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# Effect of mechanical (monotonic and cyclic) stress on the corrosion resistance of chromium-plated steel rods

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**Abstract**

Providing high hardness, low friction coefficient, as well as, relatively good corrosion resistance, chromium-plated coatings are widely used for steel cylinder rods in marine environment. Nevertheless, a uniform network of microcracks in chromium coating is evolving under mechanical loadings during the service-life of cylinder rods. The propagation of these microcracks is in the origin of the premature corrosion of the steel substrate. The aim of the study was to evaluate the relationship between mechanical stresses, the evolution of the microcracks network and the corrosion resistance of chromium coatings. After monotonic pre-loading tests, it was demonstrated by microscopic observations that the microcracks propagated for stress levels higher than the yield stress of the substrate (520 MPa) and have passed instantly through the whole thickness of the coating and reached the steel substrate. The density of microcracks increases with the level of total strain, the inter-crack distance go from 80 µm at 1% of total strain to approximately 65 µm at 5%. Electrochemical measurements have shown that the higher the level of plastic strain applied during the mechanical loading, the more the corrosion potential of the sample decreases until reaching that of the steel substrate of approximately -0.65 V/ECS after 2 hours of immersion. The polarization curves also evidenced an increase in the corrosion current density with the strain level. Moreover, we note the absence of the characteristic passive region of the reference samples that have not undergone any loading. After cyclic loadings, no microcracks propagation was observed after $10^4$ cycles when maximal stress was lower than the yield stress. However, a decreasing of the corrosion potential was observed for samples which were submitted to a cyclic loading. Nevertheless, the current density and the characteristic passive region were not modified.


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*Keywords:* Chromium coating; Cracks propagation; Corrosion resistance; Polarization curves

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## 1. Introduction

Since 1924 [1], chromium-electroplating process is a well-established practice in industrial needs, such as aerospace, automotive and general engineering [2]. This fact is due to a combination of properties offered to steel by a chromium coating, such as, high hardness, low coefficient of friction and corrosion resistance [3]. These properties depend highly of electroplating parameters: temperature of plating solution, plating current density, concentrations of chemical compounds in plating solution and duration of process [3-4]. Nevertheless, after many decades of practice, some aspects of this process are still not fully understood. One of them is an appearance and evolution of microcracks network during electroplating process [3-5]. The origin of microcracks initiation is related to the residual tensile stresses, when the thickness of chromium coating reaches 0.5 µm [6]. The first explanation of residual tensile stresses is due to the release of trapped atoms of hydrogen during electrolysis, with the following shrinkage of chromium coating [4]. In [3], authors highlight that these trapped atoms of hydrogen could play a role of catalyst to accelerate the chromium phase transformation. Therefore, β-Cr with HCP or FCC crystal arrangement will be transformed in more stable α-Cr (BCC) with shrinkage of 15 % vol. [5]. It has been proved that the presence of these microcracks is favorable for penetration of corrosion agents, such as chlorides [7- 9]. Moreover, chromium microcracks network could develop due to the mechanical loadings, which can deteriorate corrosion resistance of the structure. Nevertheless, this phenomenon was not much studied in the literature. Concerning the cracking of a brittle coating on a ductile substrate under monotonic tensile loading, Agrawal and Raj [10] showed that cracks passing through the whole thickness of the coating were observed periodically when the stress applied was higher than the yield stress of the substrate. The inter-crack distance decreases with increasing of the stress applied. Under a cyclic loading, the cracks propagation is more difficult to predict because of the complex interaction between the different cracks. Most of authors who tried to model this phenomenon used a probabilistic model to take into account the random behavior of the cracks network [11-13].

The aim of the study was to evaluate the relationship between mechanical stresses, the evolution of the microcracks network and the corrosion resistance of chromium coatings. Experimental procedure of 2 steps was used to establish this link for monotonic and cyclic tensile loading. At first, mechanical pre-loadings were carried out till different levels of total strain (for monotonic loadings) and different numbers of cycles (for cyclic loadings). The second step was to evaluate the corrosion performance of chromium-plated pre-loaded specimens thanks to electrochemical measurements.

