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UTILISATION OF ELECTROCHEMICAL METHODS FOR CHARACTERIZATION OF SOME CORROSION INHIBITORS FOR STEEL AND COPPER

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ABSTRACT

The effect of chromate and molybdate on the corrosion inhibition of copper and steel has been investigated in two eutectics solution at room temperature. We used stationary electrochemical methods and optical microscopy for the characterization of these materials. For steel, the molybdate inhibitor appears less efficient than the chromate one; for copper the polarization curves present an anodic passivation domain only in the chromate inhibited medium. The possibilities of galvanic coupling between them were simulated. This simulation has shown that, between copper and steel, the risk is more important in chromate medium than in molybdate one.

KEYWORDS: molybdate, chromate, corrosion inhibitors, cooper, steel

1. Introduction

We can controlled corrosion of metals by reducing the oxidation tendancy, by isolating the substrate from the environment or by reducing the aggressiveness of the environment. The use of corrosion inhibitors is a good method to minimize or to eliminate the corrosion. They can act either by forming a passive layer or by forming an insoluble compound that clogs the areas susceptible to corrosion or by inhibiting one stage of the redox system (oxidation or reduction reactions) [1]. For many years we used chromium for a variety of industrial application such as leather tanning, metallurgy electroplating, catalysis for corrosion inhibitors and wood preservatives. Under extremes conditions chromates protect more metals and alloys than any other commercial corrosion inhibitor, butbecause of its environmental toxicity and the risk to human health, chromates are being replaced by less toxic inhibitors, [2-5]. Attention was focused on the ion molybdate because of the chemical structure similarity and expected behavior between chromate ions and the elements of the VI group of periodic table[6-7]. Molybdate present a low toxicity and for that it is used to protect many materials, including copper and steel. The aim of this work is a comparative study between chromate and molybdate inhibitors in two eutectic solution at room temperature.

2. Experimental details

This study was carried out with two metals: steel DD11 (0.07%C, 0.2%Mn, 0.011%P, 0.011%S, 0.009%Si, 0.029%Al) and copper DHP 99.93% (99.95%Cu + Ag and 0.024%P). Table 1 presents the mechanicals properties of these materials. These metals have two shapes: plate (1.2*1.2cm^2) for steel and tube (1.5cm and Φ1.5) for copper.

The plate samples were polished with abrasive paper (until granulometry 1000) and the tubes were filled with resin, but because of there shape, they are not polished, but only degreased in ultrasounds bath for 1-2 min, then dried with hot air. The eutectic solutions contain 12-13wt% NH_4Cl and 27-28wt%$NaNO_3$. They are different by te nature of corrosion inhibitors, one of them contains the chromate and the other one contains the molybdate. The used volume of these solutions was 110cm^3.

Electrochemical tests were carried out using a classical three electrodes cell with graphite as counter electrode, saturated calomel electrode SCE (+0.242V vs. SHE) as reference electrode and the samples as working electrode. The potentiodynamic polarization curves were obtained using an EG&G potentiostat model 263 at a constant voltage scan rate of 0.166mV/s. The surface morphologies were observed with a digital microscope Hirox KH7700.

***Table 1**. Mechanical properties of metals*

Type of metal	Mechanical properties		
	Rp	Rm	A50
	[MPa]		[%]
Steel DD11	283	383	35.2
Cu DHP 99,93%	82	256	47.6

***Table 2.** Values of free potential (mV/SCE) and corrosion current density (µA/cm^2)*

Metals	Solutions			
	with chromate		with molybdate	
	E	I	E	I
	[mV/SCE]	[µA/cm^2]	[mV/SCE]	[µA/cm^2]
Steel plate	- 480	1 – 2	- 580	837
Cu tube	- 190	31.0 – 32.0	- 340	21 – 23

3. Results and discusions

As shown in table 2, we can observed that, for steel alloy, in the eutectic solution inhibited with chromate the values of free potential reach the stability value around -480 mV/SCE and in the eutectic solution inhibited with molybdate the values of free potential reach the stability value around -580mV/SCE. For copper, in the eutectic solution inhibited with chromate, these values grow up to -190mV/SCE, but when the eutectic solution contains molybdate inhibitor the values of free potential are about two times more negatives (-340mV/SCE). In the cae of steel, the values of corrosion current density calculated by QuickCalc software M352 from polarization curves, show between the both inhibited solution a difference of a factor 800, and on the contrary for copper theses values are approximately the same, wich means that a combination of both corrosion inhibitors is not accepted.

