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Influences of the rate and of the direction of plastic deformation on the corrosion behaviour of compressed iron-based alloys

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ABSTRACT

After having been subjected to intense stresses metallic alloys can be partially or totally affected by a permanent geometric change. The resulting much higher dislocations densities may lead to severe microstructure disorder inducing possibly changes in the surface reactivity of the piece, after or not machining. It is thus interesting to specify the effects of plastic deformation on the local corrosion resistance of metallic alloys, by taking into consideration the local orientation of the surface with respect to the deformation tensor. In this work two metallic alloys, pure polycrystalline iron and a ternary Fe-10Ni-18Cr alloy, both (re-)melted and (re-)solidified in the same conditions were cut, uni-axially deformed and tested in corrosion in a sulphuric solution, by applying the Stern-Geary, Tafel and cyclic polarization methods, to highlight the links of dependence of parameters as open circuit potential, polarization resistance, corrosion current densities and passivation characteristics, on the amplitude and direction of mechanical plastic deformation. Some tendencies obviously exists, notably concerning the corrosion resistance in the active state for iron or some of the passivation characteristics, but the variation observed in many cases remain not well established. The microstructure texture is suspected to superpose its influence on the deformation one.

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KEYWORDS

Pure iron;
Ternary stainless austenitic steel;
Plastic deformation;
Orientation;
Corrosion;
Sulphuric solution.

INTRODUCTION

The shaping by plastic deformation (forging, stamping ...) necessarily leads to strongly increased dislocation densities in metallic materials. This may induce for these alloys noticeable changes in their mechanical properties as well as for their behaviour in corrosion. This is true at the scale of the whole piece, but galvanic corro-

sion phenomena may also occur between different zones of the external surface of the piece, for instance between a not deformed or a slightly deformed part and a considerably deformed other part. A simple case is the one of a revolution piece which presents successive different sections leading to different plastic deformation rates after uniaxial sollicitation in traction or in compression along the piece axis. A lot of works have been

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realized for several decades about the dependence of the corrosion behaviour and the plastic strain. Unfortunately, although it was often concluded that plastic deformation tends to accelerate corrosion^[1], the reported observations are rather variable.

Stainless steels having been subjected to cold-working were among the first metallic materials which were concerned by such studies of the dependence of corrosion on plastic strain, this for solutions as sulphuric acid^[2], other acids with or without corrosion inhibitors^[3] or solutions containing chlorides^[4]. More recently works have been also carried out about cold-rolled Ti-based alloys in contact with solutions of sulphuric acid^[5] or with other oxidant solutions such as the Ringer's one^[6], alloys based on Al^[7] or Mg^[8] ...

In the present work steels are considered again, in a simple sulphuric acid solution (H₂SO₄ 2N) too, but in particular conditions possibly leading to a better control of the samples (simple uni-axial plastic deformations by compression, samples issued from a same ingot of pure iron and from a same ingot of a ternary Fe-18Cr-10Ni alloy (the chemical compositions are thus simple and constant)), and taking into account the orientation of the characterized surfaces with respect to the deformation axis.

EXPERIMENTAL

Elaboration of the alloys

The two metallic materials devoted to this study, pure iron (thereafter simply named "Fe") on the one hand and the Fe(bal.)-10Ni-18Cr (in weight percents, simply named "FeNiCr") were prepared as cylindrical primary samples as follows:

- selection of small parts of pure Fe, Ni and Cr and weighing to obtain about 50g with the desired weight composition in the case of the FeNiCr alloy,
- fusion using a High Frequency Induction Furnace (CELES), with as operating parameters a frequency of 110kHz and a voltage of 4000V,
- aspiration of the liquid in a silica tube in which the alloy solidified.

This allowed obtaining cylindrical ingots the diameter and length of which were of about 10mm and several centimeters respectively. These metallic cylinders

were then cut using an automatic precision cutter Isomet 5000 (Buelher), which allowed obtaining cylindrical samples of about one centimeter long. A first one per alloy was studied in its initial not-deformed condition while the three others will be thereafter compressed at different rates.

