Multilayers coatings for corrosion resistance enhancement of chromium electrodeposits

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Chromium multilayers coatings were obtained from three different bath solutions, they were prepared using a square wave current function. Two temperatures were studied, 35°C and 55°C varying current density 10 and 70 Adm^{-2}. The combinations of different microstructures were studied: columnar and equiaxial.
The chromium multilayers were characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Salt Spray (fog) Test. In general the coatings are microcracked, have small grain size and show an unexpected very good corrosion resistance, in some cases coatings do not form red rust even after 700 h of salt spray test.

Keywords: Multilayer coating; Chromium coatings; Corrosion resistance; Microstructures; Columnar; Equiaxial; Salt spray (fog) test; Grain orientation; Scanning electron microscopy

1. Introduction

Chromium coatings produced from chromic acid solutions have a high microhardness, a good wear and corrosion resistance. Moreover, the properties that depend on microstructure can be modified by the electrolyte composition and /or plating parameters such as temperature and current density.

Some studies have been done to improve the chromium properties, particularly corrosion resistance. Corrosion resistance is influenced not only by the coating thickness but also by surface defects like cracks (depth and width). Several methods are used to improve the corrosion resistance like: plasma nitriding [1], mechanical polishing [2], r.f. magnetron sputtering [3], pulsed-current electrolysis [4-9] with or without reversing polarity [10], etc.

In previous work it has been characterized the single layer chromium coatings at different plating conditions [11,12] obtaining equiaxial and columnar microstructures.

Table 1. Operating conditions

CHEMICAL	Bath A (gL^{-1})	Bath B (gL^{-1})	Bath C*
Cr_2O_3	250	250	Commercial
SO_4^{2-}	2.5	0.6	Commercial
SiF_6^{2-}	-------	10	Commercial
	Operating Conditions		
Temperature °C		35 and 55 ± 1	
Cathodic current density (A/dm^2)		10 and 70	

* A self-regulating high speed (SRHS) bath

As each microstructure has their particular mechanical, physical and corrosion characteristics, it could be expected that if these two microstructures are alternated the final properties of the coating would improve. For this reason in this paper it has been studied the chromium multilayers properties in particular their corrosion resistance, obtaining multilayer chromium coating by pulsed electrolysis. Alternating sublayers using two different current densities to form the equiaxial and columnar microsctructures. Then the purpose of this study is to improve corrosion resistance.

2. Experimental Procedure

Three baths have been chosen, the standard bath (A), one using two catalyst (H_2SO_4 and SiF_6) (B) and one self-regulating high speed (SRHS) bath, commercial (C). Table 1 presents the different electrolytes used for the electrodeposition of chromium multilayers.

Multilayers were obtained by alternating sublayers, the first deposited at 10 Adm^{-2} then the following sublayer at 70 Adm^{-2}. Two working temperatures were used, 35 and 55 °C, they were thermostatically controlled at ± 1 °C. These plating conditions were systematically used for the different bath solutions. Substrate used was low carbon steel AISI 1018.

The sublayer chromium thickness obtained were 1 and 0.2 μm, the plating time was set to obtain a 50 μm of total coating thickness.

The fabrication of chromium multilayers was achieved by using a square-wave current. The current density was switched between 10 and 70 Adm^{-2} to change the microstructures as we have reported previously [11,12]. The sublayer thickness for both current density was kept equal i.e. the sublayer plating time was set in a condition that the sublayer thickness at 10 Adm^{-2} is equal to the sublayer thickness at 70 Adm^{-2}. The cycle $t_{10} + t_{70}$ was repeated until