## 2. Material and methods

Microalloyed carbon steel rods (diameter: 22 mm) were delivered with a conventional chromium-electroplated coating of 20 µm thick (OVAKO Redon, France), as illustrated on fig.1(a). The chemical composition of the steel substrate is given in table 1.

Table 1. Chemical composition of the steel substrate in mass %.

| C | Si | Mn | S | V | P | C.E.* |
|---|---|---|---|---|---|---|
| 0.18 | 0.35 | 1.55 | 0.025 | 0.11 | ≤0.020 | 0.55 max |

*C.E. = % C + % Mn/6 + (% Cu + % Ni)/15 + (% Cr + % Mo + % V)/5

Initial network of microcracks was revealed using an electrolytic etching (j=5-6 $A.dm^{-2}$) during 2 min, in a solution of 50 $g.L^{-1}$ NaOH and 65 $g.L^{-1}$ $Na_2CO_3$. Density of initial microcracks (fig.1(b)) was approximately of 1024 $microcracks.cm^{-1}$. The microcracks network was also observed in the cross sectional plane (fig.1(c)). Initially, microcracks do not traverse the chrome thickness; their average length was estimated to 4.75 µm ± 1.78 µm.
Mechanical tests presented in this study were performed on an MTS tensile hydraulic-testing machine with a load capacity of 250 kN. For tensile tests (monotonic and cyclic), sample dimensions are shown on fig.2. As shown on this figure, section reduction was realized thanks to an oblong shape hole, in order to concentrate stress in the gauge length of the sample and protect the chromium coating. For monotonic tensile tests, the total strain rate was $\dot{\epsilon} =$

$3.10^{-4}$ $s^{-1}$, the strain was measured by an extensometer Epsilon. The cyclic tensile tests were performed with a load ratio of R=0 at 10 Hz.

The electrochemical tests were performed with a three electrodes cell. The working electrode was a chromium electroplated steel specimen cut from pre-loading samples with an exposed surface area of 1.2 $cm^2$. The exposed surface area was defined using Lacomit varnish (Agar Scientific Ltd, UK) to avoid interference in the electrochemical measurements from the substrate material. The counter electrode was a platinum wire with a large surface area and the reference electrode was a saturated calomel electrode (SCE: 0.241 V vs SHE). A solution of 50g.$L^{-1}$ NaCl was used as electrolyte. Firstly, the corrosion potential ($E_{corr}$) was measured in order to approach steady-state conditions. Then, polarization curves were plotted in the range of $E_{corr}$-300 mV to $E_{corr}$+2500 mV with a sweep rate of 0.5 mV.$s^{-1}$.

Two reference surface states were also studied, a sample of microalloyed carbon steel without chromium coating (Fe-C steel) and microalloyed carbon steel with chromium coating (Fe-C/Cr initial state). In both reference cases, no mechanical pre-loading was applied.

Electrochemical data were obtained from at least two separate experiments. All electrochemical tests were performed with an AMEL 2551 potentiostat (AMEL, Italy).

