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Corrosion behaviors of Cr(N,O)/CrN double-layered coatings by cathodic arc deposition

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Abstract

In this study, the Cr(N,O)/CrN double-layered coatings on tool steel were deposited using cathodic arc deposition process. CrN layer was first deposited on tool steel as an interlayer to ensure better adhesion. Then Cr(N,O) was deposited as a surface layer. The Cr(N,O) composition was varied by changing the O_2/N_2 flow ratios during the coating process. The phase structure, chemical composition, and morphology of coatings were observed by utilizing X-ray diffractometer, Auger electron spectrometer and AFM. The corrosion behavior of coatings was investigated using polarization and immersion tests. Polarization test of coatings was carried out in the solution of 3.5 wt.% NaCl. For immersion test, Cr(N,O)/CrN double-layered coatings were exposed under H_2SO_4 environment for 26 h. The results showed that the corrosion resistance of Cr(N,O)/CrN double-layered coatings with thinner thickness with thinner thickness was better than that of CrN single layer since pinholes of coatings was inhibited by double layer structure.

Keywords: Cathodic arc deposition; CrN; Cr(N,O); Corrosion

1. Introduction

Due to process cleanliness and environmental comprehensively, research into PVD coatings has been an essential task to develop various advanced surface modification materials for industrial manufacturing. Chromium nitride (CrN) deposited by PVD technology has been identified as one of the more promising protective coatings for plastic injection molding applications. Critical features of CrN coating include better wear resistance, corrosion resistance, heat resistance, and most importantly, ease of mold release [1–5]. When CrN is exposed to high temperatures, a dense and stable Cr_2O_3 nano-layered film is formed on the surface as a protective scale [6]. Previous study concluded that the Cr_2O_3/CrN double-layered coatings exhibited excellent oxidation resistance and corrosion resistance in molten A356 aluminum alloy bath [7]. The oxide layer serves as a protective layer to provide superior oxidation resistance to the underlying CrN.

Cr_2O_3 can be deposited with various technologies including thermal spray [8,9], sputtering [10–12], CVD [13–15], ion implantation [16] and cathodic arc deposition (CAD) [17,18]. In particular, CAD is known to be a superior technology with certain advantages including high deposition rate, low process temperature and easy to obtain dense structure with stoichiometric composition. However, the limitation of CAD is droplet contamination resulting in pitting corrosion problem of coated tool steel. Among the researches for improving corrosion resistance of coated steel systems, multi-layered and multi-phased structures of PVD coatings are particularly interesting. An insight into the corrosion mechanisms of these composite coatings will undoubtedly be beneficial to improve the performance of tool steels.

In this study, Cr(N,O)/CrN double-layered coatings on tool steel were conducted by using CAD process. CrN layer was first deposited on tool steel as an interlayer, followed by

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Table 1
Details of the deposition parameters of CAD coating processes

Ar^+bombardment	−1000 V bias for 1 min
Substrate temperature (°C)	200
Chamber pressure (Pa)	3.3
Substrate bias voltage (−V)	150
Evaporator current (A)	70
Source to substrate distance (cm)	15
CrN interlayer	
Deposition time (min)	35
N_2 flow rate (sccm)	300
Cr(N,O) top layer	
Deposition time (min.)	25
N_2 flow rate (sccm)	230
O_2 flow rate (sccm)	23, 46, 69, 92, 115, respectively

the deposition of Cr(N,O) as the surface layer under the conditions of various flow rate of reactive oxygen gas. Corrosion behavior of the Cr(N,O)/CrN double-layered coating was evaluated by electrochemical measurements and correlated with the microstructural factors, such as crystallographic orientation and chemical composition. The purpose of this study is to improve the corrosion resistance of Cr-based PVD coatings for plastic injection mold applications.

