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## Mechanical and electrochemical properties of a cast carbon steel. Part 2: Behaviour in corrosion

Patrice Berthod<sup>1</sup>, Elodie Conrath<sup>2</sup>

<sup>1</sup>Institut Jean Lamour (UMR CNRS 7198), department CP2S, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

<sup>2</sup>Faculty of Sciences and Technologies, University of Lorraine, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

E-mail: patrice.berthod@univ-lorraine.fr

### ABSTRACT

A ferrite-pearlitic steel, elaborated by foundry with a cylindrical shape has been mechanically studied in compression and hardness in a first part of the present work. In this second part the equivalent samples were tested in corrosion in a sulphuric acid solution by varying both the initial deformation rate and the cutting orientation with respect to the sample axis. Stern-Geary linear polarizations were successively run during half an hour of immersion with recording of open circuit potential and polarization resistance, while cyclic polarizations were performed between the cathodic domain and the anodic solvent's wall. No systematic differences were noted on the cyclic polarization curves between the values, obtained for the different deformation rates and orientations, of the various parameters describing the corrosion state changes (active → passive and passive → active), although that some tendencies were seen. In contrast the linear polarization runs showed that the  $R_p$  value more clearly depends on both the hardening amount and the surface orientation. It was notably found again that the polarization resistance decreases, and the deduced corrosion rate increases, when the plastic relative deformation is higher, and also, by combining the present results with previous ones, that there is possibly a continuity of evolution of the parallel/perpendicular  $R_p$  order from the negative deformations in compression to the positive deformations in traction.

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### KEYWORDS

Carbon steel;  
Plastic compression  
deformation;  
Corrosion;  
Electrochemical  
measurements.

### INTRODUCTION

The influence of plastic deformation on metallic materials has been studied for at least about four decades. This was for example the subject of many works driven on different types of steel, ferritic, austenitic, martensitic ... notably in aqueous acid sulphuric environments<sup>[1-4]</sup>. It was generally observed that hardening – in trac-

tion for example – tends to accelerate corrosion in the active state, while the observed effects are more variable for non-ferrous alloys<sup>[5-7]</sup>, with however a more frequent tendency to faster corrosion too. Such phenomena are potentially of great importance since many metallic pieces exposed in service to aggressive aqueous environments, often rather acid, are simultaneously subjected to stress high enough to induce permanent

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deformation, and therefore they are sometimes exposed to stress corrosion in the periods when they are mechanically solicited, and sometimes to simple corrosion when the previous stresses are not longer applied. This later phenomenon may cause heterogeneous corrosion over the whole metallic piece, notably by galvanic phenomena.

In this second part of a work concerning the effect of the hardening by plastic deformation in compression on some mechanical<sup>[8]</sup> and chemical properties of a cast carbon steel solidified following a special procedure, the corrosion behaviour of the deformed samples will be examined, concerning the active state as well as the passive state, here too by considering additionally the possible influence of the orientation of the electrode surface with respect to the deformation direction, which may be in contact with outside after machining.

### EXPERIMENTAL

#### Elaboration of the steel and preparation of the electrodes

One can first remind that the carbon steel in consideration<sup>[8]</sup> was solidified in a tube for obtaining a cylindrical shape (diameter 10mm  $\times$  length of about 4 cm) by aspiration from the liquid alloy melted by high frequency induction under 300mbars of pure argon. It was thereafter cut in several cylindrical parts (length of about 1 cm) and uni-axially compressed until the required deformation rates were reached (final relative deformations: -9.19% and -20.25%). The not-deformed part and the different deformed parts were then cut following a special procedure to obtain two samples with a surface parallel to the deformation axis (one for the metallographic examination and the hardness measurements<sup>[8]</sup> and one for the present corrosion study), and two samples with a surface perpendicular to the deformation axis (for the same mechanical and corrosion purposes).

The electrodes were prepared by inserting the not-covered end of a partially plastic-covered copper wire in a notch locally realized on the metallic sample with a hand saw, by embedding the sample and the not plastic-covered part of the wire in a {ESCIL: Araldite CY230 resin and hardener HY

956}-mixture, and by polishing with SiC papers up to 1200 grit and {1  $\mu$ m hard particles}-paste the emerging metallic surface.

