Temperature effect on crack density and crystalline phase of electrodeposited chromium

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Homogeneous, crystallized and crack-free chromium (Cr) coating was electrodeposited on stainless steel at 85 $^{\circ}$C with a current density of 80 A/dm^2, evidenced by the surface and cross section metallographs of the coating. X-ray diffraction analyses indicate the coating is largely composed of body centred cubic α-Cr. The effect of temperature on the generation of cracks, surface hardness and cathodic current efficiency were also investigated. The reduction in crack density with increasing temperature may be interpreted in terms of the decreasing inhibition of lateral grain growth.

1. Introduction

Hard chromium (Cr) deposition is widely used as a surface modification method to improve the hardness, wear resistance, erosion resistance and shiny appearance of engineering tools and components such as internal combustion engine components, hydraulic cylinders, rolls and surgical tools. These modifications can find their applications in modern industry including automotive, aerospace, mining and petrochemistry etc. [1-4]. Quite often, if not always, the Cr deposits contain macro and/or micro cracks. The presence of these defects may decrease internal stresses and thereby the brittleness, however, as the initiator of the propagation of further cracks and severe corrosion, their emergence may compromise the mechanical and corrosion resistance of deposits. No need to emphasize more that, in many aspects, it will offer benefits if the crack density in deposits can be reduced effectively. As such, many approaches have been developed.

The most common method is the utilization of a duplex system, where a plate of bright crack-free Cr is first deposited, and following this, an ordinary cracked or micro-cracked Cr deposition is carried out. But in practice, it is not easy to produce this system consistently [2,5]. Another way to reduce crack density is the application of pulse current. During reverse period in pulse current, stress relief and/or anodic reaction takes place on the sample surface, resulting in less hydrogen adsorption and hence less chromium hydride formation, which are thought to be the possible initiators of internal stress. Nonetheless, the deposits obtained by this method usually have less hardness and poor wear resistance [6, 7]. The addition of organic additives containing carboxylic or aldehyde groups into chromic anhydride solution can also contribute to the reduction of crack density [8]. However, in these cases, the deposits are mainly composed of amorphous Cr which usually possess lower hardness than crystallized chromium and are not suitable as an inner layer to enhance corrosion resistance [9,10]. Clearly, a technique that can be used to prepare crack-free and crystallized Cr deposits is still highly desirable. In recent years, many studies have shown that the temperature of electro deposition could influence the structure and composition of the deposits in a large extent [11-13]. As such, in this paper, we investigated the effects of deposition temperature on the deposited Cr, and by optimizing the deposition temperature, the crystalline phase Cr with low crack density could be successfully obtained. It is likely that this will enrich our understanding on the mechanism of generation of cracks and crystallized Cr, which may lead to the design and manufacture of Cr deposits with improved service performance.

2. Experimental

Cr coatings were electrochemically deposited from hexavalent Cr bath consisting of 250 g/L CrO$_3$ and 2.5 g/L H$_2$SO$_4$. Analytical grade chemicals and distilled water were used to prepare the solution. The coatings were deposited on polished and electro-cleaned substrate of AISI 304 stainless steel. The electro deposition was performed at a current density of 80 A/dm^2 for 1 h with the stainless steel acting as the cathode and lead being the anode.

Metallurgical observations were carried out on a LEICA MEF4A Metallurgical Microscope. X-ray diffraction pattern was recorded on an XRD-6000X

(Shimadzu Corporation, Japan). Micro Vicker hardness was measured on the surface with a load of 50 g and dwell time of 15 s on an HXD-1000TM Microscopic Hardness Meter (Shanghai Taiming Optical Instrument Co., China). Current efficiency was evaluated on the mass variation of stainless steel before and after deposition.

