

## Annealing effects on microstructure and mechanical properties of chromium oxide coatings

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### Abstract

Reactive radio frequency magnetron sputter-deposited chromium oxide coatings were annealed at different temperatures and times. The influence of annealing temperature on the microstructure, surface morphology and mechanical properties was examined by X-ray diffraction, nanoindentation, pin-on-disc wear and scratch tests, respectively. X-ray results show that the chromium oxide sputtered at room temperature in low oxygen flux is primarily amorphous. Annealing below 400 °C did not cause much change, while annealing at higher temperature of 500 °C caused a significant change in microstructure and mechanical properties. Hardness increased from 12.3 GPa to 26 GPa, and the wearability improved with higher annealing temperature due to the formation of crystalline Cr<sub>2</sub>O<sub>3</sub> phase, which occurs at 470 °C. Annealing time had little effect on mechanical properties and microstructure, although coating surface roughness increased with a longer annealing time. Coating adhesion was improved by annealing, due to residual stress relief and possible interfacial interdiffusion.

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### 1. Introduction

Chromium oxide coatings exhibit high hardness, low friction, high wear and corrosion resistance, and good optical characteristics [1–4]. Many techniques have been developed to deposit chromium oxide coatings, including reactive radio frequency (RF) magnetron sputtering, which is most suitable for industrial production. It is possible to achieve high quality Cr<sub>2</sub>O<sub>3</sub> stoichiometric coating with nearly 30 GPa hardness combined with good scratch resistance [5]. Hardness and wear resistance are important properties of chromium oxide for protective coatings applications. Several attempts have been made to obtain high hardness and good wear resistance by controlling the coating deposition parameters [2,6–8].

Previous research shows that hardness of chromium oxide coatings strongly depends on the stoichiometric polycrystalline Cr<sub>2</sub>O<sub>3</sub> phase present in the coating. Sputter deposition param-

eters, such as oxygen partial pressure (controlled by oxygen flow rate), radio frequency, substrate bias and temperature have influence on the microstructure and mechanical properties of

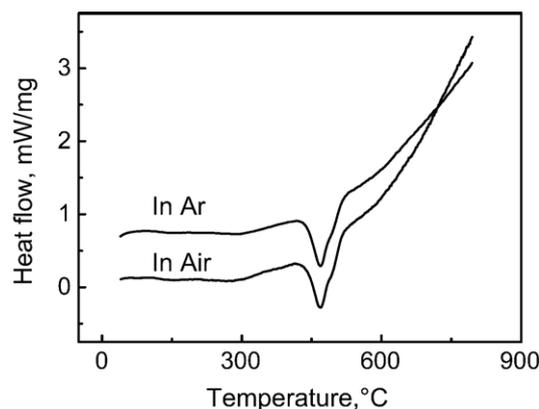


Fig. 1. DSC analysis of chromium oxide coating performed in Ar and in air, showing phase transformation at 470 °C.

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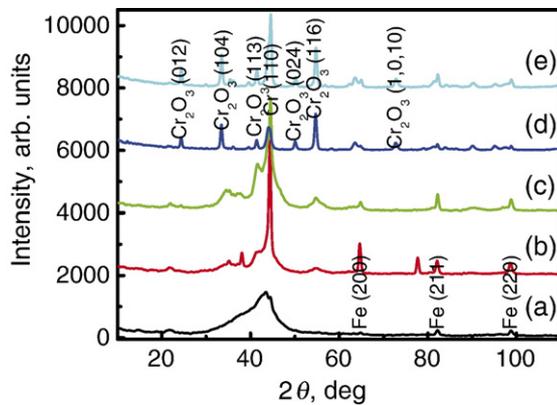


Fig. 2. XRD patterns of chromium oxide coatings annealed at different temperatures and times: (a) as-deposited, (b) 400 °C for 1 h, (c) 400 °C for 3 h, (d) 500 °C for 1 h, and (e) 500 °C for 3 h.

