Adhesion of DLC Film Prepared on WC-FeAl Substrate by Sputtering

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Abstract. DLC films were prepared on WC-25vol%FeAl and WC-25vol%Co substrates using r.f. magnetron sputtering at substrate temperature range between room temperature and 773K. The Raman spectra was analysed using \( I_{G2} / I_G \) (\( I_G = I_G1 + I_G2 \)). The critical loads of sputtered WC-25vol%FeAl specimen were higher than those of sputtered WC-25vol%Co specimen over a wide range of temperatures between room temperature and 573K. TEM observation revealed the existence of an aluminium oxide between the DLC film and FeAl binder.

1. Introduction
It is well known that WC-Co hard metals are used in a variety of scientific and industrial applications. Over the last few decades significant research was carried out to replace the cobalt binder by alternative binder systems to overcome some of its shortcomings, such as, poor corrosion resistance, high cost, its scarcity of supply and environmental toxicity. FeAl intermetallic compound might be one of the most promising candidate, because of good oxidation resistance, being much less expensive and also less toxic. An attempt was made by Subramanian et al. using melt infiltration technique [1] and by Schneibel et al. using liquid phase sintering of mixed powders technique [2] to prepare WC-FeAl composites. However, insufficient mechanical properties were obtained in both investigations for practical use. Recently, we have successfully improved mechanical properties using pulse current sintering method under pressure application [3, 4].

Diamond-like carbon (DLC) films have a range of technological applications, because of their optical, electrical and mechanical properties [5]. Particularly, they can be used as a coating film for cutting tools and dies because of its own high hardness, low friction coefficient and excellent smooth surface. However, in many cases, an additional metallic interlayer, such as tungsten, titanium, silicon and/or chromium, should be prepared owing to improve the interface adherence between DLC films and cemented carbide substrates. In this paper, the adhesion of the DLC film prepared on WC-FeAl substrate by r.f. magnetron sputtering was investigated using the scratch test and transmission electron microscopy.

2. Experimental
Fe (99.5mass%, 5 μ m), Al (99.9mass%, 10 μ m), Co (99.9%, 5 μ m) and WC powders (2.5 μ m) with the composition of WC-25vol%FeAl (Fe-40at%Al) and WC-25vol%Co were dry blended using an automatic agitator for 3.6ks. The blended powder mixtures were poured in a graphite die with
15mm in inner diameter and subsequently consolidated under a pressure of 50MPa in vacuum using pulse current sintering method. The heating rate, sintering temperature and holding temperature were 1.67K/sec, 1373K and 180 sec, respectively. The obtained compacts were polished using a planar grinding machine with a grinding wheel of 240 mesh roughness and subsequently to a mirror gloss with diamond abrasive finishing. Vickers hardness tests were performed under the load of 10kgf. The microstructures of the compacts were investigated using a scanning electron microscope (SEM) and a field emission transmission electron microscope (FE-TEM) equipped with energy dispersive X-ray spectral analysis system.

DLC films were deposited on WC-25vol%FeAl and WC-25vol%Co substrates using r.f. magnetron sputtering system with a graphite disk target (50mm in diameter), mounted on the cathode at a distance of ~100 mm from a substrate table. The base pressure of the deposition chamber was around 1.0 $\times$ 10$^{-3}$ Pa. Pure argon (99.999% purity) was used as inert gas in the chamber. The sputtering target was pre-sputtered for about 5 min before deposition to remove any surface impurities that may have been present on the target. The films were deposited at temperatures of room temperature, 373, 473, 573, 673 and 773K, using a resistance heater located behind the substrate holder. The process pressure was 1 Pa with r.f. power of 300W. WC-25vol%FeAl and WC-25vol%Co compacts were used as substrate materials and a standard chemical cleaning procedure was maintained before deposition. Raman spectra of the deposited films were obtained using a Raman spectrometer (Renishaw, inVia) with a green laser of argon ion laser 514.5 nm. The spectra were recorded from 800 to 2000 cm$^{-1}$.

Thickness values of the films were determined from an atomic force microscope (AFM) line analysis. Scratch tests were conducted using a commercialized scratch tester (RHESCA, CSR-2000). A cartridge with a diamond stylus having a radius of 5 μm was swung parallel to the surface of a DLC film sample on a X-Y translator with a tilt-table and moved horizontally, normal to the swing. As the sample moved, the stylus was gradually pressed down upon the sample until the friction force abruptly increased. The load which leads to the abrupt increase of friction coefficient is defined as the critical load.

### 3. Results and discussion

Figure 1 shows SEM micrographs of WC-25vol%FeAl and WC-25vol%Co compacts. FeAl phase was formed through the combustion synthesis reaction between Fe and Al powders, and confirmed by X-ray diffraction measurement. Both of the compacts consist of WC particles (white color) and binder (gray color) lying among them. Binder pools with about 10 μm were dispersed in places in a similar way. Vickers hardness of the compacts was 1200 and 1150, respectively.