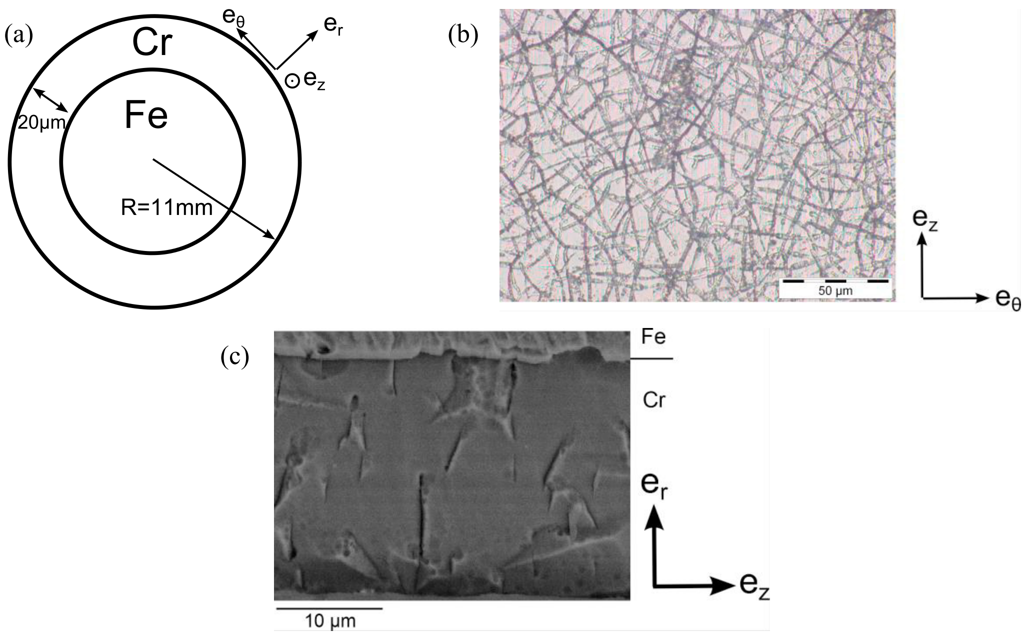


Fig. 1. (a) illustration of the cylinder cross section; (b) surface view (optical image); (c) cross section view (SEM image)

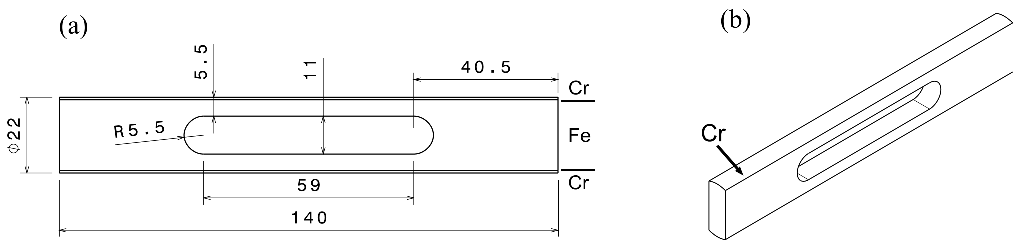


Fig. 2. (a) tensile sample dimensions; (b) isometric view

## 3. Results and discussion

### *3.1. Effect of a monotonic loading on corrosion resistance*

Two tensile tests were performed for two different levels of total strain (1% and 5%). The stress-strain curves are shown on fig.3. Fig.4 presents micrographs of surface view of samples subjected to 1% (fig.4(a)) and 5% (fig.4(b)) of total strain. We can see on these pictures that microcracks propagate for these severe levels of stress (higher than the yield stress of the material, cf. fig.3). The density of propagated microcracks increase with the level of pre-strain, it was estimated to 80 ± 5 µm for 1% of total strain, and 65 ± 3 µm for 5% of total strain.

The consequences of propagation of microcracks in chromium on corrosion resistance of the substrate were investigated by electrochemical measurements. Open circuit potential ($E_{corr}$) curves were carried out during 2 hours in order to achieve steady-state conditions of working electrode in testing electrolyte. Fig.5 shows the evolution of a potential during the immersion time for pre-loaded samples and two Reference samples. We can note that carbon steel potential value tends towards -650 mV vs SCE. This fact is due to the oxidation of carbon steel surface in electrolyte containing chlorides. On the contrary, when the steel is covered by chromium coating (Fe-C/Cr initial state) the potential decreases slightly in time and stabilizes at around -500 mV vs SCE. For pre-loaded samples, the following tendency was observed: the higher the level of plastic strain applied during the mechanical loading, the more the corrosion potential of the sample decreases, until reaching a potential value close to that the steel substrate of approximately -650 mV vs. SCE after 2 hours of immersion (case of Fe-C/Cr ε=5 % sample).

