

한국표면공학회지
Journal of the Korean Institute of Surface Engineering
Vol. 34, No. 5, Oct. 2001
<연구논문>

Characterization of oxide scales formed on TiCrN coatings

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TiCrN coatings are widely used as protective coatings to increase the service life of cutting tools, forming tools and machine components because they have high hardness and superior resistance to wear and corrosion. In engineering application, TiCrN is frequently exposed to oxidative atmosphere at high temperatures. Hence, the oxidation property of TiCrN was studied by several investigators¹⁻³. Yet, more studies including microstructure and compositional changes of TiCrN during oxidation are still needed. Their paper aims at describing the high temperature oxidation behavior of TiCrN, based upon the TEM/EDS analyses.

Coatings having compositions of $Ti_{14}Cr_{52}N_{34}$ and $Ti_{36}Cr_{26}N_{38}$ were deposited on a steel substrate (Fe-4.49Cr-1.31Mo-1.10Si-0.96V-0.42Mn-0.37C-0.03P-0.03S, wt%) by an arc-ion plating method. Detail deposition parameter are described elsewhere³. The prepared coatings were oxidized at 800°C for 50 h in air. The oxidized specimens were investigated by a high-resolution TEM equipped with EDS.

Fig. 1 shows the TEM/EDS results of the $Ti_{36}Cr_{26}N_{38}$ coating after oxidation. It was previously found that, under the given oxidation condition, $Ti_{36}Cr_{26}N_{38}$ formed an outer TiO_2 layer followed by

an inner Cr_2O_3 layer due to the selective oxidation of more active element of Ti from the initial oxidation stage³. The bright-field image shown in Fig. 1 (a) displays the oxide scale (spot 1, 2), the unoxidized coating layer (spot 3), and the substrate (spot 4-8). Both the oxides and the coating have quite fine grains. The outermost TiO_2 layer was lost during TEM sample preparation. Within the retained oxide layer, Cr_2O_3 is richer than TiO_2 . The corresponding line profiles of Ti, Cr, Fe and oxygen shown in Fig. 1 (b) indicate that some of the substrate element, Fe, diffuses into the oxide layer, according to the concentration gradient. The enlarge view of the oxide scale (Fig. 1 (c)) that corresponds to the spots 1 and 2 shows very fine, submicrometer-size oxide grains. The origin of void formation between the spot 1 and 2 may be partly due to the outward diffusion of Ti and Cr to form the oxide layer. The EDS spectrum of the oxide layer shown in Fig. 1 (d) again indicates that the oxide layer is composed of Cr_2O_3 and TiO_2 , containing some of dissolved iron ions. It appears that there is no significant amount of nitrogen within the oxide layer, though the initial nitrogen content in the coating was high.

Fig. 2 shows the TEM/EDS results of $Ti_{14}Cr_{52}N_{34}$ after oxidation. XRD tests showed that the oxide

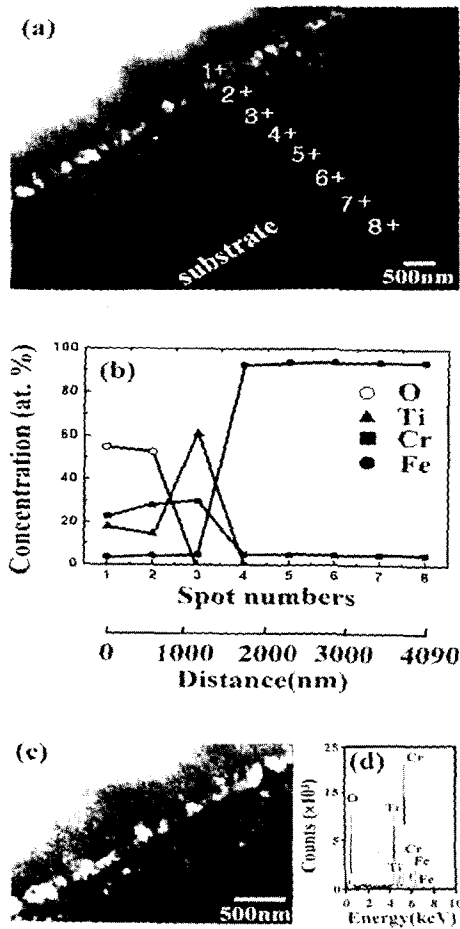


Fig. 1. $Ti_{36}Cr_{26}N_{38}$ coating after oxidation at 800 °C for 50 h. (a) TEM image, (b) EDS concentration profile, (c) TEM image around spot 1 and 2, (d) EDS spectrum of the oxide layer.

scale formed was primarily Cr_2O_3). Though Ti itself is more active than Cr, the low Ti content or activity in $Ti_{14}Cr_{52}N_{34}$ decreased the oxidizing tendency of Ti, so that Cr oxidized preferentially. The outermost oxide layer is retained in Fig. 2(a). The mappings of Ti, Cr, Fe, and oxygen shown in Fig. 2(b) delineate the oxide scale and the unoxidized coating layer. The EDS spectrum shown in Fig. 2(c) depicts the overall oxide composition. It is seen that the Cr_2O_3 -rich scale contains some Ti and Fe ions. As did in $Ti_{36}Cr_{26}N_{38}$, the substrate element, Fe, diffused outwardly to a certain extent.

The above results may be summarized as follows. During oxidation, substrate elements, particularly iron, diffuse outwardly into the scale to a certain extent. The scale consists primarily of TiO_2 and Cr_2O_3 , of which forming-tendency strongly depends on the Ti/Cr ratio in the coating. When the Ti content is high, TiO_2 forms. When the Cr content is high, Cr_2O_3 forms more easily. The growing oxide scales are not pure but have foreign ions such as iron, within the solubility limit.

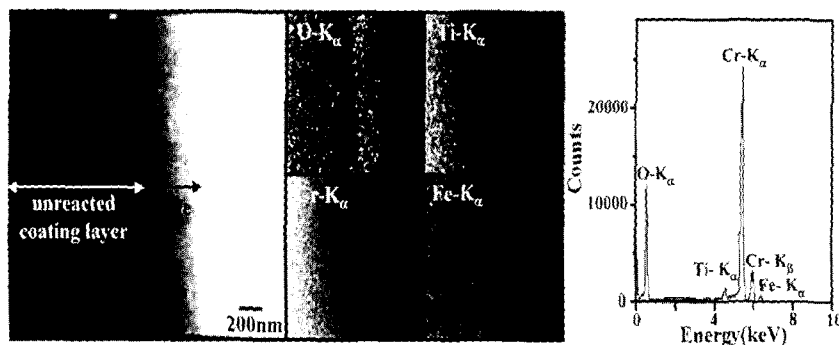


Fig. 2 TEM bright-field image, elemental mappings, and an EDS spectrum taken at the oxide layer. $Ti_{14}Cr_{52}N_{34}$ after oxidation at 800 °C for 50 h.

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