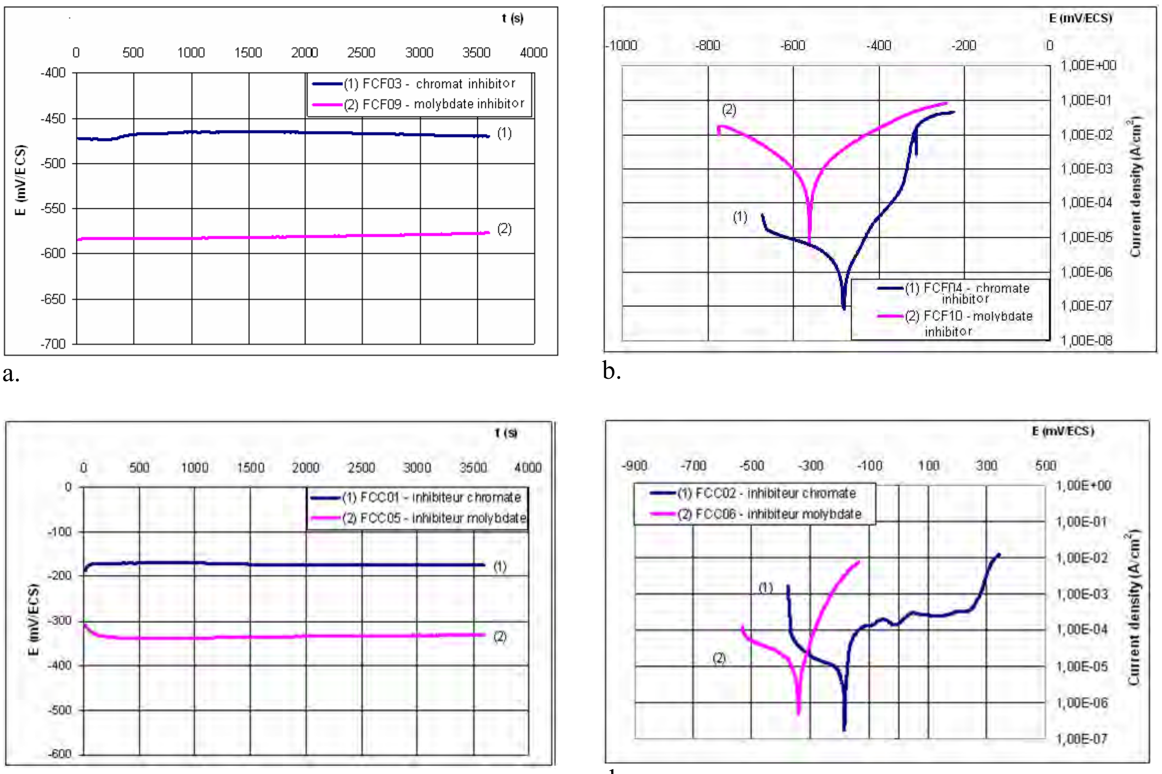
The corrosion potential values deduced from the potentiodynamic polarization curves, (fig.1) have not the same magnitude in both cases; the steel plate is a little less noble in the solution inhibited with molybdate. The values of current density in the molybdate solution are smaller than in the chromate (800 times). We also observed that for steel in both cases (in chromate or molybdate environment) appears not the anodic passivation plateau. According to the polarization curves, in the case of copper, the current densities for the two environments, chromate and molybdate, have approximately the same values. At the opposite, the corrosion potential is lower in the case of molybdate than in the chromate environment. Regarding the polarization curves for the chromate inhibitor we can observe a plateau of anodic passivation. This plateau means the period necessary for the protective films formation.

The optical microscopy images for all the metals in the two solutions (with inhibitor chromate or molybdate) are presented in Fig.2. These images are carried out after an important anodic polarization. It appears that in the chromate or molybdate environment the steel is attacked uniformly. At the other hand, for copper we can see in the case of chromate inhibitor a uniform corrosion but also an oxides film (green) on the surface of sample. The copper sample used for testing the efficiency of molybdate was also corroded.

In a galvanic coupling (bimetallism or differential aeration) the current intensities that are interesting are not the corrosion current densities. The coupling current intensity for the galvanic coupling is given by the intersection of the anodic part of the less noble metal curve with the cathode part of the nobler metal curve, taken into account the area ratio. The anode is the less noble metal or the less aerated metallic zone and the cathode is the noblest metal or the most aerated metallic zone. The anode/cathode area ratio is very important, because a small anodic area relative to a large cathodic one leads to that the current density of corrosion is entirely located on a small area and that can be very penalizing.

To see if there is a real risk of galvanic coupling between these materials in the investigated media we simulate these risks. We distinguished the two solutions (with chromate and molybdate inhibitors). For our study, we considered the anode and cathode areas are equal (1cm^2).

