



Materials Science

An Indian Journal

Full Paper

MSAIJ, 14(6), 2016 [202-207]

Influence of the carbon content and of a plastic deformation on the corrosion behaviour of cast carbon steels. Part 2: Electrochemical measurements for specifying the corrosion in a sulphuric solution

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ABSTRACT

In this second part the carbon steels Fe-xC (x varying from 0 to 1.6 wt.%C) were tested in corrosion in their not deformed state and in their plastically deformed states. This was done in a simple molar sulphuric solution promoting the active state, using a three-electrode cell and a potentiostat. The experiments which were carried on, follow-up of the free potential, linear polarization for obtaining polarization resistance versus time, the Tafel run, led to results which globally show that an increased carbon content tends improving the corrosion behaviours while this one tends to be aggravated by plastic deformation. © 2016 Trade Science Inc. - INDIA

KEYWORDS

Cast carbon steels;
Carbon content;
Hardened state;
Corrosion;
Sulphuric acid;
Electrochemical characterization.

INTRODUCTION

The microstructures of metallic alloys can be significantly modified by plastic deformation or hardening occurring during their shaping or their use^[1]: structure initially equi-axed having thereafter acquired thereafter special orientations, changed geometry for phases, elongated grains... Many works have proved that plastic deformation may induce modifications of some alloy's mechanical properties,^[2,3]. These properties may have lost their initial isotropic character, consequently to the orientated character of these deformations. Surface reactivity properties may be also influenced by hardening, notably the behaviour in contact with aggressive liq-

uid solutions. The effect of plastic deformation by compression of pure Fe, Ni and Cu was for instance found on their electrochemical properties in a molar sulphuric solution^[4]. Some influence of permanent tensile deformation was also found for ferritic steel and ferrite-pearlitic steels^[5-7]. Other results in the case of compression plastic deformation were also brought for carbon steels and alloyed steels^[8-10]. Depending on the nature of the metals and alloys, the plastic deformation direction and on the degree of hardening, various results were obtained, showing a rather scattered effect.

In this work, these are a series of carbon steels which were studied, compressed or not. The focus was done on the influence of the state of permanent

deformation and on the microstructure resulting from the different carbon contents. The Fe-xC ($x \in [0; 1.6\text{wt.}\%]$) elaborated in the first part of this work^[10] and compressed or not were tested in corrosion in acidic media using different electrochemical methods.

EXPERIMENTAL

Elaboration and as-cast microstructures of the alloys, hardening by compression

One can remind that a series of five carbon steels (Fe-xC alloys with $x=0, 0.4, 0.8, 1.2$ and 1.6 wt.%) were elaborated from pure elements by high frequency induction foundry under inert atmosphere, as 40g-weighting ingots. These ones were cut in order to obtain different types of samples, among them two about $\{7\text{ mm} \times 4\text{ mm} \times 3\text{ mm}\}$ -parallelepipeds per steel, one for metallographic characterization and one for compression runs.

The parts destined for metallography investigations embedded in a cold resin mixture, ground with SiC papers from 120-grit upto 2400-grit and polished with $1\mu\text{m}$ hard particles until obtaining a mirror-like surface, were etched with Nital $\{\text{ethanol-4\% HNO}_3\}$ and observed by optical microscopy. This allowed verifying that the Fe-0.0C steel is wholly ferritic, the Fe-0.4C one is ferrite-pearlitic, the Fe-0.8C steel is pearlitic and the Fe-1.2C and Fe-1.6C ones are hypereutectoid, as indirectly confirmed by the Vickers macro-indentation results. However, the acicular shapes of pre-eutectoid ferrite (hypo-eutectoid steel) and pre-eutectoid cementite (hypereutectoid steel), of the Widmanstätten type, were noted a little curious and not expected.

The parallelepipeds especially prepared for the compression tests were plastically deformed using a 150kN-capacity testing machine and negative longitudinal permanent deformations were obtained (from -7% to -3% from 0 wt.%C to 1.6 wt.C).

Corrosion properties

For each alloy an as-cast parallelepiped part and the plastically deformed parallelepiped parts were immersed in a liquid cold resin mixture by keeping a not covered upper part. After total stiffening they

were extracted from the plastic mould. They were then a little sewed to create in which the denuded part of an electrical wire was inserted by compression using a vice. Incorporated again in the mould additional liquid cold resin mixture was poured this time to immerse the upper part of the sample as well as the denuded copper, in order to totally isolate them from the electrolyte in which the electrode will be immersed. The emerging metallic part of the obtained electrode (working surface) was finally ground with papers from 120-grit to 1200-grit, washed and dried.