3. Results and discussion

To examine the effect of temperature on the deposition of Cr, electro depositions were conducted at 55 ^{o}C, 60 ^{o}C, 65 ^{o}C, 70 ^{o}C, 75 ^{o}C and 85 ^{o}C using Sargent solution, *i.e.* using chromic acid as Cr source. When temperature is lower than 70 ^{o}C, bluish silver Cr coatings with higher density of cracks was obtained, as evidenced by the metallographs (Fig. 1 d, e and f). While grey Cr coatings with marginal cracks were obtained if the deposition temperature is over 70 ^{o}C, see Fig. 1a and b. It is clear that the increase of deposition temperature yields a considerable reduction in the crack density of coating. Cross section observations (Fig. 1 g and h) reveal a homogeneous coating with the thickness of a few tens of microns was deposited on stainless steel, demonstrating reasonable throwing power.
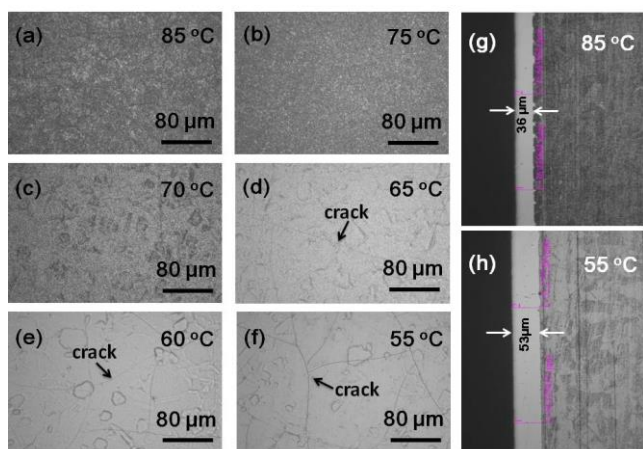

Fig. 1. Metallographs of surfaces of coatings deposited at 85 ℃(a), 75 ℃(b), 70 ℃(c), 65 ℃(d), 60 ℃(e), 55 ℃(f), and cross section of coatings deposited at 85 ^{o}C (g) and 55°C (h).

To study the underlying mechanism, X-ray diffraction patterns of coating were recorded and are depicted in Fig. 2. For the coating obtained at 85 ^{o}C, the strong peaks at 44.3 ^{o}, 64.6 ^{o}, 81.7 ^{o} and 98.0^{o} are distinguishable, which can be ascribed to the α-Cr (110), (200), (211) and (220) reflections, respectively, suggesting that the coating is mainly composed of body centred cubic (b.c.c.) α-Cr. In addition, weak peaks at 43.6 ^{o}, 50.9 ^{o} and 74.4 ^{o} are identifiable, which may stem from the reflections of β-Cr (111), (200) and (220) respectively, implying the presence

of small fraction of face centred cubic β-Cr. The emergence of Cr_2H (101) and (110) reflections at 42.9 ^{o} and 67.8 ^{o} respectively is indicative of the presence of hexagonal Cr_2H. By sharp contrast, XRD profiles of coatings obtained at 55 ^{o}C and 70 ^{o}C resemble the characteristics of amorphous Cr. The results above reveal that the coating changes from amorphous phase to α-Cr one when the temperature is increased from 55 ^{o}C to 85 ^{o}C.
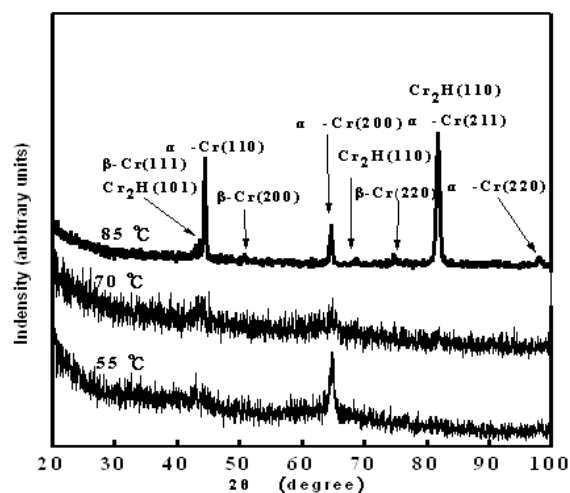

Fig. 2. XRD patterns of Cr coatings deposited at different temperatures

The rationale for the generation of crack is still a topic open for discussion. Snavely [14] argued that the successive deposition of hexagonal Cr hybrids and their decomposition to b.c.c. Cr and hydrogen cause the shrinkage in volume, yielding stress and subsequently cracks in coating. In Nielsen's view [15], a possible source of residual tensile stresses in electrodeposits can be understood as a result of grains accommodating boundary misfit at grain coalescence. The higher the inhibition of lateral grain growth, the higher the nucleation rate and so the higher number of grains that coalesce thereby leading to higher residual tensile stresses. It seems not impossible, but quite unlikely, that the phase transformation can be provoked to account for the drop of crack density at higher temperature. As for the cracked coatings, *i.e.* deposited at lower temperatures, the expected b.c.c. Cr which usually possesses low porosity and could form a protective surface coating and slower the corrosion rate of the substrate [16,17] is virtually not the prevailing phase, instead amorphous Cr governs. This implies that the phase transformation may not be the main cause for the generation of cracks here. The drop of crack density with increasing temperature may be explained using Nielsen's theory. At high temperatures, the inhibition of lateral grain growth decreases and the residual tensile stresses are not high enough to initiate the generation of cracks, but this needs further investigation.

