

## TiZrAlN의 500-700°C 사이에서 공기 중 산화

### Oxidation of TiZrAlN nanocomposite thin films in air at temperatures between 500 and 700°C

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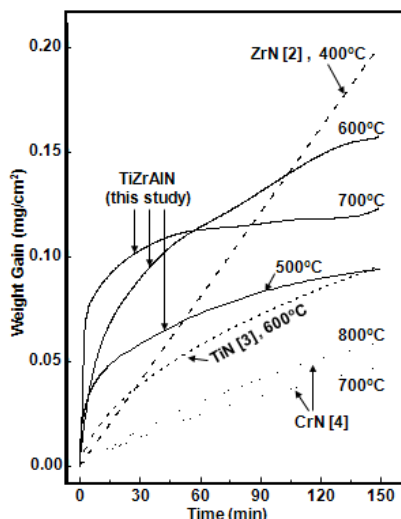
**초 록:** Quaternary TiZrAlN nanocomposite thin films with a composition of 20.7Ti-22.2Zr-2.7Al-54.4N (at.%) were deposited by the closed-field unbalanced magnetron sputtering (CFUBMS) method and oxidized in air at temperatures between 500 and 700°C. The oxides formed were TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. The films had inferior oxidation resistance because the amounts of ZrO<sub>2</sub> and TiO<sub>2</sub> were large while the amount of Al<sub>2</sub>O<sub>3</sub> was small. The oxidation progressed primarily by the inward diffusion of oxygen and the outward diffusion of nitrogen.

#### 1. 서론

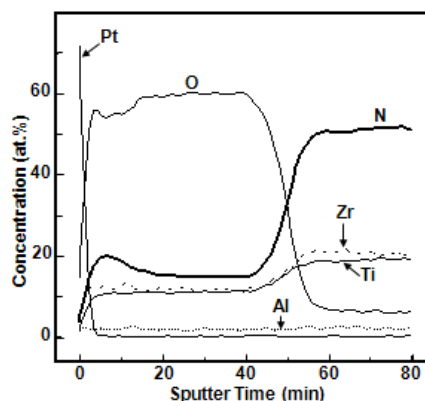
Hard TiN films have been widely applied to carbide tools and cutting inserts because of their good wear resistance and thermal stability. However, they cannot endure high speed and lubrication-free machining due to the decrease in wear resistance at elevated temperatures. Hence, superhard TiZrAlN nanocomposite films have been recently developed [1]. Because such films are frequently exposed to oxidative atmospheres during use, their high temperature oxidation resistance is vital to their success in practical applications. In this study, TiZrAlN nanocomposite thin films were deposited by the closed field unbalanced magnetron sputtering (CFUBMS) method and oxidized in air at temperatures between 500 and 700°C to study their oxidation kinetics and the mechanism of oxidation. TiZrAlN nanocomposite films were deposited on 304 stainless steel substrates using CFUBMS to obtain film thicknesses of 1-2 μm. Their average composition was 20.7Ti-22.2Zr-2.7Al-54.4N (at.%), as measured by Auger electron spectrometer (AES) analysis. Prior to deposition, a titanium interlayer was deposited with a thickness of about 300 nm to enhance the adherence of the film. Detailed deposition parameters are described elsewhere [1]. The films were oxidized for up to 20 h in air at temperatures between 500 and 700 °C in a thermogravimetric analyzer (TGA) and characterized by AES, an X-ray photoelectron spectrometer (XPS), and a transmission electron microscope (TEM operated at 200 keV). The TEM sample was prepared by milling in a focused-ion-beam (FIB) system.

#### 2. 본론

Fig. 1 shows the weight changes of the TiZrAlN films in the temperature range of 500-700°C in air. Competition between weight gain due to scaling and weight loss due to the evolution of nitrogen occurred simultaneously during oxidation of the TiZrAlN film. The oxidation rates of the test sample increased as the temperature increased from 500 to 600°C. At 700°C, the initial fast oxidation rate decreased after a short period. This is because the escape of nitrogen from the film accelerated and the thin film began to oxidize almost completely. This inferior oxidation resistance was attributed mainly to the presence of Zr in the film, as can be seen from the weight gain curve of the ZrN film [2]. ZrN oxidizes to anion-deficient, oxygen-permeable ZrO<sub>2</sub>. The TiZrAlN film oxidizes faster than TiN [3] and CrN films [4].



