Corrosion Behavior of Nitride and Cr–Al–N Coatings Formed on AISI D2 Steel

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In the present work, the corrosion behavior of Cr–Al–N coating formed on the pre-nitrided AISI D2 cold work tool steel by thermo-reactive diffusion technique in the powder mixture consisting of ferro-chromium, aluminum, ammonium chloride and alumina at $1000\,^{\circ}$C for 2 h was investigated. The phases formed in the coating layers were Cr_2N, $(Cr,Fe)_2N_{1-x}$, AlN, and Fe_2N which were confirmed by X-ray diffraction analysis. The uncoated, nitrided, and Cr–Al–N coated specimens were placed in corrosive media (3.5 wt% salt solution). A standard saturated calomel electrode was used as a reference and graphite as a counter or auxiliary electrode. The effectiveness of the coatings in preventing corrosion was tested in the NaCl solution by electrochemical impedance studies using the Nyquist plots and potentiodynamic studies as well. Conclusively, the application of nitride and Cr–Al–N layers on AISI D2 steel increased its surface hardness and corrosion resistance. The corrosion resistance of Cr–Al–N coatings is higher than that of uncoated and nitrided steels.

1. Introduction

Chromium nitride is a typical transition metal nitride coating with high hardness, good wear resistance, and corrosion resistance and is widely used in die casting, metal forming, and tool machining applications to increase productivity and tool life [1]. It was reported that alloying CrN coating led to a hardness enhancement by adding Mo or Al, a significant reduction in the friction coefficient by incorporation, and improvement in wear resistance by alloying with Ti [2]. $Cr_{1-x}AlN$ films can be obtained in a wide range of compositions due to the high solubility of CrN for AlN [3, 4]. Therefore, CrAlN coating is a good candidate as an alternative to conventional CrN coatings, especially for high-temperature oxidation-resistance applications [5, 6]. CrAlN coatings have been successfully produced through different physical vapor deposition (PVD) methods such as dc (direct current) magnetron sputtering [7, 8], arc ion plating [9, 10], and cathodic arc evaporation [1, 11]. The benefits of Cr and Al materials presented the characteristics of corrosion resistance, oxidation resistance, and lubrication [12]. The main objective of the study was to investigate the corrosion behavior of Cr–Al–N coated AISI D2 tool steel by thermo-reactive deposition technique in 3.5% NaCl.

2. Experimental procedure

The workpiece material used in this study was AISI D2 steel containing 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. Before treatment, the samples were prepared metallographically. AISI D2 steel was gas nitrided for the purpose to enrich the surfaces with nitrogen of the steels in a nitrogen and ammonia atmosphere at $560\,^{\circ}$C for 8 h. Then, Cr–Al–N coating was performed on the pre-nitrided steel samples by thermo-reactive deposition (TRD) process. The TRD process was performed at $1000\,^{\circ}$C for 2 h utilizing in a pack box containing ferrochromium, aluminum, ammonium chloride and alumina powders. Ferrochromium, aluminum, ammonium chloride, and alumina were used as a metal supplier (Cr, Al), activator, and filler materials, respectively. Characterization of Cr–Al–N coated AISI D2 steel was carried out by using following devices and methods: (i) nitrided and Cr–Al–N coated AISI D2 steel were investigated. The depth of coating layers was measured by optical micrometer attached to the optical microscope. (ii) Micro-hardness of uncoated steel, nitride layer and Cr–Al–N coating layer were measured from cross-sections of the samples under the load of 10 g.

The corrosion properties of uncoated and coated samples were characterized by two electrochemical methods, namely potentiodynamic polarization and electrochemical impedance measurements. The tests were conducted in a three-electrode system test unit with a graphite counter electrode and an Ag/AgCl, 3 M KCl electrode as the reference electrode using a PCI4/750/ZRA potentiostat-galvanostat (Gamry Instrument) controlled by a computer, with an active area of 2.269 cm². To simulate the aggressive environment, all the electrochemical characterizations were performed in a 3.5 wt% NaCl solution pH values of which is 5.96 at $22\,^{\circ}$C. Before the electrochemical measurements, samples were allowed

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to stabilize at their open circuit potential for 30 min. The calculated polarization resistance (R_p) gained from the potentiodynamic polarization tests were used to the instantaneous interfacial reaction rates, i.e., corrosion rates. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation. Electrochemical impedance studies were carried out in the frequency range from 10.000 to 0.01 Hz. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from the Nyquist plot by fitting the data using EIS 300 software.

3. Results and discussion

Figure 1 shows the cross-sectional optical and scanning electron microscope (SEM) micrographs of the nitrided and Cr–Al–N coated AISI D2 tool steels. Cr–Al–N coating layer was dense and exhibits laminar microstructure with a well-defined coating/substrate interface. The depth of the Cr–Al–N layer is examined 11.8 ± 1.3 μm. The coating exhibits a higher hardness of 20.67 ± 1.6 GPa than that of the nitrided layers (9.2 ± 0.32 GPa) and uncoated steel (5.50 ± 0.8 GPa). XRD pattern of the Cr–Al–N coated AISI D2 steel of which phases are Cr_2N, $(Cr,Fe)_2N_{1-x}$, AlN and Fe_2N.

