

Oxidation of CrAlN thin films at 800 °C and 900 °C in air

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CrAlN films with a composition of 31.3Cr-12.9Al-55.3 N (at.%) were deposited on steels by closed field unbalanced magnetron sputtering to a thickness of 1.2 μm. They consisted of dense, polycrystalline CrN and AlN fine columns. Their oxidation characteristics were studied at 800 °C and 900 °C for up to 20 h in air. The formed oxides consisted primarily of crystalline Cr₂O₃ incorporated with Al₂O₃. The amount of Al in the film was not large enough to precipitate out Al₂O₃ from Cr₂O₃. The oxide layers were thin and compact so as to make CrAlN films more protective than CrN films. During oxidation, Cr, Al and nitrogen diffused outward, whereas oxygen diffused inward. At the same time, Fe diffused outward from the substrate toward the outermost oxide surface owing to the concentration gradient.

Key words: Thin films, Sputtering, Oxidation, Transmission electron microscopy (TEM), CrAlN.

Introduction

Chromium nitride (CrN) films are widely used to increase the service life of cutting tools, die molds and machine components, because of their high hardness, good adhesion to most substrate materials, and superior resistance to wear and corrosion [1-6]. However, they are inevitably degraded by oxidation during service at high temperatures. CrN oxidizes via a progressive displacement of nitrogen by oxygen and the formation of Cr₂O₃. The oxidation limit of CrN film is commonly known to be about 750 °C [5], though it depends strongly on the Cr_{1-x}N_x stoichiometry, deposition method, film grain size, orientation, thickness, and surface roughness. In order to further improve mechanical properties and thermal stability of CrN films, CrAlN films were developed [7-12]. CrAlN films were deposited by reactive sputtering [5, 6], arc-evaporation [9], arc-ion plating [10], lateral rotating cathodic arc [11], closed field unbalanced magnetron sputtering [12] on substrates such as Si [7], a Ni alloy [8], cemented carbide [9], and steels [10-12]. The substitutional replacement of the smaller Al atoms into the Cr sites led to the refinement of the grains and an increase in the hardness, elastic modulus, and resistance to wear and oxidation. During high-temperature oxidation, both the Cr and Al in the films formed protective oxides on the surface, which limited the diffusion of oxygen into the films. Depending on investigators, Cr_{1-x}Al_xN films oxidized into amorphous Al₂O₃-rich scale [7], (Cr₂O₃+α-Al₂O₃) dominated by Cr₂O₃ [8, 9], crystalline and amorphous Al₂O₃ [10], (Cr₂O₃+CrAlO) [11], or

Cr₂O₃ and amorphous Al₂O₃ that crystallized above 900 °C [12].

Despite previous oxidation studies [7-12], the high-temperature oxidation behavior of the CrAlN films under diverse conditions needs to be investigated for wide applications, because the thermal stability of films depends sensitively on the deposition method and parameters that affect their crystallinity, composition, stoichiometry, thickness, surface roughness, grain size and orientation. In this study, CrAlN films were deposited on a steel substrate by closed field unbalanced magnetron sputtering. This study aims to investigate the oxidation behavior of CrAlN films at 800-900 °C in air. The oxidation mechanism was proposed by performing the Au-marker test. Transmission electron microscopic (TEM) analyses were performed to investigate the scale morphology, which has not been studied up to now in detail.

Experimental Procedures

CrAlN films were deposited on 1×10×15 mm³-sized AISI H13 tool steels by closed field unbalanced magnetron sputtering with vertical magnetron sources of Cr and Al targets (99.99% purity) in an (Ar+N₂) atmosphere. The deposition parameters are listed in Table 1. The chemical composition of the film was 31.3Cr-12.9Al-55.3N (at.%), according to the electron probe microanalysis (EPMA; Jeol JXA-8900R). Oxidation tests on the films were carried out at 800 °C and 900 °C for up to 20 h in atmospheric air. Subsequently, the films were evaluated by a field-emission scanning electron microscopy (FE-SEM; Jeol JSM7000F), X-ray diffraction (XRD; Mac Science M18XHF-SRA) with Cu-K_α radiation, X-ray photoelectron spectrometry (XPS;