The hardness of coating is another concern pertaining to engineering applications, since hardness is directly related with the wear resistance property. A coating with high hardness is more difficult to deform under high loads, giving rise to a delay in plastic deformation [18]. The surface hardness of coatings is plotted in Fig. 3, wherein it can be observed that the hardness value varies marginally when temperature was increased from 55 $^{\circ}$C to 65 $^{\circ}$C, but decreases precipitously with further increase of temperature. A combination of these results enables one to propose that it is not easy to obtain a crack-free Cr coating without sacrificing the hardness property.
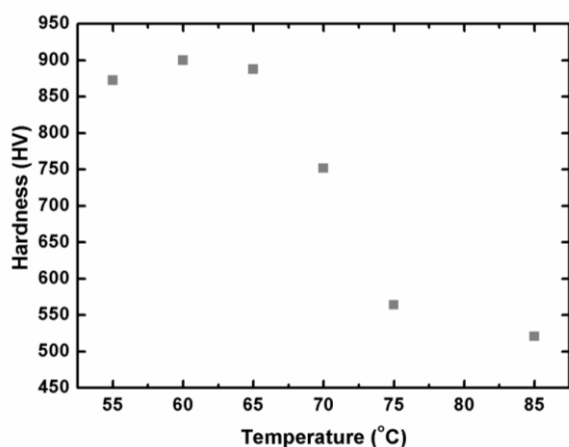

Fig. 3. Surface hardness of coatings deposited at different temperatures

For economic and ecological considerations, the cathodic current efficiency (η) is calculated using Eq. 1 and shown in Fig. 4.

$$\eta = \Delta m / (I \cdot t \cdot K) \times 100\% \qquad (1)$$

Where Δm is the mass variation of stainless steel before and after deposition, g; I is current, A; t is time, h; K is electro-chemical equivalent of Cr, 3234 g/(A·h).
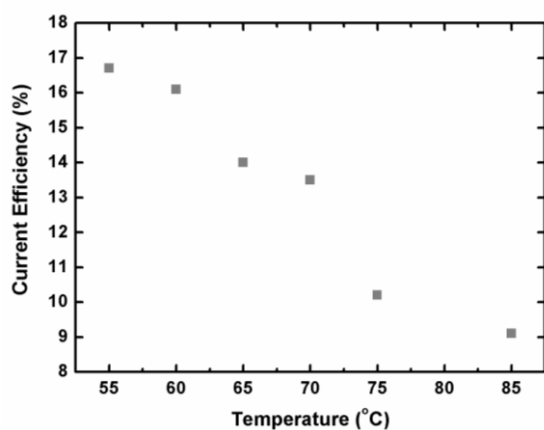

Fig. 4. Cathodic current efficiency for coatings deposited at different temperatures

Apparently, at the present current density, cathodic current efficiency decreases substantially when temperature is increased from 55 $^{\circ}$C to 75 $^{\circ}$C and then diminishes slowly, which may be explained using the deposition theory of Cr, *i.e.* the alternate formation and dissolution of cathodic colloidal membrane $Cr(OH)_3 \cdot Cr(OH)CrO_4$ [19].

4. Conclusions

A simple and economic method is described for the electro deposition of homogeneous, crack-free and b.c.c. α-Cr coatings from a bath containing chromic acid and sulfuric acid with a current density of 80 A/dm^2 at high temperatures (> 70 $^{\circ}$C). By contrast, electro depositions conducted at low temperature (from 55 $^{\circ}$C to 70 $^{\circ}$C) yield cracked amorphous Cr coatings. But it needs to be mentioned that this reduction of crack density is accomplished at the sacrifice of surface hardness and cathodic current efficiency by up to 370 HV $_{0.05}$ and 8%, respectively.

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