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Study of Two Factors Possibly Influencing the Obtaining Conditions and the Stability of the Passive State of Cast Carbon Steels in Acidic Aqueous milieu. Part 2: Hardened State

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Abstract

In this second part of the work carried out about the conditions of passivation and of stability of this state for carbon steel, this is the possible influence of a preliminary plastic deformation, issued from cold rolling or from stress existing during service, which was examined. Parts of the same Fe-xC steels, with x=0, 0.4, 0.8, 1.2 and 1.6 (weight percents) as studied in their as-cast states in the first part, were compressed until reaching significant amount of plastic deformation. The resulting hardened steels were mounted as electrodes and subjected to cyclic polarization in molar sulphuric solution. As for the as-cast state, all the samples were able to get passive for polarization at potential high enough, and fall again in the active state when potential is decreased under a critical value. The conditions of obtaining the passive state as well as to maintain it were noted. The current density of corrosion in the passive state is low but it tends to be higher than for the not deformed alloys.

Keywords: Cast carbon steels, Hardened state, Corrosion, Acidic solution, Passive state, Electrochemical measurements.

Introduction

Contrarily to cast irons which are poured into mould to solidify with the final shape of the wished pieces, the shaping of steels is often carried out by plastic deformation. Hot and cold-rolling, deforming blooms into sheets… induce significant microstructure modifications [1]. Hot and cold work lead to specific microstructures of hardened states: special orientations, phases geometrically changed, elongated grains, high dislocation concentrations... This may have important consequences on properties of all types as demonstrated by a lot of work, concerning mechanical properties [2,3], magnetic properties [4]… In the mechanical field the tensile, compression or shear strength, hardness may be modified. This was seen for not-alloyed or highly alloyed steels, copper alloys, aluminium alloys... after cold-rolling or hot-rolling [5], extrusion [6] or plastic

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deformation in torsion [7]. These properties may have lost their initial isotropic character, consequently to the orientated character of these deformations. Chemical properties may be themselves influenced by hardening, such as the corrosion behaviour. Carbon steels, which can be concerned by plastic deformation for their shaping, can be mechanically strengthened by hardening but they are intrinsically not resistant against corrosion. Besides coatings, a possibility for preserving them from to fast corrosion is to anodically polarizing them in order to access to a passive state with which they may be less threatened by corrosion. Accessing to passivation can be achieved even in contact with an acidic milieu, by applying to them a constant potential high enough. In the first part of the present work [8] cyclic polarizations were performed for a series of carbon steels containing between 0 and 1.6 wt.%C, in order to know the conditions of passivation and of keeping the passive state. These conditions may involve if the steels are preliminarily hardened during their shaping for example.

The purpose of this second part of the same work is to characterize the passivation and loss of passivation of pre-hardened versions of these steels in order to see if hardening may change the conditions previously specified. For that the same steel grades were compressed and subjected to cyclic polarization in the same molar sulphuric solution.

Experimental

Origin of the alloys

One can remind that the five synthetic carbon Fe-xC steels (x=0, 0.4, 0.8, 1.2 and 1.6 wt.%) characterized here were elaborated by melting and solidification in a high frequency induction furnace under 300 mbars of pure Ar. The compact ingots, all of about 40g, were cut for obtaining parallelepipeds with as approximate dimensions 7 mm × 4 mm × 3 mm. The control by optical microscope of the ground, polished than Nital-etched metallographic samples showed all steels were ferritic (Fe-0C), ferritic-pearlitic (Fe-0.4C), pearlitic (Fe-0.8C) or hyper-eutectoid (Fe-1.2C and Fe-1.6C).

A second set of parallelepipeds were kept for the compression runs which are described just after.

Compression runs

The parallelepipeds especially prepared for the compression tests were plastically deformed using an Alliance RF/150 testing machine from MTS Systems. This one, equipped with a 150kN-cell for the force measurement, was driven by the Testworks4 software. The tests were continued until reaching a permanent deformation important enough to get a really hardened version of the steels. The reached levels of stress are about 220, 730, 590, 750 and 960 MPa for the Fe-0C, Fe-0.4C, Fe-0.8C, Fe-1.2C and Fe-1.6C steels, respectively. The longitudinal permanent deformations □zz achieved are respectively: -7.1% (Fe-0C), -4.5%, -5.6%, -3.2% and -3.1% (Fe-1.6C) respectively. The recorded stress-strain curves are presented in Figure 1.

