

Corrosion behavior of TiAlN film on AISI 4140 steel

Thipusa WONGPINIJ¹, Pornwasa WONGPANYA^{1,*}, Chanan EUARUKSAKUL²,
Pat PHOTONGKAM² and Nirun WITIT-ANUN^{3,4}

¹School of Metallurgical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

²Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand

³Department of Physics, Faculty of Sciences, Burapha University, Chonburi 20131 Thailand

⁴ThEP Center, Commission on Higher Education, Ministry of Education, Bangkok 10400, Thailand

Abstract

The corrosion behavior of uncoated and TiAlN coated on AISI 4140 steel were studied by an electrochemical technique in 3.5 wt% NaCl solution at pH value of 2, 7 and 10 at room temperature. The corrosion potential (E_{corr}), pitting potential (E_{pit}), corrosion rate (R_{mmy}) and passive region in polarization curves were analyzed and compared. After electrochemical testing, samples surface was characterized by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) and X-ray photoemission electron microscopy (X-PEEM). The results indicated that the TiAlN coated samples yielded better corrosion resistance than the uncoated samples. The coated samples had lower corrosion rate (R_{mmy}) than uncoated samples at all pH condition. In addition, the TiAlN coated sample tested in solution at pH 7 showed the widest passive potential region.

Keywords : TiAlN film, AISI 4140 steel, NaCl solution, Electrochemical technique

Introduction

AISI 4140 low alloy steel, containing chromium, molybdenum and manganese, is widely used in automotive industry and engineering application. The AISI 4140 low alloy steel is the most attractive steel because it does not have only good mechanical properties but it is also cheap and is easily fabricated as compared to other steels. Examples of automotive parts produced from AISI 4140 low alloy steel are shaft, connecting rod, crankshaft, screw, gear and etc. In order to enhance mechanical and chemical properties of automotive parts in particular for abrasion, wear and corrosion resistance, surface technology has been extensively applied e.g. nitriding, carburizing, chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spraying and etc. The widely used surface technology is physical vapour deposition because it is a clean technology and its performance fulfils requirement of engineering application.⁽¹⁾ Titanium nitride (TiN) is a popular PVD film because it has a good combination of wear resistance and corrosion resistance. Unfortunately, TiN cannot be used at high temperature because its limitation is poor oxidation resistance at temperature above 500°C.⁽²⁾ In order to improve oxidation resistance of TiN, aluminium was added into TiN film; subsequently TiAlN film was produced.⁽³⁾ TiAlN film remains hardness and oxidation resistance at high temperature,

thus it significantly increases life time of engineering part as compared to TiN film.⁽⁴⁾ TiAlN film is not only used at high temperature, but it is also widely used in the automotive part at room temperature. Since the automotive part and engineering part were used in service environments e.g. lubricant, engine coolant and humidity; corrosion is possible to be appeared. Therefore, corrosion test by an electrochemical method is a proper approach to solving the problem of metal corrosion. This paper concentrates on the evaluation of the corrosion behavior of TiAlN film deposited on AISI 4140 steel by DC Magnetron Sputtering. The corrosion behavior of the as deposited samples and uncoated samples in 3.5 wt% NaCl solution at pH 2, 7 and 10 was tested by an electrochemical method. After electrochemical testing, the corroded surface of samples was investigated by scanning electron microscopy (SEM) with chemical composition analysis by X-ray photoemission electron microscopy (X-PEEM).

Materials and experimental procedures

Sample preparation

The AISI 4140 steel was surface-coated with TiAlN film. The chemical composition of the AISI 4140 steel was determined by emission spectrometer as shown in Table 1. The samples were cut in to rectangular

*Corresponding author E-mail : au_thip@hotmail.com

Table 1. Chemical composition of 4140 steel (in wt.%).