The electrochemical tests were carried out using the model 263A potentiostat of Princeton Applied Research driven by the M352 software of EGG/Princeton. They were of two types:

Measurement of the Open Circuit potential (E_{ocp}), then linear polarization from $E_{\text{ocp}} - 20\text{mV}$ up to $E_{\text{ocp}} + 20\text{mV}$ at the constant rate of $+10\text{mV}/\text{min}$: this allowed determining the polarization resistance R_p (from the slope of the straight line part centred on E_{ocp}), every 10 minutes from $t=0$ and $t=30\text{min}$: $t=0$ (immersion of the electrode) $+2\text{ min}$ (half of experiment since its duration is 4 min), $t=10 + 2\text{ min}$ (half of experiment) and $t=20 + 2\text{ min}$ (half of experiment)

Just after these 30 minutes (34 to be more accurate) a Tafel experiment was carried out; this started with the measurement of the new E_{ocp} ; thereafter an increasing potential was applied from $E_{\text{ocp}} - 250\text{mV}$ up to E_{ocp} at $+1\text{mV}/\text{s}$ from E_{ocp} at $t=30\text{ min}$ (duration: from $t=30\text{ min}$ to $t=30\text{ min} + 500\text{ seconds}$), whose results allowed accurately specifying the values of the corrosion potential (E_{corr}) and of the current density of corrosion (I_{corr}), and also getting the values of the anodic and cathodic Tafel coefficients (β_a and β_c).

The Working Electrode (the sample) was 1200-grit ground just before immersion and each electrochemical series of experiments (3 liner polarization and Tafel), the Counter Electrode (or auxiliary electrode) was a platinum one, and the electrode of potential reference was a Saturated Calomel one.

The electrolyte of test considered for these electrochemical experiments was a very simple and classical acidic one: H_2SO_4 1M.

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RESULTS AND DISCUSSION

Follow-up of free potential and of polarization resistance

The values of recorded E_{ocp} and of determined polarization resistance successively obtained during the 30 minutes of immersion before Tafel experiment are presented in TABLE 1 for the Fe-0.0C steel, TABLE 2 for the Fe-0.4C steel, TABLE 3 for the Fe-0.8C steel, TABLE 4 for the Fe-1.2C steel and TABLE 5 for the Fe-1.6C steel. Except for the not-deformed Fe-0.0C which was obviously protected against corrosion by a passivation layer possibly earlier developed during the preparation (and curiously remaining stable during half an hour in the acidic solution, in addition at a potential not really high) – test to remake – all the samples were in an active state, as suggested on one hand – only for the Fe-0.0C, Fe-0.4C and Fe-0.8C steels – by the potentials comprised between -0.44 V/ENH (standard potential of the Fe^{2+}/Fe redox couple) and the 0V/ENH of the H^+/H_2 redox couple, and on the other hand by the rather low polarization resistance. However one must note that the corrosion potential tends decreasing under -0.44V/ENH and the Rp value tends

TABLE 1 : Evolution of the free potential (E_{ocp}) and of the polarization resistance (Rp) of the Fe-0.0C steel during the first half hour after immersion, in its not deformed state (ND) and in its deformed state (DF)

Fe-0.0C (ND)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-308.2	-308.1	-306
Rp ($\Omega \times cm^2$)	728.23	612.1	794.5
Fe-0.0C (DF)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-230.7	-215.5	-210.6
Rp ($\Omega \times cm^2$)	46.39	26.07	19.97

TABLE 2: Evolution of the free potential (E_{ocp}) and of the polarization resistance (Rp) of the Fe-0.4C steel during the first half hour after immersion, in its not deformed state (ND) and in its deformed state (DF)

Fe-0.4C (ND)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-247.4	-206.3	-222.4
Rp ($\Omega \times cm^2$)	97.58	88.46	53.81
Fe-0.4C (DF)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-474.0	-463.4	-452.4
Rp ($\Omega \times cm^2$)	117.7	62.83	33.73

to increasing over the $100 \Omega \times cm^2$ for Fe-0.8C and not-deformed Fe-1.2C steels. Concerning the effect of hardening no significant influence may be noted, except for the Fe-1.2C the plastic deformation of which decreased the corrosion resistance.