The polarization curves for all samples shown in Figure 6 confirm previous results. Moreover, the curves evidence a slow increase in the corrosion current density ($j_{corr}$) with the strain level. It can be also observed that the cathodic parts for all samples are not affected and are the same. On the contrary, only anodic part of polarization curve of steel sample with chromium-electroplated coating (Fe-C/Cr initial state) clearly shows a passive region (j= 0.59 mA.cm$^{-2}$). In case of 1 % pre-loaded sample, a passive region was shifted towards a higher current densities (j = 7 mA.cm$^{-2}$). For 5 % pre-loaded, we noted the absence of the characteristic passive region and almost a superposition with the anodic branch of the steel substrate sample.

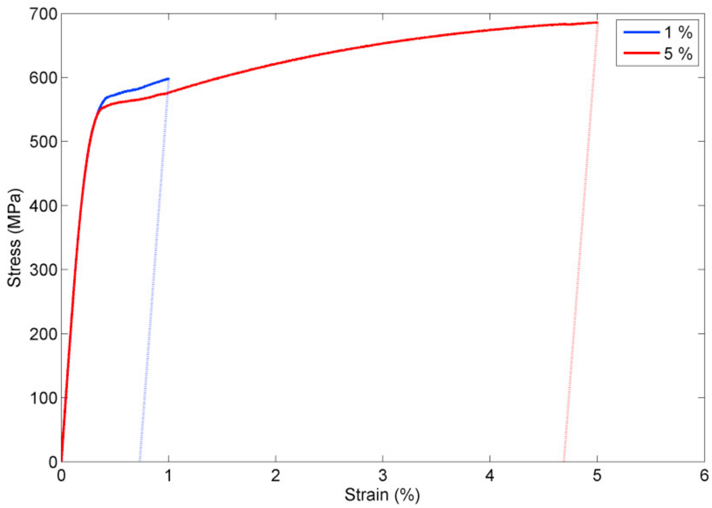


Fig. 3. Stress-strain curves for chromium-plated steel rods. Pre-loading till two different levels of total strain: 1 % and 5 %

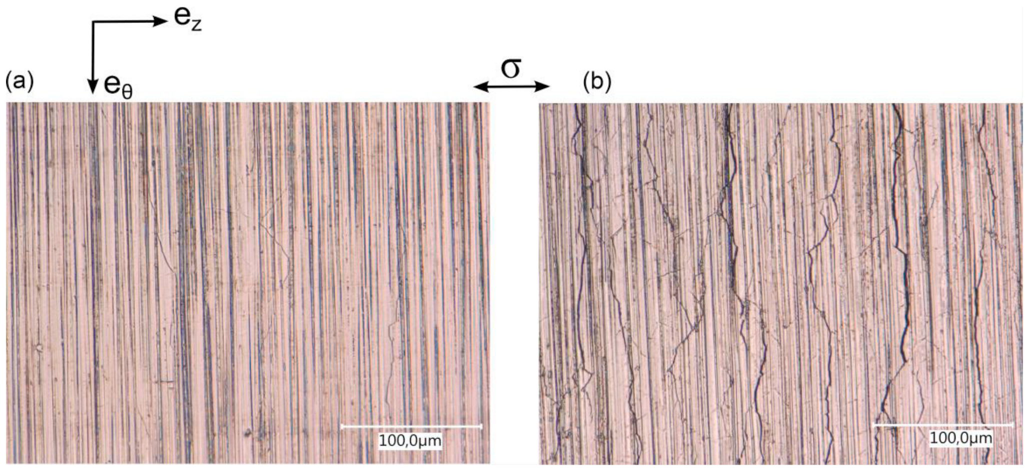


Fig. 4. Microscope observations of specimens at: (a) 1 % pre-strain and (b) 5 % pre-strain

