

# Corrosion Behavior of Hard Coated Ti-Zr-N Film on the Tool Steels

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To investigate the corrosion behavior of tools steel surface in various coating film, the surface of hard coated Ti-Zr-N film on the tool steel by using magnetron-sputtering methods was researched using various experimental methods. STD 61 steels were manufactured by using vacuum furnace and solutionized for 1hr at 1050 °C. Steel surface was coated with Ti-Zr-N film at 150 °C and 100W for 1h by using DC-sputtering equipment. Surface characteristics of Ti-Zr-N film coated specimens were investigated by OM, XRD, FE-SEM and nano-scratch tester. And corrosion behaviors of the coated specimen were investigated by polarization test and electrochemical impedance spectroscopy(EG&G Co, PARSTAT 2273. USA). It was found that Ti-Zr-N film coated sample had a thick coated layer and showed a good wear resistance and corrosion resistance of surface compared with ZrN and TiN coated sample. The corrosion resistance and mechanical property of Ti-Zr-N film coated STD 61 alloy increased as sputtering time increased.

**Keywords :** *Ti-Zr-N film, STD 61 steel, magnetron-sputtering, corrosion behavior*

## 1. Introduction

STD 61 has been widely used for tools, metallic mold and die for press working because of its favorable mechanical properties such as high toughness, and creep strength as well as excellent oxidation resistance.<sup>1)</sup> Recently, many studies were attempted to improve the wear resistance of tool steel materials by coating with the inert bioinert nitrides such as TiN and ZrN.<sup>2)</sup> TiN and ZrN possess the same crystal structure(cubic) and share similar properties, such as high melting point, good chemical and thermal stability, high grade hardness and metallic conductivity. Both of these nitrides are known to be stable refractory compounds.<sup>3)</sup>

However, these substances have not been applied in tools steel at the same time like a composite. The methods of coating currently in use are sputtering, ion plating, and laser ablation. Physical vapor deposition could physically bond the interface between the substrate and coating film so that surface strength and surface roughness could be minimized.<sup>4)</sup> DC-sputtering is already used for the purpose of hardening the surface of metal alloys after the drastic development of hardware for sputtering experiments and

in controlling plasma. Unlike carburizing done at high temperature, sputtering is done at low temperature using plasma so that surface hardening could be obtained while minimizing material change. We can get the composite film by using sputtering on the tools surface.<sup>5)</sup>

In this study, to investigate the corrosion behavior of tools steel surface in various coating film, the surface of hard coated Ti-Zr-N film on the tool steel by using magnetron-sputtering methods was researched using various experimental methods.

## 2. Experimental details

### 2.1 Preparation of samples

In this study, STD 61 tool steel was used for substrate with following composition; 0.30% C, 0.73% Si, 0.69% Mn, 0.12% S, 4.95% Cr, 1.01% Mo, 0.41% V. Heat treatment was subsequently performed at 1050 °C for 1 hr in an argon atmosphere to homogenize the microstructure, followed by furnace cooling. Specimens for electrochemical test were prepared by standard sequential metallographic polishing with emery papers and then given a polish with 0.3 μm Al<sub>2</sub>O<sub>3</sub> slurry. All polished specimens were ultrasonically cleaned and degreased in acetone.

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**Table 1. The condition of TiN, ZrN, Ti-Zr-N film deposition**

Coating condition	TiN film	ZrN film	TiN/ZrN film
Target	Ti(99.998%)	Zr(99.99%)	Ti/Zr(99.998%)
Base Pressure	10 <sup>-6</sup> Torr	10 <sup>-6</sup> Torr	10 <sup>-6</sup> Torr
Working Pressure	10 <sup>-3</sup> Torr	10 <sup>-3</sup> Torr	10 <sup>-3</sup> Torr
Gas	N <sub>2</sub> (35sccm)	N <sub>2</sub> (35sccm)	N <sub>2</sub> (35sccm)
	Ar(5sccm)	Ar(5sccm)	Ar(5sccm)
Operation temperature	150 °C	150 °C	150 °C
Pre-sputtering	20min	20min	20min
Sputtering time	1hr	1hr	1hr
Sputtering power	200W	200W	200W