![Figure 1. SEM micrographs of (a) WC-25vol%FeAl compact and (b) WC-25vol%Co compact.](image)

Figure 2 shows the Raman spectrum of DLC films deposited on WC-25vol%FeAl substrates at different temperatures. The thickness of the obtained DLC film was about 800nm and slightly tended to increase with increasing the substrate temperature. In this study, 4 peak curve fitting technique is adopted to unify the curve fitting way for all spectra. The analysis of Raman spectra using 4 peaks...
was carried out by several researchers [6, 7]. Iwaki et al. pointed out at least 4 peaks are necessary to obtain the best curve fitting [8]. Referring to their studies, an assumption is made as follows: (1) the spectrum is composed of 4 peaks at 1190 cm$^{-1}$ (D1 peak), 1380 cm$^{-1}$ (D2 peak), 1500-1560 cm$^{-1}$ (G1 peak) and 1590 cm$^{-1}$ (G2 peak) (2) the peak is fitted by Gaussian line shape, (3) D1, D2 and G2 peaks do not shift, i.e., 3 peak positions are fixed except for G1 peak. The origins of G1 and G2 peaks should be assigned to disordered graphite and ordered graphite. The peak summation of G1 and G2 peaks is equal to the intensity of G peak. As well known, G band is Raman active E$_{2g}$ mode in graphite. Therefore, Nakao et al. pointed out the intensity ratio of G2 to G peak ($I_{G2}/I_G$) may also be useful for the evaluation of the magnitude of ordered graphite structure [9]. Figure 3 shows the relationship between $I_{G2}/I_G$ and the substrate temperature for DLC films prepared on WC-25vol%FeAl compact. The value of $I_{G2}/I_G$ increases at the substrate temperature 673K sharply. Some work on the thermal stability of DLC films have been reported. Tallant et al. showed the significant conversion of DLC films to nano-crystalline graphite on heating at temperatures above 573K [10]. Our study is well coincident with the result above.

![Figure 2](image2.png)  
**Figure 2.** Raman spectra of sputtered films prepared on WC-25vol%FeAl substrates at different temperatures.

![Figure 3](image3.png)  
**Figure 3.** The relationship between $I_{G2}/I_G$ and the substrate temperature for sputtered films prepared on WC-25vol%FeAl substrates.

Figure 4 shows the relationship between the critical load and the substrate temperature for WC-25vol%FeAl and WC-25vol%Co compacts. With increasing the substrate temperature up to 573K, the critical loads of both of specimen increased. The drop of the critical loads at 673K is due to graphitization of the DLC films. It should be noted that the critical loads for WC-25vol%FeAl substrate are 10 ~ 30% higher than those for WC-25vol%Co substrate. Figure 5 shows a bright field image of the interface between the DLC film and WC-25vol%FeAl substrate. The DLC film shows a typical halo pattern. It is noticeable that there exists a thin film with ~3nm between the DLC film and FeAl binder. As shown in fig.5 (b), oxygen was detected clearly in EDX spectra. Graupner et al. have reported that Al$_2$O$_3$ films were easily formed at room temperature even under ultra high vacuum condition [11]. Therefore, the thin film observed at the interface between the DLC film and FeAl binder is considered as an aluminum oxide. On the other hand, no film was observed at the interface between DLC film and Co binder for WC-25vol%Co substrate. Nie et al. prepared duplex Al$_2$O$_3$/DLC films on Al alloys using a combined micro-arc oxidation and plasma-immersion ion implantation.
technique and investigated the influence of C$_2$H$_2$/Ar ratio on the interfacial adhesion between the DLC and alumina layers [12]. They clarified an adequate condition led to an excellent adhesion. Therefore, the excellent adhesion between the DLC film and WC-25vol%FeAl substrate might be attributed to the existence of thin alumina film.

![Figure 4](image.png)

**Figure 4.** The Relationship between the critical loads and substrate temperatures for DLC/WC-25vol%FeAl and DLC/WC-25vol%Co specimen.

![Figure 5](image.png)

**Figure 5.** (a) The bright field image of the interface between the DLC film and WC-25vol%FeAl substrate. (b) Energy dispersive spectra at the interface. (c) Energy dispersive spectra in FeAl binder.
4. Conclusion
DLC films were successfully prepared on WC-25vol%FeAl substrate using r.f. magnetron sputtering. The critical loads of sputtered WC-25vol%FeAl specimen were higher than those of sputtered WC-25vol%Co specimen over a wide range of temperatures between room temperature and 573K.

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