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# High temperature oxidation of WC-ZrN superhard nanolayered film

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The high-temperature oxidation behavior of WC-ZrN superhard nanolayered film deposited on steel was studied at 600 °C for up to 10 h in air. The oxide scale consisted primarily of  $\beta$ -ZrO<sub>2</sub>. During oxidation, C and N escaped from the film into the air, while oxygen from the air diffused into the film. Substrate elements such as Fe and Cr diffused outwards toward the oxide surface. The oxidation of the WC-ZrN film resulted in the destruction of the original nanolayers. The WC-ZrN film displayed poor oxidation resistance, because of the formation of  $\beta$ -ZrO<sub>2</sub>, which formed together with some amount of W-oxides.

Key words: Tungsten carbide, Zirconium nitride, Film, Nanolayer, Oxidation.

#### Introduction

Hard films such as TiN, TiAlN and CrN have been successfully sputter-deposited onto high-speed steels and cemented-carbide tools. They increased the cutting speed and reduced lubricants needed during machining. The conventional hard films, however, suffer from low hardness and oxidation resistance at elevated temperatures, making them difficult to cut at high speed and to machine lubrication-free. Especially in field of machining, the disposal of cooling lubricants causes serious environmental problems. Therefore, superhard nanocomposite films with high hardness and good thermal stability have attracted enormous interest to be adapted for high speed machining tools. Superhard means a microhardness exceeding 40 GPa.

Previously, superhard nanocomposite films such as WC-TiAlN [1-3], and WC-C [4] were synthesized, and their physical and mechanical properties were studied. However, WC-ZrN superhard nanolayered films are not yet adequately studied. The aim of this study is to characterize the oxidation behavior of WC-ZrN superhard nanolayered films deposited on a steel substrate by the arc ion plating method. The advantage of multi-layered films is that any residual stress can be effectively reduced to increase coating adherence because soft intermediate layers are inserted between hard layers. Since the films are frequently exposed to oxidative atmospheres during service at high temperatures, oxidation is an important property. However, the high-temperature oxidation behavior of multi-layered films has been less extensively studied compared with single or bi-layered films. In this paper, the oxidation characteristics of the multi-layered WC-ZrN superhard films were studied at 600 °C in air.

#### **Experimental Procedure**

Stainless steel substrates (SUS 304; 70%Fe-19%Cr-11%Ni, in wt.%) having a size of  $10 \times 10 \times 2 \text{ mm}^3$  were mechanically polished, rinsed with acetone ultrasonically, cleaned for 5 minutes under an Ar glow discharge condition of 1.33 Pa with a bias DC voltage of 700 V. The films were deposited under a base pressure of  $2.7 \times 10^{-3}$  Pa and a working pressure of (0.4 Pa of Ar plus 0.8 Pa of N<sub>2</sub>) using the arc ion plating method. The targets used were WC and pure Zr. The target current was 90 A for WC and 80 A for Zr. For good adhesion of the film, a 0.5 µm-thick Zr bond film and a 0.3 µm-thick ZrN interlayer were deposited with a bias DC voltage of 400 V and 200 V, respectively. Above these films, alternating WC-ZrN and WC-Zr multi-layers were deposited with a bias DC voltage of 200 V up to the target thickness of  $\sim 2.4 \ \mu m$ . Each (WC-ZrN)/(WC-Zr) layer set was repetitively deposited 35 times, and the final layer was designed to be a WC-ZrN film. Periodic arrangements of nanometrethick layers of two different compositions yielded a large enhancement in hardness. The average composition of the film prepared was 11.9%W-14.8%C-40.5%Zr-32.8%N (in at.%), according to the electronprobe microanalysis (EPMA). ZrN was roughly three times richer than WC in the film.

Oxidation tests on the films were carried out in 1 atm of static air at 600 °C. The oxidized samples were inspected by an EPMA, an X-ray photoelectron spectrometer (XPS), a scanning electron microscope (SEM), and a transmission electron microscope (TEM operated at 200 kV) equipped with an energy dispersive spectrometer (EDS). The TEM sample was prepared by milling in a focused-ionbeam (FIB) system, which had a liquid-gallium-metal ion source and a maximum accelerating voltage of 30 kV.

