A comparative study of the electrochemical corrosion behavior between Cr₂N and CrN coatings

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ABSTRACT
Thick Cr₂N and CrN coatings were successfully prepared by arc ion plating (AIP) at a high deposition rate of more than 15 μm/h. The electrochemical corrosion behavior of Cr₂N and CrN coatings in 3.5 wt% NaCl solution was investigated comparatively using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results showed that the corrosion current (Icorr) of Cr₂N coating was only 0.85 nA cm⁻², which was lower than that of CrN coating of 5.5 nA cm⁻². And its charge transfer resistance (Rct) of ~7.19 × 10⁶ Ω cm² increased by about two orders of magnitude compared to that of CrN coating, indicating that Cr₂N coating has better corrosion resistance. Additionally, the nitride coatings showed different surface morphologies after corrosion tests, where the relatively slight corroded surface of Cr₂N coating may be related to its larger range of passive region and higher pitting potential (Epit).

Introduction
Hard nitride coatings, especially Cr-based nitride coatings, play an important role in various industrial fields such as automotive, aviation and machining due to the high hardness and excellent chemical/thermal stabilities of the coatings [1–3]. So far, nitride coatings have been prepared by several techniques, including physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma nitriding and plasma spraying [4–7], among which PVD is widely used because of its environment-friendly process and the advantage of producing high-quality coatings.

However, most PVD coatings are limited to a thickness of a few microns owing to the large buildup of stresses in coatings during deposition. For instance, the maximum thickness of TiN coating without spalling was only about 6–7 μm [8]. Such thin coatings are not suitable for the applications in abrasive or erosive environments. To provide durable protection, increasing the thickness of coatings will be a feasible way in principle. It was reported that the thick coating exhibited improved load-bearing capacity and wear resistance compared to the corresponding thin coatings [7]. The density of pores in the coating was greatly reduced as the coating thickness increased, which thus improved the corrosion resistance [9]. There will be an increasing demand for thick coatings with the growing harsh industrial environments. In recent years, a number of studies have reported a wide variety of PVD coatings with high thickness based on the composition and structure design [10–12]. Moreover, the rapid preparation of thick coatings has been achieved due to the development of PVD techniques [13,14].

A great deal of work has been done previously to study the mechanical, oxidation/corrosion and wear performance of CrN coatings [15–18]. For instance, Gui et al. investigated the influence of N2 flow rate on the microstructure evolution, mechanical and corrosion performances of CrNx films. It was found that CrNx film deposited at 100 sccm nitrogen flow rate, which consisted of Cr2N and Cr phases, exhibited highest hardness and lowest corrosion current [19]. However, the work by Shan et al. reported that the CrNx coating with better corrosion resistance was composed of Cr₂N and CrN phases [20]. Hence, the performance of coatings is not completely dependent on their phase compositions. Typical chromium nitride Cr₂N and CrN coatings are intrinsically resistant to corrosion. Nevertheless, there has been little agreement on the corrosion resistance of two nitride coatings since it is closely related to microstructure of the coatings [21–23]. For instance, the intrinsic corrosion resistance of Cr₂N coating was thought to be better than that of CrN coating, whereas biased CrN coating exhibited superior corrosion protection due to its...
Table 1. Chemical compositions of the gun steel CrNi3MoV (wt%).

|   | Cr  | Ni  | Mo  | V   | C   | Mn | Si  | S   | P   | Fe  |
|---|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|
|   | 1.28| 3.14| 0.37| 0.2 | 0.4 | 0.41| 0.25 | 0.001| 0.012| Bal.|

denser microstructure [23]. The microstructure of coatings deposited by different techniques varies considerably, which will lead to inconsistent results regarding the corrosion performance of coatings.

Hence, in this work, a comparative study of the corrosion performance of Cr2N and CrN coatings deposited by the newly-developed arc ion plating (AIP) was performed using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

Experimental procedure

The gun steel CrNi3MoV with a geometry of 20 mm × 10 mm × 2 mm was used as the substrate. The chemical compositions of substrate steel are shown in Table 1. Substrate specimens were abraded down to a final 2000-grit SiC sandpaper, followed by ultrasonic washing in acetone and ethanol mixture for 10 min.