Compression runs

The compressed samples were obtained by subjecting them to an increasing force applied by a MTS RF/150 machine equipped with a 150kN-capacity force-measuring cell, through two compression platens. The samples were subjected to compressive deformation in the direction of their axis, with a deformation rate of 0.25 mm/min. The compression run was manually stopped as soon as the desired deformations were obtained. The relative plastic deformations really obtained were calculated from the measurements of the initial and final heights of the samples, using a numerical calliper. They are presented in TABLE 1. For the pure iron samples ("Fe") as well as for the ones made of the ternary steel ("FeNiCr") there is a not deformed or "As-Cast" (AC) sample, a "Small

TABLE 1 : Values of the obtained plastic deformation

Alloy	AC	SD	MD	HD
"Fe"	0%	-9.75%	-22.2%	-34.0%
"FeNiCr"	0%	-3.08%	-10.7%	-17.6%

Deformation" one (SD), a "Middle Deformation" one (MD) and a "High Deformation" one (HD), each of them being respectively about twice for the Fe samples than for the FeNiCr samples, due to the higher strength of the inoxidable austenitic steel by comparison to pure iron.

Preparing the electrodes

The deformed samples were cut in order to generate two electrode surfaces with two orientation with respect to the deformation axis, one perpendicular and one parallel (Figure 1). Each sample was connected to a plastic-covered copper electrical wire, then embedded in a cold resin mixture (ESCIL: Araldite CY230 and hardener HY 956). The electrode surfaces were thereafter polished with SiC papers up to 1200-grit (with each time a new 1200 paper per sample) before each series of electrochemical experiments.

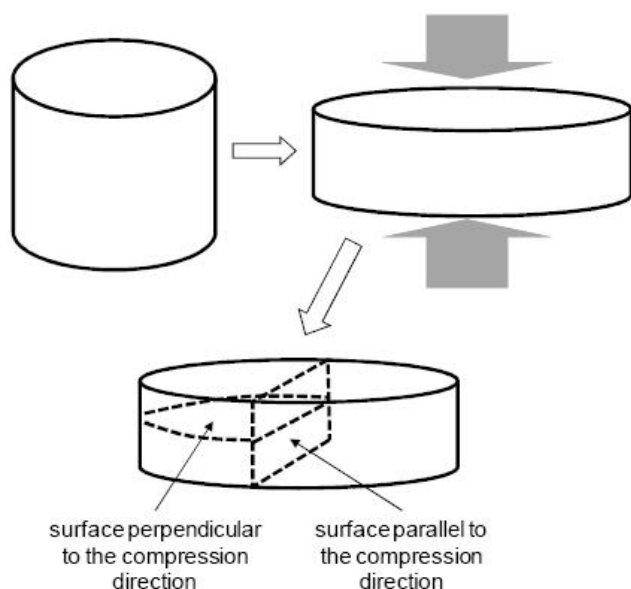


Figure 1 : Cutting procedure for obtaining a surface parallel to the compression axis and a surface perpendicular to the compression axis

Electrochemical experiments

The electrochemical runs were performed to characterize the corrosion behaviour in a sulphuric acid aqueous solution, H_2SO_4 2N. A Versastat potentiostat from EG&G/Princeton Applied Research and driven by the M352 software was used, with a three electrodes cell composed of the working electrode (the studied sample), a Saturated Calomel Electrode (SCE) for the reference in potential and a graphite rod for the counter electrode. The electrochemical tests were:

- linear polarization runs from $E_{ocp} - 20mV$ to $E_{ocp} + 20mV$ at $10mV/min$,
- Tafel runs from $E_{ocp} - 250mV$ to $E_{ocp} + 250mV$ at $1mV/s$ and at $2mV/s$ (pure Fe only),
- cyclic polarization runs between $E_{ocp} - 250mV$ and $1.9V$ at $+5$ and $-5 mV/s$ (FeNiCr steel only).

RESULTS AND DISCUSSION

First linear polarizations and tafel experiments on as-cast or SD and MD deformed pure iron

After three linear polarizations for measuring three successive polarization resistances during the time necessary to obtain the cell equilibrium, Tafel experiments were performed to get the values of both corrosion potential and corrosion currents.

After these experiments the electrode surfaces were

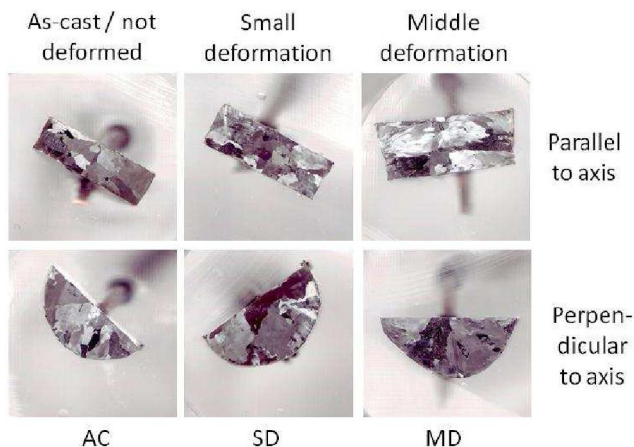


Figure 2 : Surface states of the electrodes after the $\{3 \times R_p\} +$ tafel experiments

examined since the electro-chemical runs allowed observing the microstructures of the alloys. These ones are shown in Figure 2 which presents the electrodes surfaces scanned using a simple office scanner, revealing the progressive grain deformation especially for the parallel-type electrodes.