## 2.2 Deposition of Ti-Zr-N film

The Ti-Zr-N coatings were deposited on the specimen surface by using the DC-sputtering system. The Ti and Zr targets were placed by positioning the substrate over each target for Ti-Zr-N layer. The deposition parameters used in the Ti-Zr-N layers were given in Table 1. Sputtering of Ti and Zr on cleaned alloys surface were performed by means of a DC and RF magnetron sputtering (CX-600S, COMDEL, Korea) system. Pure Ti and Zr (99.998 %) were used for the coating. Before coating, the working chamber was evacuated to  $1.0 \times 10^{-6}$  Torr and kept at room temperature for 2 hr. The RF power for Ti deposition was 100 W, and the working pressure was kept at  $1.0 \times 10^{-3}$  Torr. During sputtering of TiN, a reactive gas mixture of argon (Ar) and nitrogen (N<sub>2</sub>) was used for deposition onto the metal plate. The feed of Ar (99.9999 % pure) and N<sub>2</sub> (99.9995 % pure) gases was controlled by a mass-flow controller. The mixture of gas was maintained by inlet of Ar and N<sub>2</sub> gas at a ratio of 1:5 (inflation volume; Ar: 5 sccm, N<sub>2</sub>: 35 sccm) (sccm stands for standard cc/min) for 5 min. Pre-sputtering and deposition times were 20 min and 60 min, respectively. The coated samples were crystallized in Ar atmosphere at 1000 °C for 1 hr.

## 2.3 Characterization of Ti-Zr-N film coated surface

Ti-Zr-N coated specimens were investigated by OM (optical microscopy), XRD (X-ray diffractometer), FE-SEM and nano-scratch tester. X-ray diffraction was employed to identify the phases in the alloys, using a diffractometer (X'pert Pro MPD, Philips, Netherlands) and Cu K $\alpha$  radiation. Corrosion behaviors of the Ti-Zr-N film coated specimen were investigated by potentiostat (EG&G Co, PARSTAT 2273, USA). The potentiodynamic tests were carried out with a scan rate of 1.667 mVs<sup>-1</sup> from -1500 mV to 2000 mV in 3.5 % NaCl solution at 25 °C using

**Table 2. Values of corrosion current density ( $I_{corr}$ ) and corrosion potential ( $E_{corr}$ ) determined for coated STD 61 alloys from potentiodynamic polarization curves in 3.5% NaCl solution**

STD 61 Alloy	Non Coated	TiN coating	ZrN coating	TiN/ZrN coating
$I_{corr}$ (A/cm <sup>2</sup> )	$1.880 \times 10^{-6}$	$7.581 \times 10^{-6}$	$2.014 \times 10^{-6}$	$3.419 \times 10^{-7}$
$E_{corr}$ (mV)	-420	-360	-410	-589

a potentiostat (EG&G Co., PARSTAT 2273, USA). A conventional three-electrode system with high-density graphite as counter electrode and saturated calomel electrode (SCE) as reference was used. Preparation of the sample was as described above. The sample edges were carefully covered with epoxy to avoid the possible crevice attack. The electrolyte was deaerated using high-purity Ar gas for 30 min before starting the experiment. Deaeration was continued at a uniform rate during the experiment. The Tafel extrapolation was followed to determine the corrosion parameters; based on a software-based approximation. EIS tests were conducted at the open circuit potential at the frequency range of 10<sup>-2</sup> Hz to 10<sup>5</sup> Hz. A similar three electrode set-up was used for EIS studies. The amplitude of ac signal was 10 mV and 5 points per decade was used. An equivalent circuit was assigned for the acquired data and the data were curve fitted using ZSimpWin software.