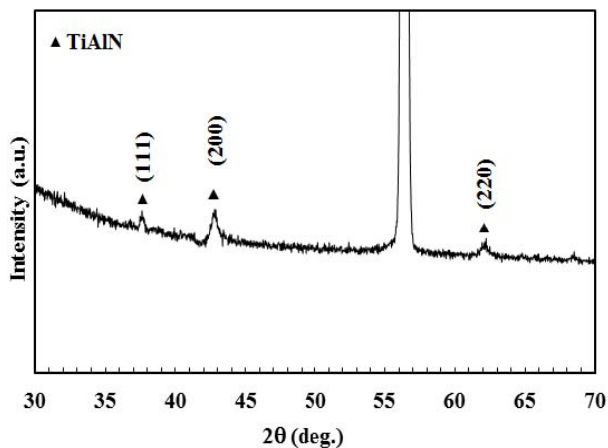
Grade	C	Mn	Cr	Si	Mo	Fe
AISI 4140	0.43	0.82	1.03	0.24	0.19	Bal.

Table 2. Deposition condition of TiAlN film.

Ar flow rate	16 sccm
N ₂ flow rate	8 sccm
Base pressure	5.0×10^{-5} mbar
Working pressure	5.0×10^{-3} mbar
Current Ti	900 mA
Current Al	300 mA
Deposition time	120 min
Target-to-substrate spacing	18 cm
Ar flow rate	16 sccm

Table 3. Chemical composition (at.%) of TiAlN film.

TiAlN film	Ti	Al	N
	32.05	6.42	61.53

**Figure 1.** XRD diffraction pattern of TiAlN film in a grazing incidence mode.

pieces size of $18 \times 18 \times 3$ mm. They were heated up to 850°C for 30 minutes and oil-quenched. After heat treatment, hardness of the samples is around 54 HRC. The samples were polished by a silicon carbide paper with various grit numbers such as 180, 320, 400, 600, 800, 1000 and 1200, respectively. Then, each sample was polished with aluminium oxide from $1.0 \mu\text{m}$ up to $0.5 \mu\text{m}$. Finally, the samples were rinsed by distilled water, acetone and were air-dried before coating.

Film preparation

The DC Magnetron Sputtering process was employed using titanium with 99.7% and aluminium with 99.9995% targets. The TiAlN film was deposited on the substrate with the condition as shown in Table 2. The composition of TiAlN coated on AISI 4140 steel

was evaluated by EDX as shown in Table 3. Main components in TiAlN film are Ti and N, whereas Al is slightly instituted in the matrix of TiN. While the crystallographic characterization of the TiAlN film was studied by a grazing incidence X-ray diffraction technique (GIXRD) as shown in Figure 1. There are three peaks of TiAlN film that are corresponded to the TiAlN (111), (200) and (220) plane at 2θ angles of 37.62° , 42.80° and 62.22° , respectively. The dominant orientation of TiAlN film in this study is the (200) plane. The strong orientation in the (200) plane is also reported by others.^(5,6) The reason for the dominant orientation of the TiAlN in the (200) plane is from the high flow rate of N_2 (over 6 sccm) during deposition process.^(7,8)

Normally, TiAlN and TiN films have similar orientation peaks e.g. in (111) (200) and (220) plane but the peaks of the TiAlN film shifts slightly to higher 2θ value than that of the TiN film. This is a result from the changes of crystallographic orientation caused by the addition of Al element in TiN film.⁽⁹⁾

Corrosion testing

The corrosion behavior of uncoated samples (AISI 4140 steel) and TiAlN coated samples (TiAlN coated on AISI 4140 steel) were evaluated by electrochemical technique. Experiments were performed using a Potentiostat analyzer. An electrochemical cell with a three electrode cell was used. The uncoated samples and TiAlN coated samples were used as a working electrode. Graphite and silver/silver chloride (Ag/AgCl electrode) were used as a counter electrode and a reference electrode, respectively. The corrosion behavior

of samples was firstly started by measuring the open circuit potential (OCP). Then, the samples were polarized to potentials ranking from -900 mV to +200 mV at a scan rate of 0.01 V/s in 3.5 wt% NaCl solution at pH 2, 7 and 10 at room temperature. The pH of solution was adjusted by addition of solution of hydrochloric acid 1 M (HCl) and solution of sodium hydroxide 1 M (NaOH) for acidic and alkaline solution, respectively. The polarization curves were used to study the corrosion behavior of the samples in solution. The polarization curves were carried out in order to obtain important corrosion parameters e.g. corrosion potential (E_{corr}), corrosion current density (I_{corr}), pitting potential (E_{pit}) and corrosion rate (R_{mmy}). After that, corroded surface was investigated by scanning electron microscopy (SEM), X-ray photoemission electron microscopy (X-PEEM) and X-ray absorption spectroscopic (XAS).