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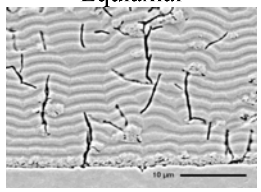
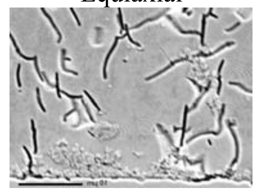
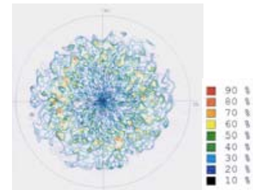
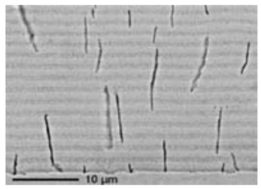
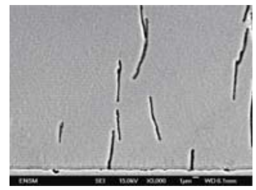
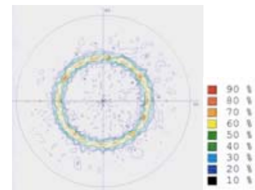
Table 2 Resume of results for multilayer coatings

	Grain size	1 µm thickness	0.2 µm thickness	Crystallographic texture
35 °C 10-70 (A/dm^2)	7 nm	Equiaxial 	Equiaxial 	
55°C 10-70 (A/dm^2)	7 nm	Columnar 	Columnar 	
Corrosion Resistance		 16 h	 700 h	

the total coating thickness was 50 µm for the different plating conditions.

The electrolytic cell was a 5-liters tank made of PTFE. Three samples shapes of the same carbon steel were used for the different analysis: a) Cylinders of about 1 cm in diameter and 7 cm long, b) parallelepipeds of about 0.9x0.9x2 cm and c) Plates of about 5x5x0.3 cm. The samples were mechanically polished and degreased in trichloromethane. Before deposition the samples were anodically etched at a current density of 50 Adm^{-2} during 1 min in the same chromium plating solution. The anodes were made of a PbSbSn alloy (3% Sb and 3% Sn) and the shape was adapted to match the samples shape.

The cylindrical samples were cut along the longitudinal axis and mechanically polished for microhardness testing and etched in a modified Murakami's reagent [13] (100 gL^{-1} K_3 [Fe (CN_6)], 8 gL^{-1} NaOH, water) for the micrographic analysis.

Several techniques were used to characterize the properties of the chromium layers. The microstructure was analyzed by SEM (JEOL 850), while grain size and crystallographic texture by XRD. The diffractometer was composed of a Phillips goniometer coupled with a device called Dosophatex ® (conceived at Ecole des Mines de Saint Etienne).

The corrosion tests were carried out in a neutral salt spray chamber in accordance to French Standard NFX 41-002. It is suggested that the tests be carried out in 5x5 cm plates. According with this standard, tests have been performed on one layer and multilayer coatings to compare. As coatings were made on steel plates of 5x5 cm, edges were protected by a varnish film and the exposition time was stopped at appearance of red rust.

3. Results & Discussion

All chromium multilayers were started by a 10 Adm^{-2} sublayer and finished by a 70 Adm^{-2} one. In general, sublayers were well formed.

3.1 Chromium multilayer microstructure.

a) Samples obtained with 1 µm sublayer thickness. At 35°C, after etched, it can be observed that chromium multilayers coatings are microcraked with some macrocracks. These coatings present the formation of equiaxial grains at the interface substrate/deposit. There are some others equiaxial grains developed inside the layers in a hazardous manner, these grains deform the continuity of subsequent sublayers producing columns emerging till to surface giving a dull aspect to the coating. In spite of very thin (1µm) sublayer thickness, the formed cracks cross the alternating layers and some of them cross the entire thickness from substrate to surface. This behavior is present only at 35° C, for the three baths tested and for 1 µm sublayer thickness, for simplicity it presents the bath A image.

At 55°C, the alternated microstructures are both columnar. The difference between them is a slight disorientation of nanograins. The 1 µm thickness sublayers are also microcracked and are perpendicular to substrate. The coatings from bath B showed the major cracks' quantity.

b) Samples obtained with 0.2 µm sublayer thickness. At 35°C, the sublayers are also microcracked, with some equiaxial grains. The coatings show the presence of equiaxial grains and these depends on the bath type. Coatings from bath A present cracks deflected from the normal to substrate while coatings from bath B show that cracks are perpendicular to the substrate and the presence of equiaxial grains is almost zero. Coatings obtained from bath C presents a lot of equiaxial grains and less cracks than the other baths. No macrocracks are detected under experimental conditions for these three baths.

