials due to their high hardness, reasonable toughness and lifetime. However, cemented carbides cannot be effectively applied in cutting aluminium-based composites, ceramics, titanium and carbon fiber-reinforced composites [1,2]. In the above cases, the high reactivity of Co to the cutting metals and the insufficient hardness of cemented carbides fail to meet the requirements for high-speed and long-life cutting [3].

One of the developments of the next generation of cemented carbides is the coating of diamond films. Diamond is the hardest material in natural environment, with such advantages as high heat conductivity, low friction coefficient and excellent chemical stability to most materials. The wear resistance of cemented carbides with diamond coatings is significantly improved, and the lifetime can be prolonged as long as 5–10 times compared with conventional cemented carbides [4,5]. Moreover, the surface roughness of the machined parts is obviously enhanced. There are many successful methods for coating diamonds on cemented carbides, including HFCVD [6,7], microwave chemical vapor deposition [8], and flame deposition [9].

The main obstacle for the applications of diamond coatings is the poor bonding strength to the cemented carbide substrates. There are both physical and chemical misfits between the diamond coatings and the cemented carbides. The thermal expansion coefficient of cemented carbides is much higher than that of the diamond, so cracks may form during the cooling and subsequent cutting process [10]. There is no chemical bonding between cemented carbides and the diamond coatings, and the Co phase in cemented carbides will promote the formation of graphite during the chemical vapor deposition, instead of the diamond phase [11,12]. The existence of impurity phases, such as graphite and amorphous carbon, is detrimental for the hardness of the diamond coating and its bonding to the substrate [13]. Therefore, avoiding the contact of the Co phase to the diamond is of significant importance for increasing the bonding strength. For the depletion of Co phase, cemented carbides are usually etched by using Murakami solution at first, in order to remove the boundaries of WC grains in the surface, and then, the samples are etched by using acid for the elimination of Co [14]. Another way is to introduce intermediate layers, for example, Si [15], W [16], B [17] and Cr [18], such that the diamond can grow without the influence of Co phase. However, the depletion of Co will leave porosity behind, and the introduction of intermediate layers will bring about some unnecessary phases.

There are other ways to remove or decrease Co phase from the surface of cemented carbides. In 1980s, Sandvick developed the first functionally graded cemented carbide with WC–Co compositions, which

* Corresponding author at: State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, Hunan, PR China.
E-mail address: yonliu@csu.edu.cn (Y. Liu).

http://dx.doi.org/10.1016/j.ijrmhm.2014.11.010
0263-4368/

Table 1

HFCVD parameters for deposition of diamond coatings on FGCC.	
Filament temperature/°C	2000
Deposition distance/mm	9 ± 1
Substrate temperature/°C	700
Gas pressure/Torr	30 ± 1
CH_4/H_2 (vol.%)	3
Deposition time/min	300
Cooling time/min	180

had a WC-rich surface, Co-rich intermediate layer and conventionally central region [19]. The sandwich-like structure can be clearly seen by naked eyes. In 1990s, there was another graded structure for WC–TiC–Co cemented carbides, on which either Co-rich or Co-poor layer can be formed [20]. In this case, the graded structure is much thinner, and usually in a scale of tens of microns. There are some reports on coating diamond on the latter graded structure, but no study on the former one is conducted. This work aims to study coating diamond on the sandwich-like graded structure, and investigate the influence of the graded microstructures on the growth and the bonding behavior of diamonds.

2. Experimental

The functionally graded cemented carbides were prepared via the carburization of carbon-deficient or η phase-containing pre-sintered WC–6Co (wt.%) specimens. The preparation process was described by the authors in Ref. [21] in detail. The FGCC specimens were cut in the cross section, grounded first with emery paper, and then polished by using diamond disks embedded with diamonds of different sizes, then a two-stepped etching method was conducted: (1) etching by using Murakami's reagent (10 g $K_3[Fe(CN)_6]$ + 10 g K OH + 100 ml H_2O) for 3 min in an ultrasonic vessel to rough the WC surface; (2) etching in an acidic solution of hydrogen peroxide (2 ml 96 wt.% H_2SO_4 + 2 ml 68 wt.% HNO_3 + 20 ml 40% H_2O_2 + 40 ml H_2O) for 3 min in order to remove Co phase in the surface. The as-etched specimens were then abraded ultrasonically in a suspension of diamond powder in a size of sub-micron (<500 nm) in acetone for 30 min. This treatment encourages the subsequent inhomogeneous nucleation of diamond during the chemical vapor deposition, by implanting ultrafine diamond fragments into the substrate surface, and by creating suitable surface defects. The diamond coatings were prepared by using a HFCVD. The deposition parameters are shown in Table 1.

