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A Study on Corrosion Characteristics of Multilayered WC-$Ti_{1-x}Al_xN$ Coatings Deposited on AISI D2 Steel

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Abstract

WC-$Ti_{1-x}Al_xN$ multilayered coatings are performed by their periodically repeated structures of lamellae of WC-Ti/WC-$Ti_{1-x}Al_xN$ materials. The WC-$Ti_{1-x}Al_xN$ coatings with variable Al content were deposited onto AISI D2 steel by cathodic arc deposition (CAD) method. The electrochemical behavior of multilayered WC-$Ti_{1-x}Al_xN$ coatings with different phases (WC-$Ti_{0.6}Al_{0.4}N$, WC-$Ti_{0.53}Al_{0.47}N$, WC-$Ti_{0.5}Al_{0.5}N$ and WC-$Ti_{0.43}Al_{0.57}N$) was investigated in deaerated 3.5% NaCl solution at room temperature.

The corrosion behaviors for the multilayered coatings were investigated by electrochemical techniques (potentiodynamic polarization) and surface analyses (X-ray diffraction (XRD), scanning electron microscopy (SEM), and glow discharge optical emission spectroscopy (GDOES)). In the potentiodynamic polarization test, the corrosion current density of WC-$Ti_{0.5}Al_{0.5}N$ was lower than others.

Keywords : GDOES, Potentiodynamic polarization test, Localized corrosion

1. INTRODUCTION

Transition metal nitrides belong to a class of materials that show an usual combination of outstanding material, amongst which are exceptional hardness, chemical stability, and high melting point[1]. Generally, nitride-based hard coatings have proved their capability to increase tool lifetime when exposed to corrosive environments.

This combination of properties has attracted considerable attention and has resulted in numerous industrial applications. Recently, the use of multilayered coatings made from transition metal nitrides TiN, Ti(Al,N) was used to demand protection against mechanical and corrosion environment[2, 3]. Also, WC is extensively employed in machine tools and protective coatings because of its high hardness, chemical stability and high abrasion resistance. Thus, multilayered WC-$Ti_{1-x}Al_xN$ coatings on AISI D2 steel were deposited by cathodic arc deposition method.

The following techniques were used to characterize these coatings; GDOES, XRD, and SEM. The corrosion performances of multilayered coatings were measured in a 3.5% NaCl solution by using electrochemical method.

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PVD coatings most often exhibit pores and pinholes through which a localized corrosion on the substrate steel takes place. This may reduce the lifetime of coated steels drastically. Thus, the calculated porosity is the criteria of the corrosion resistance of coating. Porosity was calculated from potentiodynamic polarization tests.
The purpose of the present investigation was to study the effect of aluminum on the electrochemical properties and the coating microstructures.

2. EXPERIMENTAL

2. 1 Material preparation and coating deposition

Multilayered coatings were deposited on AISI D2 steel (substrate). AISI D2 has the nominal composition in weight percent of 5.0 Cr, 1.3 Mo, 1.0 V, 1.0 Si, 0.5 Mn, 0.37 C, 0.03 P, 0.03 S and 90.77 Fe. AISI D2 steel of a disk-shaped specimen was wet-polished using a 2000 grit SiC for the final step. The base deposition of Ti and TiN layers and the alternative deposition of WC-Ti and WC-$Ti_{1-x}Al_xN$ on AISI D2 steel was repeated 10 times to build up multilayer coatings. The interlayer is deposited primarily to control and set up a residual stress gradient between the multilayer film and the steel substrate[4]. Before the deposition, sputter etch (Ti^+) cleaning for 2min at 150℃ was performed with a negative substrate bias of 700V and followed by deposition of a Ti/TiN interlayer coating. The deposition was done at 150℃ using a negative substrate bias of 200V. Coatings were deposited at a various cathodic arc current (65, 75, 80 and 85A) of aluminum target. The total thickness of the multilayered coatings was about 2.1㎛.

2. 2 Coating characteristics

XRD analysis was used for phase, preferred crystal orientation, and crystallite sizes of the WC-($Ti_{1-x}Al_x$)N coatings. The phases were identified using the JCPDS files. The chemical compositions of the coatings were determined by quantitative GDOES.