Results and discussions

Corrosion behavior

Figure 2 shows polarization curves of the uncoated and TiAlN coated samples tested in 3.5 wt% NaCl solution at pH 2, 7 and 10. The important corrosion

parameters, evaluated from the polarization curves and based on Tafel Equation (10), are shown in Table 4. Even though corrosion current density of TiAlN coated samples is higher than that of uncoated samples, but the equivalent weight (5.65 g) and density (4.81 g/cm^3) of TiAlN film are lower than the equivalent weight (26.62 g) and density (7.87 g/cm^3) of AISI 4140 steel. (11) Thus, a corrosion rate (R_{mmy}) of TiAlN coated samples is lower than that of uncoated samples and it also corresponds to the other works. (12,13) Corrosion resistance of TiAlN coated samples is attributed to the presence of titanium and aluminum atom within TiAlN film. After TiAlN film reacted with the corrosive environment, stable oxide films, which are composed of oxygen, titanium and aluminum, are generated. These oxide films are useful for corrosion resistance of TiAlN film. (14)

At pH 2, TiAlN coated sample has a narrow passive region as compared with the other samples tested at pH 7 and pH 10 as shown in Figure 2 a. This would be an effect of chloride ion from hydrochloric acid added in the solution. It is well known that increasing chloride ion leads to increase in the rate of film breakdown. (15) Moreover, the samples were severely deteriorated by exposure to the acidic solution. (16)

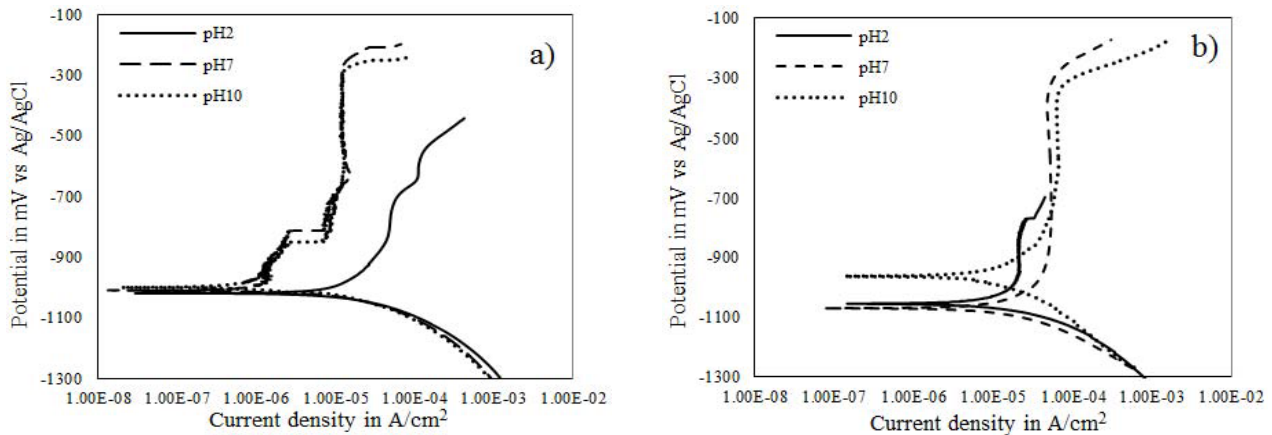


Figure 2. The polarization curves of samples in 3.5 wt% NaCl solution at pH 2, 7 and 10. a) Uncoated samples b) TiAlN coated samples.