Electrochemical measurements

After the compression tests the deformed parts were cut transversally to the deformation axis. Each half devoted to the electrochemical measurements was connected to the denuded end of a copper electrical wire, before being embedded in a cold resin with immersion of the junction in order to keep only the plastic-covered copper wire in contact with the electrolyte. Each working electrode was associated with a Pt counter electrode and a Calomel reference in potential electrode (SCE). A molar sulphuric solution (H2SO4, 1M) was poured in a three-electrode cell, in which the three electrodes were immersed. After 5 minutes a cyclic polarization was applied. This started by measuring the free potential Ecorr and by applying an increase in potential at +1 mV/s from Ecorr-250mV to 1.9 Volts. This was immediately followed by a decrease in potential at -1 mV/s until reaching again Ecorr-250mV.

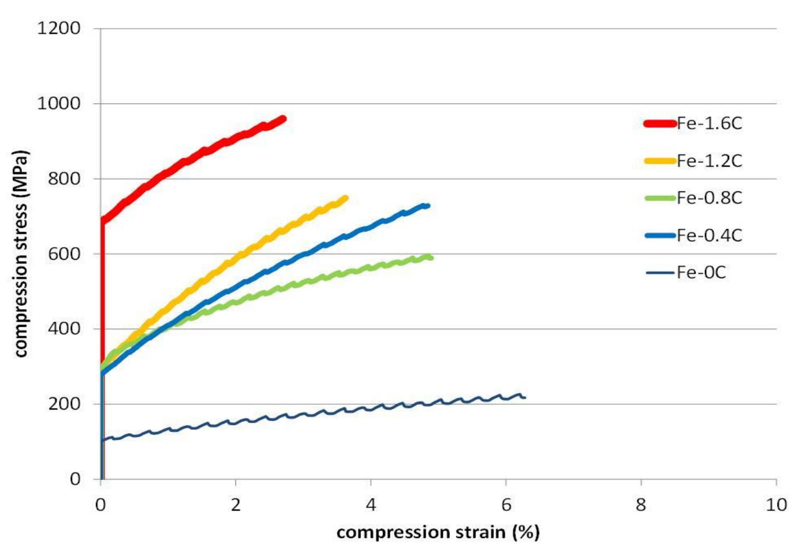

Figure 1: The stress-strain curves of the compression tests.

Results and Discussion

General aspect of the obtained polarization curves

The obtained cyclic polarization curves are plotted together in Figure 2. They all present almost superposed Tafel-type parts at low potential (between Ecorr-250 mV and Ecorrr+250mV) in the potential-increasing part and in the potential-decreasing one, parts at high anodic current density (anodic peak in the E-increasing part and sudden jump in current density in the E-decreasing one), passivation plateau (low current density and generally lower for the E-decreasing part than for the E-increasing one), a transpassivation peak at very high potential (generally only in the E-increasing part) and the solvent wall.

