Research & Reviews In

Electrochemistry

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Influence of the microstructure on the corrosion behaviour in a sulphuric solution of cast carbon steels as characterized by electrochemical impedance spectroscopy. Part 2: Effect of the preliminary hardening by compression

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ABSTRACT

In this second part this is in their plastically deformed states that the four carbon steels Fe-xC (x varying from 0 to 1.6 wt.%C) were tested in electrochemical impedance spectroscopy. Performed in the same molar sulphuric solution and following the same procedures, these EIS runs led to Nyquist semi-circles the exploitation of which allowed specifying the evolution of the transfer resistance Rtand of the double layer capacity C_{dc} with time during one hour of immersion. All these hardened steels were initially and remain in an active state characterized by low Rt values. Clear dependence of Rt and C_{dc} on immersion time and on the steel carbon content were highlighted, despite that the deformation ratios were not exactly the same for all steels. However the variations of Rt and C_{dc} versus the carbon content were inversed by comparison to the results obtained in the first part for the not deformed states. Further investigations must be done to clarify the influence of hardening on these properties, notably by imposing much higher amounts of plastic deformation.
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KEYWORDS

INTRODUCTION

Hardening during forging or use may significantly change the microstructures of metallic alloys[1]. The microstructural results of plastic deformation may be of various types, for instance structures with new special orientations, elongated grains... A lot of works have demonstrated that plastic deformation may induce modifications of some alloy's properties. Among them the most common are the mechanicalones[2,3] but it may concern also other types, magnetic properties[4] for example. Notably it was proved that tensile, compression or shear strength, hardness may be changed by hardening, for

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many metallic alloys: not-alloyed steels, highly alloyed steels, copper-based alloys, aluminium-based alloys. and this after cold-rolling/hot-rolling[5], extrusion[6] or plastic shear deformation[7].

The surface reactivity of alloys may be themselves influenced by hardening, for example the behaviourin corrosion when in contact with aqueous solutions. The effect of hardening achieved by compression oncast pure metals (Fe, Ni and Cu for instance) was found on their electrochemical properties in a 1Mol/L sulphuric solution[8]. Some effect of plastic tensile deformation was also observed for ferritic steel and ferrite-pearliticsteels[9-11]. Other results in the case of compression hardening were also reported for carbon steels and alloyed steels[12-13].

To study this for various microstructure types of carbon steels, the series of Fe-C binary alloys(Fe-xC (x $\in$ [0; 1.6wt.%]) previously elaborated by casting to specifically studying the effect of the carbon content[14], were hardened by compression, then prepared as electrodes to perform here too Electrochemical Impedance Spectroscopy runs, the results of which will be compared to the ones obtained in the as-cast conditions[14].

EXPERIMENTAL

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

One shortly reminds that a series of four carbon steels (Fe-xC alloys with x=0, 0.4, 0.8 and 1.6 wt.%) were elaborated from pure elements by high frequency induction foundry under argon (40g-weighing ingots). Among the samples which were cut in the ingots a{7 mm × 4 mm × 3 mm}-parallelepiped per steel was especially prepared forcarrying out compression run to achieve a hardened state. These deformations by compression were realized using a 150kN-capacity testing machine. The maximal stresses at which the runs were interrupted and the resulting negative longitudinal permanent deformations are given in TABLE 1.

Electrochemical measurements

As already described in the first part of this work[14], for each steel, the preparation of the working electrode started by the immersion of the compressed part in a liquid cold resin by keeping a not covered upper part. After total stiffening it was extracted from the plastic mould and partly sewed to insert the denuded part of an electrical wire. The semi-embedded metallic part was thereafter incorporated again in the mould and new liquid resin was additionally poured to immerse the upper part of the sample and the denuded copper. The emerging metallic part of the obtained electrode was ground with papers from 120-grit to 1200-grit. The counter electrode was a platinum one, and the electrode of potential reference was a saturated calomel one. The electrochemical tests were carried out in a molar sulphuric solution (Ametekpotensiostatdriven by Versastudio). The EIS tests which consisted in applying to the working electrode a sinusoidal variation $\Delta E \times \cos(\omega t)$of potential around E_{ocp} (open circuit potential), with $\Delta E = 10mV$ and $\omega = 2 \times \pi \times f$, f decreasing from 100 kHz down to 1 Hz with five values per decade. The resulting complex current I= $I_0 \times \cos(\omega t + \phi)$, dividing the complex potential, leads