2. 3 Corrosion testing

Potentiodynamic polarization curves were obtained using an EG&G PAR 273A. After immersion of the electrode in the solution for 2 h, the potential of the electrode was swept at a rate of $0.166 mVsec^{-1}$ from the initial potential of -250mV vs. open circuit potential (OCP) to the final potential of 1000mV vs. SCE. All potentials recorded were referred to the saturated calomel electrode (SCE) and the counter electrode was a high-purity graphite rod. The calculations of corrosion current density and Tafel slopes were carried out by the PARCALC Tafel analysis program included in the measurement software (M352). A solution of 3.5% NaCl deaerated with N_2 was used for the electrochemical measurements. For most the specimens, the paint adequate for saline environments was used to mask the specimen perimeters. The total exposed surface of tested sample is 0.25㎠.

2. 4 Porosity

The main problem with cathodic arc deposition is the formation of growth defects (droplets or macroparticles) formed from the cathodic arc source. These growth defects can degrade the coating properties. Also, these macroparticles can lead to an increase of the coating porosity, which appears to be a decisive factor in galvanic corrosion with the substrate. The degree of coating porosity has been determined by using electrochemical techniques. The porosity can be determined from the measured polarization resistance. W. Tato et al.[5] established an empirical equation to estimate the porosity rate (P). Porosity corresponds to the ratio of the polarization resistance of the uncoated ($R_{p,u}$) and the coated steels ($R_{p,r-u}$).

$$P = \frac{R_{p,u}}{R_{p,r-u}} \qquad (1)$$

3. RESULTS AND DISCUSSION

3. 1 Coating characteristics

The prepared specimens are designed as WC-$Ti_{0.6}Al_{0.4}N$, WC-$Ti_{0.53}Al_{0.47}N$, WC-$Ti_{0.5}Al_{0.5}N$ and WC-$Ti_{0.43}Al_{0.57}N$. Fig. 1 shows the XRD patterns of the WC-$Ti_{1-x}Al_xN$ coatings deposited by cathodic arc deposition. These data exhibit that different phases and orientation dominate when the aluminum content is varied. As the aluminum content increases, the diffraction peaks are shifted toward higher diffraction angles. TiAlN revealed the fcc structure with (111) texture with a less pronounced texture and the breadth of the diffraction peak. The greater width of the peaks indicates that the size of crystallites has reduced[6,7].

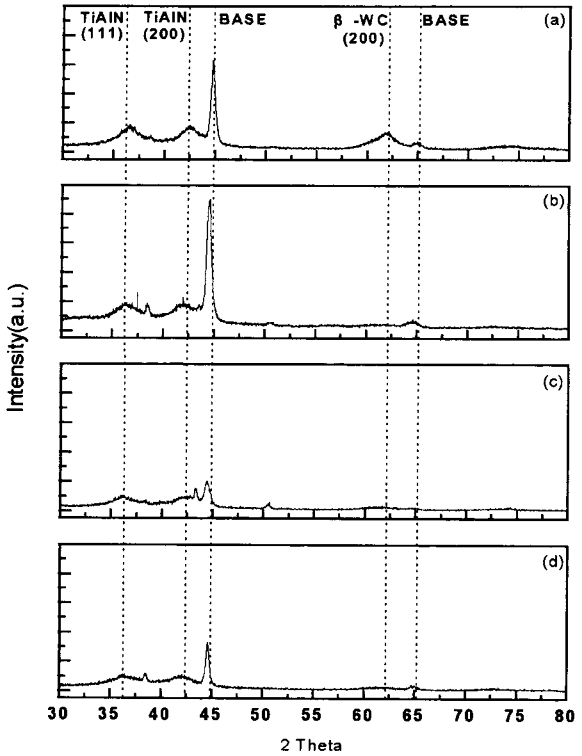


Fig. 1. XRD patterns of WC-$Ti_{1-x}Al_xN$ coatings sputtered on steel substrate;
(a) WC-$Ti_{0.6}Al_{0.4}N$, (b) WC-$Ti_{0.53}Al_{0.47}N$,
(c) WC-$Ti_{0.5}Al_{0.5}N$, (d) WC-$Ti_{0.43}Al_{0.57}N$.

