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High-temperature oxidation of magnetron-sputtered Cr–N-coated steels

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Abstract

Single-, 15-, and 30-layered Cr–N coatings deposited on a steel substrate were oxidized in air at 700 and 800 °C. Oxidation occurred via the predominant outward diffusion of Cr, Fe, and nitrogen, and the inward diffusion of oxygen. Nitrogen escaping from the coating into the air made the multi-layered Cr–N coating act as a single-layered Cr–N coating during oxidation. The oxidation product was primarily Cr_2O_3, which contained a small amount of Fe and nitrogen. The unreacted coating beneath the Cr_2O_3 scale had some iron transported from the substrate.

Keywords: Magnetron sputtering; Chromium nitride; Oxidation

1. Introduction

Chromium nitride coatings are widely used to increase the service life of cutting tools, die molds and machine components, owing to their high hardness, good adhesion to most substrate materials, and superior wear and corrosion resistance. Oxidation resistance is an important property because the coatings are frequently exposed to oxidative atmospheres during service at high temperatures. Although the oxidation of single-layered Cr–N coatings has been studied extensively [1–8], that of multi-layered Cr–N coatings has not been adequately studied. The oxidation limit of Cr–N coating is known to be ~750 °C, and the Cr–N oxidizes to Cr_2O_3 accompanied by nitrogen evolution [1–8].

The aim of this study was to characterize the oxidation behavior and mechanism of single- and multi-layered Cr–N coatings deposited by the cross-field unbalanced magnetron (CFUBM) system. The advantage of multi-layered coatings is that the residual stress can be effectively reduced in order to increase the coating adhesion because soft intermediate layers are inserted between the hard layers. The CFUBM method was developed for cost-effective industrial applications through high deposition rates [9]. The deposition of Cr–N coatings at different nitrogen pressures leads to the formation of different phases, such as α-Cr, Cr_2N and CrN. In this paper, single- and multi-layered Cr–N coatings were deposited and oxidation tested.

2. Experimental procedures

A $25 \times 25 \times 5$-mm^3 ferritic stainless steel substrate (AISI 430) was mechanically polished using 1 μm alumina powder, ultrasonically rinsed in acetone, heated at 250 °C for 10 min, and cleaned in Ar (0.4 Pa) for 20 min with the substrate biased at −800 V. The coatings were deposited by the evaporation of a pure Cr solid cathode using the CFUBM system [9]. By switching on and off the nitrogen, about 3.4–4.0-μm-thick, single- and multi-layered Cr–N coatings with alternating Cr interlayers were deposited. The detailed deposition parameters are summarized in Table 1.

Table 1
Deposition condition of Cr–N coatings by CFUBM method

Base pressure	5×10^{-3} Pa
Ar pressure	0.4 Pa
Target power density	35 W/cm^2 (DC)
Substrate/target distance	60 mm
Temperature	250±10 °C
N_2 flow rate	60 sccm
Jig rotation speed	20 rpm

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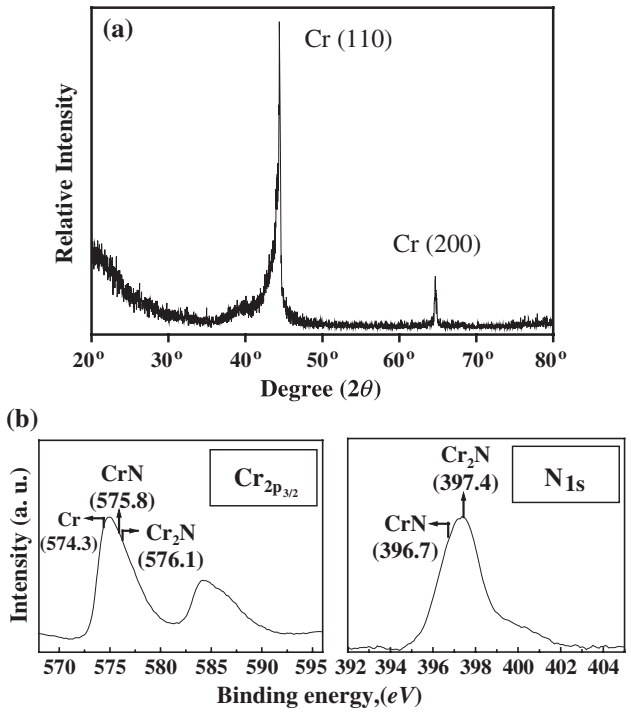

Fig. 1. Cr–N coating having 30 layers. (a) XRD pattern, (b) XPS spectra.

