CrAlMgSiN 박막의 600-900°C에서의 대기중 산화

Oxidation of CrAlMgSiN thin films between 600 and 900°C in air

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초 록: Thin CrAlMgSiN films, whose composition were 30.6Cr-11.1Al-7.3Mg-1.2Si-49.8N (at.%), were deposited on steel substrates in a cathodic arc plasma deposition system. They consisted of alternating crystalline Cr-N and AlMgSiN nanolayers. After oxidation at 800°C for 200 h in air, a thin oxide layer formed by outward diffusion of Cr, Mg, Al, Fe, and N, and inward diffusion of O ions. Silicon ions were relatively immobile at 800°C. After oxidation at 900°C for 10 h in air, a thin Cr_2O_3 layer containing dissolved ions of Al, Mg, Si, and Fe formed. Silicon ions became mobile at 900°C. After oxidation at 900°C for 50 h in air, a thin SiO_2-rich layer formed underneath the thin Cr_2O_3 layer. The film displayed good oxidation resistance. The main factor that decreased the oxidation resistance of the film was the outward diffusion and subsequent oxidation of Fe at the sample surface, particularly along the coated sample edge.

1. 서론

CrN films have been successfully applied to molding dies, wear components, and cutting tools because of their high hardness, good adhesion to most substrates, low internal stress, and superior resistance to wear and corrosion. In order to further improve their mechanical properties and thermal stability, CrSiN, CrAlN, and CrAlSiN films have been developed. In this study, CrAlMgSiN films consisting of alternating Cr-N/AlMgSiN nano-multilayers were deposited by a cathodic arc plasma process and their oxidation behavior studied between 600 and 900°C. Nano-multilayered films are attracting enormous attention because of their unique merits, including superior mechanical and lubricating properties. The purpose of this study is to investigate the oxidation characteristics of nano-multilayered CrAlMgSiN thin films for the first time.

2. 본론

CrAlMgSiN films were deposited to a thickness of 0.9-1.6 μm on both sides of a tool steels (1.5% C, 11.5% Cr, 0.8% Mo, 0.9% V, Fe = balance), with dimensions of 10x5x2 mm^3 by cathodic arc plasma deposition using two cathodes of Cr and $(Al_{0.88}Si_{0.12})_{0.7}Mg_{0.3.}$ Rotation of the substrate between two independent cathodes at a speed of 4.55 rpm during deposition yielded nano-multilayered films, whose average composition was 30.6Cr-11.1Al-7.3Mg-1.2Si-49.8N (at.%) according to the AES analysis. The CrAlMgSiN films were oxidized between 600 and 900°C in air using a TGA. Each sample was suspended by a platinum wire in an alumina reaction tube within the hot zone of an electrical furnace. The samples were characterized by an XRD with Cu-Kα radiation, XPS, AES, and a TEM equipped with an EDS with 5 nm spot size. The TEM sample was prepared by milling in a FIB system.

Fig. 1 shows analytical results of the CrAlMgSiN film that proved dense, adherent (Fig. 1a), and consisted of alternating dark/white nano-multilayers (Fig. 1b). Fig. 1c indicates the film to be polycrystalline. The AES concentration profiles shown in Fig. 1d, together with TEM/EDS analysis, indicated that the white layers were AlMgSiN (width = 4 nm), which originated from the $(Al_{0.88}Si_{0.12})_{0.7}Mg_{0.3}$ cathode, and the dark layers were Cr-N (width = 7 nm), originating from the Cr cathode. According to the XRD analysis, the film consisted of CrN, Cr_2N, and AlN (Fig. 1e). Here, the diffraction pattern of the Fe-Cr substrate was strong due to film thinness, and the JCPDS numbers were included.

Fig. 2 shows the analytical results for the oxidized CrAlMgSiN film after oxidation at 900°C for 50 h. Protruded particles ('A' in Fig. 2a) spread out over the flat oxide surface, as well as the edge of the sample. They were essentially pure Fe_2O_3 (Fig. 2b). Since Fe_2O_3 began to cover the surface (Figs. 6a and b), the oxidation time was limited to 50 h at 900°C. The EDS spectrum obtained from the flat oxide surface ('B' in Fig. 2a) is indicated that the composition was 41O-23.1Cr-9.8Al-6.2Mg-19.9Fe (at.%). Fig. 2d shows the enlarged image of the flat oxide surface ('B' in Fig. 2a). The round, tiny oxide grains indicated that oxidation occurred to a small extent. Their cross-sectional TEM image was shown in Fig. 2e (the outermost surface of the scale). The oxygen map shown in Fig. 2f indicates that spots 1-5 and 6-13 belong to oxides and the film containing dissolved oxygen, respectively. Nitrogen was absent at spots 1-13. At spots 1-5, Cr_2O_3 formed, which was incorporated with Al, Mg, Si, and Fe. Nevertheless, the formed chromia and silica layers led to the formation of the 1 μm-thick oxide scale, despite the oxidation at 900°C for 50 h.