#### Electrochemical runs

The electrochemical experiments aiming to assess the corrosion behaviour in an sulphuric aqueous solution at room temperature (H<sub>2</sub>SO<sub>4</sub> 2N) were performed using a three-electrodes cell (the studied sample as working electrode, a graphite rod as auxiliary electrode and a Saturated Calomel Electrode (SCE) as reference in potential), a potentiostat model 263A of Princeton Applied Research driven by the M352 software from EG&G/Princeton.

The experiments which were done are:

- the following of the open circuit potential ( $E_{ocp}$ ) over half an hour with the measurement of the polarization resistance every 5 minutes by linear polarization performed between  $E_{ocp} - 20mV$  and  $E_{ocp} + 20mV$  at 0.166mV/s,
- a cyclic polarization consisting of a potential-increasing part between  $E_{ocp} - 250mV$  up to 1.9V at +5mV/s, followed by a potential-decreasing part between 1.9V down to  $E_{ocp} - 250mV$  at -5mV/s,
- the potential-increasing part of the later files being also considered to perform Tafel calculations in order to specify potential and current of corrosion.

### RESULTS AND DISCUSSION

#### Results of linear polarization

The values successively obtained for the open circuit potential and the polarization resistance are displayed in TABLE 1, TABLE 2 and TABLE 3, and their evolution graphically presented in Figure 1.

The following comments can be done about these first experimental results:

#### Open circuit potential

- $E_{ocp}$  is in all cases at a level showing that the samples are in an active state,
- $E_{ocp}$  increases with time in all cases,
- if the first values recorded show differences between the two orientations (notably for the not-deformed state, curiously) the final ( $E_{ocp6}$ ) are close to one another for the two orientations (for a same deformed

**TABLE 1 : The successive values of the open circuit potential and of the polarization resistance for the not deformed sample for the two orientations**

NOT DEFORMED PARA/AXIS				NOT DEFORMED PERP/AXIS					
Time (min)		Ohm cm <sup>2</sup>	E(mV)/ENH	Time (min)		Ohm cm <sup>2</sup>	E (mV)/ENH		
3	Rp1	18, 68	-239	Eocp1	3	Rp1	17,03	-253	Eocp1
8	Rp2	13, 84	-238	Eocp2	8	Rp2	18,00	-253	Eocp2
13	Rp3	12, 71	-236	Eocp3	13	Rp3	11,41	-243	Eocp3
18	Rp4	10, 77	-234	Eocp4	18	Rp4	9,76	-238	Eocp4
23	Rp5	8, 96	-231	Eocp5	23	Rp5	8,27	-234	Eocp5
28	Rp6	8, 41	-229	Eocp6	28	Rp6	7,23	-232	Eocp6

**TABLE 2: The successive values of the open circuit potential and of the polarization resistance for the -9.19%-deformed sample for the two orientations**

DEFORMED -9.19% PARA/AXIS				DEFORMED -9.19% PERP/AXIS					
Time (min)		Ohm cm <sup>2</sup>	E(mV)/ENH	Time (min)		Ohm cm <sup>2</sup>	E (mV)/ENH		
3	Rp1	17, 47	-250	Eocp1	3	Rp1	17,14	-248	Eocp1
8	Rp2	13, 35	-248	Eocp2	8	Rp2	13,12	-244	Eocp2
13	Rp3	10, 08	-243	Eocp3	13	Rp3	10,03	-238	Eocp3
18	Rp4	7, 94	-237	Eocp4	18	Rp4	7,90	-234	Eocp4
23	Rp5	6, 68	-234	Eocp5	23	Rp5	6,70	-230	Eocp5
28	Rp6	5, 94	-232	Eocp6	28	Rp6	6,04	-228	Eocp6

**TABLE 3: The successive values of the open circuit potential and of the polarization resistance for the -20.25%-deformed sample for the two orientations**

DEFORMED -20.25% PARA/AXIS				DEFORMED -20.25% PERP/AXIS					
Time (min)		Ohm cm <sup>2</sup>	E(mV)/ENH	Time (min)		Ohm cm <sup>2</sup>	E (mV)/ENH		
3	Rp1	11, 85	-245	Eocp1	3	Rp1	20,11	-240	Eocp1
8	Rp2	8, 87	-241	Eocp2	8	Rp2	21,25	-242	Eocp2
13	Rp3	6, 68	-236	Eocp3	13	Rp3	13,47	-239	Eocp3
18	Rp4	5, 52	-233	Eocp4	18	Rp4	11,52	-237	Eocp4
23	Rp5	4, 95	-232	Eocp5	23	Rp5	9,76	-232	Eocp5
28	Rp6	4, 68	-232	Eocp6	28	Rp6	8,53	-236	Eocp6

state),

- for both orientations the final value of  $E_{ocp}$  tends to decrease when the deformation rate increases.