The values obtained for the polarization resistance, as well as the values of the open circuit potential defined as being the potential at which the current is equal to 0 during the successive linear polarizations, are presented in TABLE 2. The R_p values as well as the E_{ocp} values do not obviously vary following clear laws.

The Tafel determination on the following $I/S=f(E)$ files obtained over the $[E_{ocp} - 250mV, E_{ocp} + 250mV]$ range led to the results obtained just after the three linear polarizations for a scan rate of $1mV/s$ and just after with a second Tafel run achieved with a scan rate with twice this value ($2mV/s$). Here too (TABLE 3) no systematic evolution of E_{corr} , and also of I_{corr} , was noted versus the amount of plastic deformation as well as versus the surface orientation. This may be probably to attribute to a time before Tafel experiment not long enough to allow the whole cell reaching the equilibrium. This is the reason why that new experiments, with a period of 25 minutes before performing cycling polarization, will be performed thereafter.

Open circuit potential and polarization resistances on longer time of pure Fe samples

The open circuit potential evolution with time as well as the polarization resistance one are both graphically described in Figure 3 (E_{ocp} defined again as being

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TABLE 2 : Evolution of the polarization resistance and of the open circuit potential, before performing the Tafel experiments

Fe alloy	def. rate	Surface parallel to axis		Surface perpendicular to axis	
		Rp1, Rp2 &Rp3 (Ohm. cm ²)	E _{ocp1} , E _{ocp2} & E _{ocp3} (mV/ENH)	Rp1, Rp2 &Rp3 (Ohm. cm ²)	E _{ocp1} , E _{ocp2} & E _{ocp3} (mV/ENH)
Fe alloy	AC	49.6-66.7-52.4	-311, -315, -314	61.8-80.1-52.2	-303, -302, -297
	SD	68.5-126-117	-287, -297, -298	71.0-171-171	-278, -293, -295
	MD	57.7-72.1-42.6	-300, -299, -299	57.8-94.0-76.0	-297, -302, -301

TABLE 3 : Results of the tafel experiments

Fe alloy	def. rate	Surface parallel to axis				Surface perpendicular to axis			
		E _{corr} / ENH (mV)	I _{corr} (μA/cm ²)	β _a (mV/dec)	β _c (mV/dec)	E _{corr} / ENH (mV)	I _{corr} (μA/cm ²)	β _a (mV/dec)	β _c (mV/dec)
Scan rate: 1mV/s	AC	-318	427	61.3	143	-298	570	63.9	211
	SD	-300	209	59.0	283	-298	568	61.1	440
	MD	-298	721	58.7	168	-298	557	62.9	206
Scan rate: 2mV/s	AC	-276	1948	81.6	186	-263	1822	79.2	133
	SD	-253	733	66.2	128	-252	658	64.1	236
	MD	-260	1447	78.0	140	-263	1821	79	133

the values of potential at which I/S = 0 during the successive linear polarizations giving Rp). For the “parallel” surfaces, one can see that E_{ocp} is initially higher than after, a decrease which nearly stops thereafter. For this orientation one can note that the potential is always lower

for the two first deformation rates than for the not deformed state while the highest plastic deformation led to much higher values, even higher than for the as-cast state.