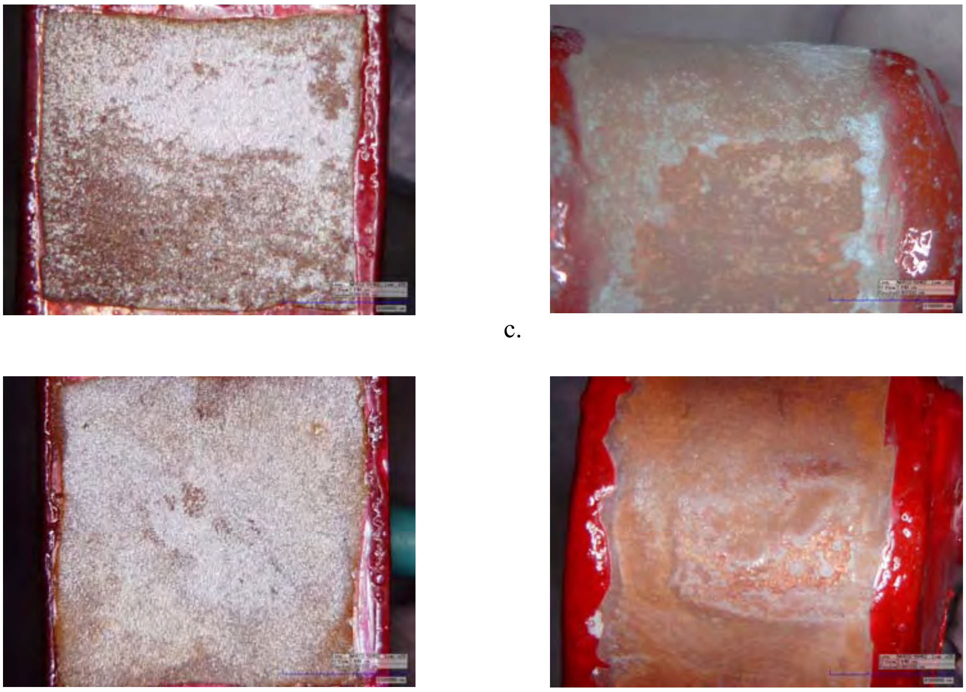
It can be observed that there are no really risks of galvanic couplings in the molybdate solution. It appears that, in medium with chromates, the galvanic coupling between steel and copper presents an important risk and this is much more important than the anode/cathode ratio areas is more little, (steel is the anode and copper is the cathode).



a. b.

c. d.

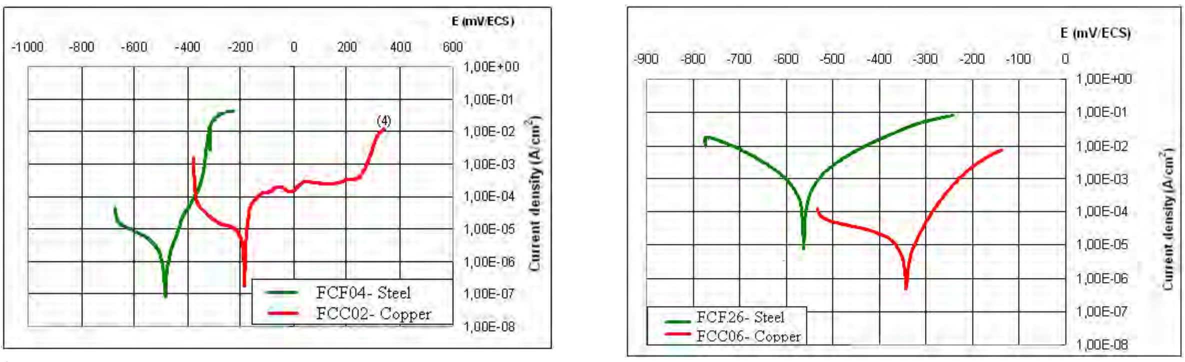
Fig.1. *Evolution of open circuit potential versus time and potentiodynamic polarization curves for steel plate (a-b) and copper (c-d) in the eutectic solutions inhibited with chromate or molybdate.*



a. c.

b. d.

Fig.2. *The optical microscopy images (x20) for steel (a. effect chromate inhibitor, b. Effect molybdate inhibitor) and for copper tube (c. effect chromate inhibitor and d. effect molybdate inhibitor).*



a. b.

Fig.3. *Simulation of galvanic coupling in eutectic solution with: a. chromate inhibitor and b. molybdate inhibitors.*

4. Conclusions

For the two metals the evolution of open circuit potential versus time varies a lot for the copper in molybdate environment where the potential is less noble than in the chromate environment.

In the case of steel, the corrosion potentials do not have the same order of magnitude, the current densities vary widely. In chromate environment, the current density is slightly smaller compared with the molybdate environment.

For copper, the corrosion potentials are slightly smaller in the case of molybdate versus the case of chromate. But the values of current density are comparable. Copper is the only metal that has presented a plateau of anodic passivation in chromate.

It was found that all metals are corroded; this corrosion was observed after a significant anodic polarization.

Even if the results obtained in molybdate inhibited media are not as good as those obtained with chromate inhibitor, nevertheless the use of molybdate does not seems such a bad possibility of substitution in the case of copper.

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