

CHARACTERIZATION OF CORROSION INHIBITORS BY ELECTROCHEMICAL METHODS

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Abstract: *Electrochemical behaviour was determined at ambient temperature for three metals (aluminium-3103, 5754 and copper) immersed in two eutectics solutions that differed by the nature of corrosion inhibitor, chromate or molybdate with the aim to replace chromate, the use of which is now very regulated. Characterization of these materials was determined by stationary electrochemical methods: potential versus time and polarization curves recording. The efficiency of these inhibitors was tested, and the possibilities of galvanic coupling were simulated too. For the three metals, the molybdate inhibitor appears less efficient than the chromate one and for copper the polarization curves present an anodic passivation domain only with the chromate inhibited medium. The simulation of the galvanic coupling risk has shown that, between Al and Cu, the risk is more important in chromate medium than in molybdate one.*

Keywords: molybdate, chromate, corrosion inhibitors, aluminum, copper, saline solution.

INTRODUCTION

Corrosion of metals can be controlled by reducing the oxidation tendency, by reducing the aggressiveness of the environment, or by isolating the substrate from the environment. A method to minimize or to eliminate the corrosion is the use of corrosion inhibitors. They work either by forming a passive layer or by inhibiting one stage of the redox system (oxidation or reduction reactions) or by forming an insoluble compound that clogs the areas susceptible to corrosion [1].

Chromium is widely used in variety of industrial applications such as leather tanning, metallurgy, electroplating, catalysis for corrosion inhibitors and wood preservatives for many years. Chromates protect in extreme conditions more metals and alloys than any other commercial corrosion inhibitor, but because of its environmental toxicity and its risk to human health, chromates are being replaced by less toxic inhibitors [2-5]. Based on the similarity of the chemical structure and expected behaviour between chromate ions and the elements of the VI group of periodic table, attention was focused on ion molybdate [6-7]. Because of his low toxicity, molybdate is used for the protection of many materials, including aluminium and copper.

The aim of this work is a comparative study between chromate and molybdate inhibitors in two eutectic solutions.

EXPERIMENTAL DETAILS

This study was carried on with two metals: aluminium and copper. Two types of aluminium alloys were used, 3103 (0.5%Si, 0.7%Fe, 0.1%Cu, 0.9%Mn, 0.3%Mg, 0.1%Cr, 0.2%Zn, 0.1%Ti+Zr) and 5754 (0.18%Si, 0.34%Fe, 0.02%Cu, 0.4%Mn, 2.66%Mg, 0.01%Cr, 0.01%Zn, 0.02%Ti, 0.002%Pb, 0.004%Ni, 0.011%Ga, 0.007%V),[8] and the copper is DHP 99.93% (99.95%Cu+Ag, 0.024%P). Table 1 presents the mechanicals properties of these materials. These metals have two shapes: tube (1.5cm and Φ 1.5cm for the copper and for the aluminium 3103) and plate (1.2*1.2cm² for the aluminium 5754). The plate samples were polished with abrasive paper (until granulometry 1000) and

the tubes were filled with resin but because of their shape, they are not polished, but only degreased in an ultrasonic bath for 1-2min, then dried with hot air.

The eutectic solutions contain NH_4Cl about 12-13wt% and NaNO_3 about 27-28 wt%. They are different by the 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 .

Table 1. Mechanical properties of metals.

Type of metal	Mechanical properties		
	Rp (MP)	Rm (MPa)	A50 (%)
Al 5754 (plate)	140	220	18.5
Al 3103 (tube)	140	155	8
Cu DHP 99,93% (tube)	82	256	47.6

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 0.166 mV/s. The surface morphologies were observed with a digital microscope Hirox KH7700.

RESULTS AND DISCUSSIONS

As shown in table 2, we can observe that, for aluminium alloys, even if we don't use the same corrosion inhibitors, the values of free potential are close and it reaches the stability value around -650 mV/SCE. For the 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 case of aluminium, the values of corrosion current density calculated by QuickCalc software M352 from polarization curves, show between the both inhibited solutions, a difference of a factor of 10 to 50; on the contrary for copper these values are approximately the same, which means that a combination of both corrosion inhibitors is accepted.

Table 2. Values of free potential (mV/SCE) and corrosion current density ($\mu\text{A}/\text{cm}^2$).