The Tafel experiments

The curves obtained for the four first steels (Fe-0.0C to Fe-1.2C) are plotted together in Figure 1 for the not deformed states (possible comparisons) and in Figure 2 for the deformed states (comparison not possible since various rates of permanent deformation among the alloys). In the corrosion potential obviously increases from the ferritic steel and the three others, as well as the corrosion current, as suggested

TABLE 3 : Evolution of the free potential (E_{ocp}) and of the polarization resistance (Rp) of the Fe-0.8C steel during the first half hour after immersion, in its not deformed state (ND) and in its deformed state (DF)

Fe-0.8C (ND)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-501.9	-494.0	-487.9
Rp ($\Omega \times cm^2$)	113.0	71.23	52.56
Fe-0.8C (DF)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-497.6	-491.7	-481.3
Rp ($\Omega \times cm^2$)	118.4	94.14	59.66

TABLE 4 : Evolution of the free potential (E_{ocp}) and of the polarization resistance (Rp) of the Fe-1.2C steel during the first half hour after immersion, in its not deformed state (ND) and in its deformed state (DF)

Fe-1.2C (ND)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-491.3	-459.3	-448.6
Rp ($\Omega \times cm^2$)	348.3	255.7	193.2
Fe-1.2C (DF)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-447.2	-467.5	-472.8
Rp ($\Omega \times cm^2$)	10.45	18.72	23.79

TABLE 5 : Evolution of the free potential (E_{ocp}) and of the polarization resistance (Rp) of the Fe-1.6C steel during the first half hour after immersion, in its not deformed state (ND) and in its deformed state (DF)

Fe-1.6C (ND)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-487.3	-468.4	-452.7
Rp ($\Omega \times cm^2$)	101.5	30.22	18.28
Fe-1.6C (DF)	t = 0 min	t = 10 min	t = 20 min
E_{ocp}/HNE (mV)	-487.6	-475.7	-463.5
Rp ($\Omega \times cm^2$)	115.3	52.51	22.23

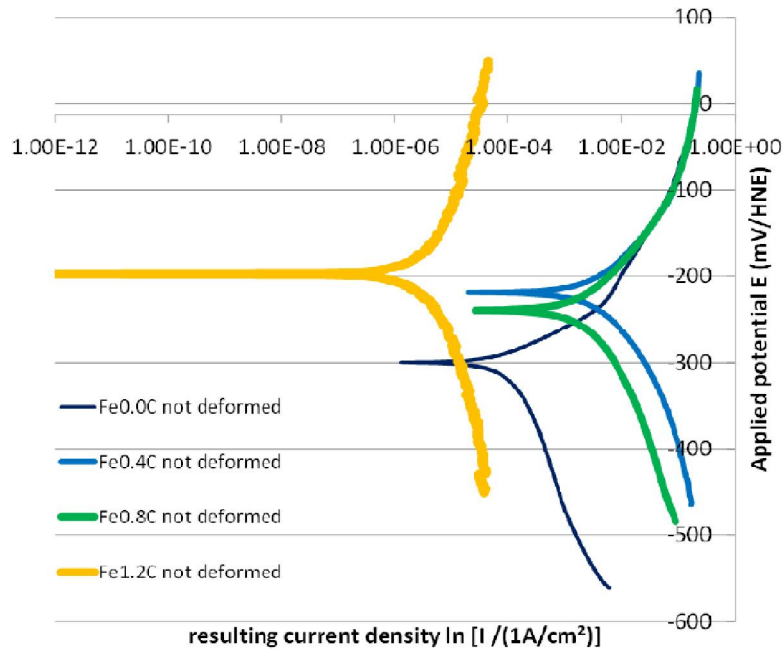


Figure 1 : The Tafel curves obtained for the four first steels (Fe-xC with x=0 to 1.2) in their not deformed states

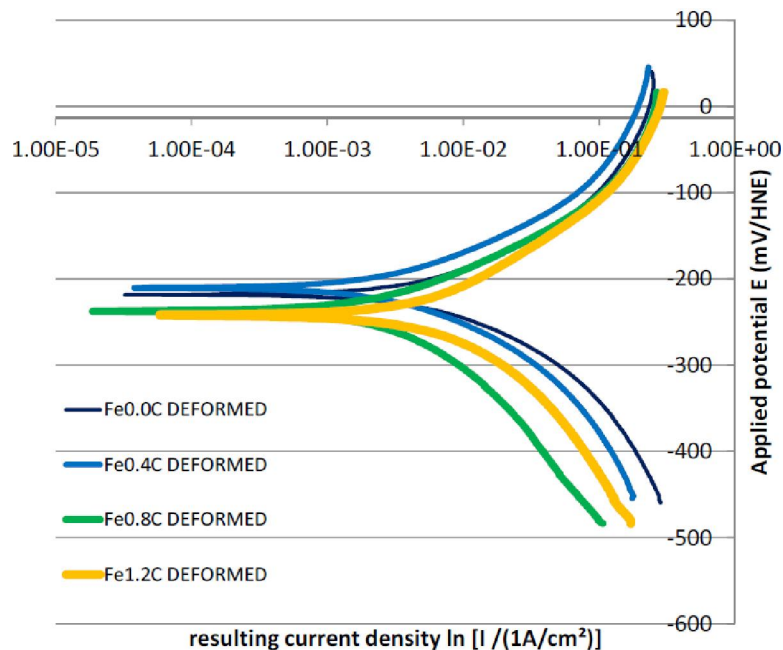


Figure 2 : The Tafel curves obtained for the four first steels (Fe-xC with x=0 to 1.2) in their deformed states