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Table 1. Deposition condition of CrAlN films by unbalanced magnetron sputtering.

target power	Cr = 1.6 A, Al = 1.8 A
substrate rotation speed	15 rpm
working pressure	Ar = 3.0 mTorr, N ₂ = 1.2 mTorr
target-to-substrate distance	90 mm
substrate bias voltage	-100 V
deposition temperature	200 °C

ESCA2000), Auger electron spectroscopy (AES; Perkin-Elmer 1660), and TEM (Jeol JEM-2100F operated at 200 keV) equipped with EDS with 5 nm spot size. The XRD patterns were obtained at 40 kV and 300 mA with a scanning speed of 10 °/min. The sputtering rate of AES was 18 nm/min for the reference SiO₂. The TEM sample was prepared by milling in a focused-ion-beam (FIB; SII SMI3050TB) system with a liquid-gallium-metal ion source and maximum accelerating voltage of 30 kV.

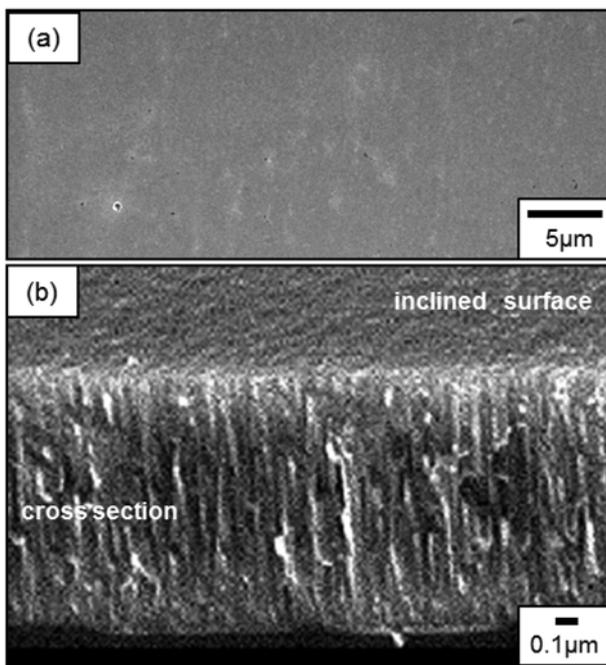
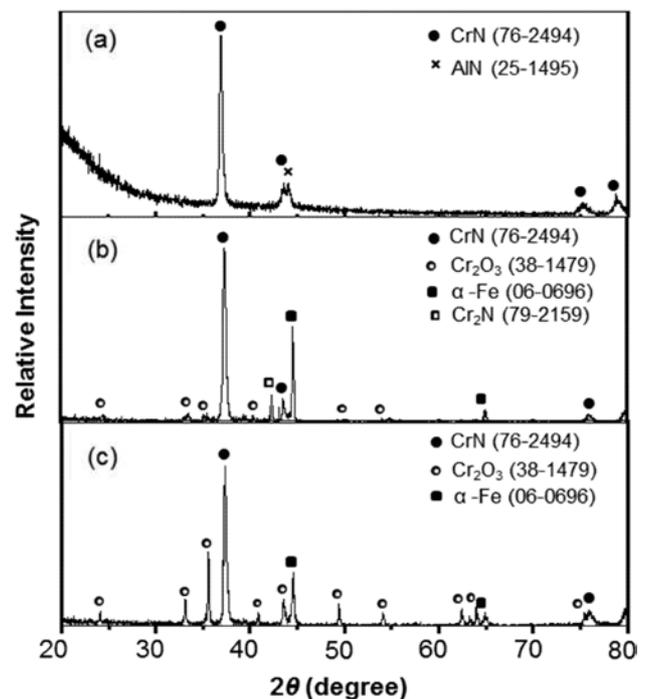
Results and Discussion

Fig. 1 shows the SEM images of the as-deposited CrAlN film. The top view displays a featureless and smooth film surface (Fig. 1(a)). The fracture surface indicates that the film with a columnar structure was dense, adherent, and approximately 1.2 μm thick (Fig. 1(b)).

