Surface & Coatings Technology 206 (2012) 2638–2644

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Study on nanocrystalline Cr_2O_3 films deposited by arc ion plating: II. Mechanical and tribological properties

Tie-Gang Wang [a,b,c], Dawoon Jeong [a], Yanmei Liu [d], Qimin Wang [a,e,*], Srinivasan Iyengar [b], Solveig Melin [b], Kwang Ho Kim [a,**]

[a] National Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 609-735, South Korea
[b] Division of Materials Engineering, Lund University, Box 118, SE-22100 Lund, Sweden
[c] State Key Laboratory of Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China
[d] Analysis and Testing Division, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China
[e] School of Mechanical and Electronic Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

ARTICLE INFO

Article history:
Received 28 May 2011
Accepted in revised form 5 October 2011
Available online 18 October 2011

Keywords:
Cr_2O_3 film
Arc ion plating
Bias voltage
Mechanical property
Friction coefficient
Wear rate

ABSTRACT

In this work, the influence of substrate bias voltage on the microhardness, adhesive strength, friction coefficient, and wear rate of AIP Cr_2O_3 films deposited on AISI 304 stainless steel substrates was investigated systematically. In the meantime, the wear failure mechanism of AIP Cr_2O_3 films in dry sliding contact was also analyzed and discussed. The results showed that the mechanical properties, adhesive behaviors, and tribological performance of AIP Cr_2O_3 films were greatly altered by applying a negative bias voltage. With increasing the bias voltage, the hardness, critical load, and tribological performance of AIP Cr_2O_3 films first were improved gradually, and then were impaired slightly again. When the bias voltage is −100 V, the Cr_2O_3 film possessed the highest hardness, the strongest adhesion, and the best wear resistance. The essence of above phenomena was attributed to the variations of microstructure and defect density in the films induced by the substrate bias voltage increase. The main wear failure mechanism of AIP Cr_2O_3 films is crack initiation and propagation under the high contact stresses, inducing the local film with small area to flake off gradually, and eventually leading to the formation of a wear scar.

1. Introduction

Chromium, a 1st row transition metal, forms a number of oxides, including CrO_3, $(CrO_3)_n$, Cr_3O_8, Cr_5O_{12}, CrO_2, and Cr_2O_3. Among these, Cr_2O_3 is the only solid chromium oxide that is thermodynamically stable at temperatures higher than 500 °C [1]. It is isostructural with sapphire (Al_2O_3) and has a corundum structure that is composed of hexagonal close-packed oxygen and chromium atoms occupying two-thirds of the octahedral sites [2]. Because of its desirable mechanical and chemical properties, such as high hardness, chemical inertness, and high-temperature stability, Cr_2O_3 has been widely used as a coating material for corrosion resistance [3] and also as a catalyst for selective oxidation reactions [4]. Moreover, because of its high solar absorbance and low thermal emittance, the Cr_2O_3 films embedded with chromium particles (black chrome) are utilized as solar absorber coatings [5].

Many methods including magnetron sputtering [6,7], chemical vapor deposition (CVD) [8,9], pulsed laser deposition [10], plasma spray [11,12], molecular beam epitaxy [13], and atomic layer deposition [14] have been used to synthesize Cr_2O_3 films. However, deviation from the exact stoichiometry of Cr_2O_3 as well as the inclusion of macroparticles, porosities, and metallic Cr phase in the layers was found to have a detrimental effect on their mechanical properties and could mask possible correlations to their nanostructures [15–17]. Due to the differences in microstructure and composition, Cr_2O_3 films exhibit different mechanical and tribological properties deposited by different methods. The hardness of a plasma sprayed Cr_2O_3 coating with 50 μm thickness was about 14.7 GPa [12], while a 200 nm thick rf-sputtered chromium oxide film with stoichiometry close to Cr_2O_3 exhibited 30 GPa hardness combined with good scratch resistance [17]. Hones et al. [16] had systematically investigated the correlation between the mechanical properties of sputtered Cr_2O_3 films and deposition parameters, such as oxygen partial pressure and substrate temperature, and found favorable deposition conditions with an oxygen partial pressure of about 15–20% of the total working pressure at substrate temperature exceeding 500 K. Using the pulsed laser deposition technique, Tabbal et al. [10] had studied the relationship between nanostructure and physical properties of Cr_2O_3 thin films grown on Silicon (100) at temperatures ranging from 20 to 950 °C. It was revealed that a significant improvement in the crystalline quality and a reduction of the residual stress occurred with increasing the deposition temperature.

* Correspondence to: Q. Wang, National Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 609-735, South Korea. Tel.: +82 51 5102391; fax: +82 51 5103660.
** Corresponding author. Tel.: +82 51 5102391; fax: +82 51 5103660.
E-mail addresses: qmwang@pusan.ac.kr (Q. Wang), kwhokim@pusan.ac.kr (K.H. Kim).

0257-8972/$ – see front matter. Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2011.10.026

These effects were accompanied by an increase of the grain size of film from 50 to 200 nm. Nanoindentation results indicated that the films with hardness and elastic modulus values as high as 20 and 220 GPa, respectively, could be synthesized at 600 °C or below, but a further increase in deposition temperature led to a deterioration of the mechanical properties. Applying arc deposition method, Hsu et al. had studied the wear and corrosion behaviors of arc deposited Cr–O–N and (Ti,Al)N coatings [18,19], as well as bias effects on the tribological behavior of cathodic arc evaporated CrTiAlN coatings [20]. However, few articles reported that nanocrystalline Cr_2O_3 films were deposited by AIP technique, and the influence of negative bias voltage on the tribological properties of Cr_2O_3 films.

