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# Characterization of Localized Corrosion in Multilayered WC-Ti<sub>1-x</sub>Al<sub>x</sub>N Coatings on AISI D2 Steel

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#### 1. ABSTRACT

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

The corrosion behaviors for the multilayered coatings were investigated by electrochemical techniques (galvanic corrosion tests, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS)) and surface analyses. The multilayer microstructure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and the chemical composition by glow discharge optical emission spectroscopy (GDOES) and Rutherford backscattering spectroscopy (RBS). The results of the galvanic corrosion test indicated small galvanic current densities. In the potentiodynamic polarization test and EIS measurement, the corrosion density of WC-Ti<sub>0.5</sub>Al<sub>0.5</sub>N was lower than others and presented higher R<sub>ct</sub> values than others after 240h immersion time. The SEM observation of the cross-sectional view and sample surfaces reveal a homogeneous structure and typical corroded surface.

#### 2. EXPERIMENTAL

Multilayered coatings were deposited on AISI D2 steel and Si-wafer. The base deposition of Ti and TiN layers and the alternative deposition of WC-Ti and WC-Ti<sub>1-x</sub>Al<sub>x</sub>N on AISI D2 steel and Si-wafer was repeated 10 times to build up multilayers. WC-Ti<sub>1-x</sub>Al<sub>x</sub>N coatings having different x values were formed as a function of aluminum target current. The total thickness of the multilayered coatings was about 2.1 

m. The elemental concentration profiles of the coated samples were determined by GDOES using a LECO (Model DS-850) instrument. The coating structure was determined using XRD method. The phases were identified using the JCPDS files. The periodic structure and the diffusion behavior of interface were determined by means of RBS of 2MeV He<sup>+</sup> incident on a WC-Ti<sub>1-x</sub>Al<sub>x</sub>N multilayered coating.

A Gamry PC3/750 instrument equipped with a zero resistance ammeter (ZRA) was used for galvanic corrosion tests of the coated samples. Potentiodynamic polarization curves were obtained using an EG&G PAR 273A. All

tests were tested in a convential three-electrode electrochemical cell. Electrochemical impedance spectroscopy measurements were performed using commercially available equipment (IM6e, Zahner-electric, Germany). A perturbation AC potential of amplitude ±10mV was applied over the frequency range 100kHz to 1mHz using a logarithmic sweeping frequency 5steps/decade.

### 3. SUMMARY OF RESULTS

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- $Ti_{0.43}Al_{0.57}N$ . 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. RBS observations were shown in order to elucidate the influence of the deposition conditions and the interdiffusion of alternative layer on the corrosion resistance of the multilayered coatings.

The measured galvanic evolutions are respresented in Fig. 5. All multilayered coatings show small galvanic current densities ( $\langle 3.5\mu\text{A/cm}\rangle$ ). The corrosion current density ( $1.883\mu\text{A/cm}\rangle$ ) of WC-Ti<sub>0.5</sub>Al<sub>0.5</sub>N was lower than others. It can be clearly seen that the WC-Ti<sub>0.5</sub>Al<sub>0.5</sub>N coating leads to a higher impedance in the EIS spectra. The WC-Ti<sub>0.5</sub>Al<sub>0.5</sub>N coating presents higher R<sub>ct</sub> values than others after 240h immersion time, as shown in Fig. 9. This result indicates that the WC-Ti<sub>0.5</sub>Al<sub>0.5</sub>N coating exposed to the corrosive environment formed the corrosion products plugging the pores and increasing the resistance pathway.

A typical SEM morphology of WC- $Ti_{0.43}Al_{0.57}N$  coating shows the severe localized damage with intergranular attack of the steel substrate. The major corrosion mechanism for the coatings results from electrolyte penetration through the defects. This is responsible for the hydrogen evolution causes to reduce the diffusion layer thickness. Thus, this reaction accelerates the corrosion reaction.

The major corrosion mechanism for the coated steels aries from electrolyte penetration in the porosity, which may eventually lead to the development of localized corrosion. Especially, the steel substrate exposed to the electrolyte will continue to undergo hydrosis reactions  $(M^{2+} + H_2O \Rightarrow M(OH)^+ + H^+)$ , which lower the pH.

## 4. REFERENCES

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