Table 4. The important values from the polarization curves of uncoated and TiAlN coated samples.

pH	Samples	E_{corr} (mV)	I_{corr} ($\mu\text{A/cm}^2$)	E_{pit} (mV)	R_{mmy} (mm/y)
2	Uncoated	-1020	6.0	-	0.0663
	TiAlN	-1056	3.5	-768	0.0134
7	Uncoated	-1010	0.45	-208	0.0049
	TiAlN	-1071	0.65	-250	0.0024
10	Uncoated	-998	0.4	-250	0.0044
	TiAlN	-965	1.0	-315	0.0038

At pH 7 and 10, the passive region of TiAlN coated sample is clearly observed in polarization curves as shown in Figure 2 b. The TiAlN coated samples tested at pH 7 (Epit: -250 mV) shows higher pitting potential than the TiAlN coated samples tested at pH 10 (Epit: -315 mV) and pH 2 (Epit: -768 mV), respectively. The width of passive region of TiAlN coated sample indicates the stability of the passive film. The reason, why the TiAlN coated sample has the widest passive region at pH 7, is might be from the fact that the aluminium oxide responsible for corrosion resistance is stable in solution having pH 5-8.⁽¹⁷⁾

Microstructure evaluation

Figure 3 shows surface images of uncoated and TiAlN coated samples after corrosion test. Significantly, the pH of 3.5 wt% NaCl solution affects the degradation of samples. The samples at pH 2 show more degradation than the samples at pH 10 and pH 7, respectively. Therefore, the corrosion product on surface of the samples at pH 2 is higher than that of the samples at pH 10 and pH 7 for uncoated and TiAlN coated samples.

In order to understand corrosion resistance of TiAlN film, the TiAlN coated sample at pH 2 selected to be surface-investigated by X-ray photoemission electron microscopy (X-PEEM) and to be chemical-analyzed by XAS spectra because it shows the worst corrosion resistance in a group of TiAlN coated samples, as shown in Figure 4 and Figure 5, respectively.

Two areas e.g. non-corroded area (area 1: TiAlN film) and corroded area (area 2) were investigated and compared. There are five main components in the film e.g. Ti, N, Fe, O and Al which were examined by XAS spectra. Such components can be used to explain how TiAlN film inhibits corrosion. Obviously, there are three peaks of Ti L-edge, N K-edge and O K-edge corresponded to photon energy ranges of 455-465 eV, 390-420 eV and 530-550 eV, respectively for non-corroded area or TiAlN film.⁽¹⁸⁻²⁴⁾ This means that there are a lot of important elements responsible for corrosion resistance e.g., Ti and N in the film; this area is thus not corroded. There is no peak of Al. This might be from the fact that there is a low content of Al dissolved in the TiAlN film as described previously in the part of film preparation and as shown in Table 3.

At the corroded area (area 2), not only chemical states of main components that are responsible for corrosion resistance of TiAlN film e.g., Ti L-edge, N K-edge and O K-edge appear, but XAS spectrum of Fe L_{3,2}-edge at a photon energy of 700-730 eV also

occurs.^(20,21) These mean that two components, i.e., Ti and Fe, are oxidized. The oxidation of Ti to produce titanium oxide (TiO_x) is a vital key for corrosion protection of TiAlN film.⁽²⁵⁾ While, the spectra of Fe L_{3,2}-edge from the pore area in Figure 5 d reveals the oxidation of the Fe into rust (Fe_xO_y) on the surface. This can be used to confirm that there is corrosion in the pore area.⁽²⁶⁾