In part I [21], we studied the influence of substrate bias voltage on the film growth process, microstructure, and characteristics, including the phase constituents, grain size, lattice constant, chemical compositions, as well as surface and cross-section morphologies. In the present work, we further investigate how the negative bias voltage affected the mechanical properties, adhesive behaviors, and tribological performance of AIP Cr_2O_3 films deposited on AISI 304 stainless steel substrates. In the meantime, the wear failure mechanism of AIP Cr_2O_3 films in dry sliding contact is also explored.

2. Experimental details

2.1. Deposition of the Cr_2O_3 films

The mirror-polished AISI 304 stainless steel (Cr—18.5, Ni—9.4, Mn—0.8, Si—0.4, P—0.1, Fe balanced, all in weight percent) substrates with the size of 30×25×1 mm were used to deposit chromium oxide films at various bias voltages by using an arc ion plating system. The arc cathode with a diameter of 80 mm for the Cr (99.99 wt.% purity) target was at a distance of 350 mm from the rotating substrate holder. A schematic diagram of the coating system had been elaborated in the previous studies [22,23]. After the substrates were cleaned in an ultrasonic cleaner bath by using acetone and alcohol solution for 20 min, respectively, and then were placed on the substrate holder opposing the target surface in the vacuum chamber. Prior to the Cr_2O_3 film deposition, the substrates were also cleaned by Cr ion bombardment under −700 V negative bias voltage for 3 min, which would remove contaminants and ensure good adhesion of the deposited films. After that a Cr interlayer with the deposition time of 5 min was introduced to provide critical metal-to-oxide bonding and to reduce stresses. In order to avoid poisoning of the target during the oxide film deposition process, the protective gas (Ar) at a fixed flow rate was introduced into the vicinity of Cr target. The purity of argon and reactive gas (O_2) was 99.999%. The thickness of all Cr_2O_3 films in this work was kept about 3.5 μm by controlling the deposition time. Under the same conditions, the deposition rate of Cr_2O_3 films with different bias voltages had been accurately measured in advance, respectively. The detailed deposition parameters for nanocrystalline Cr_2O_3 films fabricated by arc ion plating technique are listed in Table 1.

Table 1
Detailed deposition parameters for nanocrystalline Cr_2O_3 films fabricated by arc ion plating technique.

Parameters	Value
Base pressure (Pa)	3.5×10^{-3}
Working pressure (Pa)	3.0×10^{-1}
Deposition temperature (°C)	300
Arc current (A)	55
DC bias voltage (V)	0, −25, −50, −100, −150, −200, −250
Ar:O_2 gas flow ratio (sccm)	40:20
Substrate rotation speed (rpm)	25
Film thickness (μm)	~3.5
Distance between the target and substrate (mm)	350

2.2. Mechanical property measurements

The microhardness of the Cr_2O_3 films was evaluated using a microhardness tester with a Knoop indenter (Matsuzawa, MMT-7) under a load of 25 g and a dwelling time of 10 s. All the hardness values were measured with the indentation depths of less than one-tenth of the film thickness which would avoid the influence of substrate effect [24]. The distance between two indentations was not less than three times the minor diagonal to prevent stress-field effects from nearby indentations. At least 20 separated measurements were taken on each sample to obtain a mean value. The calibration of the film hardness values was regularly checked by measuring on a stainless steel sample.

The adhesive strength between the Cr_2O_3 films and stainless steel substrates was evaluated by a scratch tester (J&L Tech, Scratch test JLST022) with a Rockwell C diamond stylus (cone apex angle: 120°; tip radius: 200 μm) that was moved across the sample surface. During the scratch tests, the normal load was increased gradually up to 100 N with a loading rate of 1 N/s and a translation speed of 0.2 mm/s, and the scratch length was set as 20 mm. The friction force, friction coefficient, and acoustic emission signals were also recorded during the scratch tests in order to measure the critical load. These investigations were complemented by observation of scratch track with an optical microscope (OM, Olympus PMG3-613U W/Acc) and a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) to confirm the starting point of adhesion failure. The values of critical load presented in this paper are the average of five measurements made on the identical specimen.

2.3. Friction and wear tests

The tribological behaviors of the Cr_2O_3 films deposited at different bias voltages were evaluated by sliding wear tests via a conventional ball-on-disk friction and wear instrument (J&L Tech, Tribometer). An alumina ball (6.15 mm in diameter, 1800 $HV_{0.2}$) was chosen as a counterpart for the evaluation of tribological performance of the films. The sliding wear tests were conducted with a sliding speed of 0.1 m/s, a constant normal load of 5 N, and a total of 12,000 rotation cycles (6 mm in diameter of wear track).

The friction coefficient was continuously recorded during the whole testing processes by a computer. Before the sliding wear test, both the specimen and the counterpart were ultrasonically cleaned in acetone and ethanol for 20 min, respectively. All experiments were repeated three times in controlled room temperature (~20 °C) and relative humidity (25–30% RH). In all tests no film perforation occurred. According to Archard's classical wear equation [25], the specific wear rate k can be calculated by the following equation [26]:

$$k=\frac{V}{SL} \tag{1}$$

where V is the wear volume of the Cr_2O_3 films calculated by the dimensions of wear tracks, and S, L are the total sliding distance and the applied load, respectively. In addition, the film worn tracks after wear tests were evaluated using a FE-SEM (Hitachi S-4800) coupled with an energy dispersive X-ray spectroscopy (EDS, Oxford ISIS), and an OM (Axiovert 200 MAT, Carl Zeiss).

3. Results and discussion

3.1. Microhardness

Fig. 1 shows the variation of Knoop microhardness of AIP Cr_2O_3 films deposited at various bias voltages. It can be seen that all the films presented a higher hardness, and the highest film hardness was obtained when the bias voltage is −100 V. With increasing the