**Fig. 1.** Oxidation kinetics of the TiZrAlN nanocomposite thin film at 500, 600, and 700 °C in air. For comparison, oxidation kinetics of the ZrN film at 400 °C [2], the TiN film at 600 °C [3], and the CrN film at 700 and 800 °C [4] were superimposed.



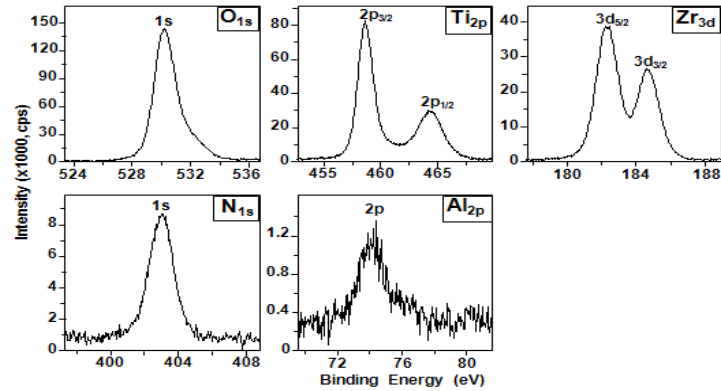
**Fig. 2.** AES depth profiles of the TiZrAlN nanocomposite thin film after oxidation at 600 °C for 7 min in air. The penetration rate is 18 nm/min for the reference SiO<sub>2</sub>.

Fig. 2 shows the AES depth profiles of the oxidized TiZrAlN film. To understand the oxidation mechanism, a thin Pt film was sputter-deposited on top of the TiZrAlN film prior to oxidation. From the location of inert Pt, it can be seen that oxygen diffused inwardly to react with Ti, Zr, and Al, while nitrogen diffused outwardly to escape from the surface, presumably as N<sub>2</sub> gas. The concentration of Al remained almost constant at a low level.

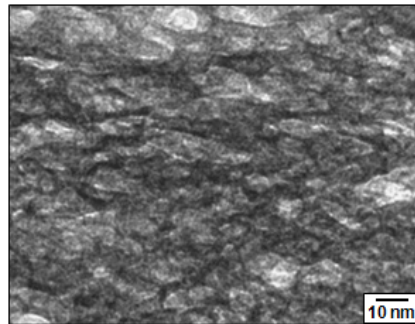
Fig. 3 shows the XPS spectra of the oxidized TiZrAlN film. The intensity of the spectra decreased in the order of O1s, Ti2p, Zr3d, N1s, and Al2p. The surface oxide film consisted of TiO<sub>2</sub> (binding energy, E<sub>b</sub>, of Ti2p<sub>3/2</sub> = 458.6 eV), ZrO<sub>2</sub> (E<sub>b</sub> = 182.2 eV for Zr3d<sub>5/2</sub>), and Al<sub>2</sub>O<sub>3</sub> (E<sub>b</sub> of Al2p = 74.2 eV). The N1s spectrum was weaker than the O1s spectrum, owing to the partial liberation of nitrogen. The asymmetric O1s spectrum (E<sub>b</sub> = 530.1 eV) indicated the involvement of more than one oxide. The N1s spectrum of the unoxidized film had a E<sub>b</sub> = 396.3 eV, because nitrogen existed in the form of nitrides. However, the N1s spectrum shifted to a higher binding energy of E<sub>b</sub> = 403.0 eV after oxidation (Fig. 3). This peak shift may have occurred due to the formation of nitrides with foreign elements such as oxygen, Ti, Zr, or Al. The nitrogen escape would deter the formation of a dense, continuous protective scale and thereby enhance the inward diffusion of oxygen.

Among the oxides formed on the film, α-Al<sub>2</sub>O<sub>3</sub> is of principal interest because it grows very slowly on account of its highly stoichiometric structure. It is generally accepted that α-Al<sub>2</sub>O<sub>3</sub> grows primarily by the inward diffusion of oxygen along the grain boundaries, although there is some component of outward growth as well [5].

In this study, Al was oxidized mainly by the oxygen that diffused inwardly. Nevertheless, the amount of Al in the TiZrAlN film was too small to protect the film. Neither dense nor continuous  $\text{Al}_2\text{O}_3$  oxide scale formed on the film. Pure TiN oxidizes by the inward diffusion of oxygen [3]. Similarly, Ti in the film oxidized primarily by the inward diffusion of oxygen in this study. Like Al, Zr also has a high affinity for oxygen. The solubility and diffusivity of oxygen in  $\text{ZrO}_2$  are relatively high. As expected, Zr in the film was oxidized by the inward diffusion of oxygen. In this study, competitive oxidation of Al, Ti, and Zr occurred depending on their activities and availabilities in the film.

