Improving the Corrosion Resistance of Hard Chromium by Using Periodic Cathodic Current

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Abstract :
Hard chromium plating using hexavalent chromium solution is extensively used for surface treatment to improve hardness, friction performance and wear resistance.
The corrosion resistance of chromium deposit is not as efficient as end-users want it: many research works have been performed to increase the corrosion resistance of chromium electro-deposit.
We have study the influence of the current density, the temperature and the bath composition on the structure of the chromium deposit. Through this study it appears that it is possible in some cases to increase drastically the corrosion resistance using multi-layers deposits of different structure without modifying the mechanical properties (in particular micro-hardness)

Introduction:

Hard chromium plating using hexavalent chromium solution is extensively used for surface treatment to improve hardness, friction performance and wear resistance.
The corrosion resistance of chromium deposit is not as efficient as end-users want it: many research works have been performed to increase the corrosion resistance of chromium electro-deposit.
The corrosion resistance is influenced not only by the thickness deposit but also by the width, depth and density by surface unit of microcracks.
Several methods have been used to improve the characteristics : plasma nitriding (1), mechanical polishing (2), r.f. magnetron sputtering (3), pulsed-current electrolysis (4 - 9) with or without reversing polarity (10). Following the method, the objective is to modify the surface deposit or to avoid formation of cracks.
In a previous study (11), we showed that it exists mainly two types of microstructure :

- by formation of equiaxed structure (figure 1)
- by formation of a columnar structure (figure 2)

each structure depends on the temperature and the current density of the chromium electrodeposition.
The equiaxed structure presents a grain size of about 15 nm, low microhardness (600HV100), low residual stress (200Mpa) and an isotropic structure. These deposits have few cracks but they cross the deposit.
The columnar structure shows a fine grain size of about 6-8 nm, high microhardness (1000HV100), high residual stress (1Gpa) and a well-defined texture (<111> fibre), these deposits are microcracked.

The idea of the research work was to realize a multilayer chromium deposit alternating the two microstructures to obtain a variation in the properties of the deposits. To be concretely realized and industrially applicable, we choose to fix the temperature and to have the cathodic current density varying between two values to obtain the two structures. Following the study previously realized (11) it appears that the temperature at which the change of microstructure is well defined (varying only as a function of current density) is 35°C.
On an other hand, it is interesting to study the properties of multilayer chromium deposit which presents a columnar structure because many other authors(and we confirm that) have shown and that the columnar structure shows the best characteristics in terms of microhardness, abrasion and wear resistance. This microstructure is obtained mainly between 50 and 60°C, whatever is the current density. For our study we choose to work at 55°C with varying periodically current density.

Experimental procedure

Two different electrolytes have been used for the electrodeposition of multilayers chromium.
The first one (Sergent'bath) has the composition :

- 250g/L of Chromium trioxyde (CrO_3)
- 2.5 g/L of sulphate ions (SO_4^{2-})

The second one is a fluosilicic catalyst bath:

- 250 g/L of Chromium trioxyde (CrO_3)
- 0.6 g/L of sulphate ions (SO_4^{2-})
- 10 g/L of SiF_6^{2-}

The working temperatures used were 35 and 55°C and they were thermostatically controlled in the rang of ± 1°C.
The current densities were switched between 10 and 70 A/dm². These plating conditions were systematically used for the different bath conditions.
The electrolytic cell was a 5 liters tank made of PTFE. For the different experiments steel substrates (XC 48) have been used as cathodes. The geometry of the cathodes was adapted to the function : plate for corrosion test (5x5x0.3 cm) and cylinders (1cm in diameter and 7 cm long) for microhardness measurement and SEM examination.
The anodes were made of a Pb-Sb-Sn alloy (3%Sb and 3% Sn) : the shape of the anodes was adapted to the cathode shape.

