

TiAlSiN 코팅의 대기중 고온산화 속도와 스케일 분석

High-temperature Oxidation Kinetics and Scales Formed on the TiAlSiN film

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**초 록:** Ti<sub>0.26</sub>Al<sub>0.16</sub>Si<sub>0.01</sub>N<sub>0.57</sub> (at%) coatings were synthesized on stainless steel 304 by using arc ion plating systems (AIPS). Targets employed for the deposition were Ti, AlSi(67:33at%) and AlSi(82:18at%). The thickness of TiAlSiN coatings is 4μm. The oxidation characteristics of the deposited coatings were studied by thermogravimetric analysis (TGA) in air between 800 and 900 °C for 75 hr. The oxide scale formed on the TiAlSiN coatings consisted of rutile-TiO<sub>2</sub> layer and α-Al<sub>2</sub>O<sub>3</sub>. At 800 °C, the coatings oxidized relatively slowly, and the scales were thin and adherent. When oxidized above 900 °C, TiO<sub>2</sub> grew fast over the mixed oxide layer, and the oxide scale formed on TiAlSiN coatings was prone to spallation. Microstructural changes of the TiAlSiN coatings that occurred during high temperature oxidation were investigated by EPMA, XRD, SEM and TEM.

1. 서론

Transition metal nitride films such as TiN and CrN are widely used for cutting tools or die molds because of their high hardness and superior resistance to wear and corrosion, however they are inevitably degraded by oxidation during service at high temperatures.[1] To further increase the oxidation resistance, nano-multilayered CrAlSiN, AlTiSiN, TiAlCrSiN films were deposited on a steel substrate by the cathodic arc plasma process, and their high-temperature oxidation behavior was studied by oxidizing in air between 800 and 900°C using TGA in this study. It is important to note that nano-multilayered films are of increasing interest due to their superior mechanical and lubrication properties in advanced tribological applications where single layer films are insufficient. The oxidized films were characterized by XRD, XPS, AES, EPMA, and TEM.

2. 본론

Figure 1 shows the SEM/TEM/XRD results of the film. Surface grinding marks that were made prior to deposition were visible owing to the film thinness, along with microdroplets (Fig. 1a). The film consisted of a few nanometer-thick, alternating Al-Si-N/Ti-Si-N nanocrystalline layers parallel to the substrate surface (Fig. 1b).

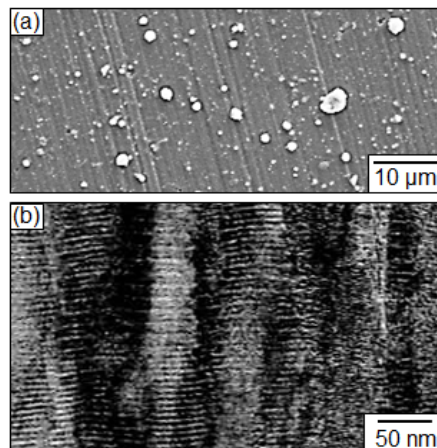


Fig. 1 TiAlSiN film deposited on the steel substrate. (a) SEM top view, (b) cross-sectional TEM image.

Figure 2 shows the AES depth profiles of the film after oxidation at 800°C for 5h. During oxidation, nitrogen diffused

outward to escape from the surface, and oxygen diffused inward. Based on the maximum concentration point of noble Au, it is seen that the outwardly diffusing  $Al^{3+}$  ions formed the outer most  $Al_2O_3$  layer, while the inwardly diffusing  $O^{2-}$  ions formed the underlying oxide layer. The high-temperature oxidation resistance of the film mainly depends on  $\alpha-Al_2O_3$ , which grows very slowly due to its highly stoichiometric structure.  $SiO_2$  also resists oxidation but was not identified by AES due to its small amount.

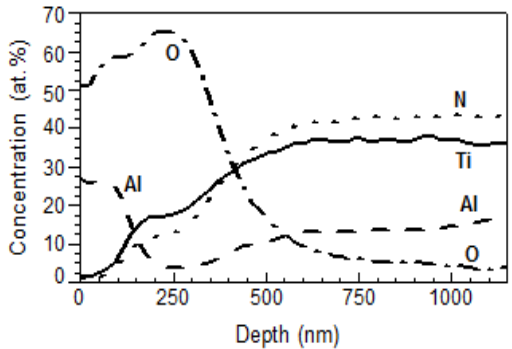


Fig. 2 AES depth profiles of the TiAlSiN film after oxidation at 800 °C for 5 h.

### 3. 결론

The  $Ti_{2.6}Al_{1.163}Si_{1.012}N_{5.65}$  thin film initially oxidized to an  $\alpha-Al_2O_3$  layer containing some  $TiO_2$  through the outwardly diffusing Al and some Ti ions, below which a rutile- $TiO_2$  layer containing some  $Al_2O_3$  formed through inwardly diffusing oxygen ions at 800°C. Later, another  $TiO_2$ -rich surface layer formed over those preformed ( $Al_2O_3$ -rich)/( $TiO_2$ -rich) bilayers, because Ti continuously diffused outward from the film. Silicon tended to accumulate underneath those oxide layers, due to its thermodynamic nobility. At 900 °C, the oxidation rate increased with partial scale spallation. The outer  $TiO_2$  layer, the intermediate  $Al_2O_3$  layer, and the inner  $TiO_2$ -rich layer intermixed with some  $Al_2O_3$  and  $SiO_2$  formed at 900 °C.

### 감사의 글

본 연구는 2014년도 산업통상자원부의 재원으로 한국에너지 기술평가원(KEPTEP)의 지원을 받아 수행한 연구 과제입니다. (No.20143030050070)

### 참고문헌

1. H. Ichimura and A. Kawana, Journals of Materials Research 8, (1993) 1093.