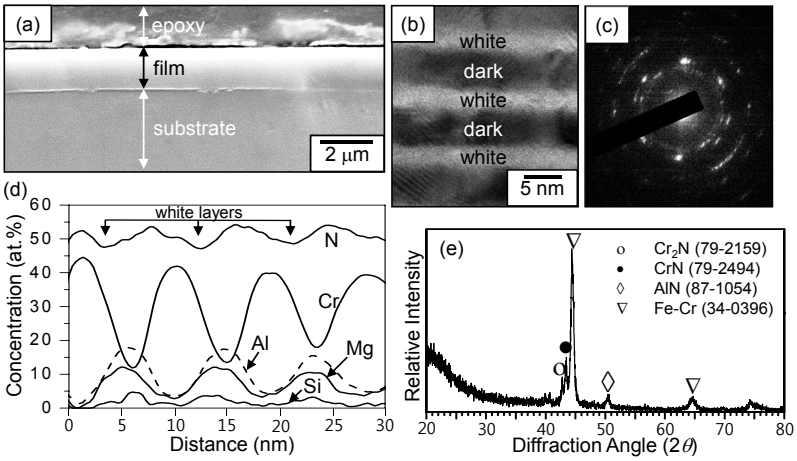

Fig. 1. CrAlMgSiN film deposited on the steel substrate. (a) SEM cross-sectional image, (b) cross-sectional bright field (BF) TEM image of the film, (c) SAED of the film, (d) AES depth profiles across the film, (e) XRD pattern.

The good oxidation resistance of the film owes primarily to the presence of Cr and Si. The Al and Mg dissolve in the chromia and silica layers. The main factor that decreased the oxidation resistance of the film was the outward diffusion of the less protective Fe through the nano-multilayered film. The edge of the sample was the weak point in terms of oxidation resistance.

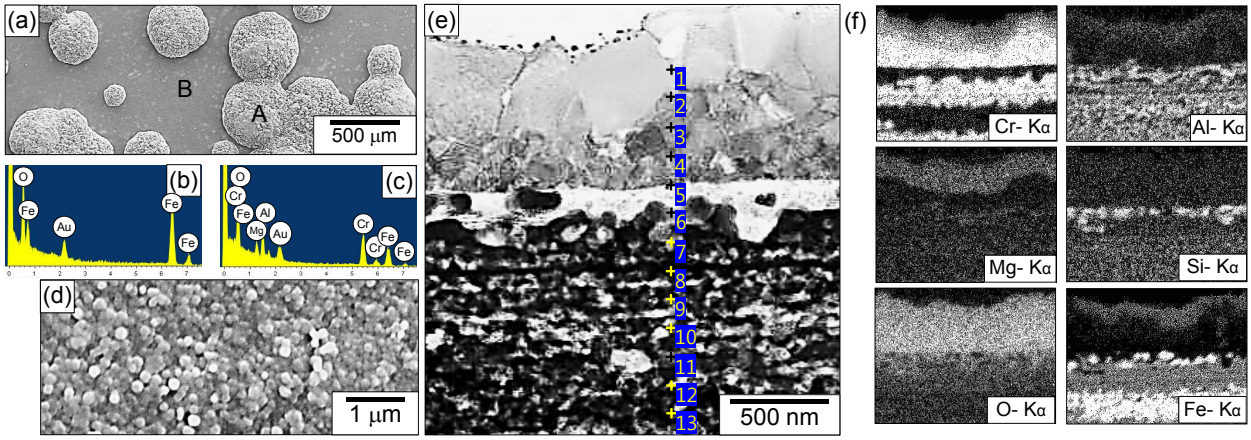

Fig. 2. CrAlMgSiN film after oxidation at 900°C for 50 h in air. (a) SEM top view, (b) EDS spectrum of 'A', (c) EDS spectrum of 'B', (d) SEM top view of 'B', (e) cross-sectional TEM BF image, (f) EDS mappings of (e).

3. 결론

CrAlMgSiN films were deposited on tool steel substrates by a cathodic arc plasma deposition method, and their high-temperature oxidation behavior investigated. The following observations were made.

(1) The film consisted of alternating layers of nanometer-size polycrystalline (CrN, Cr_2N) and AlMgSiN. During oxidation, Cr, Al, Mg, and Fe diffused outward to form the oxide scale at 600-900°C. At the same time, oxygen diffused inward, whereas nitrogen diffused outward. Si did not diffuse much owing to its strong bonding in SiO_2.

(2) The scale consisted primarily of a Cr_2O_3 layer, where Al, Mg, Si, and Fe were dissolved. Chromia formed preferentially during oxidation because the amount or activity of Cr in the film was the greatest. As the oxidation progressed, a SiO_2-rich underlayer formed, owing to consumption of Cr, Al, and Mg in the Cr_2O_3 layer. The Cr_2O_3 layer, with or without the SiO_2-rich underlayer, provided good oxidation resistance. The rapid oxidation that was observed in the oxidation curve at 900°C was due to the oxidation of Fe to form Fe_2O_3 all over the surface, including the edge of the sample.

감사의 글

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