



Dry sliding tribological behavior of Cr coatings electrodeposited in trivalent chromium sulphate baths

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ARTICLE INFO

Article history:

Received 12 September 2016

Revised 19 January 2017

Accepted in revised form 20 January 2017

Available online 10 February 2017

Keywords:

Trivalent chromium

Annealing

Morphology

XRD

Hardness

Friction coefficient

Wear rate

ABSTRACT

In this study, tribological properties of Cr coatings obtained from Cr(III) sulphate baths with complexing agents (formate-urea, glycine and oxalate) prepared on 316Ti stainless steel have been investigated. Surface morphology and wear scar and debris were examined by scanning electron microscopy. The surface microhardness of the different coatings was performed to determine the mechanical properties of the coatings. Cr coatings phase composition was identified by X-ray diffraction. To assess the tribological behavior of the coatings, dry sliding wear test against a 100Cr6 steel ball was performed with a ball on flat configuration. Investigation of friction coefficient has shown that Cr coatings deposited in Cr(III) baths have better tribological properties as compared to those of Cr coatings deposited in Cr(VI) baths. Heat treatment (at 400 °C and 600 °C) of Cr coatings deposited in Cr(III) baths deteriorates their tribological properties i.e. the friction coefficient increases. Attempts have been made to describe the wear mechanisms of Cr coatings by observing wear tracks.

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1. Introduction

Chromium coatings are widely used in a variety of industries. Plating operations are used to fabricate two types of chromium coatings, functional and decorative. Functional chromium coatings consist of a thick layer of chromium typically 1.3 to 760 µm [1] to provide a surface with functional properties such as hardness, corrosion resistance, wear resistance and a low coefficient of friction. Applications of functional chromium coatings include strut and shock absorber rods, hydraulic cylinders, crankshafts and industrial rolls. Carbon steel, cast iron, stainless steel, copper, aluminum are substrates commonly used with functional chromium. Decorative chromium coatings consist of a thin layer of chromium typically 0.003 to 2.5 µm [1] to provide a bright surface with wear and tarnish resistance when plated over a nickel layer. It is used for plating automotive trim/bumpers, bath fixtures and small appliances.

Hard chromium electrodeposition is extensively used in modern industry due to its good corrosion and wear resistances. Commonly, chromium coatings are deposited from hazardous hexavalent chromium baths. In view of a very high toxicity of Cr(VI) compounds, the development of alternative process for hexavalent chromium plating is urgently needed. According to EU Regulation (EC) No 1907/2006 ("REACH") the

use of chromium trioxide baths for functional and decorative chromium plating will be forbidden or severely limited after 1 September, 2017.

Among many potential alternatives, trivalent chromium (Cr(III)) plating is considered as a very promising technology to replace conventional hexavalent Cr plating. Functional disadvantage of hexavalent chromium plating is low cathode efficiency, which results in bad throwing power. This means it leaves a non-uniform coating, with more on edges and less in inside corners and holes. To overcome this problem the part may be over-plated and ground to size, or auxiliary anodes may be used around the hard-to-plate areas. Trivalent chromium yields higher cathode efficiency and better throwing power. Better throwing power means better production rates. Less energy is required because of the lower current densities required [2]. The process is more robust than hexavalent chromium because it can withstand current interruptions.

Due to its low cathodic efficiency and high solution viscosity a toxic mist of water and hexavalent chromium is released from the bath. Wet scrubbers are used to control these emissions. The discharge from the wet scrubbers is treated to precipitate the chromium from the solution because it cannot remain in the waste.

Additional toxic waste created from hexavalent chromium baths include lead chromates, which are formed in the bath because lead anodes are used. In the case of Cr(III) bath, the electrolysis is carried out using an insoluble anode (Pt, titanium-manganese dioxide anodes (Ti/MnO₂) or composite TiO_x/PtO_y) anodes which do not decompose [2]. Therefore, trivalent Cr electrodeposition has attracted significant attention in recent years [3–5]. The most common trivalent chromium

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plating solutions typically contain a Cr(III) salt such as CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$ [6,7].