TABLE 1 : The maximal values of the stress underwent by the samples when the compression runs were stopped and the resulting permanent deformations

Fe-x wt.% x=…	Maximal stress applied (MPa)	Relative longitudinal deformation (%)
0	220	-7.1
0.4	730	-4.5
0.8	590	-5.6
1.6	960	-3.1

to the complex impedance, the variation versus ω of which was plotted according to the Nyquist $\{-Z_{im}$ versus $Z_{real}\}$ representation. This was repeated six times every ten minutes.

Here too, since the half circle may be not complete or passed under the x-axis, the minimal value of Z_{real} was taken as being a good estimation of the electrolyte resistance Re and the maximal value of Z_{real} was taken as equal to $\{Re + Rt\}$, with consequently the determination of the transfer resistance Rt. In addition, knowing that the summit of the half circle is obtained when$Rt \times C_{dc} \times \omega = 1$ the values of the corresponding frequency f(-Z_{im} max) was noted, converted into pulsation ω(-Z_{im} max) according to ω(-Z_{im} max) = 2 π f(-Z_{im} max): this allowedspecifying the value of the double layer capacity: $C_{dc} = 1 / (Rt \times C_{dc})$.

Evolution of the Nyquist diagram with time

The plot of the point $\{-Z_{im}(\omega)$ versus $Z_{real}(\omega)\}$ for the six successive times over one hour (t=0 min, 10 min, 20 min, 30 min, 40 min, 50 min and 60 min) is shown in Figure 1 for the deformed Fe-0.0C steel, in Figure 2 for the Fe-0.4C one, in Figure 3 for the Fe-0.8C one and in Figure 4 for the Fe-1.6C one.

After plastic deformation it appears that, for all steels, the half circle becomes smaller and smaller with time. In all cases too, the curves are a little
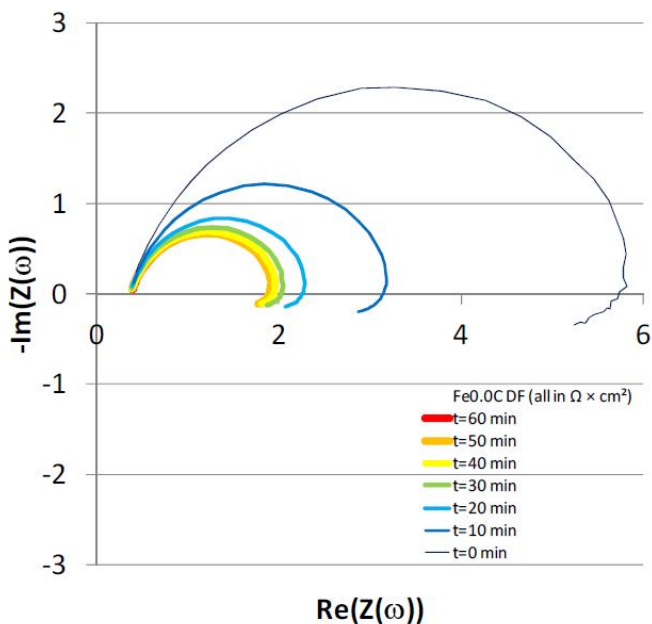
greater for the three other alloys (-Z_{im} strictly negative for 1Hz). Since the electrolyte remains seemingly constant with time, this is the transfer resistance which seems decreasing with time for all the deformed steels. In addition, the change of the semicircle is fast during the beginning of immersion and thereafter it stabilizes.