The coatings were prepared by an arc ion plating machine (DH-7, Beiyu vacuum technology, Shenyang, China). The target material employed in deposition process is pure Cr (99.9 wt%), and the reactive gas is N2 (99.999%). The specimens were hanged on a rotating stand at an average distance of 200 mm from the target. The rotation rate during deposition was 10 r/min. Prior to deposition, the specimens were bombarded-cleaned with Ar ions under voltage of −700 V for 5 min and then with metallic Cr ions under voltage of −200 V for 2 min to clear the surface contamination and improve the interfacial adhesion. The Cr2N and CrN coatings were prepared by controlling the N2 partial pressure in vacuum chamber, where the N2 partial pressure for Cr2N and CrN coatings were 0.1 and 1 Pa, respectively. The other deposition parameters are as follows: bias voltage of −100 V, arc current of 200 A, duty cycle of 20% and deposition time of 1 h.

Electrochemical corrosion behavior of Cr2N and CrN coatings were evaluated by potentiodynamic polarization and EIS, which were performed in 3.5 wt% NaCl electrolyte using a PARSTAT 2273 electrochemical workstation. A standard three-electrode system that consists of a Pt plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode (RE) and coating specimens as working electrode (WE) was adopted, where the back of coating specimens was connected to the copper wire and then coated with the paraffine, leaving an area of 1 cm² for electrochemical tests. Before electrochemical tests, the specimens were immersed in the NaCl electrolyte for 1 h to obtain a steady open circuit potential (OCP). Potentiodynamic polarization test was performed at a scan range of −0.4 to 0.8 V vs. OCP and a scan rate of 0.5 mV s⁻¹. The electrochemical polarization was analyzed by Echem Analyst software. EIS test was conducted at OCP with an amplitude of ±10 mV and a frequency range from 100 kHz to 10 mHz. The EIS data were fitted and analyzed by ZSimplWin software based on the suitable electrical equivalent circuit (EEC).

Phase constitution of the as-deposited coatings was analyzed by X-ray diffraction (XRD, X’Pert PRO, PANalytical Co., Almelo, the Netherlands). The morphologies of specimens before and after corrosion test were observed by scanning electron microscopy (SEM, Inspect F50, FEI Co., Hillsboro, OR).

Results and discussion

Figure 1 shows the surface, cross-sectional morphologies and corresponding XRD patterns of the as-deposited coatings. The surfaces of nitride coatings are homogeneous and intact without cracks and micropores. Some microdroplets with sizes mostly below 2 μm distribute on the coating surface, which is a typical feature of AIP coatings. The number of microdroplets on Cr2N coating is smaller than that on CrN coating. Cross-sectional images present that the coatings are dense and well adherent to the substrate. The thickness of as-deposited coatings is around 16.3 and 19.7 μm, respectively, corresponding to the deposition rate of over 15 μm/h, which is rather high among the reported PVD coats [13,15,24]. The XRD patterns confirm that the coatings deposited at the nitrogen partial pressure of 0.1 and 1 Pa are mainly composed of Cr2N and CrN phases, respectively. Besides, weak diffraction peaks of Cr were detected by XRD, which may originate from the metallic microdroplets.

Figure 2 displays potentiodynamic polarization curves of Cr2N and CrN coatings immersed in 3.5 wt% NaCl solution. The curves for two coatings are similar that include three typical regions of activation, passivation and over-passivation. The corresponding electrochemical parameters (corrosion potential (ECorr), corrosion current (Icorr), range of passive region (ΔEpass), passive current (Ipass), pitting potential (Epit)) are listed in Table 2. The Ecorr of CrN coating (~−22 mV) is slightly positive compared to Cr2N coating (~−108 mV). The Icorr of Cr2N coating is only 0.85 nA cm⁻², which is an order of magnitude lower than that of CrN coating of 5.5 nA cm⁻², suggesting that Cr2N coating exhibits a better corrosion resistance. In addition, the passive region of Cr2N coating is more pronounced and the Ipass is smaller as compared to CrN coating, which indicates that Cr2N coating is more...
susceptible to passivation. And Cr$_2$N coating has better pitting resistance as evidenced by its higher $E_{\text{pit}}$. Figure 3 shows the surface morphologies of nitride coatings after electrochemical corrosion tests. It can be observed that a number of pinholes distribute on the corroded surface of Cr$_2$N coating, whereas the CrN coating presents more serious corrosion. Similar phenomenon was also observed on the surface of CrN-coated H13 steel after potentiodynamic polarization in 0.5 M H$_2$SO$_4$ solution [25]. This is caused by the corrosive damage to the coatings by Cl$^-$ at extremely high polarization voltages, where the relatively imposed voltage is higher for CrN coating due to its smaller range of passive region and lower $E_{\text{pit}}$, thus inducing severe corrosion as indicated by the ultimate high current density. A number of studies have compared the corrosion resistance between Cr$_2$N and CrN coatings, but there are no consistent results [21–23]. Microstructural defects such as microdroplets and pores in PVD coatings have a detrimental effect on the corrosion performance [16], of which the fewer droplets in Cr$_2$N coating in this study may partially promote its better corrosion resistance. In addition,
the high Cr activity of Cr₂N coating contributes to the dissolution of Cr and the formation of more stable chromium-rich oxide layer thus increasing the corrosion resistance [21].