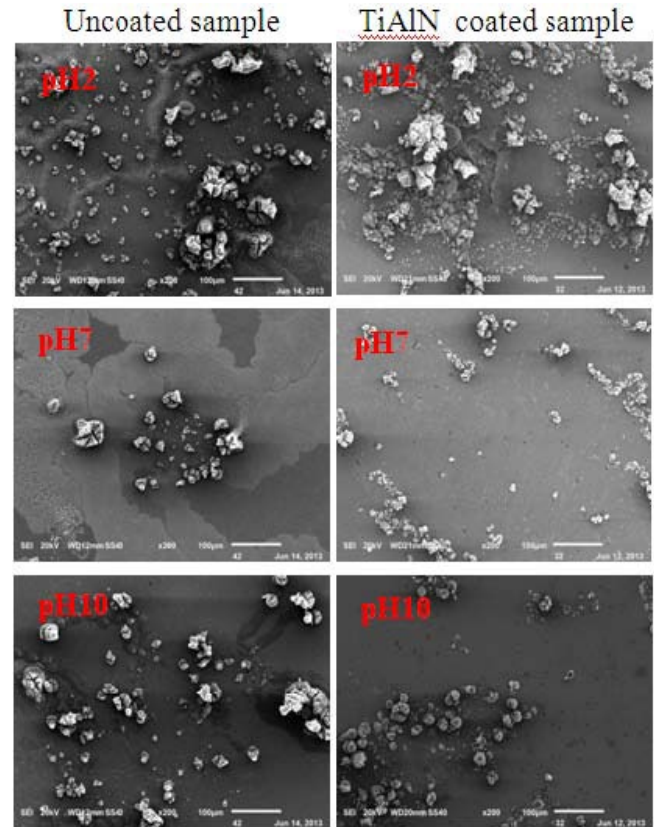


Figure 3. SEM images of surface of uncoated and TiAlN coated samples tested in 3.5 wt% NaCl solution at 27°C.

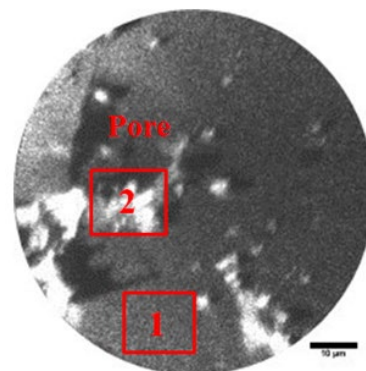
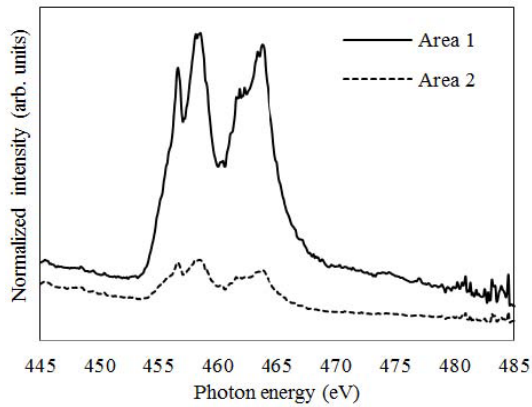
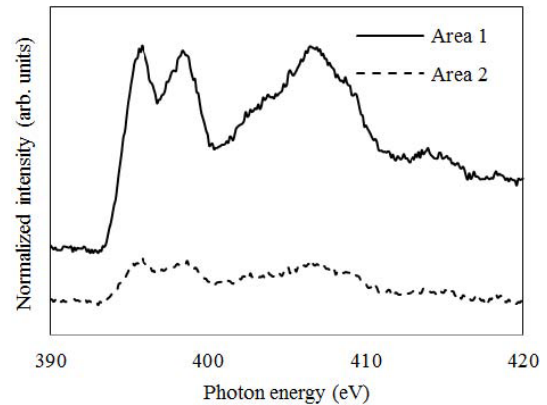


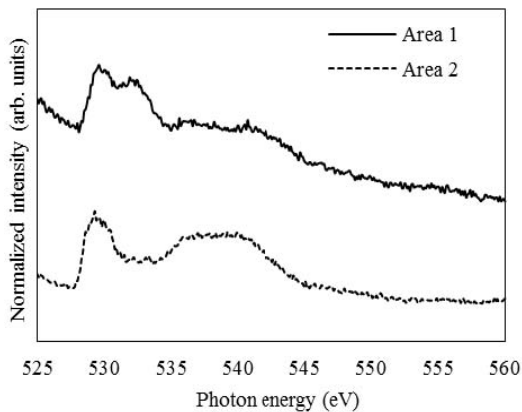
Figure 4. Synchrotron X-PEEM image of TiAlN coated samples at pH 2.



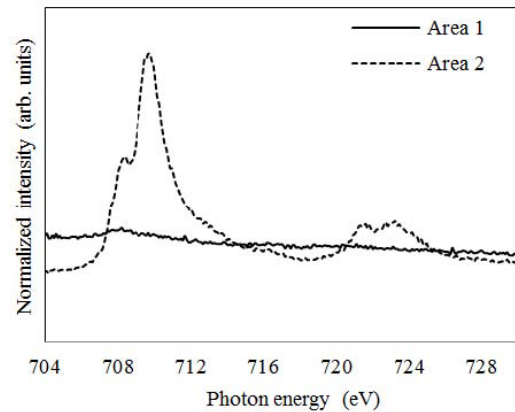
a) XAS spectra of Ti L-edge.



b) XAS spectra of N K-edge analysis of the samples after the corrosion test.



c) XAS spectra of O K-edge



d) XAS spectra of Fe L-edge

Figure 5. XAS spectra of TiAlN coated sample tested in 3.5 wt% NaCl solution at pH 2.