chromium oxide coatings. An increase in oxygen partial pressure could be beneficial for the  $\text{Cr}_2\text{O}_3$  phase formation, but at the same time may increase the possibility of target poisoning [2,8]. Radio frequency and substrate bias are often responsible for high residual stresses, leading to coating crazing and spalling [9]. High substrate temperature limits coating applications to components, which can withstand high deposition temperatures. As-deposited chromium oxide coatings prepared by reactive RF magnetron sputtering often contain both polycrystalline  $\text{Cr}_2\text{O}_3$  and lower hardness amorphous phases [2].

In this paper, sputter-deposited chromium oxide coatings on low carbon steel substrates were annealed at high temperatures

in order to obtain stoichiometric polycrystalline  $\text{Cr}_2\text{O}_3$  phase. The influence of annealing temperature and time on the coating microstructure, hardness, wear resistance and adhesion strength was investigated.

## 2. Experimental details

Deposition of chromium oxide coatings on low carbon steel substrates was performed by unbiased reactive magnetron sputtering at a total pressure of  $10^{-1}$  Pa of mixed Ar and  $\text{O}_2$  atmosphere (99.99% purity) at 350 W RF power. Ar flux was 20 standard cubic centimeters per minute (sccm), and oxygen flux was 2.3 sccm. Steel substrates were polished and ultrasonically cleaned in acetone prior to deposition. Distance between the substrate and the target was 55 mm. In order to enhance coating adhesion, steel substrates were etched in Ar plasma, and then a pure Cr interlayer was deposited for 15 min with the thickness of 800 nm. Total deposition time for the chromium oxide coating was 1 h, which resulted in a 4  $\mu\text{m}$  thick coating.

Differential scanning calorimetry (DSC) measurements of the coatings were performed from room temperature to 800 °C in Ar gas and in air. Later coatings were annealed in air for either 1 or 3 hours at various temperatures according to the DSC analysis results.

The coating microstructure was examined using Rigaku D/max-RB X-ray diffractometer with a Cu source. Surface morphology, hardness and Young's modulus of the coatings were characterized using Hysitron Triboindenter with a Berkovich diamond indenter tip. The indenter tip was loaded at a constant rate of 150  $\mu\text{N/s}$