Scanning electron microscopy (Quanta FEG 250 Environmental SEM) was used to observe the surface morphologies of the substrates and the diamond coatings. Energy dispersive X-ray spectroscopy was utilized to analyze the chemical compositions in the surface. The quality of the diamond coatings was assessed by Raman spectroscopy (Lab RAM Aramis) at an excitation wavelength of 532 nm. Scratch tests were used to quantitatively determine the bonding strength of the diamond coatings to WC–Co substrates. The scratch tests were carried out by using Multi-Specimen Test System from CETR Instruments (Model UMT-3), equipped with a Rockwell C diamond cone indenter. The included angle of the diamond cone is 120°, and the radius of the hemispherical tip is 200 μm. A scratch length of 9 mm was used with a progressively normal loading of 1 to 50 N. During the scratch test, the values of the

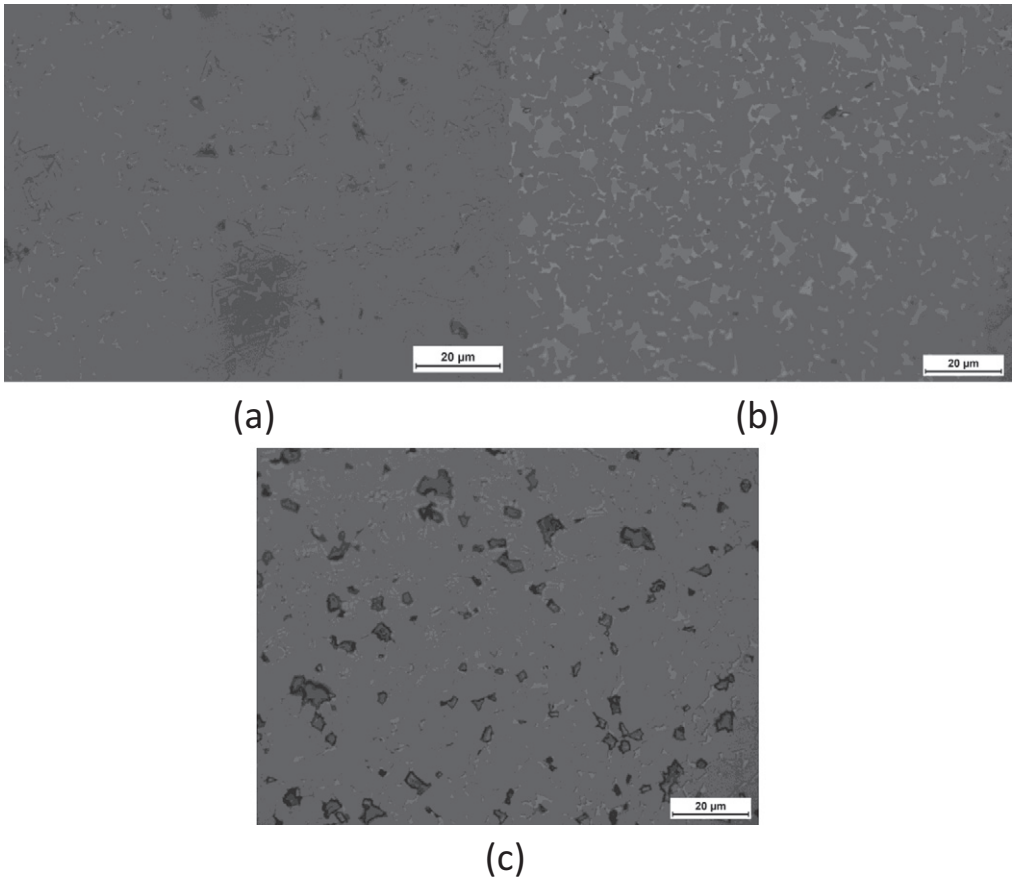

Fig. 1. Microstructures of FGCC: (a) surface with a coarse WC and Co-poor structure; (b) intermediate layer with Co-rich structure; (c) center part with WC + Co + η structure.