## 3. Results and discussion

### 3.1 The microstructure of Ti-Zr-N film coated surface

Fig. 1 is OM micrographs of STD 61 tool steel. Fig. 1(a) is the sample of non-heat treated STD 61 alloy and Fig. 1 (b) is sample of heat treated STD 61 alloy in Ar atmosphere at 1050 °C for 1 hr and then furnace cooling. It was shown the martensitic structure both of them, but, heat treated sample was finer structure than non-heat treated sample. The spherical MC, M<sub>3</sub>C and M<sub>23</sub>C<sub>6</sub><sup>(6)</sup> precipitates were uniformly formed with black dot in the heat treated STD 61 tool steel as shown in Fig. 1.

Fig. 2 shows the XRD results of TiN, ZrN and Ti-Zr-N coated STD 61 alloys. These samples were crystallized in Ar atmosphere at 1000 °C for 1 hr. It can be seen that TiN(111), ZrN(111), Fe(110), and Fe(200) peaks appeared on the surface, respectively. The researcher reported that the preferred growth direction of TiN and ZrN film was (111) and (200) orientations.<sup>(7)</sup> Therefore, we can confirmed that growth orientation of TiN and ZrN film was (111) and (200) directions on the coated surface. The Ti-Zr-N coated surface showed the uniformly ordered finer

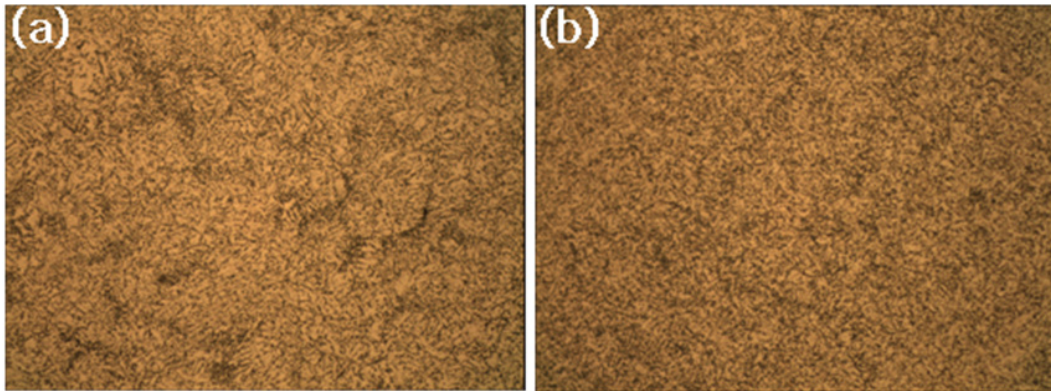


Fig. 1. OM micrographs showing the microstructure of STD 61 alloy. a) before heat treatment, and b) after heat treatment.

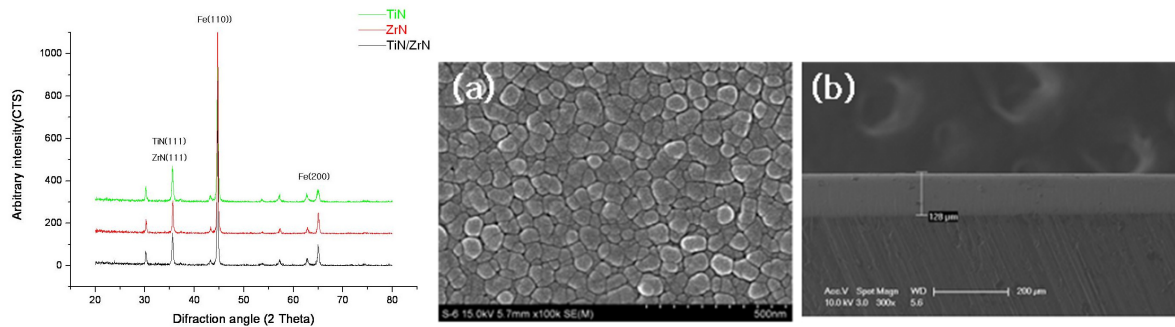


Fig. 2. FE-SEM surface morphology and X-ray diffraction patterns of Ti-Zr-N coated STD 61 alloy.

