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Investigation of microstructure and mechanical properties of multi-layer Cr/Cr_2O_3 coatings

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ABSTRACT

Single and multi-layer Cr/Cr_2O_3 coatings were deposited by reactive magnetron sputtering with the total thickness of 7 μm on steel substrates. X-ray diffraction analysis showed that single and multi-layer Cr/Cr_2O_3 coatings have different preferred crystal orientations. Columnar microstructure was detected by transmission electron microscopy both in metal chromium and ceramic chromium oxide layers. Grain size increased with the coating thickness. The value of single and multi-layer coating's fracture toughness is between 4 and 6 $MPa{\cdot}m^{1/2}$ measured with the Berkovich tip indentation, and it is between 2.8 and 3.9 $MPa{\cdot}m^{1/2}$ when measured with the Vickers indenter. The adhesion is about 192.1 and 246.7 J/m^2 for single and multi-layer coatings, respectively.

1. Introduction

Chromium oxide exhibits good optical, magnetic and mechanical properties, so it can be used as a selective solar ray collector and for other applications as a protective coating against wear, corrosion, and oxidation [1–6]. Among various chromium oxides, Cr_2O_3 is most chemically stable under ambient conditions [7]. The performance and reliability of chromium oxide coatings is often limited by their mechanical properties. Nanoindentation methods are routinely used for elastic modulus and hardness coatings characterization, although the main chromium oxide coatings failure model is fracture and delamination, thus it is important to investigate the coating fracture toughness and adhesion properties. Up to now, there has been no discussion of chromium oxide coatings fracture toughness in the literature.

Various techniques have been used to deposit Cr_2O_3 coatings, including sputtering [1,2,4,8–10] electron-beam evaporation [11,12], chemical vapor deposition [6,7], electrochemical deposition [13], and chemical spray pyrolysis [14], based on different applications. Various deposition methods result in different chromium oxide coatings microstructure, which controls their properties, so it is important to know the microstructure of specimens prepared by different deposition methods. Magnetron sputtering has become the process of choice for the deposition of a wide range of industrially important coatings. Examples include hard, wear-resistant, low friction, corrosion resistant, decorative coatings and coatings with special optical or electrical properties. Quality films and coatings can be deposited by magnetron sputtering, but unfortunately they are typically highly stressed. With the increase of coating thickness, the residual stress typically increases. Several studies showed that coating thickness plays an important role in enhancing both physical vapor deposition (PVD) coated tool cutting performance and resistance to abrasive and erosive wear [15]. Graded systems have been employed to obtain thicker coatings without losing performance in terms of coating adhesion and fracture toughness [16]. It is also likely that thicker coatings will improve corrosion resistance in aqueous environments by eliminating through-thickness pin-hole defects.

In this paper X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques were used to characterize the microstructure of multi-layer chromium oxide coatings prepared by reactive radio frequency magnetron sputtering technique. Fracture toughness and adhesion were also investigated.

2. Experimental details

Chromium oxide coatings were deposited on $W_{18}Cr_4V$ high speed steel substrates by reactive magnetron sputtering from 50 mm Cr target (99.95% pure) in Ar/O_2 plasma at a total pressure of 10^{-1} Pa. Distance between the substrate and the target was 55 mm. Deposition was performed in mixed Ar and O_2 atmosphere with 350 W radio

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frequency (RF) power. Argon flow rate was kept at 15 standard cubic centimeters per minute (sccm), while oxygen flow rate was 6 sccm. Prior to coating deposition substrates were cleaned in acetone and ethanol for 10 min in order to remove organic contaminants, and then etched for 15 min in Ar plasma at RF power of 100 W to further clean the substrate surface. Chromium interlayer of 500 nm thick was sputtered for 10 min, after which oxygen gas was introduced into the sputtering chamber for the chromium oxide reactive sputter deposition, then 3 μm thick chromium oxide coating was deposited in 30 min. After that, the oxygen gas valve was shut down and next chromium interlayer was deposited. By repeating these steps Cr/Cr_2O_3 multi-layer structure was achieved. The substrate was electrically grounded and its temperature reached 473 K during deposition.

The coating microstructure was examined using Rigaku D/max-RB X-ray diffractometer with a Cu source (λ = 1.54056 Å). Each sample was exposed to the X-ray beam at 40 kV and 150 mA. The scanning region of the diffraction angle (2θ) was from 10° to 110° at 0.02° step size. TEM sample was prepared by FEI Focus Ion Beam (FIB) equipped with field emission scanning electron microscope. Tecnai F20 TEM was used to characterize interfaces and microstructure of chromium oxide multi-layers. TEM operating voltage was 200 kV. Fracture toughness was measured using Hysitron triboindenter and microhardness test instrument. Adhesion between chromium oxide coatings and steel substrates was evaluated by means of a scratch test using CETR Micro-Tribometer model UMT-2. The normal load was continuously increased at a rate of 0.25 N/s, while the conical diamond tip (120° angle, 200 μm tip radius) was moving at a constant velocity of 0.05 mm/s.