Trivalent chromium has a tendency to form various complexes in aqueous solutions; a weak complexing agent should be used to prevent formation of undesirable complexes [8–11]. It is well known that chromium is coordinated with water molecules which can be substituted with ligands very slowly in the stable esa-aquo complex $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ [12]. During electrolysis hydrogen evolution causes a significant pH increase near the electrode surface, at pH values higher than 4.5 coordinated water molecules may be converted to OH^- groups, which leads to formation of μ -hydroxo-bridged species further transforming into oligated (high molecular weight polymers) compounds which can precipitate near the cathode surface limiting the availability of Cr^{3+} and hindering the desired reduction reaction. Limiting parts of the described phenomena is possible to reduce by using appropriate complex agents for Cr^{3+} such as oxalic acid, formate, urea, and glycine. These organic compounds form with Cr^{3+} complexes with secondary ligands consisting of carbamidic, glycine or oxalic groups. They are thermodynamically more stable than its esa-aquo complex; so the organic ligands may sequester a considerable amount of chromium ions from its esa-aquo complex, making them available for the reduction reaction at the cathode. This suggests that electrodeposition of good quality chromium deposit is possible due to the formation of active chromium–carbamid $[\text{Cr}(\text{carbamid})_n(\text{H}_2\text{O})_{6-n}]^3$, chromium–glycine $[\text{Cr}(\text{H}_2\text{O})_4(\text{Gly})]^{2+}$ or chromium oxalate $[(\text{H}_2\text{O})_n\text{Cr}(\text{Cr}_2\text{O}_4)]^+$ and $[(\text{H}_2\text{O})_n\text{Cr}_2(\text{Cr}_2\text{O}_4)]^{4+}$ complexes. These complexes delay the formation of the stable oligomeric species, and thus provide a prolonged working lifetime in the Cr(III) plating electrolytes [8,13].

The carbon existing in these complex agents in the bath will get incorporated in the coating accompanying the reduced chromium metal. As a result, a Cr–C coating is formed [14–16]. According to <http://www.pfonline.com/articles/an-overview-of-hard-chromium-plating-using-trivalent-chromium-solutions> [17] the history of alternative processes to hexavalent hard chromium plating is a long but generally not successful story. The substitution of hexavalent chromium processes by trivalent ones seems to be the best way but currently, no processes have reached significant industrial development.

The purpose of this investigation was to consider the effect of oxalate, glycine, formate-urea as the complexing agents on the properties of Cr(III) deposits.

2. Experimental

2.1. Preparation of specimens

Chromium coatings were electrodeposited on an AISI 316Ti stainless steel (Fe-17.5 Cr-10.4Ni-0.48Mo-0.59Si-0.69Ti-0.12Cu, in wt%) substrate from the electrolytes listed below in Table 1. These trivalent

chromium electrolytes based on the SO_4^{2-} formate-urea electrolyte ($\text{Cr(III)}_{\text{f-u}}$) [3,18,19], glycine ($\text{Cr(III)}_{\text{g}}$) and oxalate ($\text{Cr(III)}_{\text{ox}}$) electrolytes [13] were chosen because while using them Cl gas is not released at the anode [2]. All the compositions of the solutions listed in Table 1 are taken from literature.

For the sake of comparison of tribology properties, Cr(VI) coating was also prepared in 120 g/l CrO_3 and 2.5 g/l Limeda Ch-3, $i_k = 40 \text{ A/dm}^2$, $t = 50^\circ\text{C}$, $\tau = 10 \text{ min}$. The additive Limeda Ch-3, which represents a mixture of sodium fluorosilicate $\text{Na}_2[\text{SiF}_6]$ and sulphate $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (potassium aluminium sulphate dodecahydrate) compounds was created in the Institute of Chemistry, Vilnius, Lithuania. The supplier ChromTex, Lithuania.