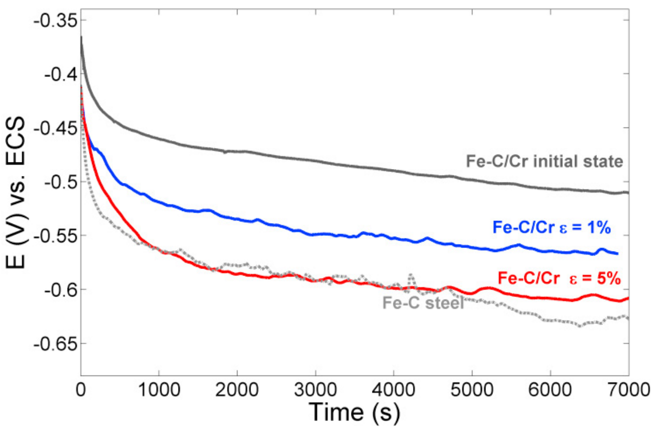


Fig. 5. $E_{corr}$ vs. time during immersion in 50 g.L$^{-1}$ NaCl solution of pre-loaded samples and two Reference samples

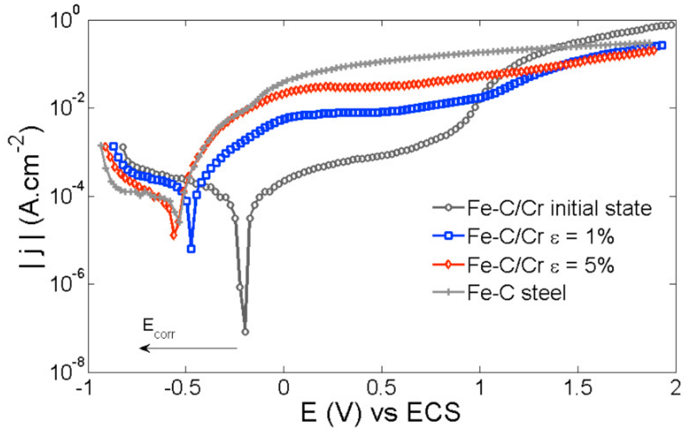


Fig. 6. Polarization curves for all preloaded samples and two Reference samples (scan rate V= 0.5 mV.s$^{-1}$) carried out after 2 h of immersion in 50 g.L$^{-1}$ NaCl

### 3.2. Effect of a cyclic loading on corrosion resistance

To characterize samples submitted to more representative stresses to the service-life conditions, cyclic loadings were performed with maximum stress lower than the substrate yield stress. The tests were performed for 10, 100, 1000 and 10000 cycles with a maximal stress of 80% of the yield stress of the substrate (which corresponds to a total strain of 0.2%) at a load ratio of R=0. Even if no microcracks propagation was observed in chromium coating either with optical microscope, either with SEM, corrosion resistance of the substrate was quantified by electrochemical measurements and compared with the reference state. Open circuit potential ($E_{corr}$) curves were carried out during 1 hour in order to achieve steady-state conditions of working electrode in testing electrolyte. Fig.7 shows the evolution of a potential during the immersion time for samples which were submitted to cyclic loadings and Fe-C/Cr Reference sample.

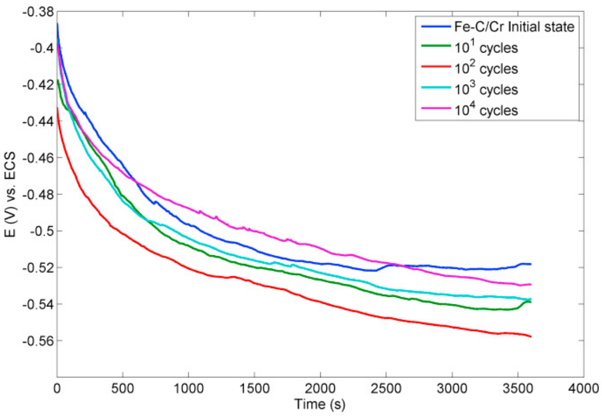


Fig. 7. $E_{corr}$ vs. time during immersion in 50 g.L$^{-1}$ NaCl solution of pre-loaded samples and two Reference samples