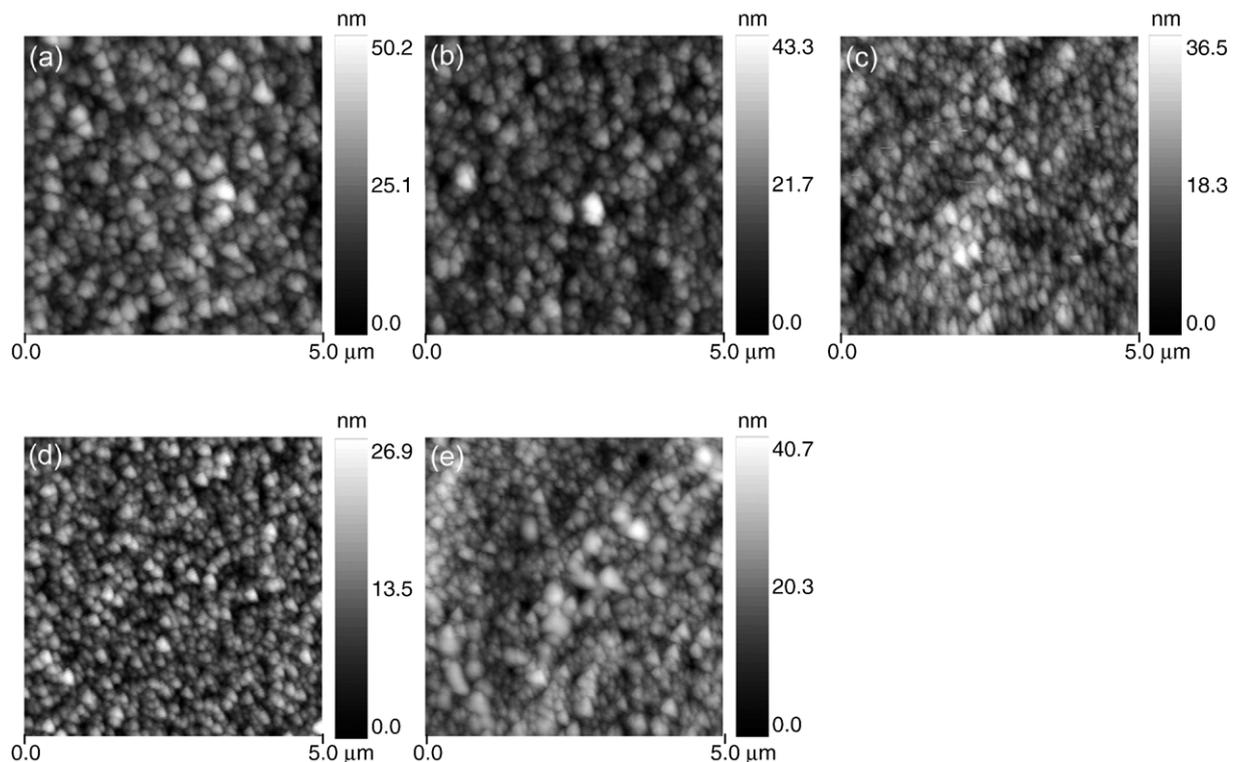


Fig. 3. Surface morphology of chromium oxide coatings annealed at different temperatures: (a) as-deposited, (b) 400 °C for 1 h, (c) 500 °C for 1 h, (d) 400 °C for 3 h, (e) 500 °C for 3 h.

to the maximum load of 3 mN. Hardness and modulus values presented are an average of ten or more indents for each test condition. Wear experiments were carried out by means of the CETR Micro-Tribometer model UMT-2 at room temperature in air. Relative sliding speed of the diamond tip was 300 mm/min with the normal load of 5 N. The wear resistance was evaluated in terms of the wear volume.

Adhesion between chromium oxide coatings and steel substrates was evaluated as a function of different annealing conditions by means of a scratch test using UMT tribometer. The normal load was continuously increased at a rate of 0.25 N/s, while the conical diamond tip ( $120^\circ$  angle, 200  $\mu\text{m}$  tip radius) was moving at a constant velocity of 0.05 mm/s.

### 3. Results and discussion

Results of Differential scanning calorimetry (DSC) measurements are presented in Fig. 1, which shows an inverse peak observed on both curves obtained in air and Argon. The inverse peak indicates that the chromium oxide coating underwent a phase transformation at about 470  $^\circ\text{C}$ . Correspondingly, the annealing tests were carried out at either 400 or 500  $^\circ\text{C}$  for 1 or 3 h in air.

Fig. 2 shows X-ray diffraction (XRD) patterns of the as-deposited and annealed chromium oxide coatings on low carbon steel substrates. It can be seen from Fig. 2(a) that the as-deposited chromium oxide coating is amorphous, as only a few substrate diffraction peaks are present. Some crystalline  $\text{Cr}_2\text{O}_3$  peaks appear in Fig. 2(b) with the amorphous background after the chromium oxide coating was annealed at 400  $^\circ\text{C}$  for 1 h. When the annealing time was increased to 3 h at 400  $^\circ\text{C}$ , as shown in Fig. 2(c), the diffraction peaks of  $\text{Cr}_2\text{O}_3$  phase changed a little, but the substrate diffraction peaks became weaker, compared with Fig. 2(b). Fig. 2(c) also reveals that although the annealing time was increased, the amorphous phase had not completely transform to crystalline chromium oxide phase.