by the shift of the curves from the bottom-left side to the top-right side in the graph, although the Fe-1.2C steels plays as an exception. After deformation, even if the hardening rates were not the same, all the Tafel curves are globally aggregated, as the hardening smoothed the differences issued from the various microstructures: the same high level of corrosion potential (just under $-0.2V$ /ENH) and of high corrosion density of current (of the 10^{-3} - $10^{-2}A/cm^2$ level).

Superposing the Tafel curves for the not deformed state and for the deformed state alloy per alloy (Figure 3), allows seeing that hardening led to accelerated corrosion for the ferritic steel (Fe-0.0C) and the hypereutectoid one (Fe-1.2C) (e.g. the steels with the best behaviour when not deformed) while no significant effect was noticed for the two other steels initially not so resistant (Fe-0.4C and Fe-0.8C).

The determined values of I_{corr} , presented in

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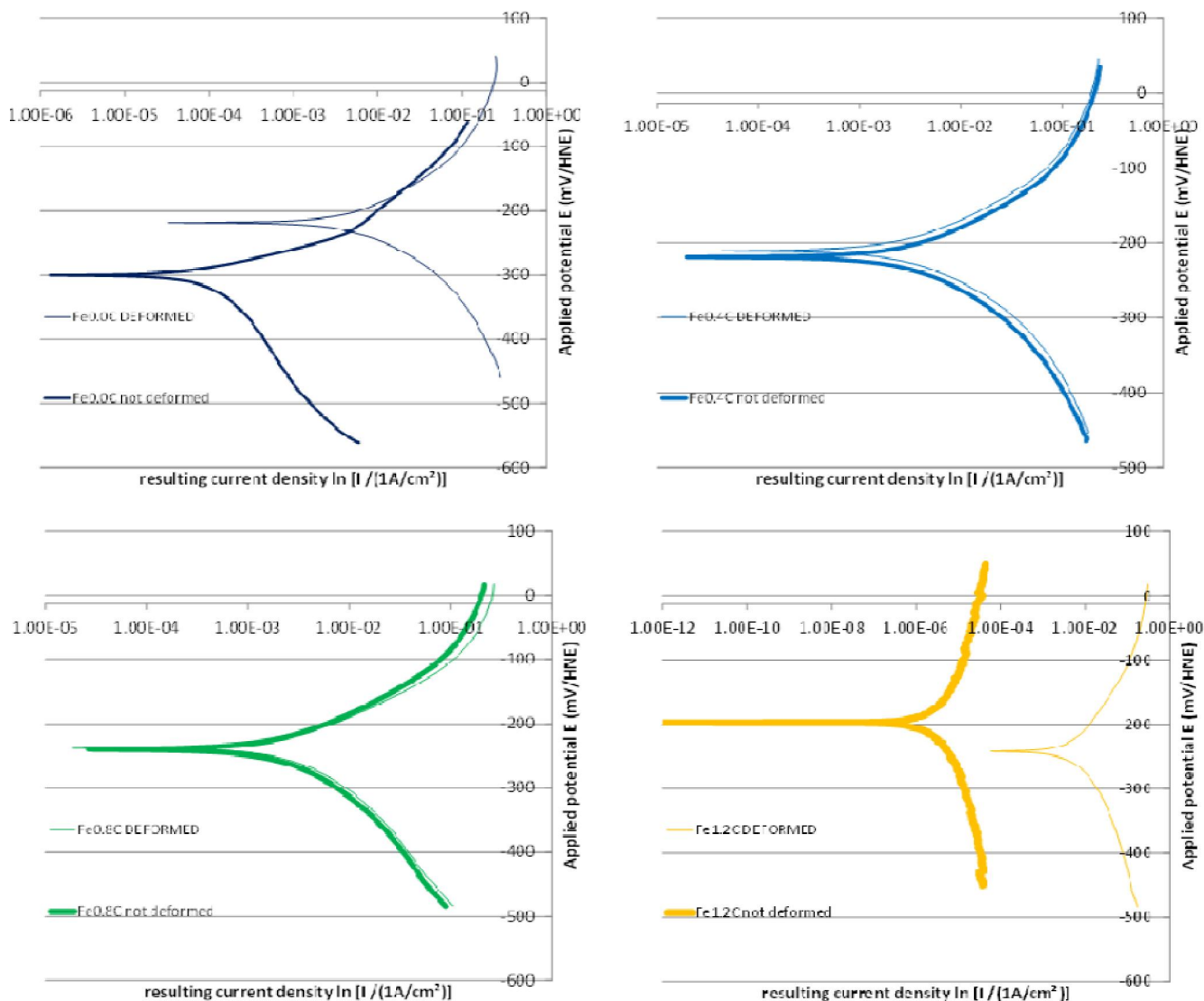