Fig. 2 shows the XRD patterns of the CrAlN films. As-deposited film consisted of face centered cubic

(FCC) CrN and FCC AlN (Fig. 2(a)). The CrN phase exhibited a strong (111) preferred orientation, which was the lowest strain energy plane of B1-type structure. Although CrN and AlN can exhibit complete solubility in the B1-type CrAlN FCC lattice [13, 14]. A weak AlN peak in Fig. 2(a) is because equilibrium was not attained. After oxidation at 800 °C for 20 h, diffraction patterns such as strong CrN, weak Cr₂N, strong α-Fe substrate, and weak Cr₂O₃ were detected (Fig. 2(b)). CrN decomposed into Cr₂N and N₂ [9, 12]. The amount of the formed Cr₂O₃ was small, indicating superior oxidation resistance of the film. The formed Al₂O₃ dissolved in Cr₂O₃, because both oxides have a corundum structure [7]. Both Cr₂O₃ and Al₂O₃ have a low diffusivity for anions and cations due to their high degree of stoichiometry. AlN in the deposited film disappeared owing to heating to form the B1-type FCC CrAlN ternary solution with a strong (111) preferred orientation (Fig. 2(b)). When the molar ratio of Al/(Cr+Al) was larger than 0.7, the structure of the CrAlN films changed from B1 (NaCl type) to B4 (wurtzite type) [8, 10]. In this study, Al/(Cr+Al) ratio is 0.24, representing that the B1-type was attained in Fig. 2(b). After oxidation at 900 °C for 20 h, diffraction patterns of CrN, α-Fe, and Cr₂O₃ were detected (Fig. 2(c)). Here, CrN peaks were still strong, and substrate peaks were clearly recognizable, reflecting superior oxidation resistance of the thin film. Owing to increased extent of oxidation, the Cr₂O₃ pattern was distinct in Fig. 2(c).

Fig. 3 shows the XPS spectra of Cr_{2p}, Al_{2p}, and N_{1s} taken from the outermost surface of the deposited

**Fig. 1.** SEM images of the deposited CrAlN film. (a) top views and (b) fractured.**Fig. 2.** XRD pattern of the CrAlN film. (a) as-deposited, (b) after oxidation at 800 °C for 20 h in air, (c) after oxidation at 900 °C for 20 h in air.

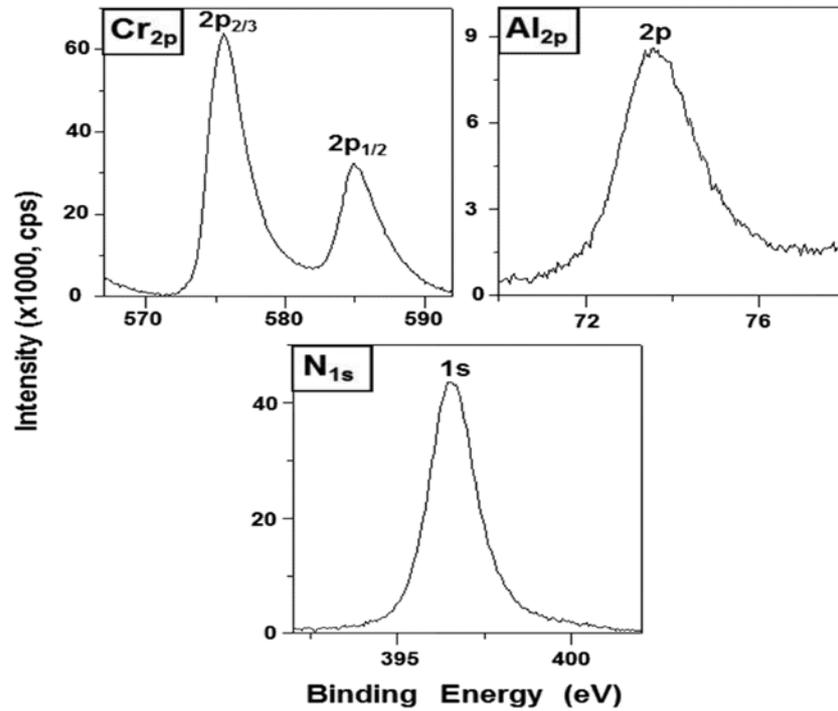


Fig. 3. XPS spectra of Cr_{2p}, Al_{2p}, and N_{1s} taken from the outermost surface of the deposited CrAlN film.