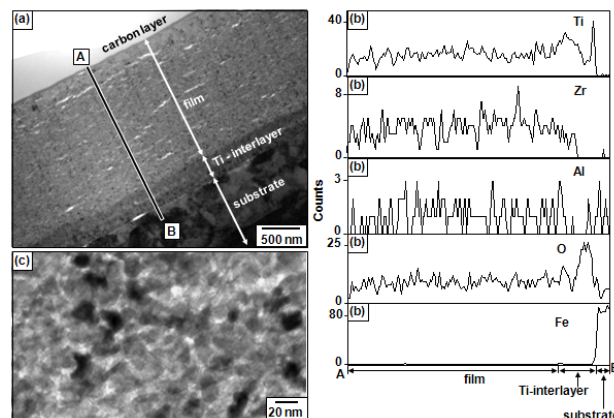


**Fig. 3.** XPS spectra of  $\text{O}_{1s}$ ,  $\text{Ti}_{2p}$ ,  $\text{Zr}_{3d}$ ,  $\text{N}_{1s}$ , and  $\text{Al}_{2p}$  obtained from the surface scale formed on the TiZrAlN film after oxidation at  $500^\circ\text{C}$  for 20 h in air.



**Fig. 4.** Cross-sectional bright field TEM image of the TiZrAlN thin film deposited.

Fig. 4 shows the TEM image of the unoxidized TiZrAlN thin film. Polycrystalline grains with sizes ranging from 3 to 15 nm were somewhat round. The XRD analysis indicated that the film consisted of a substitutional solid solution of TiN and ZrN [1].



**Fig. 5.** TiZrAlN thin film after oxidation at  $700^\circ\text{C}$  for 3.5 h in air. (a) cross-sectional bright field TEM image, (b) EDS line profiles of Ti, Zr, Al, O and Fe along A-B, (c) enlarged high-resolution image of the oxidized film.

Fig. 5(a) shows the TEM image of the oxidized TiZrAlN thin film. The original 2  $\mu\text{m}$ -thick film, a thin Ti interlayer, and the steel substrate are visible. The EDS line profiles shown in Fig. 5(b) indicate that the completely oxidized film consisted of mixed oxides of Ti, Zr, and Al. These elements were oxidized predominantly by the inwardly diffused oxygen. Oxygen can diffuse inward easily via diffusion paths such as grain boundaries of nanocrystals that consist of  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$ . Oxygen which penetrated into the film was partially blocked by the steel substrate. As the oxidation progressed further, the substrate was also oxidized by the inwardly diffused oxygen. The original nanocomposite grains were oxidized into nanometer-sized polycrystals (Fig. 5(c)). Fig. 4 shows the TEM image of the unoxidized TiZrAlN thin film. Polycrystalline grains, whose size ranged from 3 to 15 nm, were somewhat round. The XRD analysis indicated that the film consisted of a substitutional solid solution of TiN and ZrN [1].

Fig. 5(a) shows the TEM image of the oxidized TiZrAlN thin film. The original 2  $\mu\text{m}$ -thick film, a thin Ti interlayer, and the steel substrate were seen. The EDS line profiles shown in Fig. 5(b) indicate that the completely oxidized film consisted of mixed oxides of Ti, Zr, and Al. These elements were oxidized predominantly by the inwardly diffused oxygen. Oxygen can diffuse inward easily via easy diffusion paths such as grain boundaries of nanocrystals, which consisted of  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$ . Oxygen penetrated into the film was blocked partially by the steel substrate. As the oxidation progressed further, the substrate was also oxidized by the inwardly diffused oxygen. The original nanocomposite grains oxidized into nanometer-size polycrystals (Fig. 5(c)).

### 3. 결론

During oxidation of the TiZrAlN thin films, oxygen diffused inward to react with Zr, Ti, and Al, while nitrogen diffused outward from the surface. The film displayed inferior oxidation resistance because there was a sufficient amount of oxygen-permeable  $\text{ZrO}_2$  and semi-protective nonstoichiometric  $\text{TiO}_2$  in the scale. The amount of protective  $\text{Al}_2\text{O}_3$  was small because of the low Al content in the film.

### 감사의 글

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### 참고문헌

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