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The corrosive behavior of Cr/CrN multilayer coatings with different modulation periods

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ABSTRACT

Cr/CrN multilayer coatings with varied individual layer thickness were synthesized by arc ion plating. The SEM results confirmed the clear periodicity of these coatings. They are known to contain bcc Cr, fcc CrN and hcp Cr_2N phase by XRD patterns tested. The polarization curves show that the corrosion potential of the coatings with modulation periods of 603, 862, 1351 nm are more negative compared to that of the one with modulation period of 260 nm, which indicates that the lowest modulation period results in the highest corrosion resistance. The corrosion resistance of 1351 nm coating is higher than that of 603 nm and 802 nm coating. Nyquist diagrams show that these multilayer coatings are the corrosion of only coatings without the degradation of substrate. The 260 nm and 1351 nm multilayer coatings show higher charge transfer resistance but the 603 nm multilayer coatings present the lowest charge transfer resistance. These results can be attributed to the interface effect or nitride effect providing better resistance to diffusion of saline ion into the coatings, respectively. The corrosion resistance of coatings may mainly result from the interfaces and the nitride effect is secondary.

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1. Introduction

Combined erosion–corrosion presents a serious issue for engineering components exposed to corrosive slurries. For example pump impellers, values and nozzles which encounter corrosive solution with suspended hard particles show catastrophic failures under this combined attack [1,2]. Transition metal nitride coatings, such as TiN, CrN and ZrN etc., which are prepared by Physical Vapor Deposition (PVD) technology, have been developed to achieve high wear and corrosion resistance. They are found effective on using as protective coatings. In general, the transition metal nitride coatings are chemically inert and thermally stable. However the growth defects (droplets, pores, pinholes, inter-columnar voids, grain boundaries, etc.) in the coatings prepared by arc ion plating compromised their effectiveness on resisting erosion–corrosion [2,3]. These defects not only allowed the solution a direct path to the substrate but also are the "weak" parts in the coatings which form the initiation points of mechanical failure.

Different strategies have been followed to improve the coating characteristics. Effects of coatings thickness [3,4], incorporation of interlayer and composition of the coatings [5] on the corrosion behavior of single layer coatings have been studied. Thick TiN coating is expected to have good corrosion resistance but thin layer of TiN coatings is severely affected by the corrosive medium [6]. Pitting corrosion is expected to occur if the thickness of the coatings is less than 6 μm [3,6]. Incorporation of the interlayer (such as electroless deposition Ni, or PVD Ti, Cr etc.) between the substrate and coating helps in achieving good adhesion and high corrosion resistance. Alloying of the coatings (i.e. ternary coatings) can enhanced wear and corrosion resistance as compared to the binary coatings by increasing the hardness and controlling the size and the density of the micro-pores. The nanocomposite and multilayer structure [3,7] coatings are the most effective on resisting erosion–corrosion. The flat and sharp interfaces between two alternative individual layers in multilayer structure impede the inter-columnar voids and cut off the corrosive medium path to the substrate. During the chemical attack Cr easily forms dense Cr_2O_3 layer on the coating surface, which passivates the surface and prevents further corrosion attack [3]. The Cr/CrN multilayer coatings show excellent wear resistance and also provide a good corrosion protection. R. Bayon et al. [8] showed that the modulation periods (bilayer periods) of Cr/CrN multilayer coatings affected their wear and corrosion resistance. The coatings with shorter bilayer period presented longer charge transfer resistance (i.e. higher corrosion resistance) before the wear test. But after the mechanical interaction, the higher resistance value was found in

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the coatings with longer bilayer periods. The combined effects of the tribological condition and the immersion time in the aggressive electrolyte significantly reduced the corrosion resistance of the short bilayer period coatings. Under tribocorrosion condition, metal nitride coatings have mainly shown abrasive–adhesive wear mechanisms. Moreover, due to their relatively low fracture toughness, cracks can easily develop during both initial surface grinding and subsequent corrosion.

In this paper, our work concentrates on the evaluation of electrochemical behavior of the Cr/CrN multilayer coatings with different modulation periods on stainless steel substrate in 3.5 NaCl solution.

2. Experimental details

304 stainless steel substrates were mechanically polished, followed by ultrasonic cleaning in alcohol and acetone solution and then rinsing in deionized water before being located into the reactor chamber. Target was high purity chrome (99.9 at.%) with a size of diameter Φ60 mm. The distance between the target and substrate was kept at approximately 240 mm. Prior to deposition, the chamber was evacuated to a pressure of 6.7×10^{-3} Pa, and then Ar was introduced for sputtering cleaning to remove the oxide and contaminant layer on the substrate at pulse bias of −800 V and duty cycle of 30% for 5 min. The coatings were prepared at 0.6 Pa pressure in deposition chamber with a −150 V bias, duty cycle at 20% and 60 A arc current. The substrate did not rotate. The mass flow rate of Ar and N_2 gas is 30 and 35 sccm, respectively. The four coatings were prepared by arc plating under the time ratio (min:-min) of 2:2, 2:4, 2:7, 2:10 of Ar to N_2 gas being alternately fed into the chamber during deposition, which corresponded 23, 16, 11 and 8 layer in multilayer coatings, respectively. For all multilayer coatings, the inter layer near substrate and outside layer of coating is Cr and CrN, respectively.