3. 2 Corrosion testing

The results of the potentiodynamic polarization measurements of the multilayered coating are shown in Fig. 2. The anodic polarization curves of multilayered coatings reproduced some features of the substrate in shape. But, some distinctive differences between the substrate and the coated steels are evident. The corrosion current density ($1.883\mu A/cm^2$) of WC-$Ti_{0.5}Al_{0.5}N$ was lower than others, as shown in Table 1. Thus, the decrease in the corrosion current density indicates a decrease in corrosion

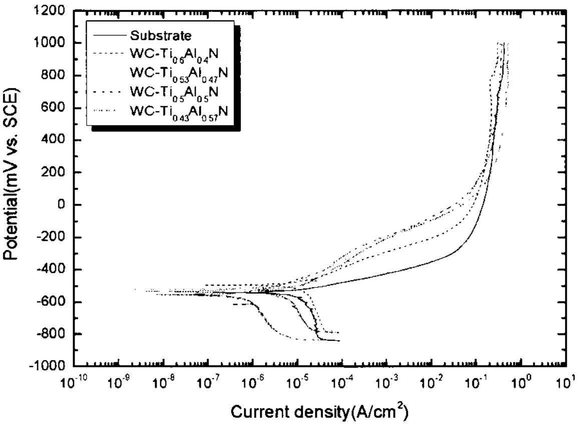


Fig. 2. Polarization curves for WC-$Ti_{1-x}Al_xN$ coatings in a 3.5% NaCl solution.

Table 1. Results of electrochemical experiments

Specimen	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_a (V/decade)	β_c (V/decade)	R_p ($\times 10^3$)	Porosity
Substrate	-541.9	14.69	0.0961	0.2231	1.988	-
WC-$Ti_{9.60}Al_{0.40}N$	-494.5	15.41	0.0918	0.6938	2.288	0.866
WC-$Ti_{0.53}Al_{0.47}N$	-520.3	2.904	0.1317	0.3969	14.805	0.133
WC-$Ti_{0.5}Al_{0.5}N$	-554.9	1.883	0.1274	73.12	29.365	0.068
WC-$Ti_{0.43}Al_{0.57}N$	-529.0	4.753	0.1684	0.396	10.808	0.184

rate. The corrosion appearance is closely related to the surface quality (coated morphology and defects). Since the coating is cathodic to the substrate from the results of potentiodynamic polarization tests (Fig. 2 and Table 1), the defects lead to localized corrosions. If the substrate is exposed to the corrosive environment, the galvanic effect is increased by an unfavorable surface ratio (large cathodic surface/anodic surface) in contact with the solution. Porosity is a characteristic of coatings, manifested by the existence in them of pores. Combining the above equation (1) with the electrochemical determinations gives a porosity of 0.866 for WC-$Ti_{0.6}Al_{0.4}N$, 0.133 for WC-$Ti_{0.53}Al_{0.47}N$, 0.068 for WC-$Ti_{0.5}Al_{0.5}N$, and 0.184 for WC-$Ti_{0.43}Al_{0.57}N$, listed in Table 1. The porosity is somewhat higher in the for WC-$Ti_{0.6}Al_{0.4}N$ coating than others. The calculated porosity values have a correlation with the corrosion resistance of coating.