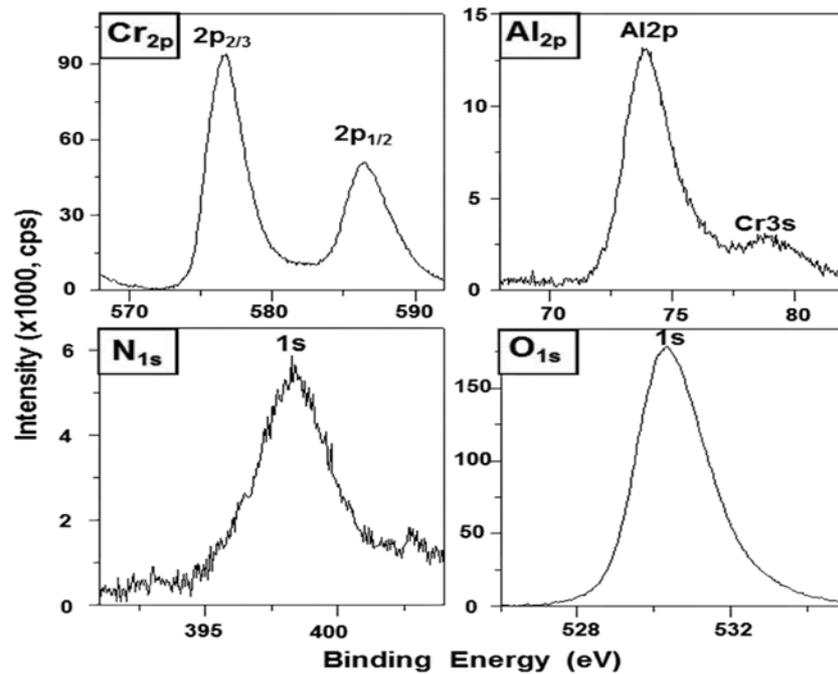


Fig. 4. XPS spectra of Cr_{2p}, Al_{2p}, N_{1s} and O_{1s} taken from the outermost surface of the CrAlN film after oxidation at 800 °C for 1 h.

CrAlN film. The Cr_{2p_{3/2}} peak was centered at 575.6 eV, which might be associated with CrN [15]. The peaks pertaining to free chromium (574.4 eV) and Cr₂N (574.5 eV) were not recognizable. The Al_{2p} spectrum showed a component at 73.6 eV, which was larger than the Al_{2p} binding energy of AlN (72.6 eV). This deviation in the binding energy may be due to incorporation of Cr in AlN. The N_{1s} spectrum showed a binding energy component at 396.5 eV associated with the nitrides.

Fig. 4 shows the XPS spectra of Cr_{2p}, Al_{2p}, N_{1s} and O_{1s} taken from the outermost surface of the CrAlN film after oxidation at 800 °C for 1 h. The composition determined from XPS was 27Cr-18Al-53O-2N (in at.%). The binding energy of Cr_{2p_{3/2}} peak was centered at 576.9 eV, which matched with Cr₂O₃ [15]. The binding energy of Al_{2p} (73.8 eV) was smaller than that of Al₂O₃ (*E_b* of Al_{2p} = 74.2 eV), which may be due to dissolution of Al₂O₃ in the isostructural Cr₂O₃. The coexistence of

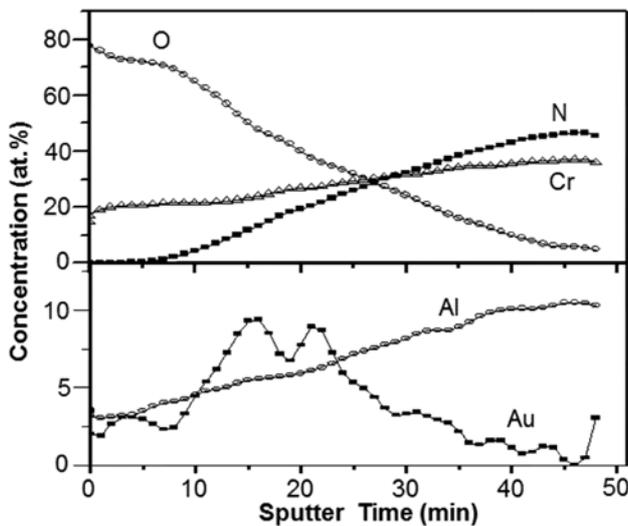


Fig. 5. AES depth profiles of the CrAlN film after oxidation at 900 °C for 12 min in air.

