

Corrosion Behavior of TiAlN film on AISI 4140 Steel

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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

application.⁽¹⁾ Titanium nitride (TiN) is a popular PVD film because it has a good combination of AISI 4140 low alloy steel, containing chromium, wear resistance and corrosion molybdenum and manganese, is widely used in resistance. Unfortunately, TiN cannot be used at automotive industry and engineering application. high temperature because its limitation is poor. The AISI 4140 low alloy steel is the most attractive oxidation resistance at temperature above steel because it does not have only good 500°C.⁽²⁾ In order to improve oxidation resistance of mechanical properties but it is also cheap and is TiN, aluminium was added into TiN film; easily fabricated as compared to other steels. subsequently TiAlN film was produced.⁽³⁾ TiAlN Examples of automotive parts produced from AISI film remains hardness and oxidation resistance at 4140 low alloy steel are shaft, connecting rod, high temperature, thus it significantly increases life crankshaft, screw, gear and etc. In order to enhance time of engineering part as compared to TiN mechanical and chemical properties of automotive film.⁽⁴⁾ TiAlN film is not only used at high parts in particular for abrasion, wear and corrosion temperature, but it is also widely used in the resistance, surface technology has been extensively automotive part at room temperature. Since the applied e.g. nitriding, carburizing, chemical vapour automotive part and engineering part were used in

deposition (CVD), physical vapour deposition service environments e.g. lubricant, engine coolant (PVD), thermal spraying and etc. The widely used and humidity; corrosion is possible to be appeared. surface technology is physical vapour deposition. Therefore, corrosion test by an electrochemical because it is a clean technology and its method is a proper approach to solving the problem performance fulfils requirement of engineering 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 pieces size of 18 x 18 x 3 mm. They were heated up to 850°C for 30 minutes and oil-quenched. After heat treatment, hardness of

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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 μm up to 0.5 μm . Finally, the samples were rinsed by distilled water, acetone and were air-dried before coating.

Table 1. Chemical composition of 4140 steel (in wt.%).
Grade C MnCr Si MoFe

AISI 4140 0.43 0.82 1.03 0.24 0.19 Bal.

Film Preparation

Table 2. Deposition condition of TiAlN film.

| | |
|-----------------------------|---------------------------|
| Ar flow rate | 16 sccm |
| N ₂ flow rate | 8 sccm |
| Base pressure | 5.0x10 ⁻⁵ mbar |
| Working pressure | 5.0x10 ⁻³ mbar |
| Current Ti | 900 mA |
| Current Al | 300 mA |
| Deposition time | 120 min |
| Target-to-substrate spacing | 18 cm |
| Coating thickness | ~500 nm |

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

TiAlN film Ti Al N
32.05 6.42 61.53

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 N₂ (over 6 sccm) during deposition process.^(7,8)

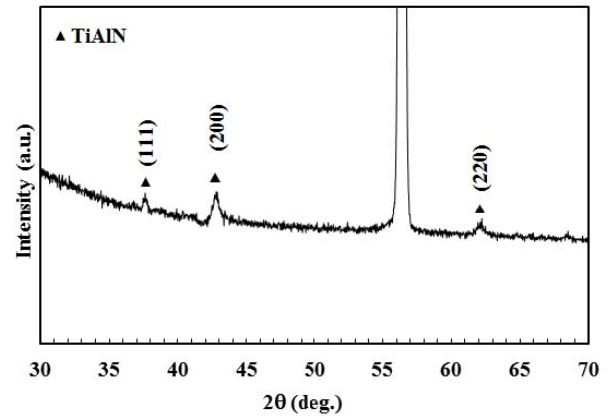


Figure 1. XRD diffraction pattern of TiAlN film in a grazing incidence mode.

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 3.5wt% 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). samples.