Figure 2 shows the potentiodynamic polarization curves of the untreated, nitrided, and the Cr–Al–N coated AISI D2 steels tested in the 3.5 wt% NaCl aqueous solution.
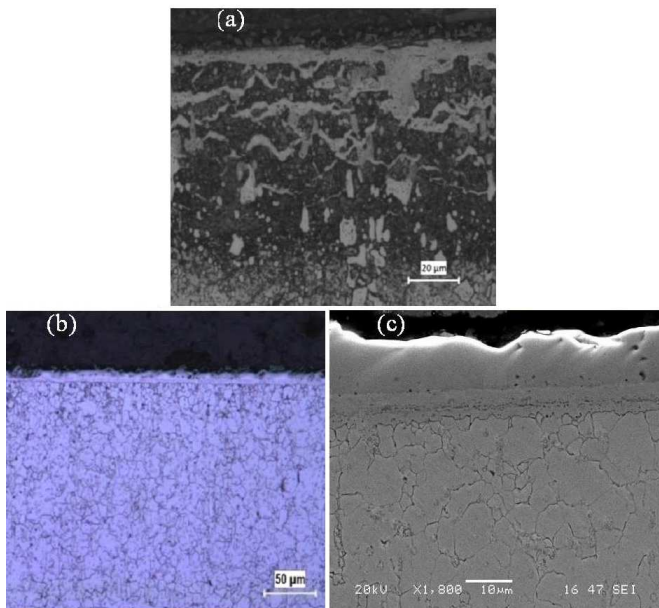

Fig. 1. The micrographs of (a) nitride, (b, c) chromium aluminum nitride coated AISI D2 steel.

The corrosion potential (E_{corr}), current density (i_{corr}) and polarization resistance (R_p) obtained by the Tafel calculations for uncoated, nitrided, and coated steels are
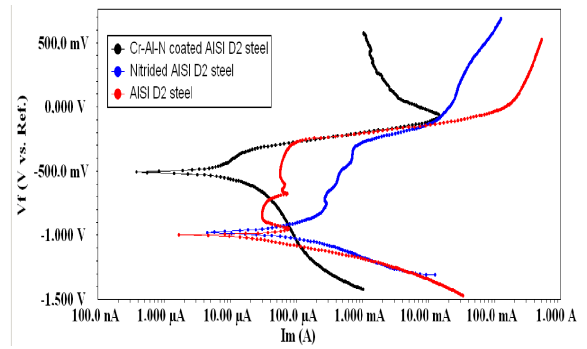

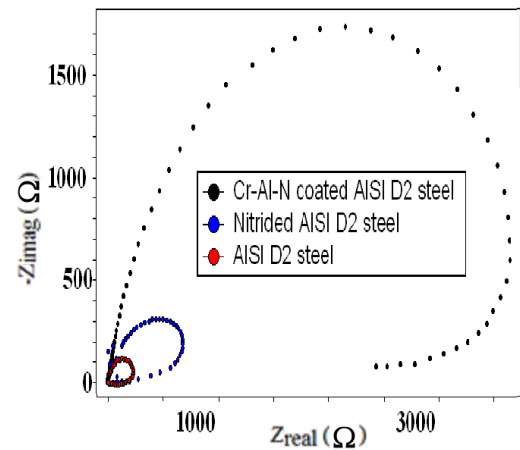Fig. 2. Potentiodynamic polarization curves for the samples.

Fig. 3. Nyquist plots of EIS data of the samples.

given in Table. Cr–Al–N coated sample has got the highest E_{corr} value which is coming upon the upper site of passive region of the uncoated and nitrided AISI D2 steels, and current density of the Cr–Al–N coated AISI D2 steel is much lower than that of the uncoated and nitrided steels. This electrochemical characteristic demonstrates the capacity of the Cr–Al–N coating for providing corrosion protection to the underlying substrate. The corrosion behavior of Cr–Al–N 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 Al_2O_3 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 [10, 13]. It is clearly evident from the corrosion results that the Cr–Al–N coatings exhibit superior corrosion resistance as compared to the CrN coating [14, 15].

As shown in Fig. 3, the EIS data of Cr–Al–N coated steel, nitrided, and untreated steel samples are also presented as the Nyquist plot, which was comprised of real and imaginary parts of the impedance as a function of

the applied frequency perturbation. A convenient way to evaluate the corrosion properties of the samples is to compare the diameters of the semi-circles in the Nyquist plot [16, 17]. The larger the arc diameter is, the better corrosion resistance of the sample was expected. As shown in

Fig. 3, the Cr–Al–N coated steel exhibited the larger arc diameter than that of the nitrided and untreated AISI D2 steels, and better corrosion resistance of these steels were evident.

TABLE

Potentiodynamic polarization parameters of the samples.

	β_a [V/dec]	β_c [V/dec]	E_{corr} [mV]	i_{corr} [$\mu A\ cm^{-2}$]	R_p [$\times 10^3\ \Omega\ cm^2$]
uncoated steel	0.0874	1.056×10^6	−1.000	20.87	1.8180
nitrided steel	0.1280	0.0761	−978.4	11.48	1.8505
Cr–Al–N steel	0.3792	0.1664	−508.7	3.78	13.2800

Note β_a, β_c, E_{corr}, i_{corr}, and R_p are the Tafel slopes of the anodic and cathodic reactions, the corrosion potential, corrosion current density, and polarization resistance, respectively.

However, the impedance arc of the sample becomes smaller thus indicating a continuous degradation in its resistance against corrosion. This corrosion behavior could be contributed to the presence of pinholes and other defects in the coating. It is well known that coating defects can provide corrosion media an easy access to the coating/substrate interface, resulting in formation of corrosion cells between coating and substrate [2, 18]. In order to fully utilize the potential of Cr–Al–N coating for corrosion protection, it is necessary to either reduce the number of coating defects or develop techniques to block the pinholes or pores associated with the defects. TRD method has important advantages for the formation of the compact, smooth and porosity free coatings and so the coating layer exhibits the higher corrosion resistance [19].

Conclusively, thermo-reactive deposited Cr–Al–N coating demonstrated a much more noble corrosion potential, the higher corrosion potential, and a lower current density when compared to uncoated and nitrided AISI D2 steel.

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