Cr and Al at the outermost oxide surface indicated that Cr and Al oxidized competitively owing their high affinity for oxygen. The nitrogen spectrum was the weakest because the oxidation inevitably accompanied the release of nitrogen from the CrAlN film.

Fig. 5 shows the AES depth profiles of the oxidized CrAlN film. In order to understand the oxidation mechanism, a thin Au film was sputter-deposited for 10 min using an ion sputter (Hitachi E-1010) on top of the film prior to oxidation, and oxidized at 900 °C for 12 min in air. From the maximum concentration point of Au, it is seen that nitrogen diffused outwardly to escape from the surface, probably as N_2 gas, while oxygen diffused inwardly [9, 12]. Pure Cr_2O_3 formed on bulk Cr is known to grow via the outward diffusion of Cr ions along the grain boundaries [16]. Likewise, Cr was seen to diffuse outwardly in Fig. 5. Al_2O_3 grows very slowly and that this primarily occurs by the inward progression of O^{2-} ions along the oxide grain boundaries, although there is some component of outward growth [17]. The amount of Al was smaller than that of Cr in the original film. Hence, the small concentration gradient of Al would diminish the driving force of Al diffusion outward, as compared to Cr. Also, the AlN is largely covalently bonded, while the CrN is a metallic bonding [12]. Hence, Al atoms in the CrAlN film would resist oxidation and their outward diffusion more than Cr atoms.

Fig. 6(a) shows the TEM image of the partially oxidized CrAlN film. Even after oxidation at 800 °C for 20 h, the scale thickness was only 0.15 μm , reflecting excellent oxidation resistance of the film. The unoxidized film had a dense, polycrystalline structure with fine columns whose width was tens of nanometer (Fig. 6(b)). The EDS line profiles shown in Fig. 6(c) indicate that the scale consisted primarily of Cr_2O_3 , where a small amount of Cr and Fe dissolved.