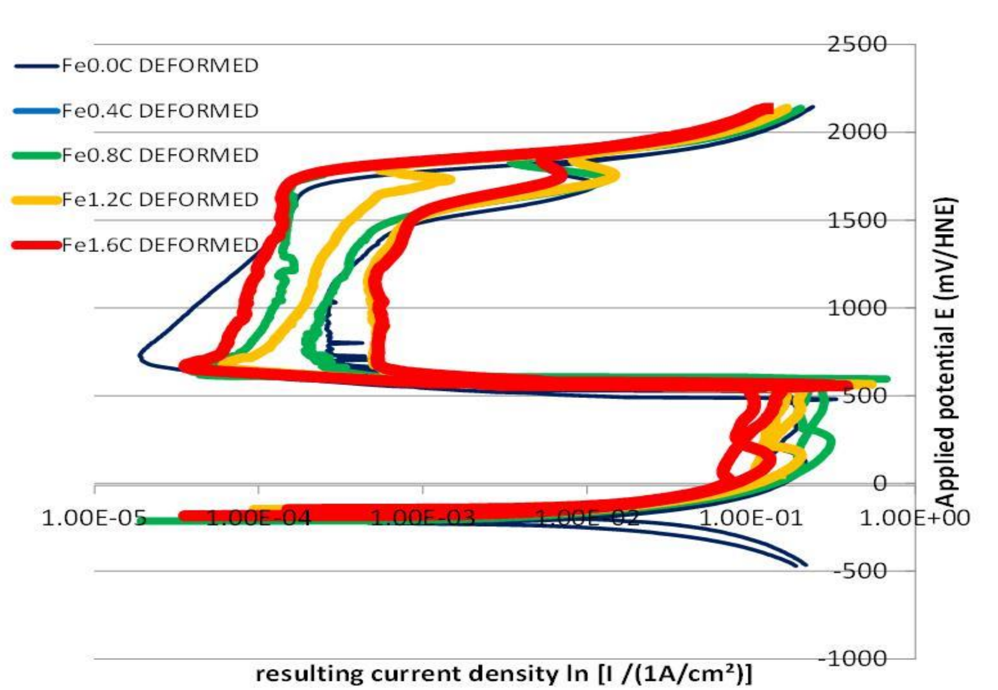

Figure 2: All the polarization curves plotted together.

Effect of hardening on the potential-increasing parts of the cyclic polarization curves

To better distinguish the different parts of each polarization curve four of them are plotted again, but separately, in Figure 3. One can better observe the different elements of description given above. In order to more efficiently reveal the consequences of the applied plastic deformation in compression to the electrochemical behaviours of the steels on the behaviours in passivation of the studied carbon steels only the potential-increasing parts of the cyclic polarization curves were plotted, the one for the as-cast steel together with the one of its hardened version. The noted differences are illustrated by some graphs: the ferritic Fe-0C as-cast and hardened in Figure 4, the pearlitic Fe-0.8C in Figure 5, and the hypereutectoid Fe-1.6C in Figure 6.

