Application of Ultrananocrystalline Diamond/Nonhydrogenated Amorphous Carbon Composite Films to Hard Coating on Cemented Carbide

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【Introduction】

Cemented tungsten carbide (WC-Co) is a sintered composite comprising tungsten carbide and cobalt binder. WC–Co has ever been employed as materials for cutting tools such as drill bits and end mills due to its high hardness and fracture toughness. In order to extend the lifetime of WC-Co cutting tools, they are coated with hard materials such as TiN, TiC, TiCN, TiAlN, amorphous carbon (so-called diamond-like carbon), and polycrystalline diamond[1]. In particular, diamond is the most promising coating substance due to its largest hardness in nature.

Nanodiamond is a new candidate as carbon-based hard coating materials for machining nonferrous metals and alloys, owing to the superior properties such as good thermal stability, low friction, and high wear resistance. Ultrananocrystalline diamond (UNCD) /nonhydrogenated amorphous carbon (a-C) composite (UNCD/a-C), which comprises diamond crystallites with diameters of less than 10 nm and an a-C matrix, is a kind of diamond related materials and has received much attention as a new candidate for applications to hard coatings because of their following characteristics: (1) high hardness and Young's modulus, (2) smooth film surface, and (3) higher temperature stability than that of hard amorphous carbon, so-called diamond-like carbon (DLC).

In the case of the deposition of diamond and related materials films on WC-Co substrates, the removal of Co on the surface or the insertion of buffer layers is required before the film deposition, since Co binder located at WC grain boundaries act as catalysts that facilitates graphitization, which results in a drastic degradation in the hardness and adhesion of the films [2,3].

Doping foreign elements such as Si have been applied to hard a-C films for improving mechanical properties, stabilizing the chemical bonding structures of the films, and relaxing internal stresses in the films. Si doping has been considered to suppress the formation of sp^2 bonds and facilitate the formation of sp^3 bonds [4].

In this study, the deposition of UNCD/a-C films by coaxial arc plasma deposition(CAPD) was applied on WC-Co substrates as hard coatings at room substrate-temperatur, and the doping effects of Si on the film growth and mechanical properties were investigated. In addition, the effects of inserting undoped UNCD/a-C buffer layers between the Si-doped films and WC-Co substrates mainly for the purpose of suppressing from Co diffusion into the films were studied since we confirmed the diffusion of Co atoms into the Si-doped films directly deposited on the WC-Co substrates.

【Experimental procedure】

Undoped and Si-doped UNCD/a-C films were deposited on WC-Co substrates with dimensions of 10 mm diameter and 5.5 mm thickness by CAPD at room substrate-temperature and base pressures of less than 10^{-4} Pa. An arc plasma gun (ULVAC ARL-300) equipped with a capacitor of 720 μF was operated at a voltage of 100 V and repetition rate of 1 Hz. The

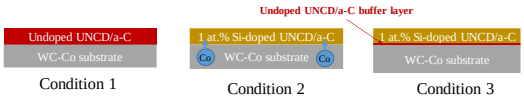

Fig. 1. Schematic diagram to the undoped and Si-doped films prepared by CAPD.

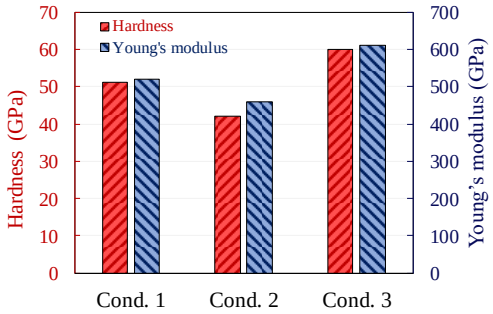

Fig. 2. Nanoindentation measurements of the undoped and Si-doped UNCD/a-C films

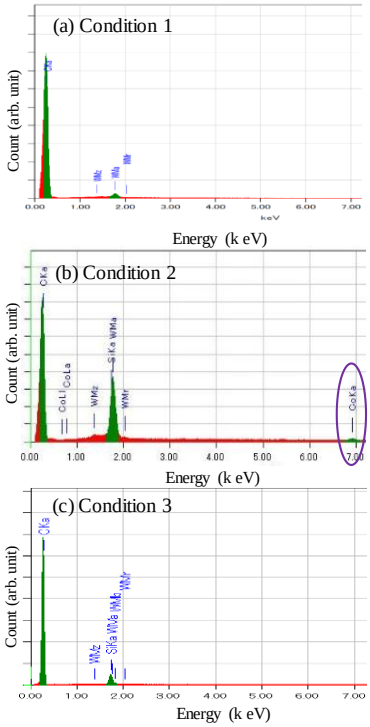

Fig. 3. Top view EDX spectra of the undoped and Si-doped UNCD/a-C films

surface of WC-Co substrates was only roughened followed by cleaning in aceton and methanol ultrasonic bath for 7 min for each one, respectively. The films deposition was carried out directly on WC-Co substrate and after inserting UNCD/a-C buffer layer with thickness of 1μm as illustrated in Fig.1.