Conclusions

The corrosion behavior of AISI 4140 steel coated with TiAlN film in 3.5 wt% NaCl solution at pH 2, 7 and 10 by an electrochemical method was studied. The following conclusions can be drawn:

- The TiAlN film oriented in plane (100), (200) and (220) with the thickness of 500 nm is successfully coated on AISI4140 steel by the DC magnetron sputtering process.
- The TiAlN coated samples exhibit better corrosion resistance than the uncoated samples at all pHs.
- The samples tested in solution at pH 2 show higher corrosion rate (R_{mmy}) than the samples tested in solution at pH 10 and pH 7 for uncoated and TiAlN samples, respectively.
- The synchrotron X-PEEM technique associated with XAS is effective for surface

Acknowledgements

The authors would like to thank Suranaree University of Technology, National Research

Council of Thailand for fund supporting this project under contract number SUT7-713-56-12-16 and Mr. Sarayut Tunmee for operating the X-ray photoemission electron microscopy (X-PEEM) measurement.

References

- Samir, K.K. and Lin, Y.J. (2007). Wear mechanisms and tool performance of TiAlN PVD coated inserts during machining of AISI 4140 steel. *Wear.* **262** : 64-69.
- Shum, P.W., Tam, W.C., Li, K.Y., Zhou, Z.F. and Shen, Y.G. (2004). Mechanical and Tribological properties of titanium-aluminium-nitride films deposited by reactive close-field unbalanced magnetron sputtering. *Wear.* **257** : 1030-1040.
- Lugscheider, E., Knotek, O., Barimani, C., Leyendecker, T., Lemmer, O. and Wenke, R. (1999). PVD hard coated reamers in lubricant-free cutting. *Surf. Coat. Technol.* **112** : 146-151.