Figure 4 displays Nyquist and Bode plots of Cr₂N and CrN coatings in 3.5 wt% NaCl solution measured at OCP. Nyquist plots for two coatings are shown as capacitive arcs at high frequency and as lines at low frequency, which is consistent with the single time constants shown in the Bode plots. The capacitive arcs at high frequency represent the impedance of coatings and the lines at low frequency correspond to mass transport during corrosion reaction. The capacitive arc of Cr₂N coating is obviously larger than that of CrN coating, indicating that Cr₂N coating exhibits a greater corrosion resistance. Based on EIS analysis, the equivalent circuit of Cr₂N and CrN coatings that describes the interface between work electrode and electrolyte is displayed in Figure 5, where \( R_{\text{sol}} \) represents the resistance of electrolyte, constant phase element (CPE<sub>dl</sub>) and \( R_{\text{ct}} \) stand for the double-layer capacitance and charge transfer resistance at the coating-electrolyte interface, and \( W \) is associated with the mass transport. Here, the use of CPE<sub>dl</sub> to replace the ideal capacitor element in equivalent circuit is due to frequency dispersion effect caused by several factors, such as surface inhomogeneous properties and roughness [26–28]. The fitting EIS results are listed in Table 3. The fit of the equivalent circuit model to the experimental data is determined from the chi-square (\( \chi^2 \)) value in the iterative modeling process, where the value of \( \chi^2 \) on the order of \( 10^{-3} \) or...
below is acceptable. In this work, the value of $\chi^2$ for Cr$_2$N and CrN coatings is 3.85 × 10$^{-4}$ and 9.06 × 10$^{-4}$, suggesting that selected equivalent circuit model is suitable. The values of $R_{sol}$ and CPE$_{dl}$ of Cr$_2$N coating are nearly equal to those of CrN coating. The values of $n_d$ are close to 1, indicating a small deviation of the specimens from the ideal capacitance behavior. $R_{ct}$ reflects the degree of difficulty in charge transfer, which is normally adopted to evaluate the corrosion resistance of coatings. In principle, the Cr$_2$N coating with high Cr activity may release metallic Cr easily. However, the $R_{ct}$ value of Cr$_2$N coating is two order magnitude larger than that of CrN coating, which is probably attributed to its sensitivity to passivation, thus inducing the formation of passive layer with decreased charge carrier density. The better corrosion resistance of Cr$_2$N coating indicated by $R_{ct}$ is consistent with the results of potentiodynamic polarization.

**Conclusions**

In this work, thick Cr$_2$N and CrN coatings were prepared by virtue of AIP at a high deposition rate of more than 15 μm/h. The electrochemical corrosion behavior of two nitride coatings in 3.5 wt% NaCl solution was studied. The corrosion current and charge transfer resistance of Cr$_2$N coating were 0.85 nA cm$^{-2}$ and 7.19 × 10$^6$ Ω cm$^2$, while those of CrN coating were 5.5 nA cm$^{-2}$ and 4.32 × 10$^4$ Ω cm$^2$. The lower corrosion current and higher charge transfer resistance of Cr$_2$N coating indicate that it exhibits better corrosion resistance than CrN coating. Furthermore, Cr$_2$N coating has larger range of passive region and higher pitting potential ($E_{pit}$), which resulted in it being slightly corroded after potentiodynamic polarization test.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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