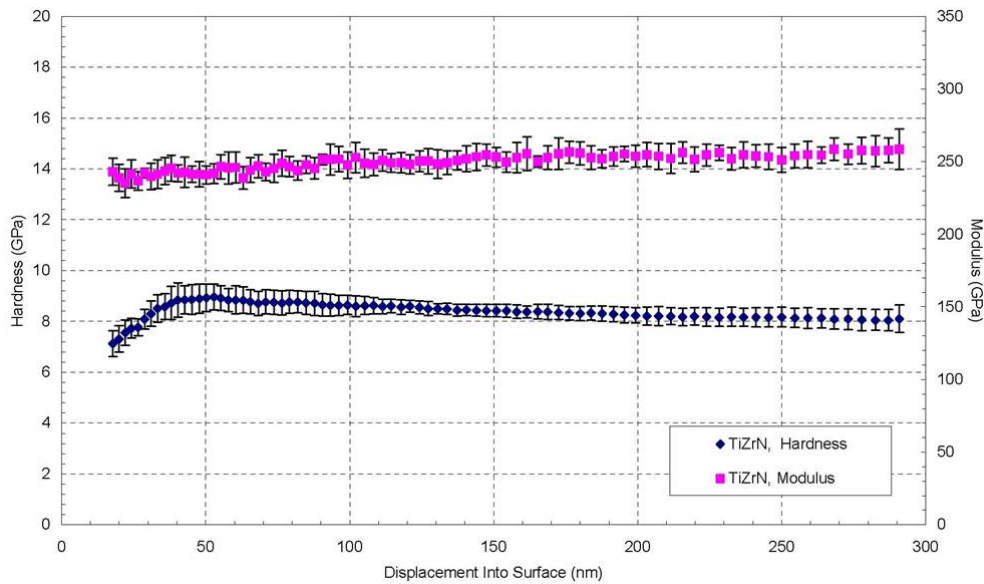


Fig. 3. Nano-hardness and elastic modulus of Ti-Zr-N coated STD 61 alloy.

granular and dense shape without defect such as macro-particle. Composite layer was composed of Ti, Zr and nitrogen with 140  $\mu\text{m}$  thickness.

### 3.2 Hardness and wear resistance of Ti-Zr-N film coated surface

Fig. 3 shows the results of nano-hardness and elastic modulus test of Ti-Zr-N coated STD 61 alloys. ZrN coated