Figure 3 : Effect of the plastic deformation on the Tafel curves obtained for the four first steels (Fe-xC with x=0 to 1.2)

TABLE 6 : Corrosion potentials (E_{ocp}), current densities of corrosion (I_{corr}) and Tafel anodic and cathodic coefficients (β_a and β_c) issued from the Tafel experiments carried out for the Fe-0.0C in its not deformed state (ND) and in its deformed state (DF)

Fe-0.0C Not Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-300.2	0.102	43.92	150.6
Fe-0.0C Plastically Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-210.3	2.93	72.30	74.89

TABLE 7 : Corrosion potentials (E_{ocp}), current densities of corrosion (I_{corr}) and Tafel anodic and cathodic coefficients (β_a and β_c) issued from the Tafel experiments carried out for the Fe-0.4C in its not deformed state (ND) and in its deformed state (DF)

Fe-0.4C Not Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-219.1	4.278	88.11	109.3
Fe-0.4C Plastically Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-210.3	3.583	84.10	88.92

TABLE 6 for the Fe-0.0C steel, TABLE 7 for the Fe-0.4C steel, TABLE 8 for the Fe-0.8C steel,

TABLE 9 for the Fe-1.2C steel and TABLE 10 for the Fe-1.6C steel. They confirm these differences

TABLE 8 : Corrosion potentials (E_{ocp}), current densities of corrosion (I_{corr}) and Tafel anodic and cathodic coefficients (β_a and β_c) issued from the Tafel experiments carried out for the Fe-0.8C in its not deformed state (ND) and in its deformed state (DF)

Fe-0.8C Not Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-239.7	2.623	96.69	120.7
Fe-0.8C Plastically Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-237.3	2.84	80.42	115.9

and give the numerical values issued from the Tafel calculations. The values of the Tafel coefficients are also given in the same TABLES. If the cathodic coefficient remains more or less close to the theoretic 120 mV / decade corresponding to the cathodic reaction $H^+ + e \rightarrow \frac{1}{2} H_2$ (gas), the anodic one, close to the theoretic 60mV / decade corresponding to the anodic reaction $Fe \rightarrow Fe^{2+} + 2 e$ for the low carbon steels, increases for the pearlitic (0.8C) and hyper-eutectoid (1.2C) steels.

General commentaries

The corrosion properties of the steels are here too influenced by plastic deformation by compression but also by the microstructure. Indeed, the polarization resistance tends increasing and the corrosion current decreasing when the carbon content increases, in the not deformed state. However, hardening, which enhances corrosion, seems deleting these differences. It is possible that the plastic deformation exposes more the ferritic part to corrosion maybe by breaking cementite. Further deformation strains may be usefully considered to enrich these first observations. The evolution of the anodic Tafel coefficient when the carbon content increases, is also interesting, but this remains to be explained.

CONCLUSIONS

Even if some interesting observations were done concerning the coupled effects of the carbon content and of the hardening on the corrosion behaviour of this family of steels, the interpretations of these influences are not easy to do. Before that the repeat-

TABLE 9 : Corrosion potentials (E_{ocp}), current densities of corrosion (I_{corr}) and Tafel anodic and cathodic coefficients (β_a and β_c) issued from the Tafel experiments carried out for the Fe-1.2C in its not deformed state (ND) and in its deformed state (DF)

Fe-1.2C Not Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-197.5	4.456	162.1	178.5
Fe-1.2C Plastically Deformed			
E_{corr}/ENH (mV)	I_{corr} (mA/cm ²)	β_a (mV/decade)	β_c (mV/decade)
-242.2	7.71	131.3	121.5

ability needs to be verified and some of these tests to be remade (notably the one concerning the not-deformed ferritic steel). This study concerning the active state will be followed by another ones concerning the passive state (potentiodynamic runs or cyclic polarizations high in potential).

ACKNOWLEDGMENTS

The authors thank Mathieu Lierre for the preparation of the solution as well as for its assistance.

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