Metals	Solutions			
	with chromate		with molybdate	
	E (mV/SCE)	I ($\mu\text{A}/\text{cm}^2$)	E (mV/SCE)	I ($\mu\text{A}/\text{cm}^2$)
Al plate	- 650	1.3 – 1.4	- 650	51 - 52
Al tube	- 650	4.5 – 5.0	- 650	58 – 59
Cu tube	- 190	31.0 – 32.0	- 340	21 – 23

The corrosion potential values deduced from the potentiodynamic polarization curves, (fig.1) have the same magnitude in both cases; the aluminium plate is a little less noble in the solution inhibited with molybdate. The values of current density in the chromate solution are smaller than in the molybdate (50 times). We also observed that an anodic passivation plateau appears only for chromate inhibitor. For the aluminium tube like for the other aluminium alloy, it is observed that in the both inhibited solutions (with chromate or molybdate) the corrosion potential has almost the same value. The polarization curves show that the current densities are similar, only a little lower in the case of chromates. 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.

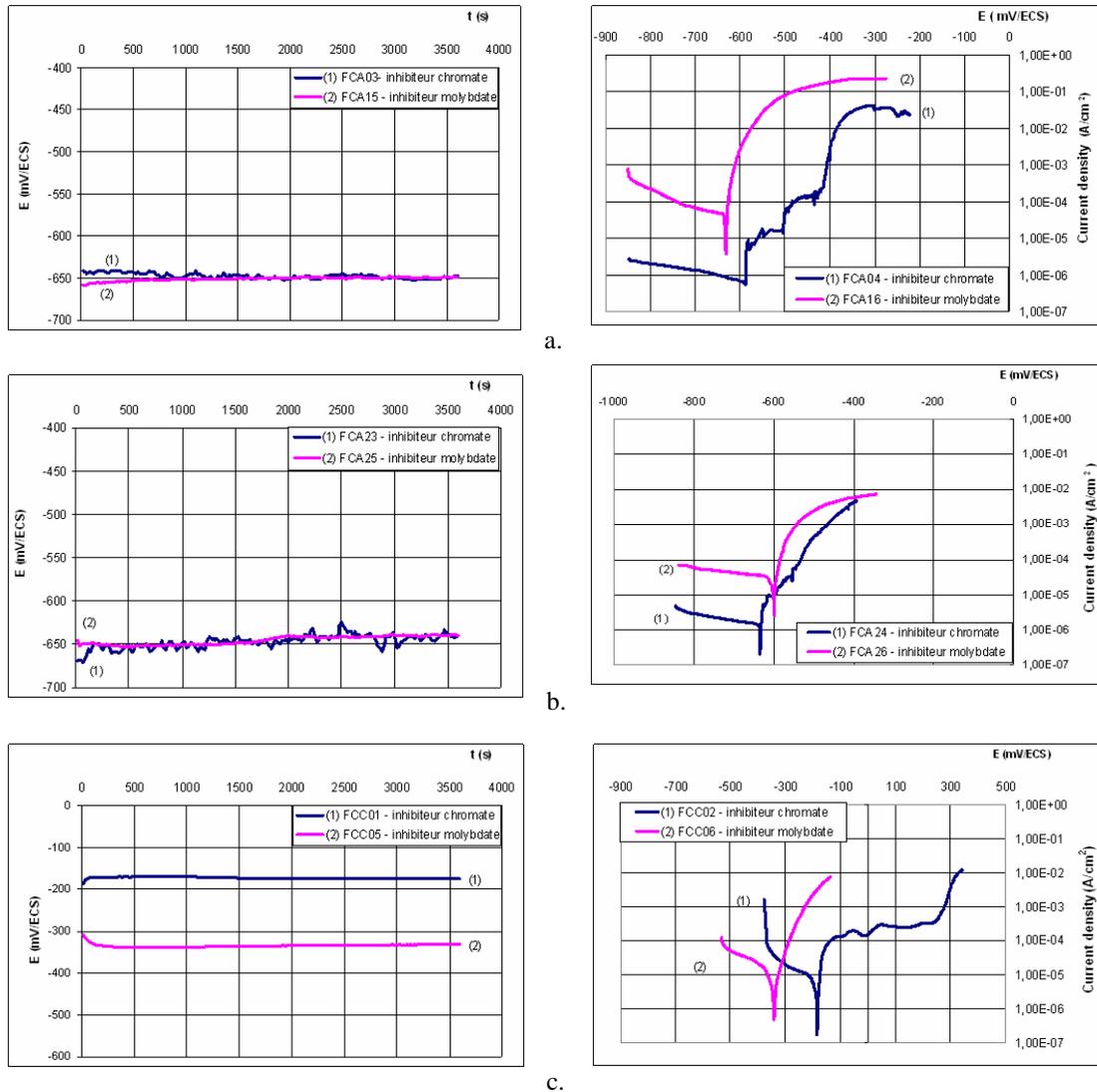


Fig.1. Evolution of open circuit potential versus time and potentiodynamic polarization curves for aluminium plate (a), aluminium tube (b) and copper (c) in the eutectic solutions inhibited with chromate or molybdate.