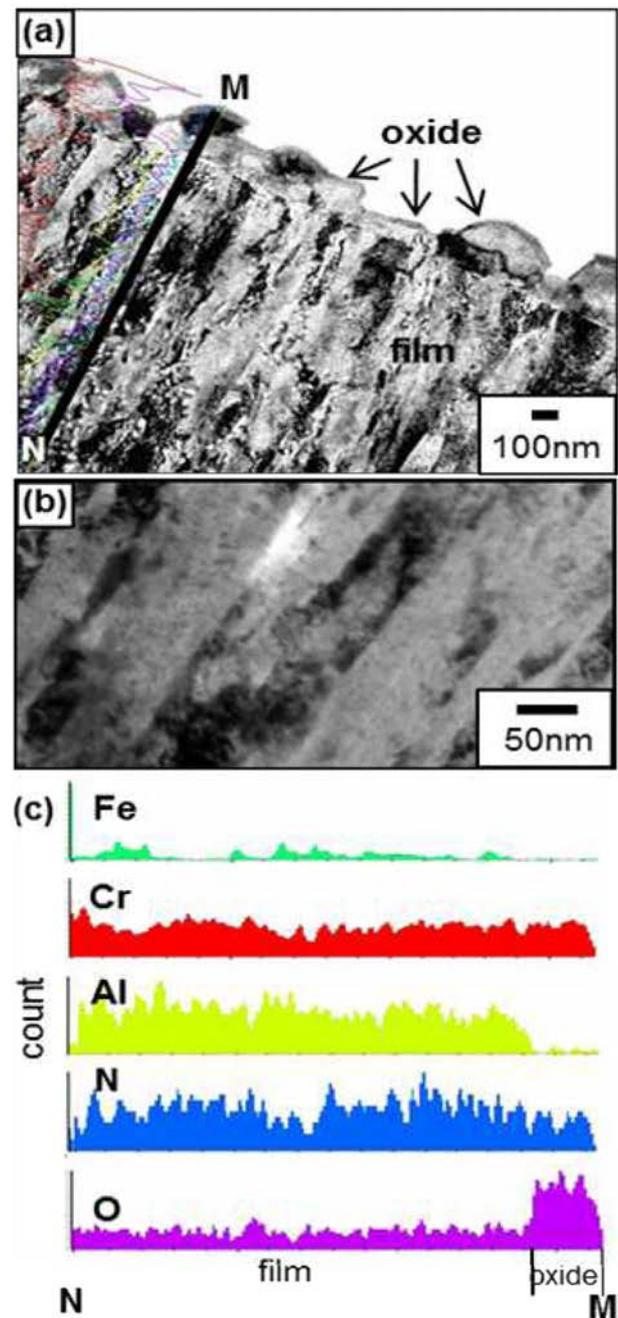


Fig. 6. TEM/EDS analytical results of the CrAlN film after oxidation at 800 °C for 20 h in air. (a) cross-sectional bright field image, (b) enlarged film image, (c) line profiles of Cr, Al, Fe, nitrogen, and oxygen.

Nitrogen existed up to the thin oxide scale. According to Banakh *et al.* [7], $Cr_{1-x}Al_xN$ film with $x < 0.2$ began to oxidize at 500 °C, exhibiting poor oxidation resistance. However, their oxidation time was fixed as 15 min, which might be too short to evaluate the real oxidation resistance.

Fig. 7(a) shows the TEM image of the partially oxidized CrAlN film. When the film oxidized at 900 °C for 20 h, the scale was still only $\sim 0.3 \mu m$ -thick. Such a scale thickness was observed when CrN films oxidized at 800 °C for 4 h [5, 6]. Therefore, it is clear