Nyquist diagram comparison between the not deformed and plastically deformed states

The plastic deformation in compression obviously induces a severe contraction of the half circle of the Fe-0.0C steel, as is to say a dramatic loss in transfer resistance (Figure 5): initially in (a curious) passive state, it clearly remains active in the acidic solution when hardened. No such change was noted for the Fe-0.4C steel which was always in an active state when not yet deformed (Figure 6). The half circles are almost superposed for the two immersion durations.

The comparison leads to scattered results for the two carbon-richest alloys: half circle smaller or greater after deformation for the Fe-0.8C (Figure 7) and the Fe-1.6C (Figure 8) steels respectively.

Evolution of Re, Rt and C_{dc} versus time for the four alloys

The electrolyte resistance does not vary signifi-

Figure 1 : Nyquist plot of the measured EIS values in the case of the deformed Fe-0.0C steel
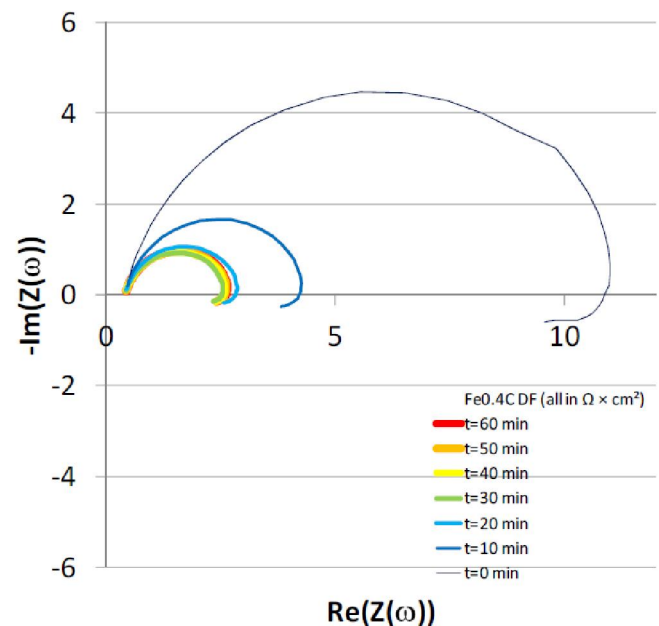