The surface and cross-section images of the multilayer coatings were observed by scanning electron microscopy (SEM) of S3600N mode. In order to clear the interface of the chromium and chromium nitride multilayer coatings and get a sharp photographic image, the multilayer coatings were immersed in an HF and HNO_3 mixed solution (1:9) for 30 min, which preferentially etches Cr over CrN. The microstructure of the multilayer coatings was analyzed by X-ray diffraction with a Cu Kα source. Potentiodynamic polarization and electrochemical impedance spectroscopy measurements were performed at 25 °C in a three-electrode cell containing 3.5% NaCl aqueous solution. The instrument used was a PARCSTAT 2273 advanced electrochemical system. A saturated calomel electrode (SCE) was used as the reference electrode, and the counter electrode was platinum. Before electrochemical measurements, the samples were immersed in solution for approximately 30 min until a steady open circuit potential was recorded. Potentiodynamic polarization tests were carried out at a scanning rate of 0.167 mV/s. Electrochemical impedance was measured by perturbing the open circuit potential of the specimens with a 10 mV ac signal with a frequency decreasing from 10^5 Hz to 1 m Hz. The specimens were covered with paraffin for electrical insulating except the surface for electrochemical measurements.

3. Results and discussion

3.1. Surface and cross-section morphology

Fig. 1 is the SEM surface morphology of the Cr/CrN multilayer coatings with different time ratio of Ar to N_2 gas being alternately

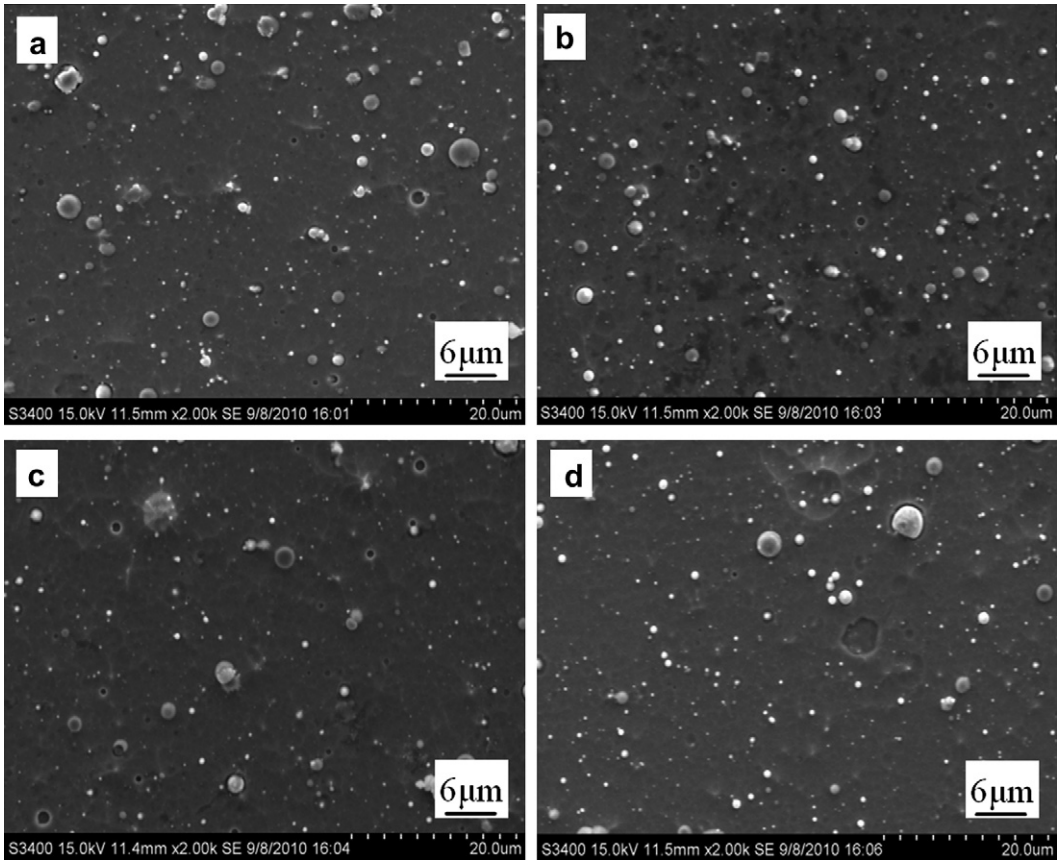

Fig. 1. The SEM image of the surface morphology of Cr/CrN multilayer coatings with different time ratio (min:min) of Ar to N_2 gas in chamber. (a)2:2, (b)2:4, (c)2:7, (d)2:10.

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