2. Experimental procedure

Specimens were made of JIS SKH51 steel bars (0.92% C, 0.28% Mn, 3.64% Cr, 0.26% Co, 1.94% V, 5.79% W, 5.04% Mo, Fe balanced), which were machined into disks of 30 mm in diameter and 5 mm in thickness. Prior to PVD treatment, the steel substrates were mechanically ground and polished to have an average surface roughness of approximately 0.1 μm. Both CrN and Cr(N,O) thin films were deposited by CAD coating system which was equipped with two oppositely positioned cathodic arc evaporators. After thorough wet cleaning in an ultrasonic bath with ethanol, the samples were then affixed to chamber holders and the chamber pressure was pumped down to 0.01 Pa. The substrates are then further cleaned by high-energy Cr ion bombardment at −1000 V bias voltage to ensure clean surface of the substrate. During ion bombardment, the pressure was kept at 0.1 Pa by charging the Ar gas only. In subsequent depositing stages, the reactive gases of N_2 and O_2 were fed into the chamber and reacted with metallic ions to form CrN and Cr(N,O) films, respectively. Surface layer processing was performed with different flow rate of oxygen gas increasing from 23 sccm to 115 sccm while the nitrogen flow was fixed at 230 sccm. Chamber pressure during depositing stage was kept at the range of 2 to 3.3 Pa depending on the reactive O_2/N_2 gas flow ratio. Deposited time was kept at 35 and 25 min for CrN and Cr(N,O) films, respectively. Details of the deposition process parameters are listed in Table 1.

Crystallographic characteristics observations of as-deposited specimens were conducted by using X-ray diffractometer (XRD; model PAN analytical X'pert PRD (MRD)) with Cu K_α radiation. Auger electron spectrometer measurements were performed by utilizing a model 670 PHI Xi Physical Electronics Auger system, which has a spot size approximately 100 μm. Scanning electron microscopy (SEM; model JOEL JSM-5600) and atomic force microscopy (AFM) were employed to investigate the thickness and surface morphology of the coatings. The ratio of porosity of the coatings was evaluated from these micrographs by an image analysis program (Matrox Inspector software). The dc potentiodynamic tests were conducted in 3.5 wt.% aqueous sodium chloride (NaCl) solution through a three-electrode cell connected to a Potentiostat/Galvanostat (Model 263A) system. A saturated calomel electrode (SCE) was used as a reference to measure the potential across the electrochemical interface. The corrosion potential was determined with the sweeping setting rate at 1 mV/s and sweeping potential range from −0.3 V to 1.0 V. Aqueous solution of 10 vol.% H_2SO_4 was prepared for immersion tests. The immersion solution was continuously stirred at ambient temperature. Weight loss of the specimens as an indicator of corrosion rate was

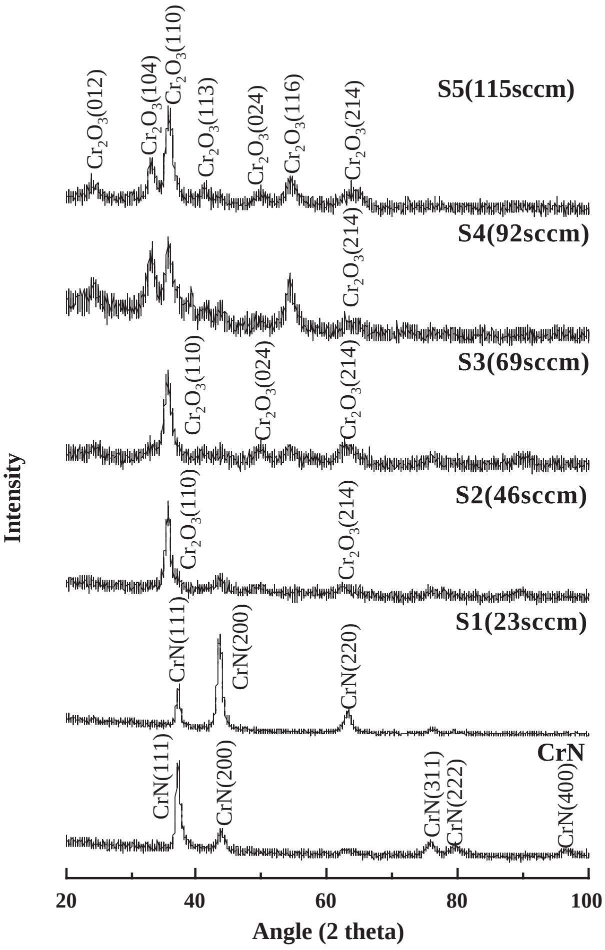

Fig. 1. X-ray diffraction patterns of specimens with various oxygen flow from 0 sccm to 115 sccm.