At 55°C the microstructure is columnar for 10 and 70Adm^{-2} .In the case of coatings from bath A when the sublayer thickness diminishes to 0.2 µm at 55°C, the cracks number decrease but they become longer. The coatings from the other baths continue to exhibit an important number of cracks Fig 1.

3.2. Crystallographic texture

Pole figures were achieved on the surface of each sample. The {200} pole figures were obtained with the Co-Kα radiation. This peak is convenient due to its low multiplicity and good intensity. A calculus of X-ray penetration shows that in the case of chromium coatings, this penetration is around 1.2 µm [11,14,15].

At 35°C**,** the different sublayer characteristics determine the final behavior of multilayer coatings especially crystallographic texture. Due to XRD penetration, the pole figure for coatings of 1 µm sublayers thickness is that of the last layer deposited, pole figure correspond then to an equiaxial microstructure.

For sublayers of about 0.2 µm, the pole figure combines the effect of equiaxial and columnar microstructures.

The sublayers of coatings obtained at 55 °C have the same microstructure, the pole figure show only the fibre <111>. The three different baths multilayer coatings show the same pole figure, for 1 and 0.2 µm sublayer thickness.

3.3 Grain size

The one layer coatings with a columnar structure obtained at 35 °C and 10 Adm^{-2} have a small grain size of about 6-7 nm and the coatings with an equiaxial microstructure that are obtained at 35 °C and 70 Adm^{-2} have a bigger grain size of about 10-15 nm. Surprisingly the grain size for multilayers coatings obtained at 35 °C is always small i.e. 6-7 nm, in spite of different current density which is an unexpected result. In the case of multilayers coatings obtained at 55 °C, due to the presence of the same type of microstructure, the grain size is always small, i.e. 6-7 nm. This value is consistent with the grain size of simple coatings.

3.4 Corrosion Tests

Simple coatings obtained at 35°C (one layer) with an equiaxial microstructure show a poor corrosion resistance, probably due to its microstructure with macrocracks, suggesting a non isolated substrate. The coatings from the three different baths with this microstructure also show the same behavior i.e. red rust appears after 16 hrs of test.

One layer coatings with a columnar structure show a slightly better corrosion resistance. As these types of coatings are microcracked, corrosion attack would be through the cracks crossing the entire layer. Actually, coatings from bath A and bath C show red rust at 38 hours, while coatings from bath B have no corrosion evidence.

Multilayer coatings obtained at this temperature, in all cases, show a poor corrosion resistance, they rusted at 16 hours. The attack is less aggressive than in the case of one layer coatings. The combination of two microstructures does not produce macrocracks but the coating is not enough insulating to protect the substrate.

Simple coatings obtained at 55 °C (one layer) show different behavior depending on type of bath. Coatings from bath A at 70 Adm^{-2} are the most attacked; red rust is observed at 48 hrs. Exceptionally coatings from bath B show no signs of corrosion after 700 h. The bath C coatings present a unique spot of corrosion; the rest of surface has no attack. It is expected that multilayer coatings obtained at 55 °C have a good corrosion resistance.

Corrosion resistance was evaluated in plates, because it is eliminated some defects due to geometry (edge effect) and it is necessary an angle within the chamber (35°) for salt spray. This is the reason to use plates. In the other hand, for real pieces it depends on several factors, geometry, applications, size, and the results could be different from the plate's results.

The table II, shows a resume of the main results presented in this paper.

4. Conclusions

This study demonstrates that multilayer coatings have a different behavior depending on the type of microstructure. The multilayer coatings obtained at 35º C i.e. alternating the two types of microstructures show very interesting properties, as a fine grain of about 7 nm. Nevertheless this kind of coatings are not enough protective to hinder the apparition of red rust, samples rusted at 16 hrs. In contrast these same coatings but obtained at 55º C i.e. both sublayers having the same type of microstructure, also show a fine grain of about 7 nm, and corrosion tests have shown its better behavior because we have not seen red rust even after 700 hrs. Finally it is interesting to note that these kind of multilayers coatings are easy to fabricate.

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