Fig. 2(d) and (e) exhibit XRD patterns of chromium oxide coating annealed at 500  $^\circ\text{C}$  for 1 and 3 h, respectively. These patterns clearly exhibit crystalline  $\text{Cr}_2\text{O}_3$  phase diffraction peaks, and no amorphous phase is observed in these specimens. It can be concluded that the chromium oxide coatings annealed

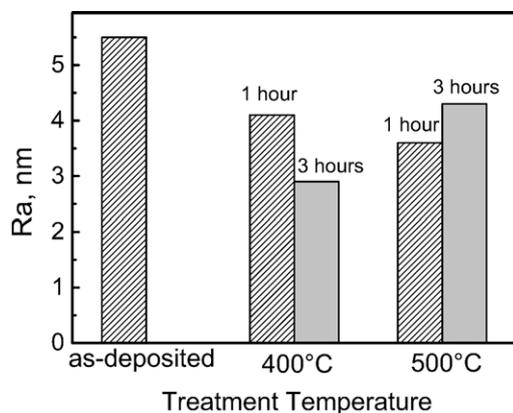


Fig. 4. The influence of annealing temperature and time on coating roughness.

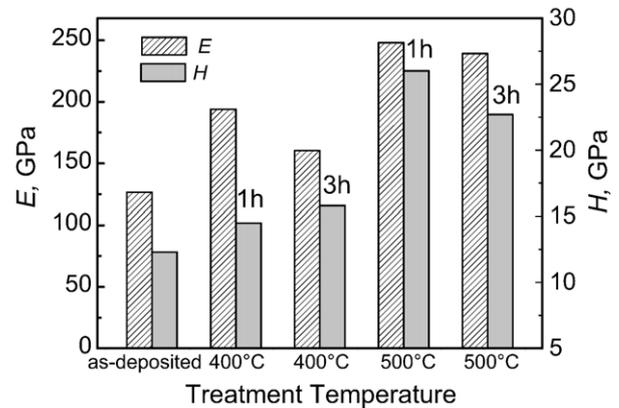


Fig. 5. Annealing effects on hardness and elastic modulus of chromium oxide coatings.

at 500  $^\circ\text{C}$  had completely transformed to the polycrystalline  $\text{Cr}_2\text{O}_3$  phase. Fig. 2(d) and (e) exhibit a little difference in width and intensity of the  $\text{Cr}_2\text{O}_3$  phase diffraction peaks. Compared with those in Fig. 2(d), the width of  $\text{Cr}_2\text{O}_3$  phase diffraction peaks in Fig. 2(e) are narrower with higher intensity, which indicates that the grain size of polycrystalline chromium oxide increased with annealing time.

Chromium oxide surface morphology was observed by using the scanning capabilities of Hysitron Triboindenter. As seen in Figs. 3 and 4, as-deposited coating exhibits island surface structure with 5.5 nm  $R_a$  roughness. When chromium oxide coatings were annealed at 400  $^\circ\text{C}$  and 500  $^\circ\text{C}$  for 1 h, their surface roughness decreased to 4.1 nm and 3.6 nm, respectively. After annealing time was increased to 3 h, at 400  $^\circ\text{C}$ , a more compact and smoother coating surface was observed in Fig. 3 (d), however, at 500  $^\circ\text{C}$ , the coating surface became coarser with  $R_a$  roughness of 4.3 nm. Higher roughness observed after annealing at 500  $^\circ\text{C}$  could be attributed to grain growth of the crystalline  $\text{Cr}_2\text{O}_3$  phase.