Figure 2 : Nyquist plot of the measured EIS values in the case of the deformed Fe-0.4C steel
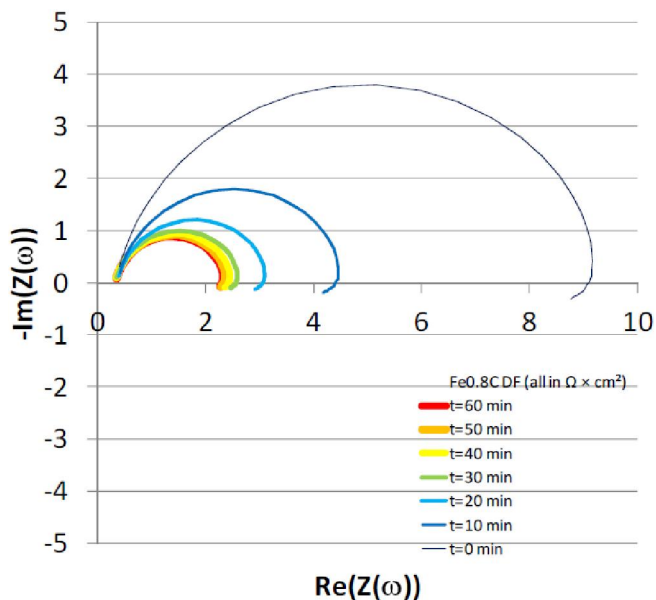
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Figure 3 : Nyquist plot of the measured EIS values in the case of the deformed Fe-0.8C steel
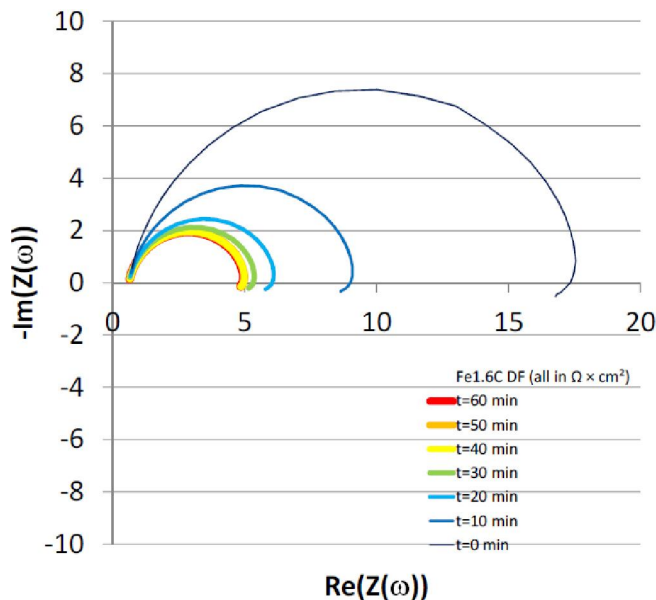
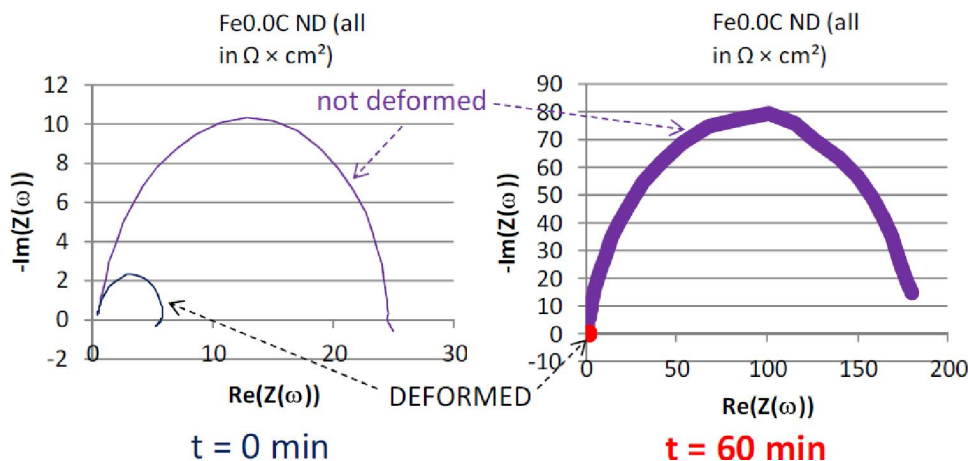**Figure 4 : Nyquist plot of the measured EIS values in the case of the deformed Fe-1.6C steel**

Figure 5 : Nyquistdiagrams superposition for the Fe-0.0C steel in its two states (not deformed and plastically deformed) for the two extreme durations of immersion
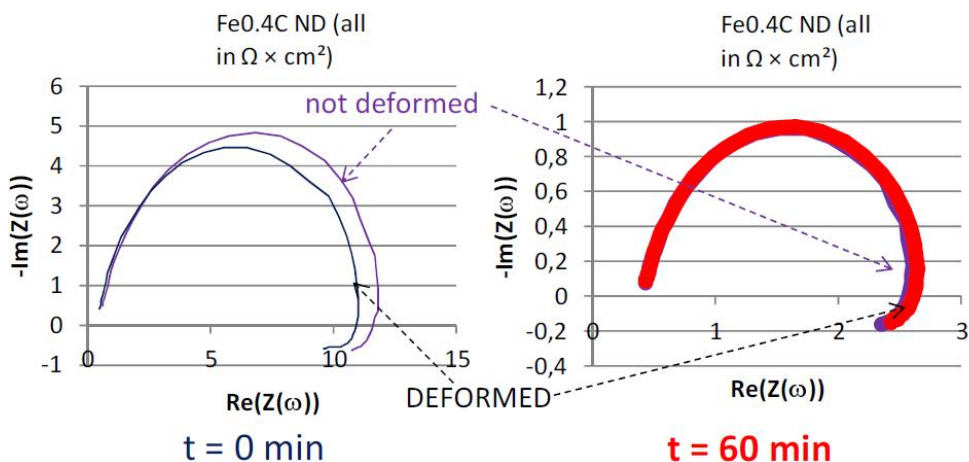