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Fig. 1. TGA curve of the WC-ZrN film, which was obtained during heating from room temperature to 800 °C in air with a heating rate of 5 °C  $\cdot$  minute<sup>-1</sup>.

## **Results and Discussion**

Figure 1 shows the TGA heating curve of the WC-ZrN film. Total weight changes were relatively small. The heating curve began to gain weight rapidly from around 600 °C, because of an increased oxidation rate of the film. Hence, an oxidation temperature was chosen as 600 °C in this study. It is noted that the oxidation limit of a CrN coating is commonly known to be about 750 °C [5], whereas that of TiN is known to be 600 °C [6]. Apparently, WC-ZrN was not an oxidation-resistant film.

Figure 2 shows TEM analytical results of the oxidized WC-ZrN film. The oxidation at 600 °C for 2 h resulted in the formation of about 350 nm-thick oxide scale on the film (Fig. 2(a)). Figure 2(b) displays the concentration profiles of W, Zr, Fe and oxygen obtained from the EDS spot analysis. The spot size employed was 0.5-nm. The



**Fig. 2.** TEM results of a WC-ZrN film after oxidation at 600 °C for 2 h. (a) bright field image, (b) EDS concentration profiles from point 1 to 7, (c) high-resolution image of point 1, (d) high-resolution image of point 2, (e) high-resolution image of point 3, (f) enlarged view of point 6, (g) selected area electron diffraction pattern of the oxide scale.

oxide scale consisted primarily of Zr, together with a lesser amount of W. Both the oxide scale and the film had a small amount of dissolved iron ions. The outward diffusion of Fe from the steel substrate through the boundaries of nanosize-grains and nanolayered films would be rapid. Zr has a highly negative standard free energy of oxide formation and was the major element, so that the Zr oxidized the most easily. Tungsten which was the minor element in the film oxidized to a lesser extent. It seemed that the extent of oxidation of Zr and W was largely proportional to their respective amounts in the film. Figure 2(c) shows the HR-image of point 1. The oxide scale consisted of nanometre-sized polycrystals. Figure 2(d) shows the HRimage of point 2. Nanometre-sized polycrystalline oxide grains and the original nanolayers are seen. A similar morphology is seen in Fig. 2(e), which is the HR-image of point 3. Figure 2(f) shows an enlarged view of point 6. The unoxidized coating consisted of ultra-thin multi-layers. Such thin nanolayers progressively became thicker as the oxidation progressed owing to the volume expansion. Scattered, fine, numerous dark spots in Fig. 2(f) indicated the local depletion of heavy elements such as W which has a high atomic number. As shown in Figs. 2(c) to (f), the oxidation of WC-ZrN film resulted in the destruction of the original nanolayers. On the other hand, the oxygenactive zirconium easily oxidizes to ZrO<sub>2</sub> that has three polymorphs, i.e., monoclinic  $\alpha$  (stable below 1,240 °C), tetragonal  $\beta$  (stable between 1,240-2,370 °C), and cubic  $\gamma$  (stable between 2,370-2,680 °C). These polymorphs are non-metal deficient, n-type semiconductors with the composition  $ZrO_{2-x}$  [7]. The SAED pattern of the oxide scale shown in Fig. 2(g) indicated that the scale consisted of  $\beta$ -ZrO<sub>2</sub>. The formation of  $\beta$ -ZrO<sub>2</sub>, instead of the thermodynamically more stable  $\alpha$ -ZrO<sub>2</sub>, is attributed mainly to the multi-component nature of the film, because the transformation of polymorphic ZrO<sub>2</sub> can be influenced markedly by not only the temperature but also the presence of impurities. W and Fe shown in Fig. 2(b) seemed to be present as a solid solution in  $\beta$ -ZrO<sub>2</sub>. Basically, Fe forms a semi-protective oxide scale and W forms a non-protective oxide scale. Hence, the dissolution of W and Fe would not increase the protectiveness of the oxide layer. When the WC-ZrN was oxidized, W formed tungsten oxides and Zr formed zirconium oxides, whereas carbon and nitrogen were released into the air. Generally, tungsten oxidizes catastrophically, because tungsten oxides such as WO2 and WO<sub>3</sub> are highly volatile, which disrupts the oxide layer. Zirconium readily reacts with oxygen to become ZrO<sub>2-x</sub>.