The samples were polished and degreased. Before deposition, the samples were anodically etched at a current density of 50 A/dm², during 1 minute in the same chromium plating solution. Two kind of chromium sub-layers have been studied : 1 µm and 0.2 µm and plating time was set to obtain a 50µm of total coating thickness.

The cylindrical samples were cut in half long way and polished mechanically for the measures of microhardness and etched in a modified Murakami's reagent (12) : 100 g/L K3[Fe(CN6)], 8 g/L NaOH, water for the micrographic analysis.

Results and discussion

Microhardness :

The microhardness is depending on the type of bath : the deposits with an equiaxed microstructure have a low microhardness. For standard deposits, microhardness is around 600HV100, for SiF_6 Bath, it is around 800HV_{100}. For the deposits with a columnar microstructure the microhardness is high, around 1000HV_{100}.
For multilayer deposits from standard and SiF6 bath realized at 35°C, the microhardness is about 1000HV_{100}.
In the case of deposits realized at 55°C, the microhardness is always around 1000HV_{100}.

Corrosion tests :

The corrosion tests were carried out in a neutral salt spray chamber. Corrosion resistance of single and multiplayer coatings was tested. Deposition was made on steel plates (5x5 cm). A varnish film protected the edges. The exposition time of the plates depends on the attack degree of the surface. The results are showed in figure 3.

Deposits at 35°C :

We present the corrosion resistance as function of exposition time.
In a general manner, single deposits with an equiaxed structure show a poor corrosion resistance, because of this kind of microstructure show macrocracks, the substrate is not isolated. The coatings from the different baths show a poor corrosion resistance.
Single deposits with a columnar structure, showed a “slight better” corrosion resistance. This type of deposits are microcracked, corrosion attack will be through the network cracks.
In all cases, multilayers deposists realized at 35°C showed a poor corrosion resistance. The attack is less aggressive than in a single deposit. The combination of two microstructures does not product macrocracks, but the coating is not sufficiently performing to protect the substrate as the different figures show it.

Deposits at 55°C :

Single deposits obtained at 55°C show also a poor corrosion resistance, for instance, deposits from standard baths at 70 A/dm² are the most attacked (figure 3).
Multilayer deposits realized at 55°C are expected to show a good corrosion resistance. The figure show that the corrosion signs are present, mainly in the edges where coating is affected by the high current density. In the centre of the samples there are no traces of corrosion.
Figure presented in the photographies show that after 700 h of salt spray test there are no corrosion traces or pits.

Conclusion:

Multilayers deposits realized at 35°C are microcracked, but the deposits have not a good corrosion ressitance.
Multilayers deposit realized at 55°C are also microcracked. They have a “normal” microhardness (about 1000 HV100). These deposits show a very good corrosion resistance.
This study demonstrates that the multilayers deposits alterning sublayers of columnar moicrostructure result in a good corrosion resistance, without modifying notably the microhardness. Further investigations will study the mechanical properties in view of an industrial major application.