### Polarization resistance

- Rp is in all cases lower than 25  $\Omega$  cm<sup>2</sup>, confirming that all samples are in an active state,
- Rp decreases with time in all cases,
- for all times it also decreases when the deformation rate increases, for the two orientations,
- there is no real differences at all times between the two orientations for the not-deformed state and for the -9.19% rate, while Rp is at all times higher for the perpendicular orientation than the one for the

parallel orientation (almost twice).

### Results of cyclic polarization

The obtained curves of cyclic polarization are presented in Figure 2 (not-deformed sample), Figure 3 (plastic deformation rate: -9.19%) and Figure 4 (plastic deformation rate: -20.25%) by uncoupling their potential-increasing part and their potential-decreasing part, in order to better compare the results between the two orientations for a same permanent relative deformation rate.

In all cases it is obvious that, whatever the deformation state, the samples were in an active state and succeed to passive when the potential applied by the

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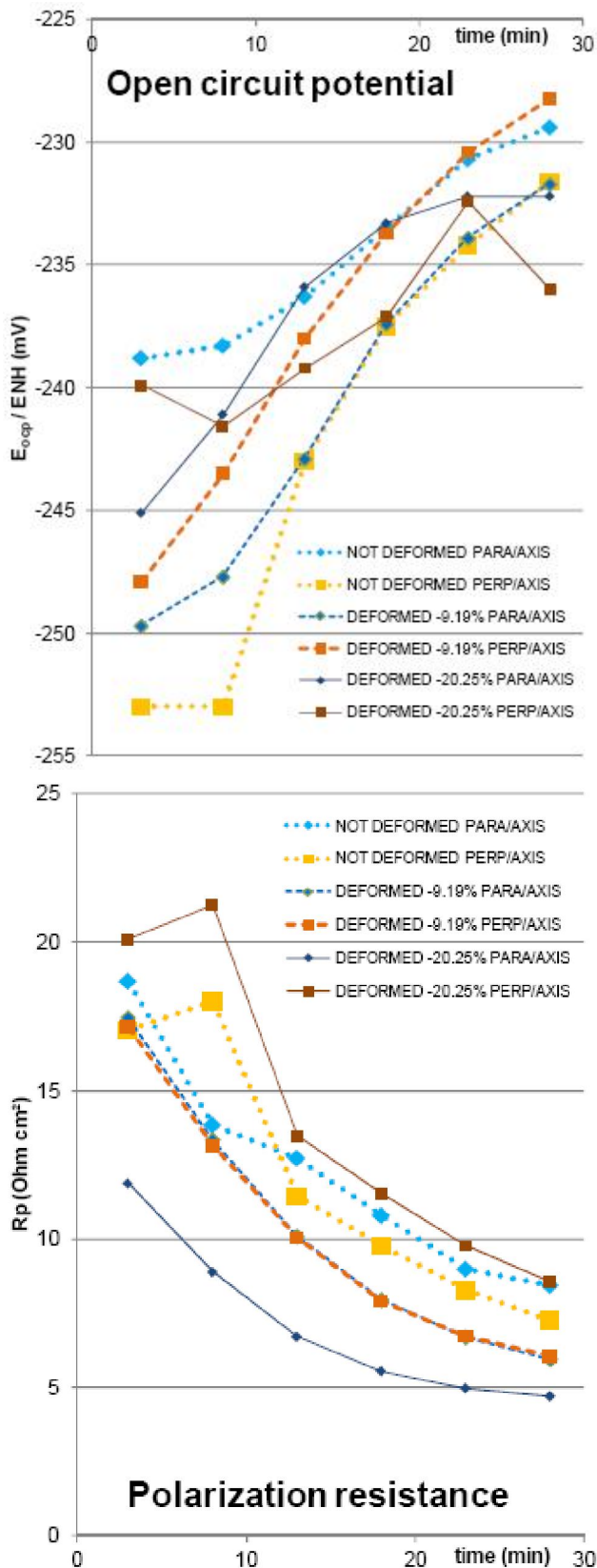


Figure 1 : The open circuit potential (left) and the polarization resistance (right) plotted versus time for all the deformation states and for the two orientations