Hardness and elastic modulus of chromium oxide coatings annealed at different conditions are presented in Fig. 5. It can be seen that annealing treatment can significantly increase both hardness and elastic modulus. Hardness of the as-deposited amorphous chromium oxide coatings is 12.3 GPa. After annealing at 400  $^\circ\text{C}$  for 1 h, hardness increased to 14.5 GPa, and then did not

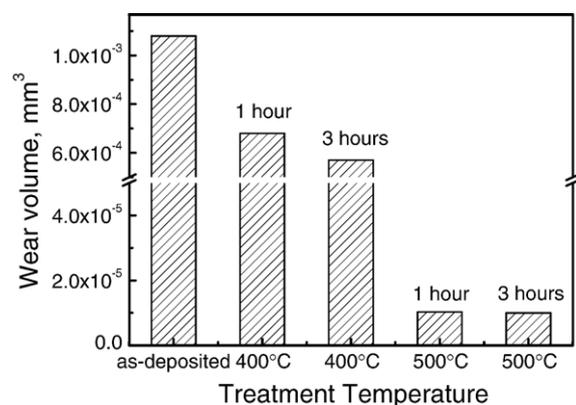


Fig. 6. Effects of annealing temperature and time on the wear volume.

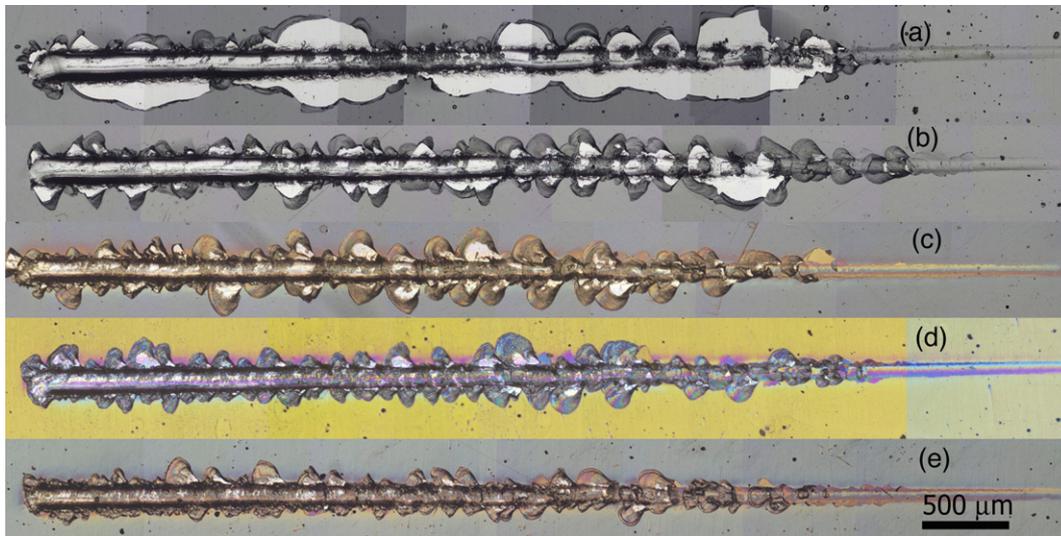


Fig. 7. Scratch tracks in chromium oxide coating: (a) as-deposited, annealed at (b) 400 °C for 1 h, (c) 400 °C for 3 h, (d) 500 °C for 1 h, (e) 500 °C for 3 h.

change much with longer annealing time. In contrast, when the coating was annealed at 500 °C for 1 h, its hardness increased to 26 GPa due to the formation of  $\text{Cr}_2\text{O}_3$  polycrystalline phase, and then slightly decreased due to  $\text{Cr}_2\text{O}_3$  grain size growth with prolonged annealing time of 3 h [10]. Elastic modulus of the coatings increased with annealing temperature, while longer annealing time caused a slight modulus reduction.

Fig. 6 shows the effect of annealing treatment on the wear behavior of chromium oxide coatings. With the increased annealing temperature, the wear volume decreased significantly, but the annealing time did not seem to affect the wear behavior. The increase of wear resistance can be attributed to improved surface roughness and increased coating hardness.

