Abstract

In the present study, the corrosion behaviors of chromium nitride (CrN) and chromium aluminum nitride (CrAlN) coatings deposited on AISI D2 steel samples are reported. Steel samples were pre-nitrided at 575°C for 8 h in the first step of the coating process, and then CrN and CrAlN coatings were performed by thermo-reactive deposition (TRD) process in a powder mixture consisting of ferrous chromium, aluminum, alumina and ammonium chloride, for CrN or CrAlN, respectively. Coating treatments were realized at 1000°C for 2 h. Coated samples were characterized by x-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and EDS analysis, and micro-hardness tester. The corrosion properties of uncoated and coated samples were characterized by potentiostatic polarization test in a 3.5 wt. % NaCl solution. CrN and CrAlN coated steel specimens exhibited higher corrosion resistance than uncoated steels.

1. Introduction

Nowadays, hard coatings with boride, carbide, nitride, or carbonitride of transition metals are widely used for tool applications, in order to increase corrosion resistance and wear [1, 2]. The coatings are used in order to isolate the steel surface from the corrosive environment and prevent the diffusion of oxygen, water vapor, or ions, which act as a source that initiates the corrosion.

Hard coatings have been deposited by different techniques: physical vapor deposition (PVD), and chemical vapor deposition (CVD) techniques, thermal spraying. As an economical alternative for producing hard coatings, an emerging technique called thermo-reactive diffusion deposition (TRD) is being used [1]. This technique was patented by Toyota in Japan and it has been applied successfully for many years at industrial level for producing several types of layers on iron-based alloys [3].

In the TRD process, the carbon and nitrogen in the steel substrate diffuse into a deposited layer with a carbide-forming element (CFE) or nitride forming element (NFE) such as vanadium, niobium, tantalum, chromium, molybdenum, or tungsten. The diffused carbon or nitrogen react with the CFE and NFE in the deposited coating so as to form a dense and metallurgically bonded carbide or nitride coating at the substrate surface [5]. Particularly, the coating obtained by the TRD process presents excellent adhesion with the substrate and consequently good seizure resistance. Also TRD process involves relatively simple equipment, low in cost, and environment friendly [4]. Thus the process has a wide range of practical application [5].

Nitride based hard compound coatings have high hardness, excellent wear and corrosion resistance enable them to improve tool life greatly [6, 7]. Among them, TiN and CrN are respectively the first and the second most frequently employed coatings [7]. CrN also exhibits low friction coefficient, high corrosion and wear resistance and high toughness, when compared to TiN [8]. CrN coating have been used for cutting tools, molding dies and machine parts in industry. But the oxidation resistance of CrN is limited up to 600 °C. For hard protective coatings, thermal stability is important as they are exposed to high temperatures during the cutting process. The addition of Al to CrN raises the temperature at which onset of oxidation occurs. CrAlN coatings have been reported to be stable up to a temperature of 900 °C depending upon the Al content in the coatings [9]. Therefore, CrAlN coating is a good candidate as an alternative to conventional CrN coatings, especially for high-temperature oxidation-resistance applications [10-12]. CrAlN coatings also exhibit higher hardness and a lower friction coefficient when compared to CrN coatings [9].

The main objective of this study was to investigate the corrosion behavior of CrN and CrAlN coated AISI D2 tool steel by thermo-reactive deposition technique in 3.5 wt. % NaCl solution.

2. Experimental Procedure

2.1. Coating treatment and characterization

The steel substrates used in this study was AISI D2 steel with chemical composition of 1.56% C, 0.27% Si, 0.30% Mn,
0.020% P, 0.001% S, 11.2% Cr, 0.75%Mo, 0.93% V and iron (balance). Before coating treatment, the samples were cut into discs 20 mm in diameter and 5 mm in thick and were ground by 1200 grit silicon carbide papers. The preparation of the substrates for the process consisted of ultrasonic aided cleaning with acetone and ethyl alcohol. Nitriding treatment was carried out for the purpose to rich the surfaces with the nitrogen of the steels in a gas atmosphere for 8 hours at 560°C in a tube furnace. Then, CrN and CrAlN coating was performed on the pre-nitrided steel by thermo-reactive deposition (TRD) technique. The TRD process was performed at 1000°C for 2h utilizing in a pack box containing ferro-chromium, aluminum, ammonium chloride and alumina powders. Ferro chromium, aluminum (for CrAlN), ammonium chloride, and alumina were used as a metal supplier (Cr, Al), activator and filler materials, respectively. Alumina crucible was sealed with an alumina lid and alumina-based cement. Commercial powders were used for CrN and CrAlN coating treatment. The coated samples were ground and polished up to 0.3 μm with alumina paste and then etched with 3% nital for metallographic examinations. In the scanning electron microscopy (SEM) and energy dispersive x-ray spectrometer (EDS), the samples were analyzed on the cross-sections. X-ray diffraction (XRD) analysis of the layers were performed on the surfaces of the coated sample with 20 varying from 40° to 65°, using CuKα radiation. Micro-hardness measurements of the CrN and CrAlN coating layers from surface were performed using Future-Tech FM-700 micro-hardness tester under the loads of 25 g and 10 g, respectively.

2.2. Corrosion tests

The corrosion properties of uncoated and coated samples were characterized by electrochemical methods, namely potentiodynamic polarization. The tests were conducted in a three-electrode system test unit using a PCI4/750/ZRA Potentiostat-Galvanostat (Gamry Instrument) controlled by a computer, with an active area of 0.28274 cm². To simulate the aggressive environment, all the electrochemical characterizations were performed in a 3.5 wt.% NaCl solution at room temperature, prepared with analytical grade reagents and deionized water. Before the electrochemical measurements, samples were allowed to stabilize at their open circuit potential for 30 min. Polarization measurements were made at a potential scan rate of 5 mV/s and the scanning range was set from -1 to +1 V. After electrochemical test, the corrosion potential (Ecorr), the corrosion current density (icorr) and the polarization resistance (Rp) were deduced from the Tafel (log i vs. E) plots.