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/cm³) of TiAlN film are lower than the equivalent weight (26.62 g) and density (7.87 g/cm³) of AISI 4140 steel.⁽¹¹⁾ Thus, a corrosion rate (R_{mm/y}) 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⁾

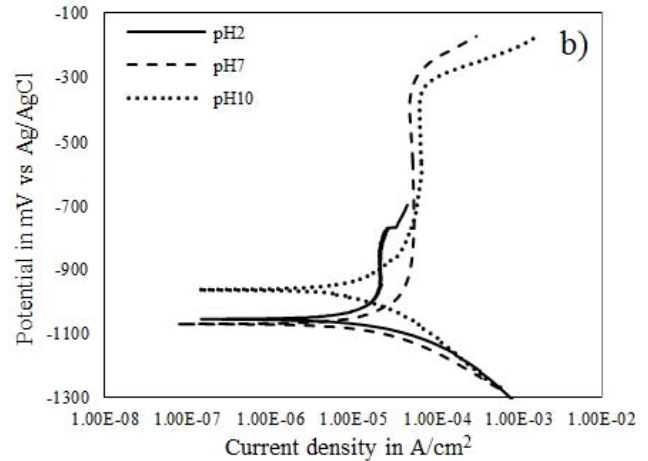
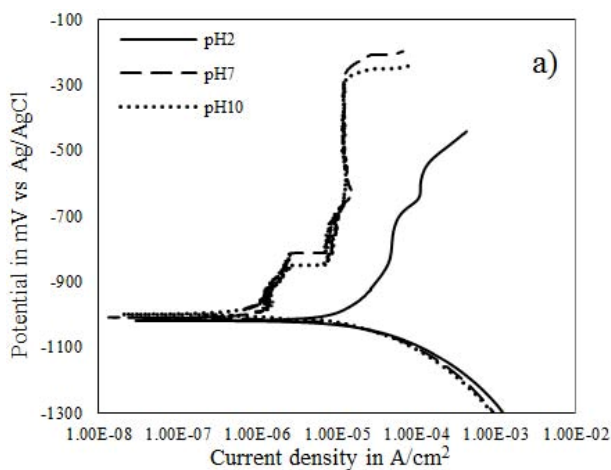


Figure 2. The polarization curves of samples in 3.5 wt% NaCl solution at pH 2, 7 and 10. a) Uncoated samples b) TiAlN coated samples

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

| pH | Samples | E _{corr} (mV) | I _{corr} (μ A/cm ²) | E _{pit} (mV) | R _{mm/y} (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 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 b). 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⁾ 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 (E_{pit}: -250 mV) shows higher pitting potential than the TiAlN coated samples tested at pH 10 (E_{pit}: -315 mV) and pH 2 (E_{pit}: -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

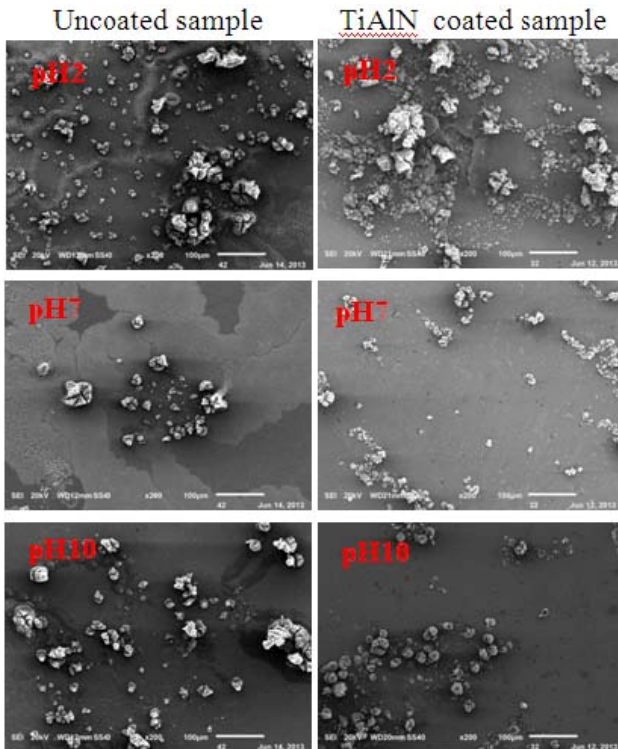


Figure 3. SEM images of surface of uncoated and TiAlN coated samples tested in 3.5 wt% NaCl solution at 27°C.

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 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 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.