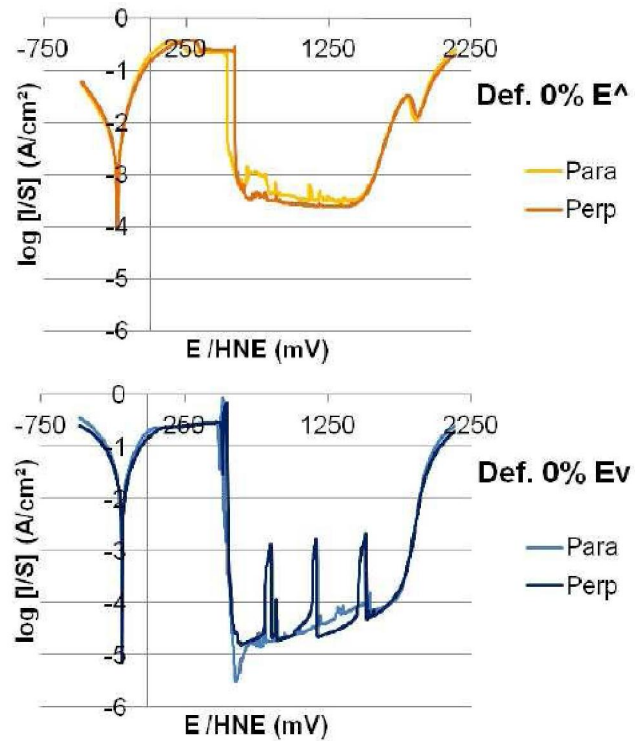


Figure 2 : The E-increasing part (top) and the E-decreasing part (bottom) of the cyclic polarization curves obtained for the parallel orientation and for the perpendicular orientation (superposed) in the case of the not deformed samples

potentiostat has become high enough, with as result a significant decrease in anodic current. When this applied potential decreased thereafter, all samples lost their passive state, with as results the appearance of very high anodic currents and, after, a new value of corrosion potential being close to the initial one.

For the not-deformed sample there is no evident dependence on the orientation, neither for the E-increasing part of the curve, nor for the E-decreasing part, although a tendency to a loss of the passive state can be suspected for the perpendicular orientation. For the -9.19% deformed state, the most visible difference between the two orientations is the anodic current in the passive state which is higher for the parallel orientation than for the perpendicular one in both the E-increasing part and the E-decreasing part. This latter difference is also the single noticeable one concerning the curves for the -20.25% deformed state but in the opposite direction by comparison with the -9.19% deformed state.

Some small differences between the potentials at which the samples become passive and at which they lose their passive state can be noted but there are not



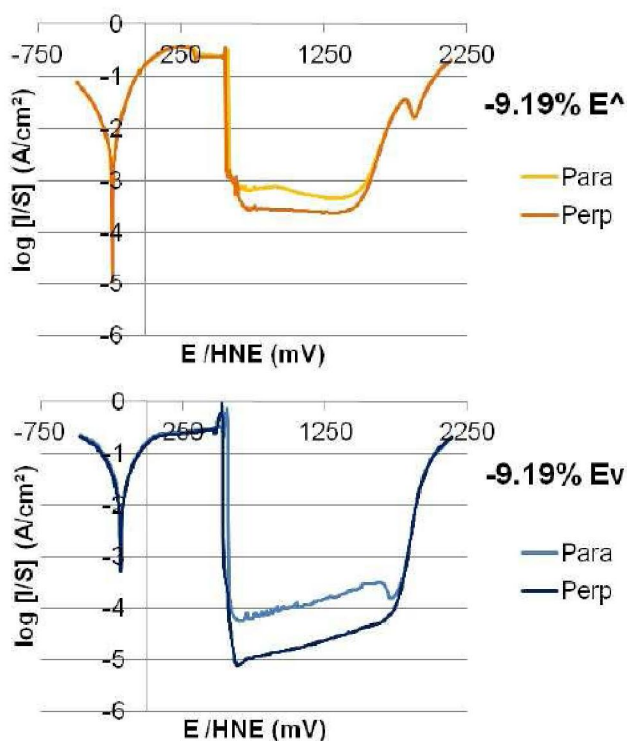


Figure 3 : The E-increasing part (top) and the E-decreasing part (bottom) of the cyclic polarization curves obtained for the parallel orientation and for the perpendicular orientation (superposed) in the case of the -9.19% deformed samples