4. Yang, Q., Seo, D.Y., Zhao, L.R. and Zeng, X.T. (2004). Erosion resistance performance of magnetron sputtering deposited TiAlN coatings. *Surf. Coat. Technol.* **188-189** : 168-173.
5. Kim, C.W. and Kim, K.H. (1997). Anti-oxidation properties of TiAlN film prepared by plasma-assisted chemical vapor deposition and roles of Al. *Thin Solid Films.* **307** : 113-119.
6. Adibi, F., Petrov, I., Greene, J.E., Wahlström, U., Sundgren, J.E. (1993). Design and characterization of a compact two-target ultrahigh vacuum magnetron sputter deposition system : Application to the growth of epitaxial Ti_{1-x}Al_xN alloys and TiN/Ti_{1-x}Al_xN superlattices. *Journal of Vacuum Science & Technology A.* **11** : 136-142.
7. Shew, B.Y., Huang, J.L. and Lii, D.F. (1997). Effects of r.f. bias and nitrogen flow rates on the reactive sputtering of TiAlN films. *Thin Solid films.* **293** : 212-219.
8. Chakrabarti, K., Jeong, J.J., Hwang, S.K., Yoo, Y.C. and Lee, C.M. (2002). Effects of nitrogen flow rates on the growth morphology of TiAlN films prepared by an rf-reactive sputtering technique. *Thin Solid Films.* **406** : 159-163.
9. Hsu, C.H., Lu, J.K., Lai, K.L. and Chen, M.L. (2005). Erosion and corrosion behaviors of ADI deposited TiN/TiAlN coatings by cathodic arc evaporation. *Materials Transactions.* **46** : 1417-1424.
10. Uhlig, H. H. (1971). *Corrosion and Corrosion Control*. John Wiley & Sons Inc., New York : 37-59.
11. Linna, R. (2012). *High temperature behavior of arc evaporated ZrAlN and TiAlN thin films*. Linköping University, Sweden.
12. Souto, R.M. and Alanyali, H. (2000). Electrochemical characteristics of steel coated with TiN and TiAlN coatings. *Corros. Sci.* **42** : 2201-2211.
13. Liscano, S., Gil, L., Leon, O.A., Cruz, M. and Staia, M.H. (2006). Corrosion performance of duplex treatments based on plasma nitriding and PAPVD TiAlN coating. *Surf. Coat. Technol.* **201** : 4419-4423.
14. Ting Liu, K. and Gong Duh, J. (2008). Grain size effects on the corrosion behavior of Ni_{50.5}Ti_{49.5} and Ni_{45.6}Ti_{49.3}Al_{5.1} films. *J. Electroanal. Chem.* **618** : 45-52.
15. Mazhar, A.A., Arab, S.T. and Noor, E.A. (2001). The Role of chloride ions and pH in the corrosion and pitting of Al-Si alloy. *J. Appl. Electrochem.* **31** : 1131-1140.
16. Christine, T. and Alan, R.P. (2005). Effect of Temperature and pH on the Corrosion resistance of nitinol. In : *Proceeding of ASM Materials & Processes for Medical Devices Conference*. California.
17. Gaute, S. (2003). Corrosion of Aluminium Alloys. <http://www.Sintef.no/static/mt/norlight/seminars/norlight2003/postere/Gaute%20svenningsen.pdf>.
18. Guiot, E., Wu, Z.Y., Gota, S. and Gautier-Soyer, M. (1999). Polarized O K edge spectra of Fe₂O₃ (0001) nanometric films: A full multiple scattering interpretation. *J. Electron Spectrosc.* **101-103** : 371-375.
19. Frazer, B.H., Gilbert, B., Songderegger, B.R. and Stasio, G.D. (2003). The probing depth of total electron yield in the sub-keV range : TEY-XAS and X-PEEM. *Surf. Sci.* **537** : 161-167.
20. Hocking, R.K., Wasinger, E.C., Groot, F.M.F., Hodgson, K.O., Hedman, B. and Solomon, E.I. (2006). Fe L-Edge XAS Studies of K₄[Fe(CN)₆] and K₃[Fe(CN)₆] : A Direct Probe of Back-Bonding. *J. Am. Chem. Soc.* **128** : 10442-10451.
21. Wasinger, E.C., Groot, F.M.F., Hedman, B., Hodgson, K.O. and Solomon, E.I. (2003). L-edge X-ray Absorption Spectroscopy of Non-Heme Iron Sites : Experimental Determination of Differential Orbital Covalency. *J. Am. Chem. Soc.* **125** : 12894-12906.
22. Yoon, W.S., Kim, K.B., Kim, M.G., Lee, M.K., Shin, H.J., Lee, J.M., Lee, J.S. and Yo, C.H. (2002). Oxygen contribution on Li-ion intercalation-deintercalation in LiCoO₂ investigated by O K-edge and Co L-edge X-ray absorption spectroscopy. *J. Phys. Chem. B.* **106** : 2526-2532.

23. Esaka, F., Furuya, K., Shimada, H., Imamura, M., Matsubayashi, N., Sat, T., Nishijima, A., Kikuchi, T., Kawana, A. and Ichimura, H. (1997). XAS Study on the Intermediate Species Formed During the Surface Oxidation of CrN Films. *J. Phys. IV 7* : C2-1149-C2-1150.
24. Schedel-Niedrig, Th. (1998). X-Ray absorption spectroscopy : sensitive characterization of (model-) catalysts with the electron yield technique, *Fresen. J. Anal. Chem.* **361** : 680-682.
25. Preda, I., Soriano, L., Gutierrez, A., Palacin, S., Fernandez-Garcia, M., Belver, C., Gonzalez-Diaz, N., Vollmer, A., Bressler, P.R., and Sanz, J.M. (2005). Electronic structure of TiO nanoparticles as observed by X-ray2 absorption spectroscopy (XAS). 2nd NanoSpain Workshop. Barcelona.
26. Crocombette, J.P., Pollak, M., Jollet, F., Thromat, N. and Gautier-Soyer, M. (1994). X- ray-absorption spectroscopy at the Fe L_{2,3} threshold in iron oxides. *Phys. Rev. B.* **52** : 3143-3150.