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 environment the aluminium plate is attacked uniformly and that in the other case, it is very well see that the corrosion is a localized. For aluminium tube we can observe a figure of pitting corrosion. 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 corrode.

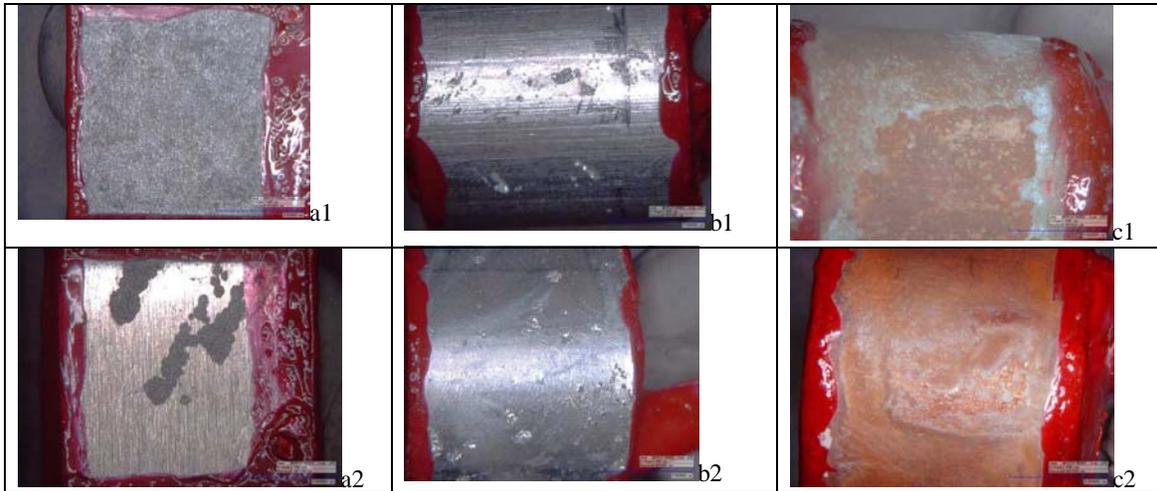
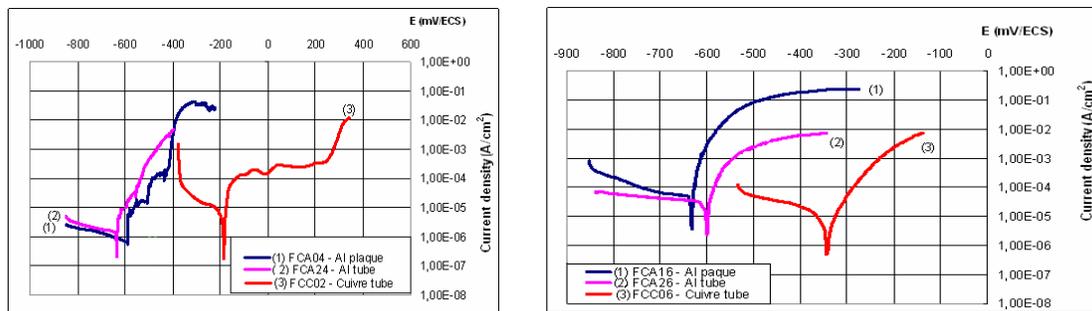


Fig.2. The optical microscopy images (x20) for aluminium plate (a1. effect chromate inhibitor, a2. Effect molybdate inhibitor), for aluminium tube (b1. effect chromate inhibitor and b2. Effect molybdate inhibitor) and for copper tube (c1. effect chromate inhibitor and c2. effect molybdate inhibitor).

In a galvanic coupling (bimetalism 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).



a.

b.

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

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

CONCLUSIONS

For all metals the evolution of open circuit potential versus time does not vary much, except for the copper in molybdate environment where the potential is less noble than in the chromate environment.

In the case of aluminum tube or plate, the corrosion potentials have the same order of magnitude, the current densities vary widely. In chromate environment, for aluminum plate, 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 was 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 so good that those obtained with chromate inhibitor, nevertheless the use of molybdate seems a not so bad possibility of substitution in the case of these metals, aluminum or copper.

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