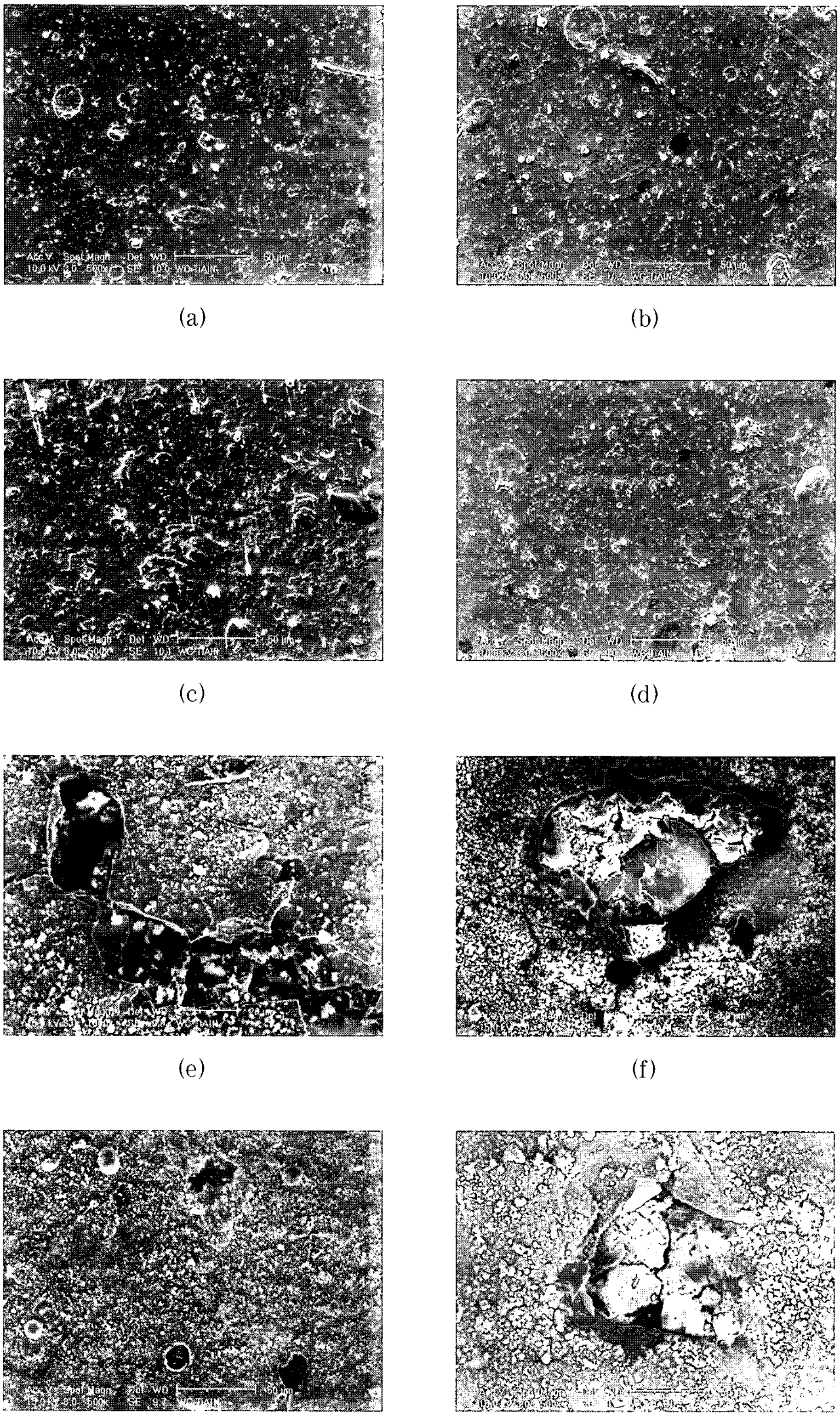
3. 3 Surface morphologies

The surfaces of coatings deposited by CAD methods are very rough. Various radii of droplets from submicrons to tens of microns are distributed to the coated layer, as shown in Fig. 3 (a-d). These droplets can form a local galvanic couple between one part as an anode and another as a cathode. Also, the differences of chemical compositions between droplets and coating matrix lead to susceptibility to localized corrosion. Fig. 3(e-h) shows a corroded surface with localized corrosion products extruding from pre-existing pores in the coating. Also, it was observed that these coatings show the typical cracking appearance of the coating. This behavior could be explained by three aspects ; the corrosion products underneath the coating, the hydrogen evolution and the aggressive anion adsorption[8-10]. For the WC-$Ti_{0.5}Al_{0.5}N$ coating, only slightly uniform corrosion is observed. This coating shows very small and shallow pits. On the other hand, the WC-$Ti_{0.43}Al_{0.57}N$ coating exhibits a severe localized corrosion. These conditions lead to local distribution of the film with formation of local anodic sites at which the current density becomes very high due to the large cathodic area provided by the unpitted passive film.

4. CONCLUSIONS

1) Multilayered WC-$Ti_{1-x}Al_xN$ coatings produced by CAD with increasing Al content are fine-grained and present the broad X-ray diffraction peak.

2) In the potentiodynamic polarization test, a substantial increase in the corrosion resistance was observed for all coated samples. The corro-



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Fig. 3. SEM surface morphologies of WC-$Ti_{1-x}Al_xN$ coatings showing ; ((a) (e) : WC-$Ti_{0.6}Al_{0.4}N$, (b) (f) : WC-$Ti_{0.53}Al_{0.47}N$, (c) (g) : WC-$Ti_{0.5}Al_{0.5}N$, (d) (h) : WC-$Ti_{0.43}Al_{0.57}N$; (a-d) : as-deposited coatings, (e-h) : after-tested coatings).

sion current density of WC-$Ti_{0.5}Al_{0.5}N$ was lower than others.

3) A typical SEM morphology of WC-$Ti_{0.43}Al_{0.57}N$ coating shows the severe localized damage. The major corrosion mechanism for the coatings results from electrolyte penetration through the defects. Thus, this reaction accelerates the corrosion reaction.

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