Figure 6 : Nyquistdiagrams superposition for the Fe-0.4C steel in its two states (not deformed and plastically deformed) for the two extreme durations of immersion
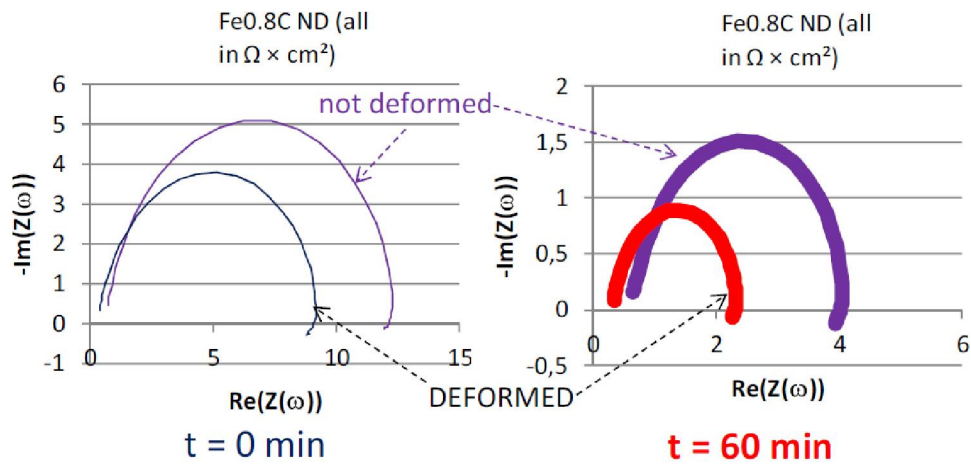
Figure 7 : Nyquistdiagrams superposition for the Fe-0.8C steel in its two states (not deformed and plastically deformed) for the two extreme durations of immersion
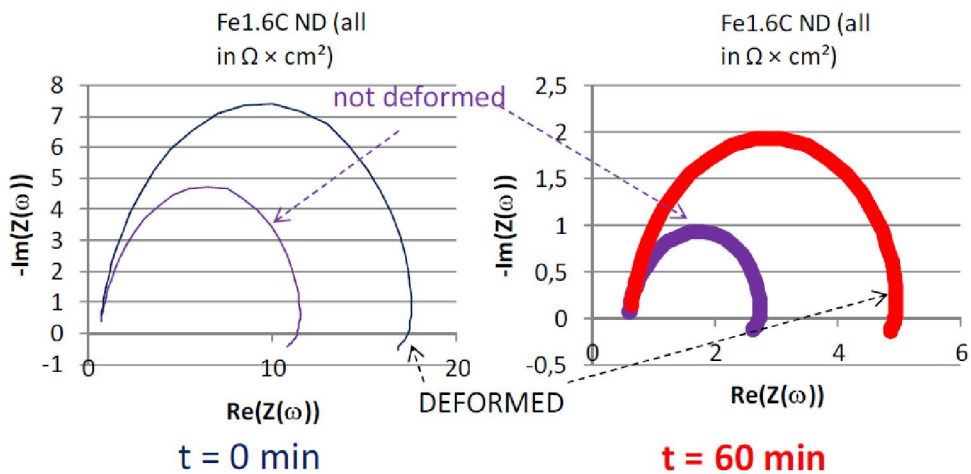