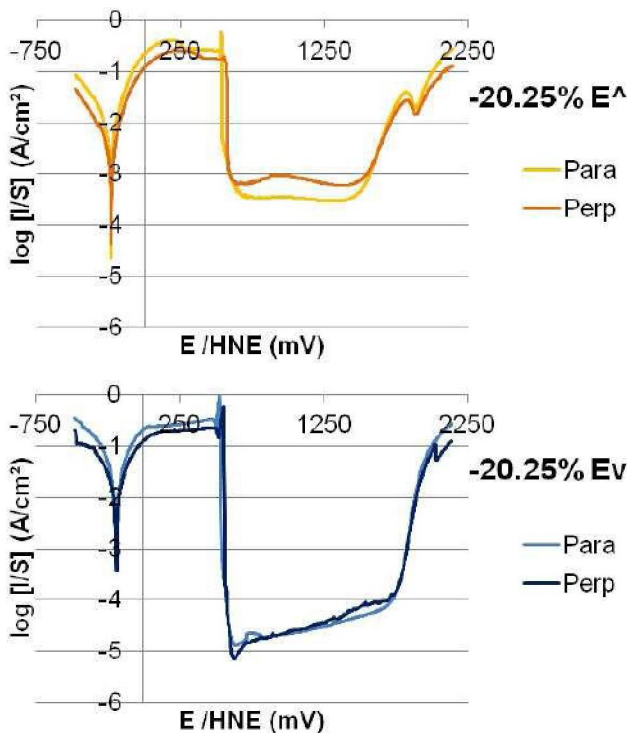


Figure 4 : The E-increasing part (top) and the E-decreasing part (bottom) of the cyclic polarization curves obtained for the parallel orientation and for the perpendicular orientation (superposed) in the case of the -20.25% deformed samples

significant, notably by comparing the results between the two orientations of the not-deformed sample.

All the polarization curves were deeper analyzed by noting the values of different characteristic points linked to the active state and the passive state. These values are displayed in TABLE 4, TABLE 5 and TABLE 6.

The following comments can be done about this second set of experimental results:

### Corrosion current densities and corrosion potential

In all cases being of several mA per  $\text{cm}^2$ ,  $I_{\text{corr}}$  determined by Tafel treatment of the files (E-increasing part) is obviously almost constant when both the deformation rate and the orientation vary; one can mention the (very) small increase with the deformation rate for the parallel orientation but which is absolutely not significant; the corrosion potential  $E_{\text{corr}}$ , issued from the same Tafel calculations, shows only a (very again) small decrease when the deformation rate increases, only for the parallel orientation too; it remains constant for the other orientation.

### Conditions of passivation

Looking to the values of the critical current density of passivation it seems that passivating seems more difficult when the deformation rate increases but without well established effect of the orientation; there is however an exception: the  $I_{\text{cp}}$  value obtained for strongest deformation and the perpendicular orientation, which is particularly low; the previous observations are not in good agreement with the values of the passivation potential since  $E_{\text{pass}}$  varies significantly with the deformation rate for the parallel orientation but it seems monotonously decreasing for the other orientation.

### Protection efficiency and stability of the passive state

Nothing general can be said about a dependence of the anodic density current in the passive state since, as qualitatively seen above on the superposed curves, the existing variations of  $I_{\text{pass}}$  are not clearly linked with the deformation rate and the orientation; the same remarks can be formulated for the potential of passivation loss  $E_{\text{Flade}}$ . The tranpassivation densities  $I_{\text{transpass}}$  of current, which characterize the resistance of the pas-

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TABLE 4 : Quantitative exploitation of the cyclic polarization curves obtained for the not deformed steel

	NOT DEFORMED PARA/AXIS			NOT DEFORMED PERP/AXIS			
	I(A/cm <sup>2</sup> )	E(mV)/HNE		I(A/cm <sup>2</sup> )	E(mV) /HNE		
Icorr (TafPC)	3,95E-03	-231	Ecorr ^	Icorr (TafPC)	4,31E-03	-232	Ecorr ^
Icp	2,34E-01	525	Epass	Icp	2,97E-01	590	Epass
Ipass	3,17E-04	549	E Flade	Ipass	2,55E-04	554	E Flade
Itranspass	3,04E-02	-187	Ecorr v	Icorr (TafPC)	3,29E-02	-182	Ecorr v