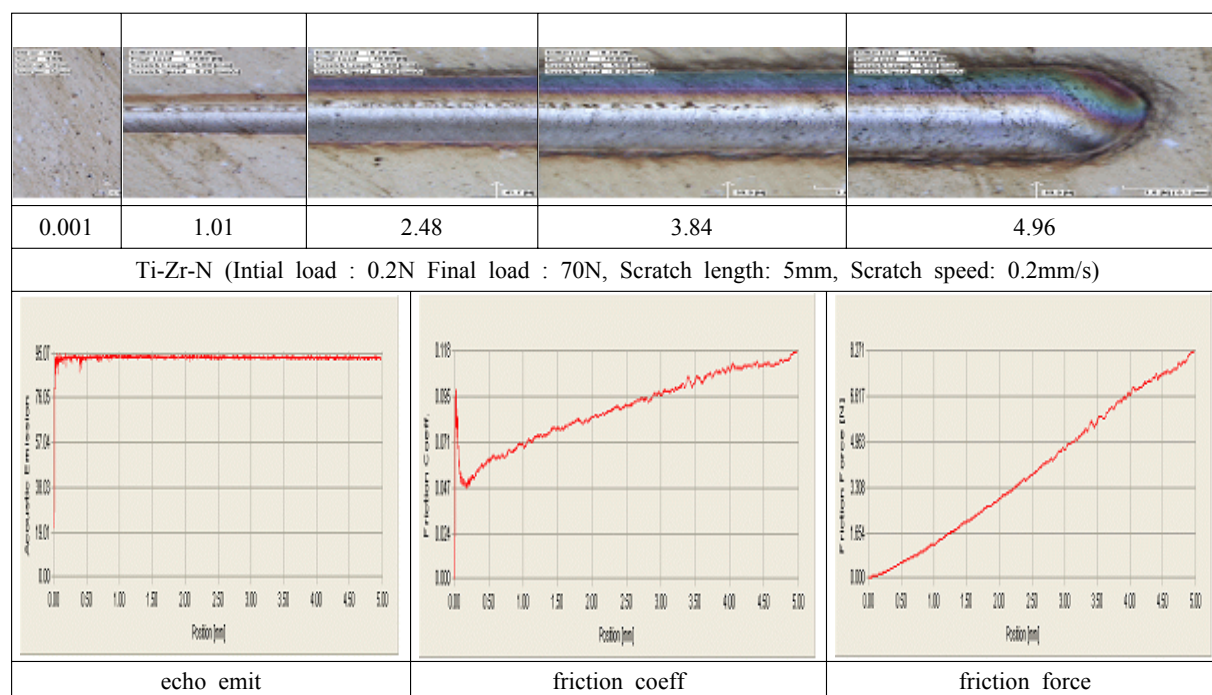


Fig. 4. Scratch test performed on a Ti-Zr-N coated STD 61 alloy.

sample showed higher value of nano hardness and elastic modulus than that of TiN coated sample. In the case of Ti-Zr-N coated sample, it showed the mixed characteristics between TiN film and ZrN film. From the previous report, TiN film has lower value of hardness than ZrN film due to more stable ZrN film.<sup>8)</sup> From the scratch test in the Fig. 4, the friction coefficient and force of Ti-Zr-N coated sample was increased with distance. Especially, friction force of Ti-Zr-N coated sample was 0.8 N at 1 mm from start position, whereas, TiN and ZrN showed the 1.1 N and 1.09 N. It is confirmed that Ti-Zr-N coated surface can be given to improve the wear and corrosion characteristics of tool surface due to dense coated layer without coating defects as shown in Fig. 2.

### 3.3 Corrosion behavior of Ti-Zr-N film coated surface

Fig. 5 shows potentiodynamic polarization curves of coated STD 61 alloys after potentiodynamic test in 3.5% NaCl solution. From the Fig. 5, TiN coated sample showed the higher corrosion potential and corrosion current density than other coated film. ZrN coated sample has the similar corrosion characteristics to non-coated sample. The corrosion current density of Ti-Zr-N coating sample was the lower value compared to other specimens. The corrosion current density is related with corrosion rate, therefore, Ti-Zr-N film has low corrosion rate. The reasons why Ti-Zr-N coated sample has the lowest value of corrosion

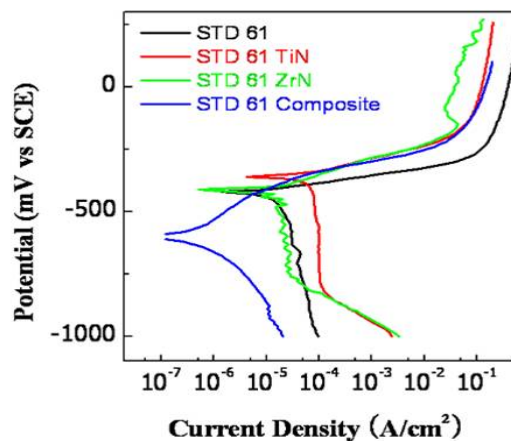


Fig. 5. Anodic polarization curves of coated STD 61 alloys after potentiodynamic test in 3.5% NaCl solution.

current density are that composite layer protects from releasing metal ion by  $\text{Cl}^-$  ions due to dense coated layer without coating defects and forms the inhibition layer by  $\text{N}^3-$  from Ti-Zr-N film.<sup>9)</sup> In the Fig. 5, polarization curve of Ti-Zr-N coated sample was shifted to left side from polarization curve of non-coated sample. It is confirmed that Ti-Zr-N film has a good corrosion resistance.