The oxidation tests were carried out in static air at 700 and 800 °C. The oxidized samples were inspected by X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GDOES), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) equipped with an energy-dispersive spectrometer (EDS), electron probe microanalysis (EPMA), Auger electron spectroscopy (AES), and transmission electron microscopy (TEM operated at 300 keV). The TEM samples were glued onto a Si dummy wafer using epoxy, mechanically polished to a thickness of ~30 μm, and ion milled to perforation.

3. Results and discussion

The XRD tests indicated that all the prepared coatings were primarily the Cr phase with (110) and (200) preferred orientations, as shown in Fig. 1(a). The grain size, D, which was obtained by applying the Scherrer formula to the bcc-Cr(110) line, was about 36 nm. The XPS spectra shown in Fig. 1(b), however, indicated that nitrogen formed Cr_2N as well as CrN, whose amounts were not large enough to show up in the XRD pattern. Hence, all the coatings were Cr having some Cr_2N and CrN.

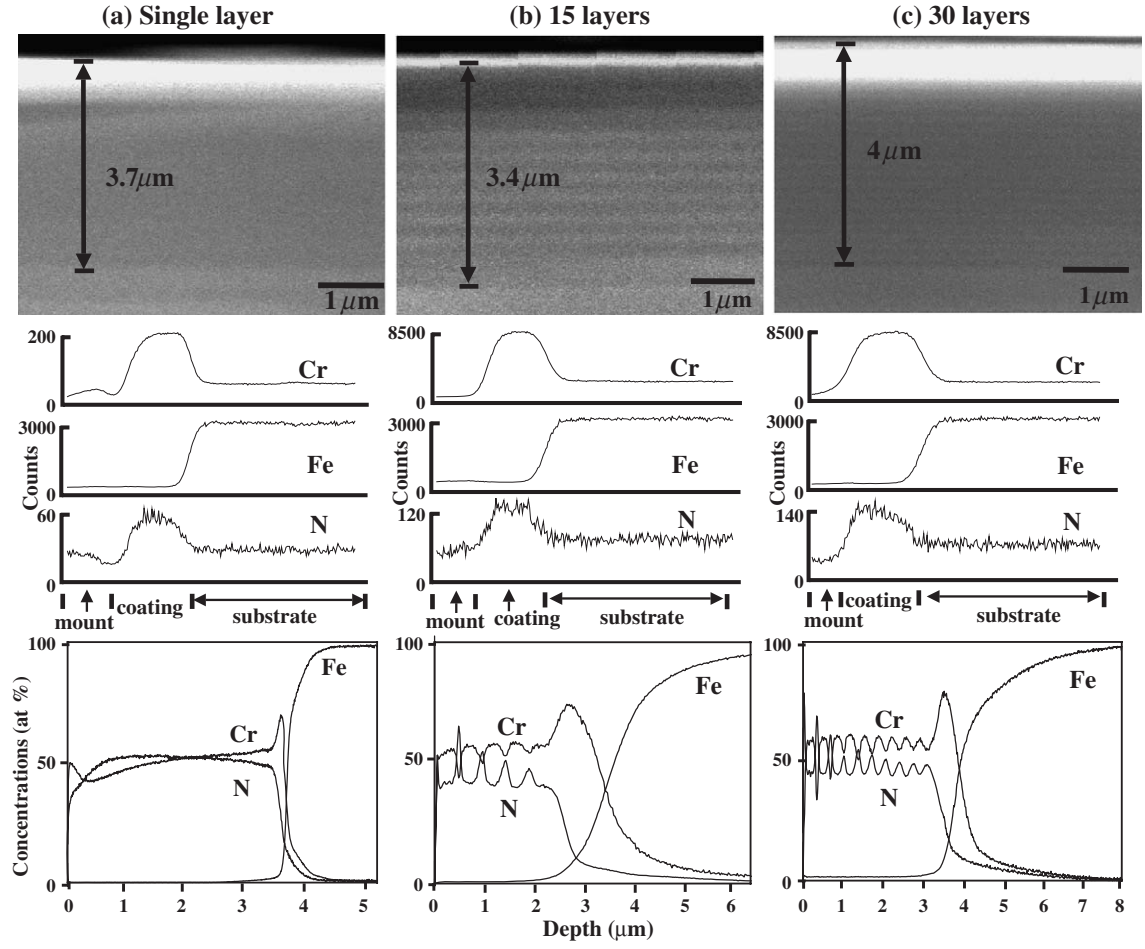

Fig. 2. SEM cross-sectional image, EPMA line profiles, GDOES concentration profiles of Cr–N coatings. (a) single layer, (b) 15 layers, (c) 30 layers.