Figure 8 : Nyquistdiagrams superposition for the Fe-0.4C steel in its two states (not deformed and plastically deformed) for the two extreme durations of immersion
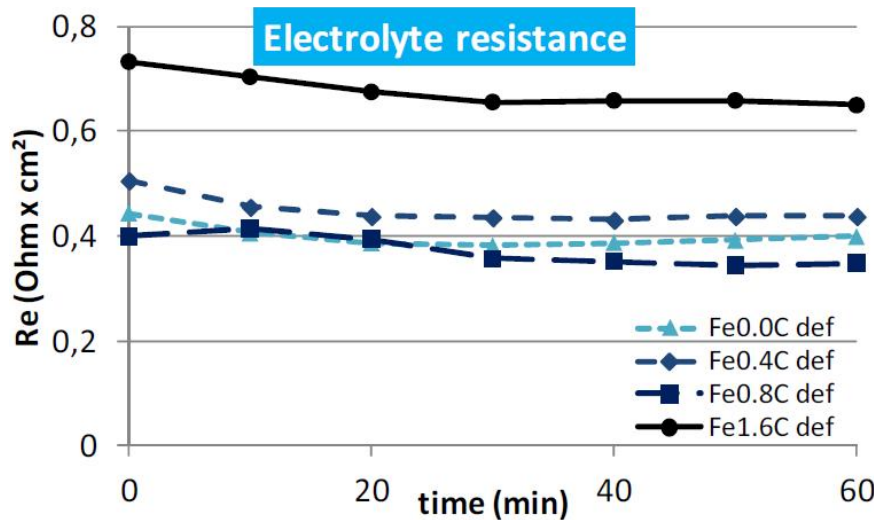

Figure 9 : Cumulated curves showing the evolution of the electrolyte resistance versus time during the I hour – immersion for the four steels in their deformed states

cantly with time for each of the four alloys (Figure 9). There are small differences between the alloys but this is only due to a not real repeatability position of the working electrode by regards to the counter

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electrode. This is with no consequences for the more important results which follow.

The transfer resistance (Figure 10) is globally the same for the deformed ferrite-pearlitic and the pearlitic steels (Fe-0.4C and Fe-0.8C), but slightly lower for the deformed ferritic one (Fe-0.0C) and significantly higher for the hyper-eutectoid steel (Fe-1.6C). However, in all cases the Rt value decreases, rather rapidly then slowly, to become stabilized after half an hour (to about 1.5, 2 and 4.5 &! × cm² for the Fe-0.0C, Fe-0.4&0.8C and Fe-1.6C deformed steels respectively).

The double layer capacity increases to stabilize after 50 minutes for the four steels (Figure 11). The curves are well ordered, suggesting that the lower the carbon content the higher the double layer capacity. The Cdc value of the deformed ferritic Fe-0.0C steel stabilizes at about 65×10^{-5}Fahrad, the Fe-0.4C one at 37×10^{-5}Fahrad, the Fe-0.8C one at 32×10^{-5}Fahrad and the Fe-1.6C one at 19×10^{-5}Fahrad.

General commentaries

If all the four hardened steels behave similarly to one another (active state for all as expected in an acidic solution, contraction of the half circle with time). The four hardened steels behaved in these fields as the not deformed Fe-0.4C, Fe-0.8C and Fe-
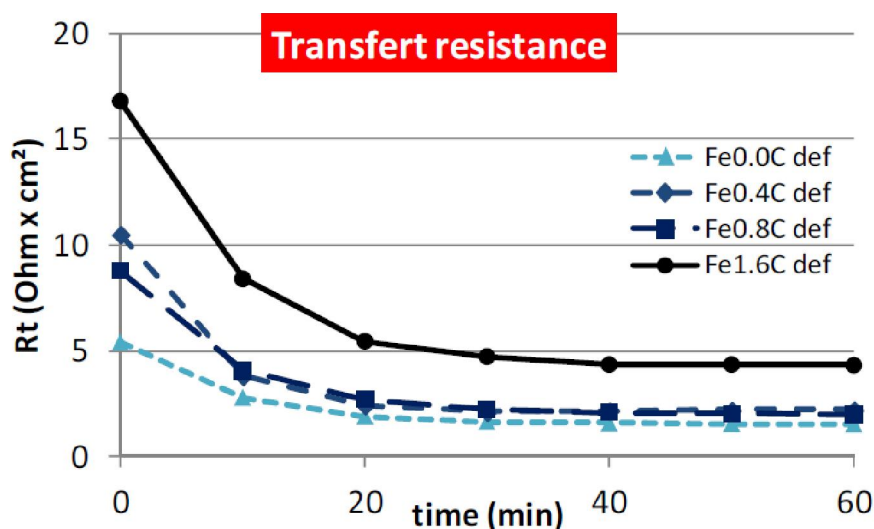