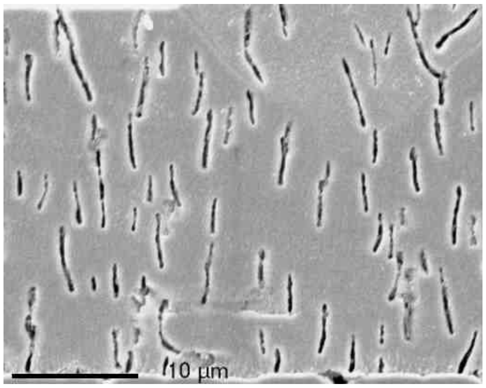


Figure 1

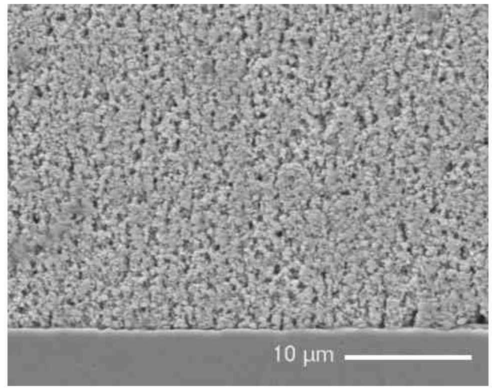
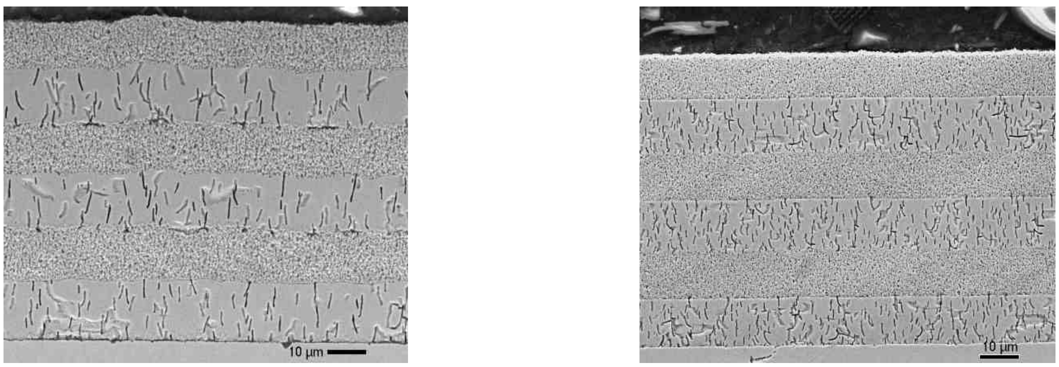


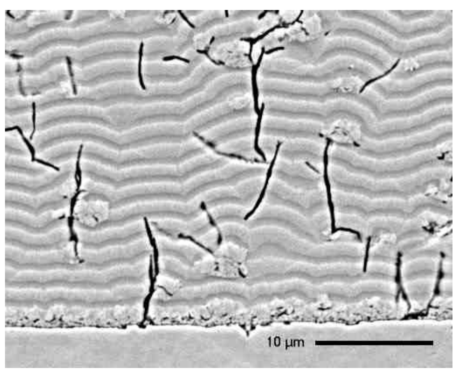
Figure 2

Deposits from standard bath: 35 °C

10 A/dm² (columnar structure) 70 A/dm² (equiaxed structure)

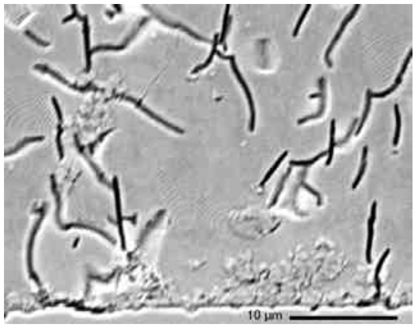


Micrographies of multilayers deposits : **35 °C** Dc : 10 et 70 A/dm² (thickness of layers : 10 µm)