Fig. 6 shows the non-destructive impedance spectra recorded for the as STD 61 alloy, TiN coated, and ZrN coated surfaces in the electrolyte. Impedance measurements were carried out after 30 min of initial immersion in the



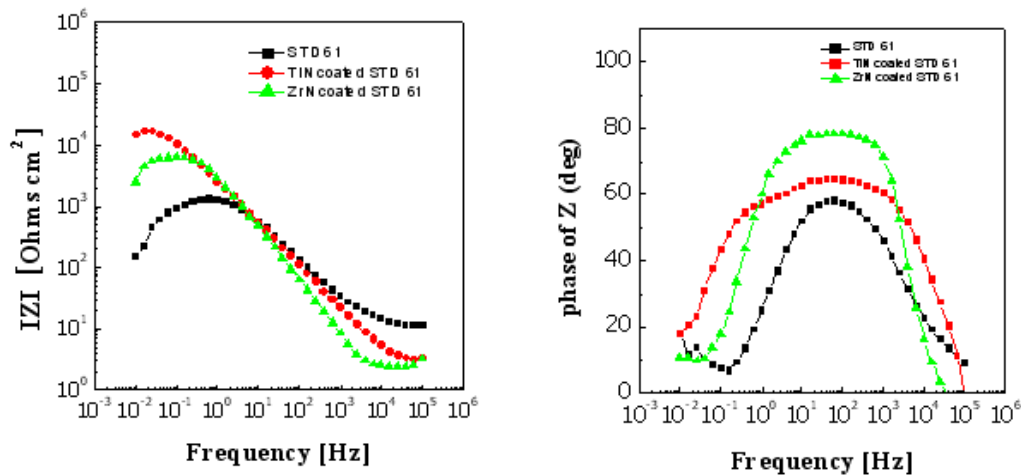


Fig. 6. EIS results of non-coated and Ti-Zr-N coated STD 61 alloy after A.C. impedance test in 3.5% NaCl solution at  $36.5 \pm 1^\circ\text{C}$ .

Table 3. Corrosion parameters obtained from EIS data after A.C. impedance test in 3.5% NaCl solution

Samples	$R_s(\Omega\text{cm}^2)$	$R_1(\Omega\text{cm}^2)$
STD 61	11.5	1,310
TiN coated STD 61	3.1	17,307
ZrN coated STD 61	2.3	6,620

electrolyte. A high impedance value of the order of  $10^5 \sim 10^6 \text{ ohm cm}^2$  was obtained at low and medium frequencies, suggesting good corrosion resistance for both the TiN and ZrN surfaces. The phase shift plot showed two time constants in the case of both the TiN and ZrN coated surfaces. This corresponds to the presence of two interfaces: the high corrosion resistant barrier layer and the outer granular surface and layer. The higher phase angles obtained for these surfaces compared with that of the non-coated surface at the high-frequency region is attributed to the TiN and ZrN film coating. The increase in phase angles at the high-frequency region may be associated with the ZrN and TiN film nature of the coated layer. The electrochemical studies suggested that the Ti-Zr-N coated surface indicates a good corrosion resistance with an enhanced passivation against  $\text{Cl}^-$  ion.

#### 4. Conclusions

- 1) The microstructure of heat treated alloy showed martensitic structure with spherical MC,  $\text{M}_3\text{C}$  and  $\text{M}_{23}\text{C}_6$  precipitates distributed uniformly in the matrix.
- 2) The ZrN coated surface showed finer granular than

that of TiN coated surface. The coated layer structures of ZrN and TiN were grown to (111) and (200) preferred orientation.

3) Nano-hardness and elastic modulus of Ti-Zr-N coated film were higher than that of other specimens. In case of Ti-Zr-N coated film, nano-hardness and elastic modulus showed the hybrid character between TiN film and ZrN film.

4) The corrosion current density of Ti-Zr-N coated film was lower than those of non-coated, TiN coated, and ZrN coated film. Ti-Zr-N coated surface had a high corrosion resistance.

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