Figure 3 shows the SEM images of the oxide scale formed on the WC-ZrN film. The scale formed after oxidation at 600 °C for 5 h in air had cracks and nodules (Fig. 3(a)). Since the Pilling-Bedworth ratios are 1.57 for ZrO<sub>2</sub> and 1.87 for WO<sub>3</sub>, the volume expansion that arose, together with the ensuing evaporation of volatile species such as tungsten oxides, made the scale prone to cracking. The cross sectional image shown in Fig. 3(b) indicated that the fragile oxide scale formed could not protect the substrate from oxidation.



Fig. 3. SEM images of the oxide scale formed on a WC-ZrN film after oxidation at  $600 \,^{\circ}$ C for 5 h in air. (a) top view, (b) cross-section.

Figure 4 shows the EPMA results of the oxide scale formed on the WC-ZrN film. The scale formed after oxidation at 600 °C for 10 h in air was nonadherent (Fig. 4(a)). Oxide scales peeled off as flakes due to the formation of non-protective, volatile W-oxides and cracks developed. The cross sectional image shown in Fig. 4(b) indicates that the oxide layer has grown out of contact with the steel substrate, resulting in development of a bucked scale. The flat scale had cracks and was partially detached. The upper part of the scale was generally more porous than the lower part of the scale. The line profiles shown in Fig. 4(c) indicated that a large portion of the film was oxidized. The nitrogen profile shown in Fig. 4(c) indicated that there was negligible amount of nitrogen left in the film owing to its escape during oxidation. The W profile was weaker than the Zr profile. The presence of W in the profile indicated that the evaporation of tungsten oxides did not occur significantly at 600 °C, although it decreased the oxidation resistance of the film.

Figure 5 show the XPS results of the oxide scale formed on the WC-ZrN film after oxidation at 600 °C for 10 h in air. Both  $Zr_{3d}$  and  $O_{1s}$  spectral lines originating from the oxide surface were strong, indicating the surface scale consisted mainly of  $ZrO_2$ . The  $W_{4f}$  spectral line was not strong owing to its small amount. As in the oxide scale, there was no preferential, selective oxidation in the outermost surface of the scale. W and Zr oxidized almost competitively in proportion to their amount in the film. The  $C_{1s}$  and  $N_{1s}$ spectral peaks were quite weak owing to their escape into air. Carbon would evolve as CO or CO<sub>2</sub> gas, whereas nitrogen as  $N_2$  gas. The quite weak  $Cr_{2p}$  spectral peak

0 350 0 Counts 50 *Ц*Т Fe (b) 100 W 0 600 Zı R 0 5 //M scale substrate A mount

(c) <sup>40</sup>

Fig. 4. EPMA results of the oxide scale formed on a WC-ZrN film after oxidation at 600 °C for 10 h in air. (a) top view, (b) cross-section, (c) line profiles along A-B.



Fig. 5. XPS spectra of  $W_{4f}$ ,  $Zr_{3d}$ ,  $C_{1s}$ ,  $N_{1s}$ ,  $O_{1s}$  and  $Cr_{2p}$  bands taken from the surface of the oxide scale formed on a WC-ZrN film after oxidation at 600 °C for 10 h in air.

indicated that a small amount of Cr diffused outward up to the surface of the scale probably to be dissolved in ZrO<sub>2</sub>. Fe from the steel substrate was not detected in Fig. 5, although not Cr but Fe was detected in Fig. 2(a). It seemed that the diffusion rate of Fe and Cr varied depending on the local composition fluctuation.

## Conclusions

A (WC-ZrN)/(WC-Zr) nanolayered film oxidized mainly into  $\beta$ -ZrO<sub>2</sub>, because Zr was richer than W in the original film. W and Zr oxidized almost competitively in proportion to their amounts in the film. During oxidation, carbon and nitrogen diffused outward from the film. Fe and Cr diffused outward from the substrate. It seemed that W, Fe and Cr were dissolved in the  $\beta$ -ZrO<sub>2</sub> in the oxide scale. The (WC-ZrN)/(WC-Zr) nanolayered film formed nanometresize polycrystals that consisted primarily of  $\beta$ -ZrO<sub>2</sub>.

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