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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 $\dot{\epsilon} =$