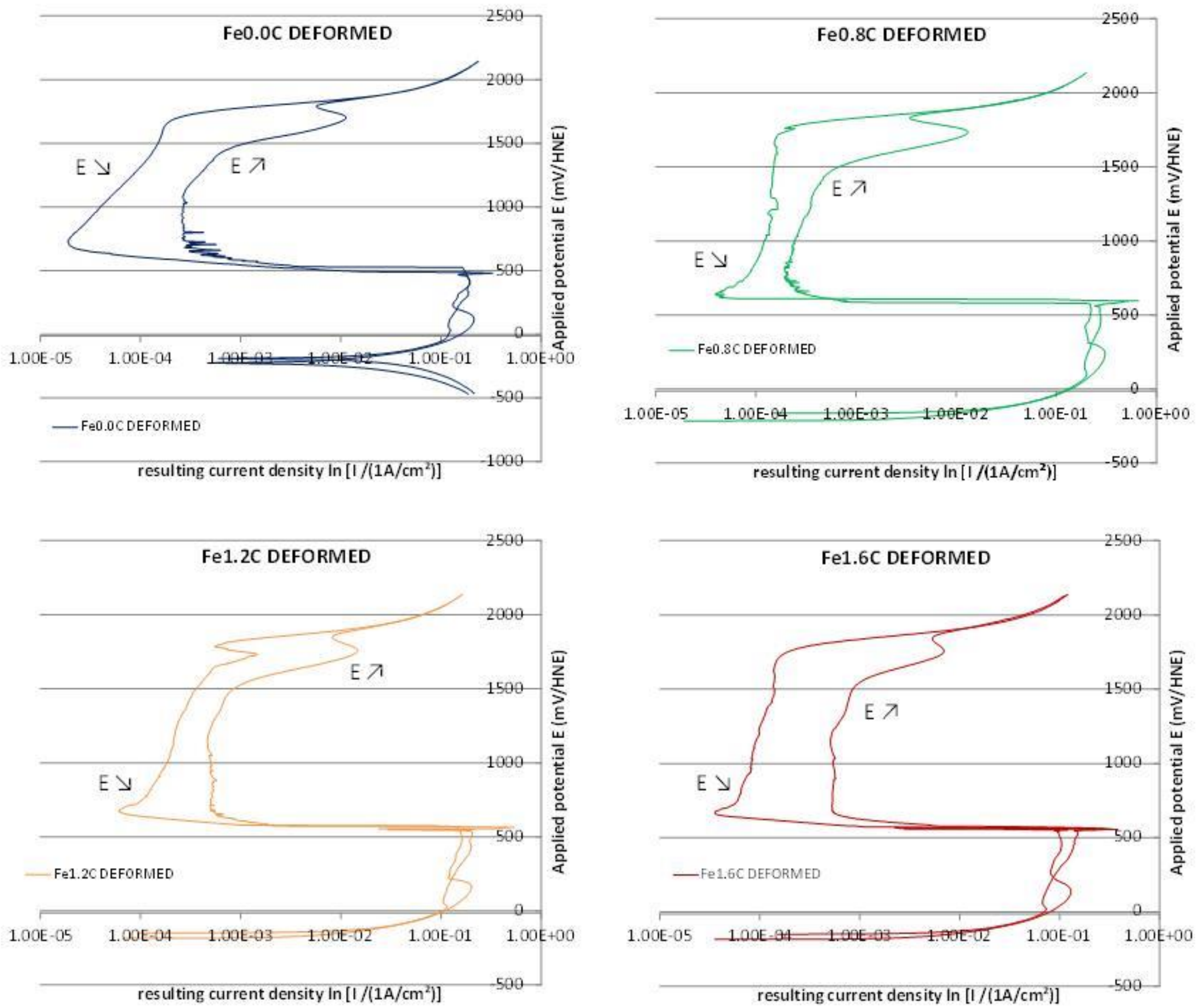

Figure 3: The whole cyclic polarization curves obtained for the ferritic steel (Fe-0C: top left), the pearlitic steel (Fe-0.8C: top right) and the two hypereutectoid steels (bottom, Fe-1.2C: left, Fe-1.6C: right).

Globally one can see that the hardening induced by the compression runs may change more or less the potensiodynamic curves, for example:

Higher corrosion current in active state in the case of the Fe-0C alloy

Tendency to an easier passivation (Fe-0C and Fe-1.6C: slightly lower anodic peak, but the contrary for the Fe-0.8C alloy)

Higher corrosion rate in the passive state for the carbon-lowest steels (and the contrary for the C-highest one)…

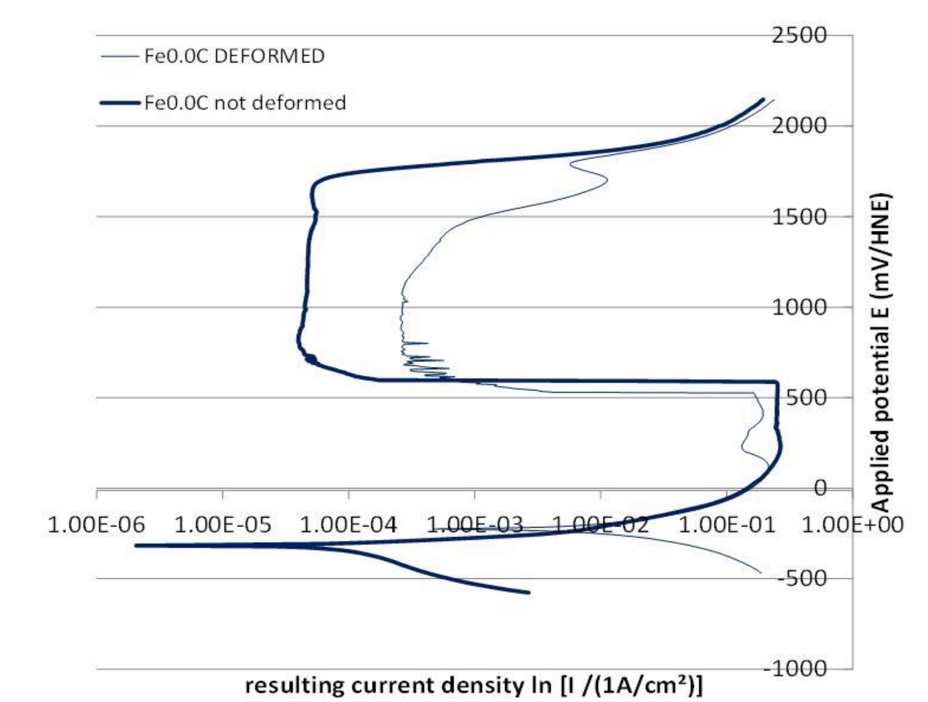

Figure 4: The cyclic polarization curves obtained for the ferritic steel before and after compression.