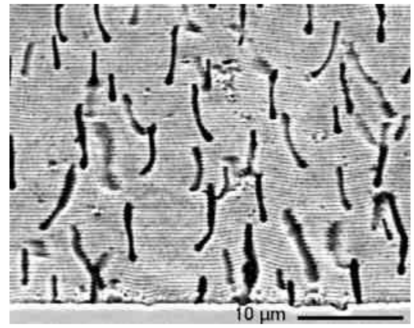


Deposit with standard bath : 35 °C 10- 70 A/dm²

Thickness of layers : 1 µm

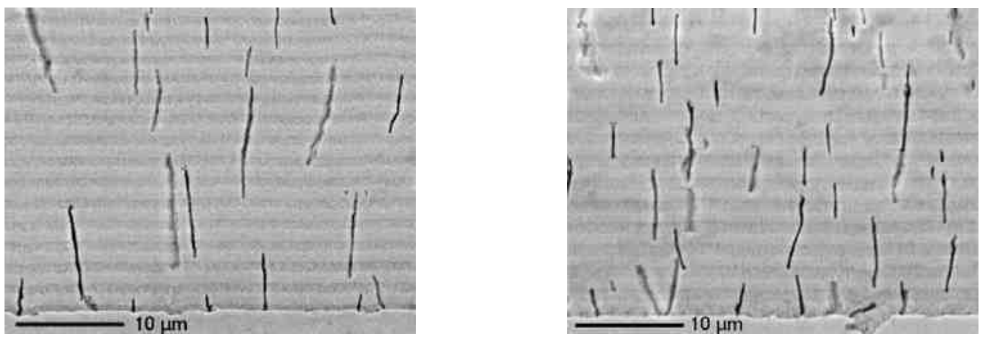


Deposit with standard bath : 35 °C

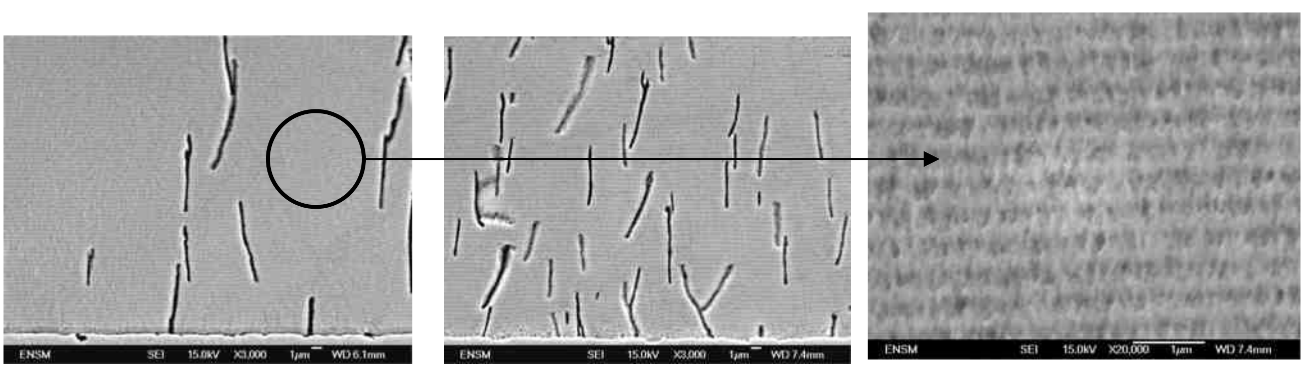


Deposit with SiF_6 bath : 35 °C

10 – 70 A/dm² - Thickness of layers : 1 µm



Deposit with standard bath : 55 °C 10- 70 A/dm²
Thickness of layers : 1 µm



Deposit with standard bath : 55 °C 10- 70 A/dm²
Thickness of layers : 0.2 µm

35 °C

10 A/dm² | 70 A/dm²

Standard

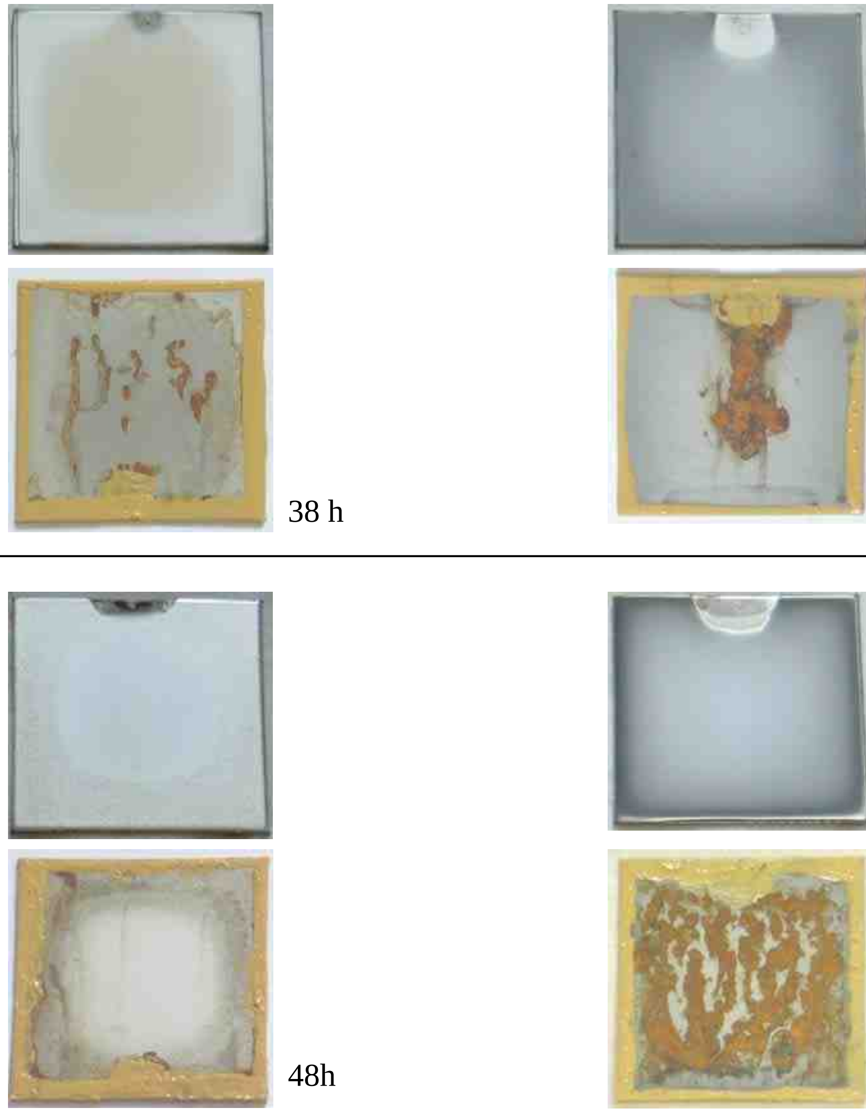
Before

After 38 h | 38 h

SiF$_6$

Before

After 48h | 16 h



Multilayers à 35 °C

Avant | Après

Standard

1 µm

16 h

0.2 µm

16 h

SiF_6

0,2 µm

16 h

55 °C

10 A/dm²

70 A/dm²

Standard

Before

After

48 h

48 h

SiF_6 *

10 A/dm²

70 A /dm²

Before

After

48h

Multicouches à 55 °C

	1 µm		0,2 µm	
Standard Before				
After		700 h		48 h