3. Results and discussion

Fig. 1 shows an FIB cut of the Cr/Cr_2O_3 coating multi-layer structure. A 500 nm metal chromium layer was deposited on high speed steel in order to achieve thick coating with low residual stress and good mechanical performance, then about 3 μm chromium oxide coating was deposited on top. Single Cr/Cr_2O_3 layer with the same thickness was deposited for the purpose of comparing the mechanical properties. The coating in Fig. 1(b) is quite dense without pores or inclusions present, so good mechanical properties can be expected. A metal interlayer between the substrate and the ceramic coating can help to relieve the residual stress and improve the coating fracture toughness, adhesion and impact resistance [17–19].

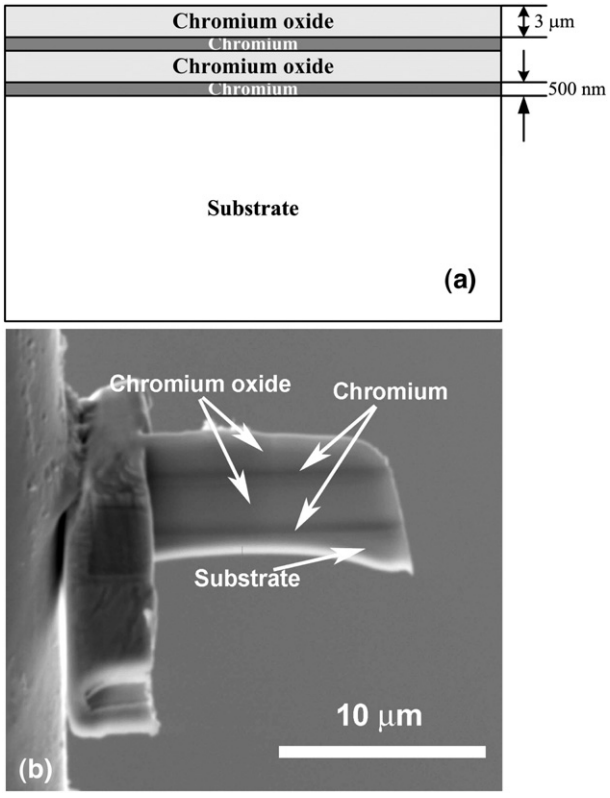

Fig. 1. (a) Multi-layer structure schematics; (b) FIB cross-section of the Cr/Cr_2O_3 multi-layer coating.

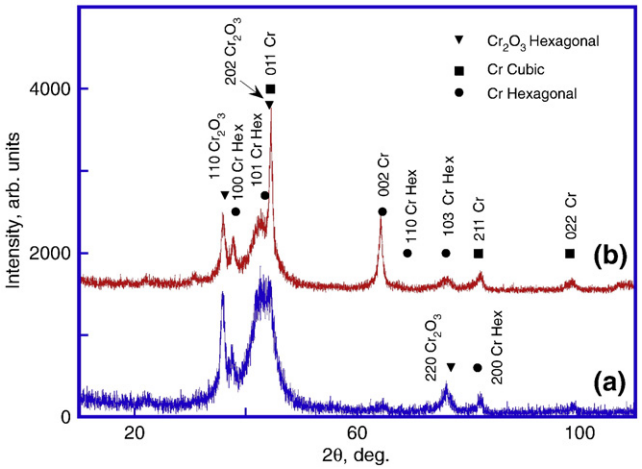

Fig. 2. XRD pattern of chromium oxide (a) single Cr/Cr_2O_3 layer; (b) multi-layer Cr/Cr_2O_3.

Considering the patterns measured in Fig. 2, the phase analysis of the single- and multi-layer chromium oxide coating samples was performed using a programme EVA [20] with direct link to the powder diffraction file [21]. The XRD patterns of the both samples show a lot of X-ray reflections attributed to Cr_2O_3 and cubic and hexagonal modifications of Cr (see Table 1). The XRD patterns were analysed by means of a programme ANALYZE [22]. The reflection profile data obtained (full width at half maximum (FWHM) *FWHM*, integral breadth β and central-angle Bragg angle $2\theta_B$ of the reflection profiles) were used for strain–size analysis of the samples.

As it is known, the broadening of the XRD reflection profiles can be caused by an influence of small-size incoherently diffracting crystallites formed due to presence of the dislocation arrays, stacking faults, twins and other extended imperfections. Additionally, the dislocations, vacancies, interstitials, substitutionals and other defects of this type result in formation of a strain in crystallites or in columns of the lattice unit cells. The strain and crystallite size broadening can be separated by integral breadth method as it is given briefly below.

The reflection profiles are described by Lorentzian function (Cauchy approximation) or by Gaussian function (Gaussian approximation) or by a combination of both reflection profile types (pseudo-Voigt function).

Table 1
Adopted from [39] structural data of the crystalline phases found in the samples

Crystalline phase	Space group[a]	*a* (Å) / α (°)	*b* (Å) / β (°)	*c* (Å) / γ (°)	Ref.
Cr, cubic	(229) $Im\bar{3}m$	2.885 90	*a* 90	*a* 90	ICSD code 64711
Cr, hexagonal	(194) $P6_3/mmc$	2.722 90	*a* 90	4.434 120	ICSD code 43526
Cr_2O_3	(167) $R\bar{3}c$	4.957 90	*a* 90	13.592 120	ICSD code 75577

[a] (Number of space group) space group symbol.