3. Results and Discussion

CrN and CrAlN coatings were produced successfully on AISI steel by thermo-reactive diffusion technique at 1000°C for 2h. The cross-sectional SEM micrographs of the (a) CrN and (b) CrAlN coated are shown in Figure 1. The coating layers were dense and exhibits laminar microstructure with a well-defined coating/substrate interface as shown in this figure. But, the surface of CrAlN coating layer has a dense and smooth microstructure than that of CrN. EDS analysis showed that, the surface of the coating layer includes higher chromium and lower iron concentration than that of the layer close to the interface the substrate as seen in Fig. 1.

The depth of the CrN and CrAlN layers are examined 8.15 ± 1.1μm and 11.8 ± 1.3μm, respectively. The phases formed in the CrN and CrAlN coating layers were CrN and Cr2N, (Cr,Fe)2N1-x, AlN and Fe2N phases respectively. The micro-hardness measurements showed that the CrAlN, CrN coatings and uncoated exhibited hardness values of 22, 27 GPa, 21, 75 GPa and 5, 58 GPa, respectively. These are the consequence of the presence of hard nitrides. Such similar results are explained by the fact that the layer are made up of the same nitride compounds [8].

Figure 1. The SEM micrographs and EDS analysis of (a) chromium nitride and (b) chromium aluminum nitride coated AISI D2 steel.

Fig. 2 shows the potentiodynamic polarization curves of the uncoated, CrN and CrAlN coated AISI D2 steels tested in a 3.5 wt.% NaCl aqueous solution. The corrosion potential
(E<sub>corr</sub>), current density (i<sub>corr</sub>) and polarization resistance (R<sub>p</sub>) obtained by Tafel calculations for uncoated and coated steels are given in Table 1. The measured corrosion potential and current values of the CrAlN coated sample (-463 mV and 3.07 μAcm<sup>-2</sup>) is much nobler than that of the CrN coated steel (-492 mV and 3.49 μAcm<sup>-2</sup>) and uncoated steel (-1000 mV and 20.87 μAcm<sup>-2</sup>). CrN and CrAlN coatings deposited on steel substrates demonstrated good corrosion resistance in 3.5 wt.% NaCl solution. Electrochemical characteristic demonstrates the capacity of the CrAlN coating for providing corrosion protection to the underlying substrate. It is clearly evident from the corrosion data that the CrAlN and CrN coatings exhibit superior corrosion resistance as compared to the uncoated substrate. The corrosion behavior of CrAlN may also have been affected because of the presence of Al. It has been reported that the addition of Al to the transition metal nitrides improves the corrosion resistance. During the chemical attack, aluminum forms an Al₂O₃ layer on the surface of the coating, which passivates the surface and prevents the coating from further attack. The presence of the passive layer leads to an additional resistance to the corrosive medium passing through the pores [8, 13]. It is clearly evident from the corrosion results that the CrAlN coatings exhibit superior corrosion resistance as compared to the CrN coating [14, 15].

![Figure 2. Potentiodynamic polarization (Tafel) curves for CrAlN coated, CrN coated and uncoated steel in 3.5 wt. % NaCl solution.](image)

### Table 1. Potentiodynamic polarization datas of coated and uncoated steels in 3.5 wt. % NaCl solution.

<table>
<thead>
<tr>
<th></th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (V/dec)</th>
<th>E&lt;sub&gt;c&lt;/sub&gt; (V/dec)</th>
<th>E&lt;sub&gt;corr&lt;/sub&gt; (mV)</th>
<th>i&lt;sub&gt;corr&lt;/sub&gt; (μAcm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>R&lt;sub&gt;p&lt;/sub&gt; (x10⁻³ Ωcm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
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<tbody>
<tr>
<td>Uncoated</td>
<td>0.0874</td>
<td>1.06x10⁶</td>
<td>-1000</td>
<td>20.87</td>
<td>1.8180</td>
</tr>
<tr>
<td>CrN coated</td>
<td>0.1689</td>
<td>0.1255</td>
<td>-492</td>
<td>3.49</td>
<td>8.9581</td>
</tr>
<tr>
<td>CrAlN coated</td>
<td>0.1464</td>
<td>0.1275</td>
<td>-463</td>
<td>3.07</td>
<td>9.6391</td>
</tr>
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</table>

**Note:** (β<sub>a</sub>, β<sub>c</sub>, E<sub>corr</sub>, i<sub>corr</sub>, and R<sub>p</sub> are the Tafel slopes of the anodic and cathodic reactions, the corrosion potential, corrosion current density and polarization resistance, respectively)

### 4. Conclusion

CrN and CrAlN coatings were produced successfully on AISI steel by thermo-reactive diffusion technique at 1000 °C for 2h. The coating layers were dense, homogeneous and exhibits lamellar microstructure. The phases formed in the CrN and CrAlN coating layers were Cr₂N and Cr<sub>2</sub>N, (Cr,Fe)<sub>2</sub>N₁₋ₓ, AlN and Fe₂N phases respectively. The micro-hardness of the CrAlN and CrN layer formed on the steel were much harder than uncoated steel. CrAlN and CrN coatings deposited on steel substrates demonstrated good corrosion resistance.

### References