SiF_6 Before				
After		700 h		700 h

Bibliography :

1 - J.P. Ge – Plat and Surf. Fin., may 1996, p.146
2 – S. Hoshino and T. Midorikawa – 2nd Intern. Chromium Coll. – St Etienne , EMSE, (1998), p.187
3 – J. Romero, A. Lousa, E. Martinez and J. Esteve – Surf. And Coat. Tech , 163-164 (2003), p.392
4 – T. Pearson and K. Dennis – Plat. and Surf. Fin., nov. 1989, p.64
5 – J.H. Chai, D.Y. Chang and S.C. Kwon – Plat. and Surf. Fin. June 1989, p.80
6 – G. Gaigner, M. Assoul, M. Wery and J. Pagetti – Mat. et Tech., 11-12, 2001, p.61
7 – Y. Kobayashi et al. – Mat. et Tech., 11-12, 2001, p.23
8 – Y. Choi, N.I. Baik and S.I. Hong - Thin solid films, 397, (2001)
9 – J. Reby, G. Vasseur, B. Sutter
10 – C. Columbini
11 – J. Torrez-Gonzalez and P. Benaben – Plat. and Surf. Fin., june 2003, p.107
12- A. Portevin and P. Bastien - "Réactifs d'attaque métallographique", ed. Dunod, Paris (1937)