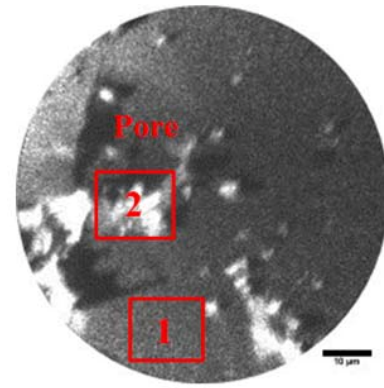
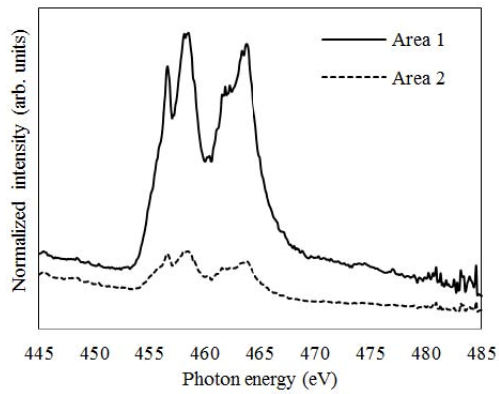


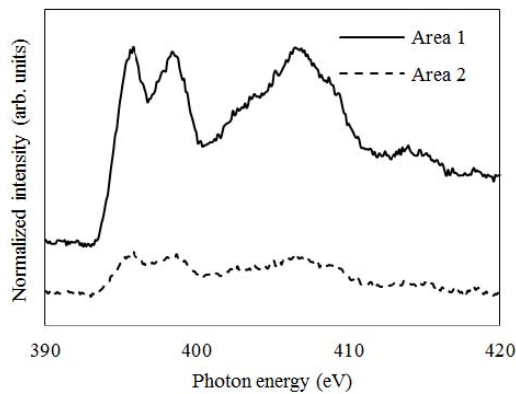
Figure 4. Synchrotron X-PEEM image of TiAlN coated samples at pH 2.

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 455-465eV, 390-420eV and 530-550eV, 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.

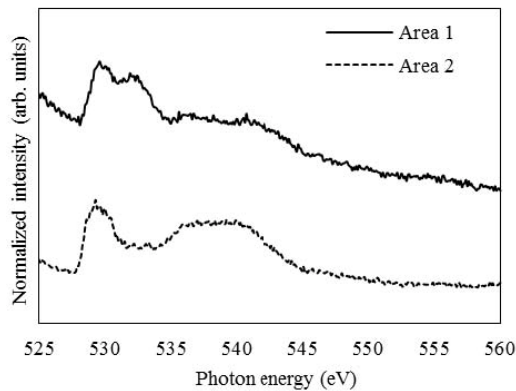
At the corroded area (area 2), not only chemical states of main components that are responsible for corrosion resistance of TiAlN film e.g., Ti L-edge, N K-edge and O K-edge appear, but XAS spectrum of Fe L_{3,2}-edge at a photon energy of 700730eV also occurs.⁽²⁰⁻²¹⁾ These mean that two components, 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 5d) 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⁾



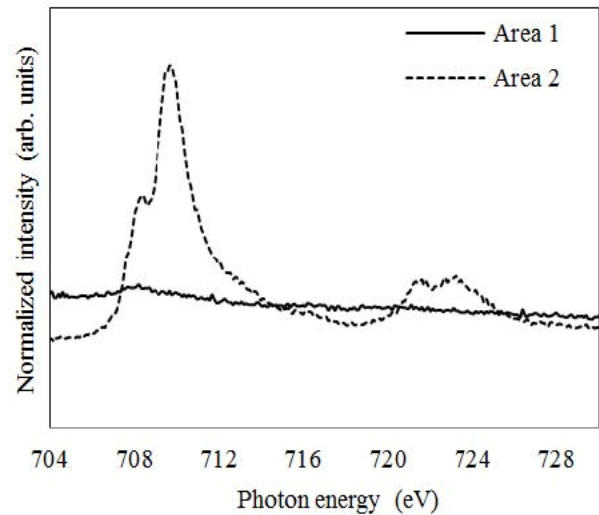
a) XAS spectra of Ti L-edge



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 3.5wt% 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:

a. 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 7 for uncoated and TiAlN samples, respectively.

The synchrotron X-PEEM technique associated with XAS is effective for surface

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