All solutions were prepared using distilled water and analytical grade chemicals (manufacturer AppliChem GmbH). The steel substrate was also treated mechanically and electropolished in the commercial solution containing 27.5 g L^{-1} sodium carbonate, 17.5 g L^{-1} sodium tripolyphosphate, 2.5 g L^{-1} sodium silicate, 2.5 g L^{-1} synthanol DS-10 (CAS No 12679-83-3) and 50 g L^{-1} sodium hydrate at a current density of 0.05 A cm^{-2} for 5 min at 50°C , using the substrate as an anode and a Ti plate as a cathode. After that samples were washed with distilled water, soaked in a hot 20 vol% HCl solution, washed again with distilled water and then immediately placed in the plating bath. Electrolyte pH was adjusted to 1.6–2.0 using H_2SO_4 or KOH.

A bath of a volume of 1 L with vertical Pt with area of $(2 \times 4 \text{ cm}^2)$ anodes and a cathode between them was maintained at a constant temperature. The cathode (substrate) and anode were disposed within the bath at a distance of 25 mm. Chromium deposits were obtained on both sides of specimen (one side's area was 1 cm^2). The cathode/anode ratio was 1:4. Chromium electroplating was performed without separation of the anodic and cathodic compartments. The current density of continuous plating was $45\text{--}50 \text{ A dm}^{-2}$ and the temperature was 48°C ; pH 1.6–2.0. The deposition thickness was 6 μm .

2.2. Characterizations

A Helios NanoLab 650 DualBeam workstation (FEI) was used for chromium coatings surface and scar morphology, debris investigation (SEM). In order to choose a typical picture for each coating, three to four locations (in the central zone) were taken. Measurements of deposit thickness were done by using the weight method. Samples were weighed before and after the electrodeposition. XRD patterns of the films were measured using an X-ray diffractometer SmartLab (Rigaku) equipped with a 9 kW rotating Cu anode X-ray tube. The grazing incidence (GIXRD) method was used in the 2θ range of 15 to 85° . An angle between the parallel beam of X-rays and the specimen surface was adjusted to 0.5° . Crystallite size was calculated using the graphical Halder-Wagner method implemented in PDXL software package (Rigaku). The approach is based on the graphical representation of linear relationship $(\beta / \tan\theta)^2$ vs. $\beta / (\tan\theta \sin\theta)$ plot (β – XRD peak physical broadening, θ – diffraction angle).

As-electrodeposited Cr samples were annealed under Ar atmosphere at 400 and 600°C , using the heating rate of $20^\circ\text{C min}^{-1}$ from room temperature to the desired temperature plateau, where they were held for 1 h and then cooled to room temperature. The microhardness tests were performed on the surface of the coatings using a PTM-3 set-up at a load of 50 g. The values of HV are the average of five indentations.

Dry sliding ball-on-plate wear tests on coated samples were carried out in the laboratory atmosphere with 30–40% relative humidity and at room temperature. For tribological measurements a CSM Tribometer (Anton Paar, Switzerland) was used. The steel ball (100Cr6) of 6 mm OD was fixed stationary. The Cr specimen was mounted on a pre-installed tribometer module, which maintained a linear reciprocal motion of 4 mm amplitude, speed 2 cm/s, load 10 N. For plotting the graphs, each data point of the coefficient of friction was obtained by taking an arithmetical average of the modular values from the central 80%

Table 1
Compositions of Cr baths used for electrodeposition of Cr (III) coatings.

Component	Cr(III) oxalate bath: gl^{-1} Markers	Cr(III) glycine bath: gl^{-1}	Cr(III) formate urea bath: gl^{-1}
	Cr(III) _{ox}	Cr(III) _g	Cr(III) _{f-u}
$\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	150	150	150
$\text{Na}_2\text{C}_2\text{O}_4$	35	–	–
H_3BO_3	30	30	30
Na_2SO_4	60	60	60
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	100	120	120
NaF	15	20	20
$\text{NH}_2\text{CH}_2\text{COOH}$	–	75	–
HCOONa	–	–	27
NH_2CONH_2	–	–	45
Deposition conditions	$i_c = 50 \text{ A/dm}^2$; $t = 48^\circ\text{C}$	$i_c = 45 \text{ A/dm}^2$; $t = 48^\circ\text{C}$	$i_c = 40 \text{ A/dm}^2$; $t = 48^\circ\text{C}$

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