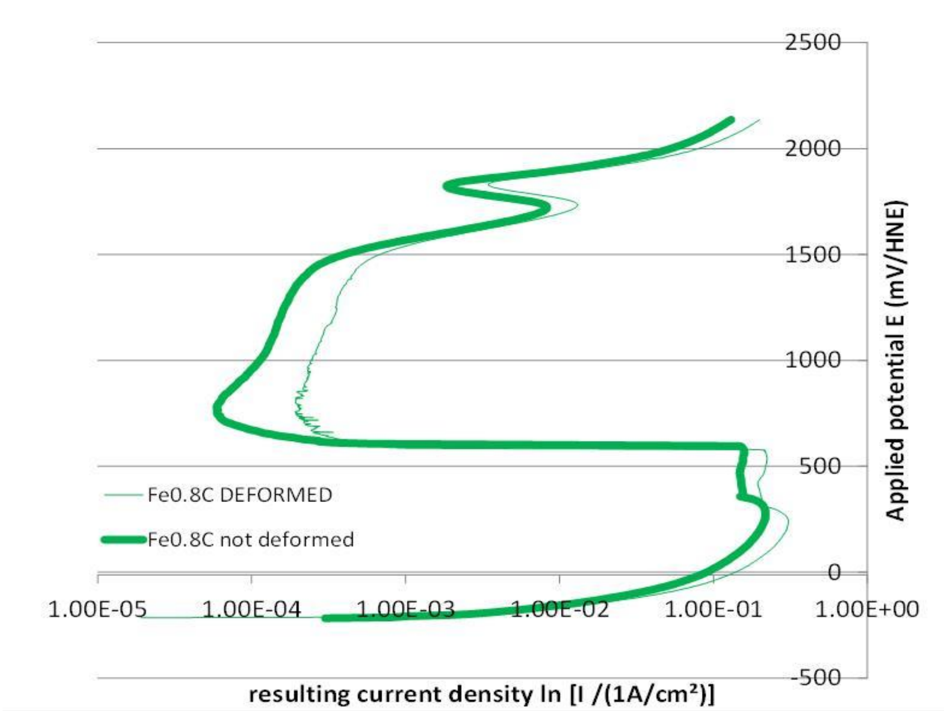

Figure 5: The cyclic polarization curves obtained for the pearlitic steel before and after compression.

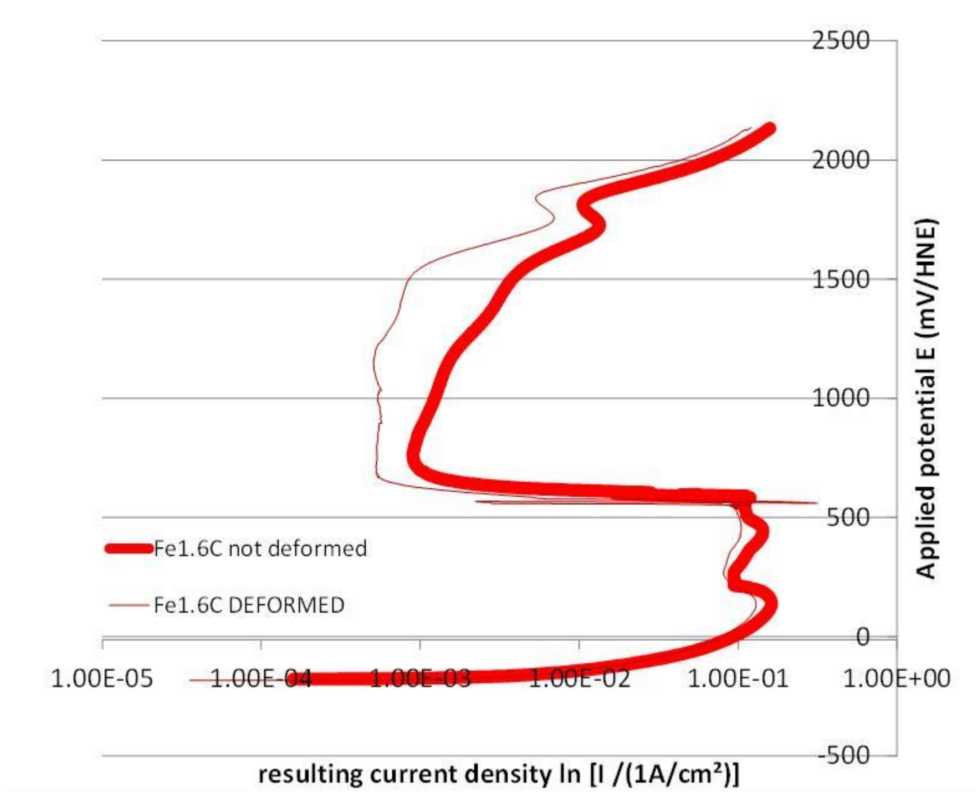

Figure 6: The cyclic polarization curves obtained for one of the hypereutectoid steels before and after compression.

