

## CrZrN 박막의 대기 중 고온산화

## High-temperature Oxidation of CrZrN Films in Air

김민정<sup>a</sup>, 황연상<sup>a</sup>, 봉성준<sup>a</sup>, 이상율<sup>b</sup>, 이동복<sup>a\*</sup><sup>a\*</sup>성균관대학교 신소재공학과(E-mail:dlee@skku.ac.kr), <sup>b</sup>한국항공대학교 항공재료공학과

**초 록:** Films of CrN, Cr<sub>40</sub>Zr<sub>9</sub>N, and Cr<sub>31</sub>Zr<sub>16</sub>N were deposited on a steel substrate by closed field unbalanced magnetron sputtering, and their oxidation behaviors at 700°C and 800°C for up to 60h in air were investigated. All the deposited films were composed of the CrN phase. Zirconium atoms in Cr<sub>40</sub>Zr<sub>9</sub>N and Cr<sub>31</sub>Zr<sub>16</sub>N films partially dissolved in the CrN phase. They advantageously refined the columnar structure, reduced the surface roughness, and increased the microhardness. The CrN film displayed relatively good oxidation resistance, owing to the formation of the highly protective Cr<sub>2</sub>O<sub>3</sub> on its surface. The Cr<sub>40</sub>Zr<sub>9</sub>N and Cr<sub>31</sub>Zr<sub>16</sub>N films oxidized to Cr<sub>2</sub>O<sub>3</sub> as the major phase and  $\alpha$ -ZrO<sub>2</sub> as the minor one. They oxidized primarily by the inward transport of oxygen. The addition of Zr could not increase the oxidation resistance of the CrN film, because the formed ZrO<sub>2</sub> that was intermixed in the Cr<sub>2</sub>O<sub>3</sub>-rich oxide layer was oxygen permeable, and developed the compressive stress in the oxide scale owing to the volume expansion during its formation.

## 1. 서론

Chromium nitride (CrN) films are widely used to increase the service life of cutting tools, die molds, metal cutting inserts, and machine components, because of their high hardness, superior wear- and corrosion-resistances, good adhesion to most substrate materials, and thermal stability. ZrN is also used as a protective and decorative film having good corrosion resistance and mechanical properties. In order to further increase the cutting speed and reduce the amount of lubrication, it is necessary to improve the properties of the binary nitrides. Hence, CrN films were recently added with Zr. For example, ternary CrZrN films with various Zr contents were deposited by closed field unbalanced magnetron sputtering, reactive magnetron sputtering, and arc-ion implantation on substrates such as steel and silicon. In this work, CrZrN films were deposited on steel substrates by closed field unbalanced magnetron sputtering, and their high-temperature oxidation property was investigated. In order to take full advantages of CrZrN films, it is necessary to understand the oxidation property because the films are frequently exposed to oxidative atmospheres during service at high temperatures. The purpose of this study is to examine the oxidation products, oxide scale structure, and oxidation mechanism of CrZrN films at 700°C and 800°C in air.

## 2. 본론

The CrZrN films were deposited on 1x10x20 mm<sup>3</sup>-sized AISI H13 tool steels by closed field unbalanced magnetron sputtering with vertical magnetron sources of Cr and Zr targets (99.99 % purity) in an (Ar+N<sub>2</sub>)atmosphere to about 4~8 mm thickness. The chemical compositions of the prepared films, which were designated as CrN, Cr<sub>40</sub>Zr<sub>9</sub>N, and Cr<sub>31</sub>Zr<sub>16</sub>N, were analyzed by electron probe microanalysis (EPMA). The surface roughness of the films was investigated by atomic force microscopy (AFM). The film hardness was measured using a nanoindenter. The oxidation tests on the deposited films were carried out at 700 and 800°C in 1 atm of air. Following oxidation, the films were inspected by field-emission scanning electron microscopy (FE-SEM) equipped with energy-dispersive spectroscopy (EDS), electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), X-ray diffraction (XRD), and a transmission electron microscope (TEM operated at 200 kV) equipped with an energy-dispersive spectroscope (EDS) with a 5-nm spot size. The TEM sample was prepared by milling in a focused ion beam (FIB) system after carbon coating.