TABLE 5 : Quantitative exploitation of the cyclic polarization curves obtained for the -9.19% deformed steel

	DEFORMED -9.19% PARA/AXIS			DEFORMED -9.19% PERP/AXIS			
	I(A/cm <sup>2</sup> )	E(mV)/HNE		I(A/cm <sup>2</sup> )	E(mV) /HNE		
Icorr (TafPC)	5,68E-03	-233	Ecorr ^	Icorr (TafPC)	5,43E-03	-229	Ecorr ^
Icp	3,18E-01	581	Epass	Icp	3,51E-01	559	Epass
Ipass	5,50E-04	571	E Flade	Ipass	2,53E-04	533	E Flade
Itranspass	3,46E-02	-183	Ecorr v	Itranspass	3,60E-02	-187	Ecorr v

TABLE 6 : Quantitative exploitation of the cyclic polarization curves obtained for the -20.25% deformed steel

	DEFORMED -20.25% PARA/AXIS			DEFORMED -20.25% PERP/AXIS			
	I(A/cm <sup>2</sup> )	E(mV)/HNE		I(A/cm <sup>2</sup> )	E(mV) /HNE		
Icorr (TafPC)	5,74E-03	-234	Ecorr ^	Icorr (TafPC)	4,22E-03	-231	Ecorr ^
Icp	5,76E-01	534	Epass	Icp	1,92E-01	555	Epass
Ipass	3,21E-04	538	E Flade	Ipass	6,07E-04	561	E Flade
Itranspass	3,96E-02	-192	Ecorr v	Itranspass	2,75E-02	-189	Ecorr v

sive scale to re-oxidation, varies but without any evident relation with the deformation rate and the orientation, but it is true that a part of this current can be linked to the start of the solvent's oxidation which forbids good accuracy.

### Corrosion potential after loss of the passive state

Each value of  $E_{corr v}$  is logically lower than the corresponding  $E_{corr}$  value for the same deformation rate and orientation. But there are no clear evolution versus these two parameters.

### General commentaries

Thus the corrosion parameters deduced from the cyclic polarization did not show well established relations with the plastic deformation rate and the orientation of the tested surface with respect to the deformation axis, despite there were variations which were seen, some of which being significant. The plastic deformation obviously does not systematically influence the passivation conditions and the resulting protection, at least in this studied range of permanent deformation and in this sulphuric solution. Further investigations can be imagined to complete the study of such possible de-

pendence, achieving much more intense plastic deformation (beyond -50% for example) and/or testing in other more or less aggressive solutions as neutral but chlorides-rich ones.

In contrast more interesting observations were done for the active state, notably concerning the polarization resistance. As for pure iron compressed or not and tested in the same solution<sup>[9]</sup> it was here seen that the polarization resistance increases with the immersion time, while it decreased in the case of another ferrito-pearlitic steel deformed in traction in a sulphuric acid solution too<sup>[10]</sup>. In the two previously cited works<sup>[9,10]</sup> it was already confirmed what was noticed in most of earlier studies about the influence of the deformation rate on the polarization resistance. Here this is confirmed again, and furthermore the decrease in  $R_p$  when the deformation rate increases is in good agreement what was found for compressed iron and for the ferrito-pearlitic steel after tensile plastic deformation. In addition, the  $R_p$  order between parallel and perpendicular, which is inverted for cast ferrito-pearlitic steels deformed in traction ( $R_{p//} > R_{p\perp}$ )<sup>[10]</sup> by comparison with after deformation in compression ( $R_{p//} < R_{p\perp}$  for -20.25%) (this

study) let think that there is maybe a monotonous evolution of this order with the algebraic value (negative in compression, positive in traction) of the plastic deformation. This may be interesting to verify with complementary tests.

### CONCLUSIONS

The surface reactivity changes with a microstructural damage resulting from plastic deformation, can be then significant, but not for all the corrosion behaviour characteristics. In the present case the effect can be detected for the active state and revealed simply by linear polarization for deducing polarization resistances then corrosion currents. By combining with the most important results of the first part, it appeared, for this cast ferrite-pearlitic steel elaborated in special conditions, that hardening increases again and the corrosion resistance decreases again when the plastic deformation rate in compression increases, but in the two cases differently if the tested surface is, after machining, parallel or perpendicular to the compression axis. These results come completing many other ones obtained in various other conditions.

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