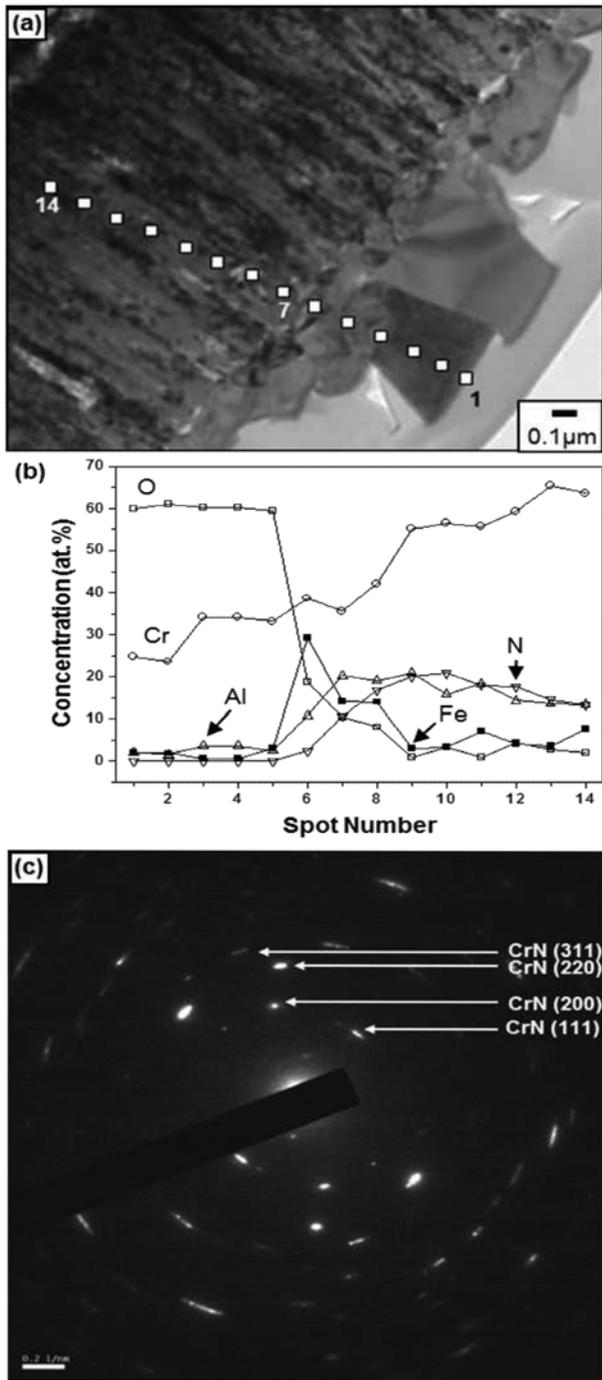


Fig. 7. TEM/EDS analytical results of the CrAlN film after oxidation at 900 °C for 20 h in air. (a) cross-sectional bright field image, (b) concentration profiles of Cr, Al, Fe, nitrogen, and oxygen, (c) selected area electron diffraction pattern at spot 14.

that CrAlN films had better oxidation resistance than CrN films [11, 12]. The concentration profiles across the scale and film are shown in Fig. 7(b). Points 1 to 5 corresponded to oxides. At point 6, new, tiny oxide grains nucleated and grew. Points 7 to 14 were the unoxidized film. Cr diffused out to form the Cr₂O₃ layer, and Al diffused out to dissolve in the Cr₂O₃ layer to a lesser amount, as explained in Fig. 5. Lin *et al.*

[12] previously suggested that amorphous Al₂O₃ may form besides Cr₂O₃ below 900 °C during oxidation of Cr_{1-x}Al_xN film with x = 0.23 and x = 0.6, because Al₂O₃ can maintain amorphous state up to 900 °C. Their suggestion was based on SEM/XRD analyses. However, Al₂O₃ was found to dissolve in polycrystalline Cr₂O₃ oxides in our TEM investigation. Around the scale/film interface such as point 6, round submicron Cr₂O₃ crystallites that were incorporated with Al and Fe ions formed. Nitrogen was absent at points 1 to 5, because nitrogen was released, without being bound to the growing Cr₂O₃ scale. 2.5% nitrogen was present at point 6. The amount of retained nitrogen in the unoxidized film was 11~21% at points 7 to 14, owing to ensuing nitrogen escape during oxidation. Fe was unevenly distributed at points 1-14, indicating that Fe diffused outward from the substrate into the oxide scale owing to the concentration gradient. Zhu *et al.* [8] suggested that pure Cr₂O₃ grains and (Cr,Al)₂O₃ formed in the outer oxide layer. However, their suggestion was based on the XRD/SEM analyses. TEM result confirms that not pure Cr₂O₃ grains but (Cr,Al)₂O₃ grains were more likely to form. When (Cr_{0.6}Al_{0.4}N, Cr_{0.4}Al_{0.6}N) films oxidized at 900 °C for 20 h [10] or (Cr_{0.77}Al_{0.23}N, Cr_{0.4}Al_{0.6}N) films oxidized at 900-1050 °C for 1 h [12], not only Cr₂O₃ but also Al₂O₃ was detected from the XRD analyses. In our study, Al₂O₃ was not detected, because our film with a composition of 31.3Cr-12.9Al-55.3N (at.%) had a lesser amount of Al. Figure 7(c) shows the selected area electron diffraction pattern of the unoxidized CrAlN film. This consisted primarily of CrN, implying that oxidation at the film surface and the inward diffusion of Fe did not affect the original film structure.

Conclusions

CrAlN films were deposited on tool steel substrates by the closed field unbalanced magnetron sputtering method, and their high-temperature oxidation behavior was investigated in order to understand their oxidation mechanism and oxide scales formed. The films displayed superior oxidation resistance due to formation of Cr₂O₃ that was incorporated with some amount of Al₂O₃. The thickness of the scales formed was approximately 0.15 and 0.3 μm when the films were oxidized for 20 h in air at 800 and 900 °C, respectively. The films oxidized via outward diffusion of Cr, nitrogen, and Al, together with inward transport of oxygen. The formed oxide was inevitably Cr₂O₃, where a small amount of Al and Fe ions dissolved, viz., (Cr,Al,Fe)₂O₃.

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