The deposited films were mechanically and structurally characterized by nanoindentation, energy-dispersive X-ray spectroscopic (EDX), X-ray photoimession (XPS). The X-ray measurements were carried out at beam line 12 of SAGA Light Source (Proposal Nos. 1610090S and 1607062S). The C1s XPS spectra were decomposed into peaks using Voigt function after subtracting the backgrounds by Shirley's method.

【Results and Discussion】

Films of Condition 1 deposited at room substrate-temperature exhibits a hardness and Young's modulus of 51.3 and 520.2 GPa, respectively. These values are larger than those of a-C films deposited on nonbiased substrates and comparable with those of hard a-C films deposited on negatively biased substrates by other methods such as sputtering and FCVA[5,6]. One reason for the large values should be the suppression of graphitization, which is induced by the catalytic effects of Co on WC-Co substrates, by realizing the low-temperature growth by CAPD. The existence of Co atoms in the films could not be clearly detected by EDX shown in Fig.3 (a) and SIMS measurements, it is seen that the diffusion of Co into the film rarely occurs.

Si-doped UNCD/a-C films were deposited with 1 at. % Si plended graphite targets, and doping effects of Si were investigated. The Si-doped film (Condition 2) deposited directly on WC-Co substrate show a degraded hardness and Young's modulus to 42 and 459 GPa, respectively as shown in Fig.2. This degradation of hardness and Young's modulus might be attributed to the films graphitization induced by the catalytic effects of the diffused Co from the WC-Co substrate into the films as detected by EDX shown in Fig.3 (b). This implies that the Si doping seems to activate the Co on the substrate surface, which increase sp^2 bonds and degrade the mechanical properties to the films.

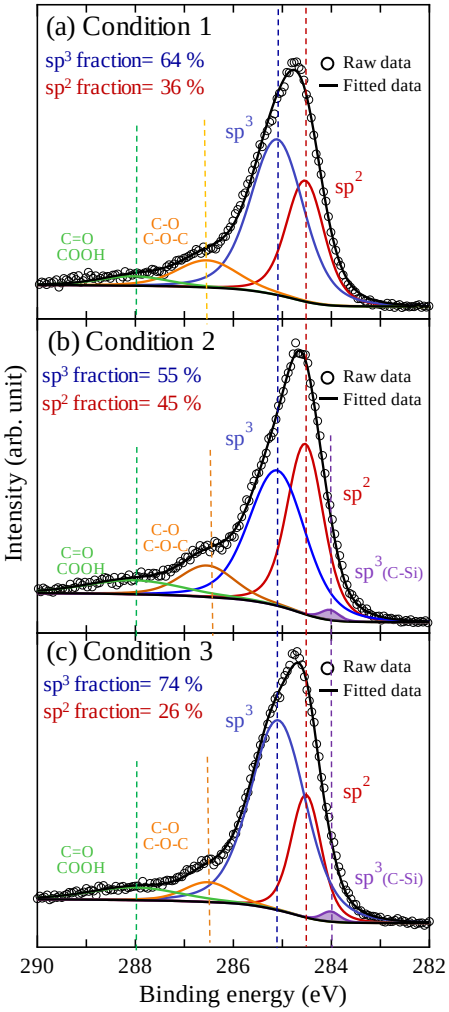

Fig. 4. Decomposed C1s XPS spectra of the undoped, and Si-doped UNCD/a-C films

By inserting undoped UNCD/a-C buffer layer (Condition 3), the Co diffusion was suppressed as detected by EDX shown in Fig.3 (c) and the hardness and Young's modulus were enhanced to 60 and 611 GPa, respectively at film thickness of 7 μm. This enhancement in mechanical proprties shows a consistence with the estimated amount of sp^3 bonds as shown in Fig.4 by the C1s XPS analysis.

【Conclusion】

The UNCD/a-C films sucsesfully deposited by CAPD as hard coating materials on WC-Co for cutting tools applications. It was found that the low substrate-temperature is effective to supress the films graphitization induced by the the catalytic effects of Co in the WC-Co substrates. Furthermore, the Si doping facilitates the formation of C-C sp^3 bonds, particularly after iserting the undoped UNCD/a-C buffer layer that inhibited the Co diffussion into the films, which resulted in the hardness enhancement.

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