After these first illustration concerning only the potential-increasing parts, the results of the exploitation of the whole cyclic polarization curves are displayed in Table 1 (characteristics values of potential and current densities noted on the E-increasing part), and in Table 2 (E-decreasing part).

Differently to what was done in the first part the comparison between the different carbon contents cannot be done here since the hardening ratio is not the same for all the steels. The analysis is therefore limited to the effect of hardening steel by steel. On the other hand some results are lacking since some of the curves cannot allow determining some characteristics. Nevertheless one can say that, concerning the values noted on the E-increasing part:

The critical current density before passivation seems be decreased by hardening (Icp decreased for 2 cases out of 3)

The passivation potential seems decreased by hardening (Epass decreased for 2 cases out of 3) (… what suggests that hardening tends favoring passivation)

The anodic current density in the passivation plateau seems to be increased by hardening (I pass mini increased for 2 cases out of three)

The potential of transpassivation start seems to be increased by hardening (E transpass increased for 2 cases out of three)

The maximal transpassivation current density (peak) seems to be increased by hardening (I transpass pass maxi increased for 2 cases out of three)

(… what suggests that the protection against corrosion brought by passivation is less efficient if hardened while the transpassivation is delayed to higher potential but with a higher intensity).

Wt.%c	**0**	**0.4**	**0.8**	**1.2**	**1.6**	**unit**
Icp	251	174	215	/	141	*mA / cm^2*
Ipass	196	/	296	191	121	mA / cm^2
Epass	538	594	551	/	975	*mV / HNE*
Epass	501	/	599	554	550	mV / HNE
Ipass mini	44.2	175	64.2	/	975	*µA / cm^2*
Ipass mini	270	/	219	582	619	µA / cm^2
Etranspass	1.313	1.384	1.391	/	1.577	*V / HNE*
Etranspass	1.400	/	1.459	1.462	1.495	V / HNE
Itranspass maxi	0.0545	4.66	7.31	/	12.4	*mA / cm^2*
Itranspass maxi	9.98	11.4	/	12.4	6.20	mA / cm^2

Table 1: Values of current densities and of potential on interest in the potential-increasing parts of the cyclic polarization curves; comparison between the as-cast version and the hardened version of the same steels.

The hierarchy concerning the current density in passive state remains for the E-decreasing part of the curves. The passive state seems to be lost sooner for the hardened state (higher value of E pass loss for 2 cases out of 3). The lack of exploitable results does not allow concluding about the effect of hardening on the maximal value of anodic current density abruptly appearing when the passive state is lost.

Wt.%c	**0**	**0.4**	**0.8**	**1.2**	**1.6**	**unit**
Ipass mini	7.25	9.43	6.37	/	/	*µA / cm^2*
Ipass mini	20.6	/	40/8	67.2	39.2	µA / cm^2
Epass loss	608	704	666	/	582	*V / HNE*
Epass loss	741	/	650	695	694	V / HNE
Ipass loss maxi	375	313	/	/	237	*mA / cm^2*
Ipass loss maxi	330	/	663	539	381	mA / cm^2

Table 2: Values of current densities and of potential on interest in the potential-decreasing parts of the cyclic polarization curves; comparison between the as-cast version and the hardened version of the same steels.

General commentaries

Even if the obtained curves were not all exploitable it seems that the plastic deformation led to modifications for the passivation properties of the studied carbon steels. A beneficial effect is the probable higher easiness to access to the passive state. Thus anodic polarization should lead to passivation without supplementary difficulty by regards to the as-cast steels. But the problem is more the anodic density of current when in the passive state which was detected as being between 3 and 6 times higher in case of hardening for the ferritic-pearlitic steels. This was not observed for the carbon-richest alloy but it is true that, thanks to its high mechanical resistance to compression, its plastic deformation rate was much lower with as results lower influence of hardening.

Conclusions

The results of the two parts of this work showed that whatever their carbon contents, cast carbon steels can access to the passive state even in contact with low-pH milieus. When anodically polarized, at constant potential higher than the minimal ones specified here, they may be maintained with a stable passivation layer, the sustainability of passivation of which remains to be determined. The carbon content may influence the conditions of passivation and of anodic protection and this must be taken into account before applying the anodic polarization at constant potential. In case of preliminary hardening (e.g. in case of cold working, hot rolling…) the corrosion rate in passive state, even lower than in active state, seems being enhanced by comparison with not-hardened versions. Consequently one must keep in mind that the brought corrosion resistance is not so good.

Acknowledgments

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