Fig. 7 gives a qualitative evaluation of adhesion between substrate and chromium oxide coatings annealed at different temperatures and times by means of the scratch test. On the as-deposited chromium oxide coating, spallation occurred during scratching, and the exposed substrate could be seen as bright spots in Fig. 7(a). This catastrophic delamination phenomenon could be attributed to high residual stresses in the coatings generated during deposition [11]. After the coating exposure to 400 °C for 1 h, the residual stresses were partially annealed, which significantly reduced the delaminated area, as seen in Fig. 7(b). With increased annealing temperature and time, adhesion was improved, as almost no coating delamination is seen in Fig. 7(c) and (d). In addition to the residual stress relief, there can be interfacial interdiffusion effects responsible for the adhesion improvement [12,13]. Fig. 8 shows high resolution micrographs of the as-deposited coatings' interfaces. There are some defects present on the substrate surface, which act as stress concentrators, so substrate treatment prior to coating deposition is very important for improving coating adhesion strength. While the interfacial layers between the substrate and the Cr, and between the Cr and the coating are amorphous, some nanocrystalline clusters are present in these amorphous layers, as seen in Fig. 8b. The incorporation of amorphous middle layer will reduce the amount of stored elastic energy in the coating by reducing its residual stress,

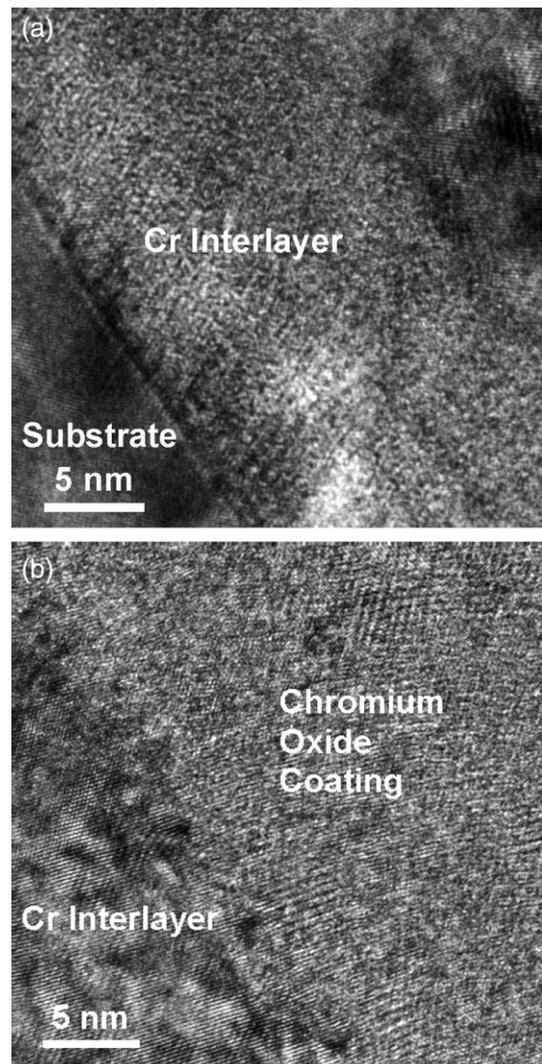


Fig. 8. HREM micrographs of the interfaces between a) the substrate and the Cr interlayer, and between b) the Cr interlayer and the coating.

allowing increasing coating total thickness without fracture failures.

#### 4. Conclusions

Effects of annealing temperature and time on microstructure and mechanical properties of chromium oxide coatings deposited on low carbon steel substrates by reactive RF magnetron sputter technique were investigated. Coatings were annealed at 400 °C and 500 °C for either 1 or 3 h. While the as-deposited chromium oxide coatings were primarily amorphous, a polycrystalline Cr<sub>2</sub>O<sub>3</sub> phase developed with annealing above the 470 °C phase transition temperature, which significantly improved coating mechanical properties. Annealing treatment also decreased the coating surface roughness, and increased its hardness, elastic modulus, wear resistance, and adhesion.

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