Figure 1 shows the TEM/EDS results of the Cr<sub>40</sub>Zr<sub>9</sub>N film after oxidation at 700°C for 30 h. The thickness of the scale was only about 0.6  $\mu$ m due mainly to formation of Cr<sub>2</sub>O<sub>3</sub> (Fig. 1(a)). The EDS spectra shown in Fig. 1(b) indicates that point 1, 2, and 3 correspond to an essentially pure Cr<sub>2</sub>O<sub>3</sub> grain, a (Cr<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>)-mixed oxide layer, and

the unoxidized film with a columnar microstructure, respectively. In Fig. 1(a), three  $\text{Cr}_2\text{O}_3$  grains or islands rose up above the  $(\text{Cr}_2\text{O}_3, \text{ZrO}_2)$ -mixed oxide layer, which indicated that they formed by the outward diffusion of Cr from the film. The oxide layer consisted of a uniform mixture of nanocrystalline  $\text{Cr}_2\text{O}_3$  and  $\text{ZrO}_2$  (Fig. 1(c)). No selective oxidation of Cr or Zr occurred throughout the oxide scale. The fact that oxygen-deficient  $\text{ZrO}_2$  oxidizes by the inward diffusion of oxygen ions may indicate that  $\text{Cr}_2\text{O}_3$  intermixed with  $\text{ZrO}_2$  within the oxide layer would oxidize mostly by the inwardly transported oxygen ions.

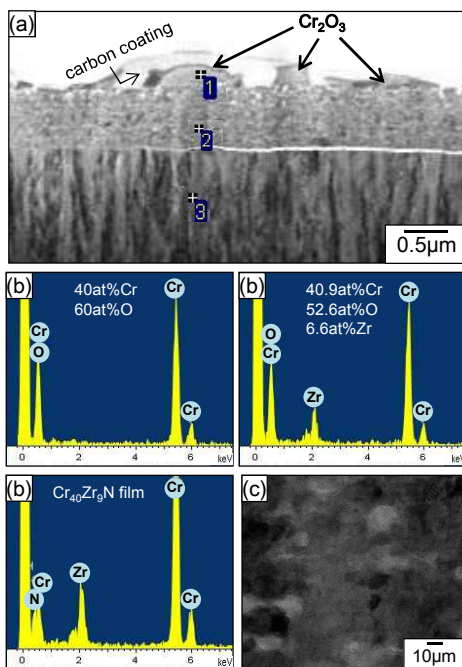


Fig. 1. TEM analysis on the  $\text{Cr}_{40}\text{Zr}_9\text{N}$  film after oxidation at  $700^\circ\text{C}$  for 30 h.

(a) cross-sectional image, (b) EDS spectra of point 1, 2 and 3, (c) enlarged image of the oxide scale (point 2).

### 3. 결론

The oxidation behavior of  $\text{CrN}$ ,  $\text{Cr}_{40}\text{Zr}_9\text{N}$  and  $\text{Cr}_{31}\text{Zr}_{16}\text{N}$  films was investigated at  $700$  and  $800^\circ\text{C}$  for up to 60 h in air. The  $\text{CrZrN}$  films consisted of the nanocrystalline, intermixed  $\text{CrN}$  and  $\text{ZrN}$ . They always oxidized to  $\text{Cr}_2\text{O}_3$  and  $\alpha\text{-ZrO}_2$ , respectively. The thin  $\text{Cr}_2\text{O}_3$  scale that intermixed with a less amount of  $\alpha\text{-ZrO}_2$  consisted of extremely fine round or ellipsoidal crystallites. The  $\text{CrN}$  film oxidized by inward diffusion of oxygen, together with outward diffusion of Cr to a small extent. Similarly,  $\text{Cr}_{40}\text{Zr}_9\text{N}$  and  $\text{Cr}_{31}\text{Zr}_{16}\text{N}$  films oxidized primarily by the inward transport of oxygen, being accompanied with outward diffusion of Cr and Zr to a small extent. Nitrogen always tended to diffuse outward into the air. The anion-deficient  $\text{ZrO}_2$  seemed to enhance the inward transport of oxygen. Hence, the addition of Zr could not increase the oxidation resistance of  $\text{CrN}$  films.

### 참고문헌

1. D. B. Lee, Y. C. Lee, and S. K. Kwon, *Surf. Coating Tech.* 141 (2001) 227.
2. M. K. Kim, G. S. Kim, and S. Y. Lee, *Met. Mater. -Int.* 14 (2008) 465.
3. S. H. Park, I. S. Han, H. J. Lee, S. C. Huh, and W. J. Park, *Met. Mater. -Int.* 15 (2009) 187.
4. G. S. Kim, B. S. Kim, S.Y. Lee, and J. H. Hahn, *Surf. Coat. Technol.* 200 (2005) 1669.
5. S. M. Kim, B.S. Kim, G. S. Kim, S. Y. Lee, and B. Y. Lee, *Surf. Coat. Technol.* 202 (2008) 5521.
6. Z. G. Zhang, O. Rapaud, N. Bonasso, D. Merces, C. Dong, and C. Coddet, *Vacuum* 82 (2008) 1332.

### ACKNOWLEDEMENT

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Korean Ministry of Education, Science and Technology (2010-0023002).