Figure 10 : Cumulated curves showing the evolution of the transfer resistance versus time during the 1 hour – immersion for the four steels in their deformed states
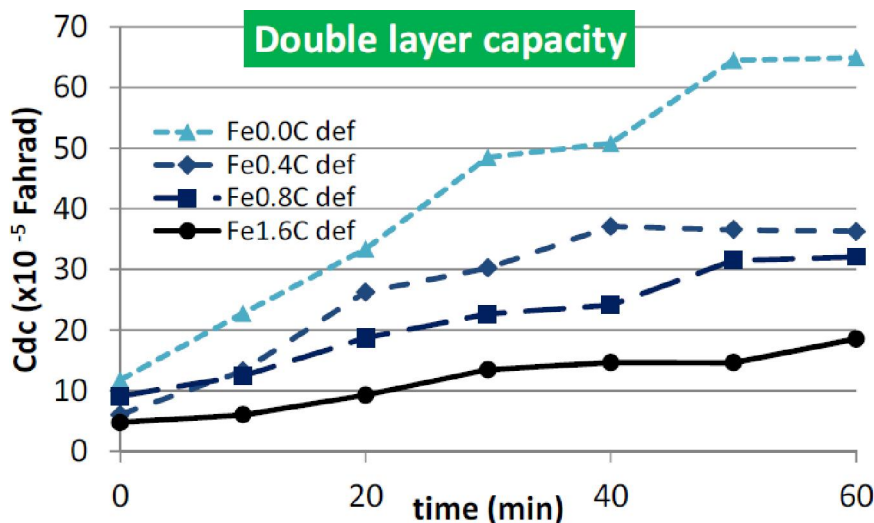

Figure 11 : Cumulated curves showing the evolution of the double layer capacity versus time during the I hour – immersion for the four steels in their deformed states

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1.6C steels studied in the first part[14]. In contrast the effect of the plastic deformation is not the same for the four steels. If the corrosion behaviour was not qualitatively modified (state still active) the evolution of the Nyquist circle was not the same. This cannot be attributed to the fact that the deformation rates were different among the steels. Although these deformation ratios were not exactly the same, the transfer resistance followed a certain law versus the carbon content (increase from the ferritic steel to the hyper-eutectoid one) as well as the double layer capacity (decrease from the ferritic to the hyper-eutectoid). These evolutions are the inverse that what was observed for the not deformed state! This is really questionable and supplementary tests, involving higher deformation rates for example, remain to be done to enlarge the investigation field and obtain more chances to establish robust conclusions.

CONCLUSIONS

The plastic deformations achieved on the four carbon alloys thus led to modifications of their responses to the EIS solicitations. Unfortunately the principal consequences of hardening were inversions in the dependence of the electrochemical properties issued from EIS on the carbon content, and curiously alloy per alloy there was no systematic direct influence of the plastic deformation itself. Supposing that the seen variations were maybe in the uncertainty range characterizing the scattering of the results, outlooks may be hardening much more the alloys (permanent deformation of -25%, -50% and so on) for enhancing the effects of hardening.

ACKNOWLEDGMENTS

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