We can note that for samples submitted to cyclic loadings, potential value tends towards values slightly lower than for Fe-C/Cr Reference sample. Moreover, no tendency for the OCP evolution with the number of cycles was observed. Only 10 cycles are enough to make the sample more negative, but the effect of the following cycles of loadings is not clear. The polarization curves for all samples shown in Figure 8 confirm previous results. Moreover, the curves do not evidence a significant variation of the corrosion current density ($j_{corr}$) between the different samples. The cathodic part is still unchanged with the cyclic loading and the anodic part clearly shows a passive region for all the samples (j=2 mA.cm$^{-2}$).

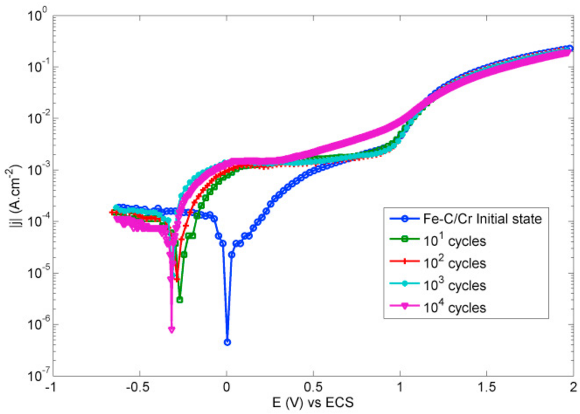


Fig.8. Polarization curves for samples submitted to cyclic loadings and one Reference sample (scan rate V= 0.5 mV.s$^{-1}$) carried out after 1 h of immersion in 50 g.L$^{-1}$ NaCl

As maximum stress is lower than the yield stress, crack propagation could be a rare phenomenon in the whole sample. Even if few microcracks propagate, the steel substrate will be exposed to electrolyte; that is why the corrosion potential is affected. Nevertheless, if the number of propagated microcracks is too low, the corrosion kinetics will be unchanged and so the current density will not be affected.

Concerning the effect of number of cycles, as described by Malésys et al. [11-12], obscuration process can probably occurred, that to say all cracks located in the stress relaxation zone of another could not propagate, which can make the probability of crack propagation still lower. If the stress intensity factor of some cracks is higher than the fracture toughness of the chromium coating, cracks will pass instantly through the whole thickness of the coating, even after 1 cycle, but the obscuration process could stop propagation of others.

## 4. Conclusions

The corrosion performances of hard-chromium coatings subjected to monotonic and cyclic mechanical loadings were compared in this work. Following conclusions can be drawn:

- Microscopic observations after monotonic tensile tests demonstrated that the microcracks propagation began for stress levels higher than the yield strength of the substrat (520 MPa). Microcracks propagate and have passed instantly through the whole thickness of the coating and reached the steel substrate. The density of microcracks increases with the level of total strain.
- No microcracks propagation was observed for stress levels lower than the yield stress of the substrate, even after $10^4$ cycles.
- After electrochemical measurements for monotonic loading, it was observed that the higher the level of plastic strain applied during the mechanical loading, the more the corrosion potential of the sample decreases until reaching that of the steel substrate of approximately -650 mV/ECS after 2 hours of immersion. The polarization curves confirm the previous results, as evidenced by the increase in the corrosion current density with the strain level. Moreover, we noted the absence of the characteristic passive region presented only for the reference sample that has not undergone any loading.
- After electrochemical measurements for cyclic loading, it was showed that the corrosion potential of pre-loaded samples was lower than Fe-C/Cr reference sample one. Moreover, no effect of number of cycles was observed, and the current density and the characteristic passive region were not modified.

These results show that the corrosion resistance of the chromium coating after mechanical loading depends on the microcracks propagation. This study could be interestingly enriched by a numerical model to predict the evolution of microcracks network under mechanical loading (monotonic and cyclic).

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