For the “perpendicular” surface, the same type of

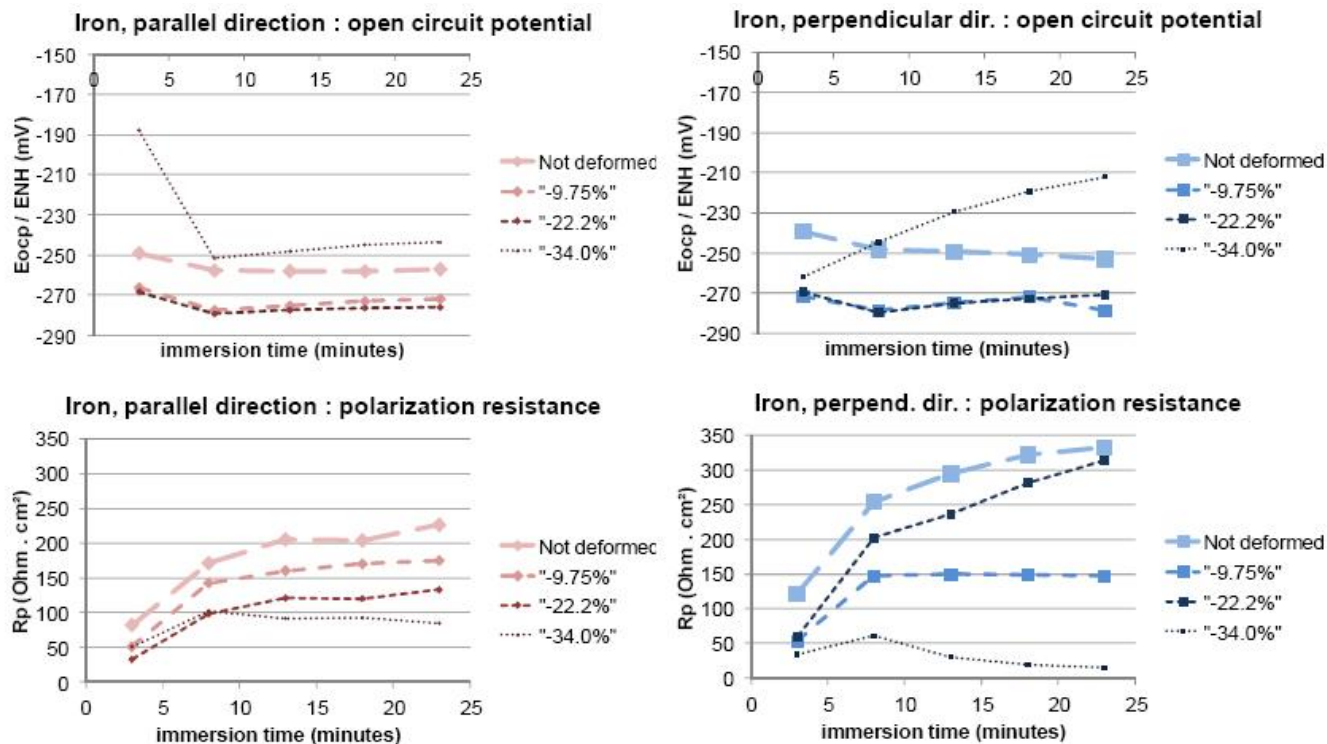


Figure 3 : Evolution of the open circuit potential and of the polarization resistance with time for the four deformation states and the two orientations

E_{ocp} evolution versus time and versus the plastic deformation rate is found again.

Concerning the polarization resistances, for the parallel orientation their evolution is very clear: first the R_p values increase with time for the four deformation states (maybe except for the highest deformation), and second, when the plastic deformation rate increases the polarization resistance decreases.

For the perpendicular orientation the R_p evolution with time is globally the same as above. The same comment concerning the dependence of the polarization resistance on the plastic deformation rate can be done. Between the two orientations, there are (often small) differences with scattered orders. This depends on the deformation rate. One can underline that there is, about the not-deformation state, an influence of the orientation which cannot be attributed to the plastic deformation: in this case it can be suggested that there is a possible effect of the crystalline growth direction during solidification on the corrosion behaviour.

Open circuit potential and polarization resistances on long time of steel samples

The E_{ocp} evolutions with time, with the plastic deformation state and with the surface orientation with respect to the sample axis, for the FeNiCr alloys, are displayed in TABLE 4 and graphically represented in

TABLE 4 : Evolution of the open circuit potential versus time and versus the plastic deformation rate, for the two surface orientations, in the case of the FeNiCr alloy

FENICR Temps (min)	PARA/ AC E/ENH (mV)	PARA/ SD E/ENH (mV)	PARA/ MD E/ENH (mV)	PARA/ HD E/ENH (mV)
3	-109	694	99	-167
8	-218	637	-88	-197
13	-216	570	-220	-198
18	-213	55	-218	-200
23	-211	-111	-216	-200
FENICR Temps (min)	PERA/ AC E/ENH (mV)	PERP/ SD E/ENH (mV)	PERD/ MD E/ENH (mV)	PERD/ HD E/ENH (mV)
3	690	-214	-166	-184
8	700	-208	-201	-210
13	700	-203	-199	-210
18	699	-198	-198	-213
23	697	-192	-198	-212

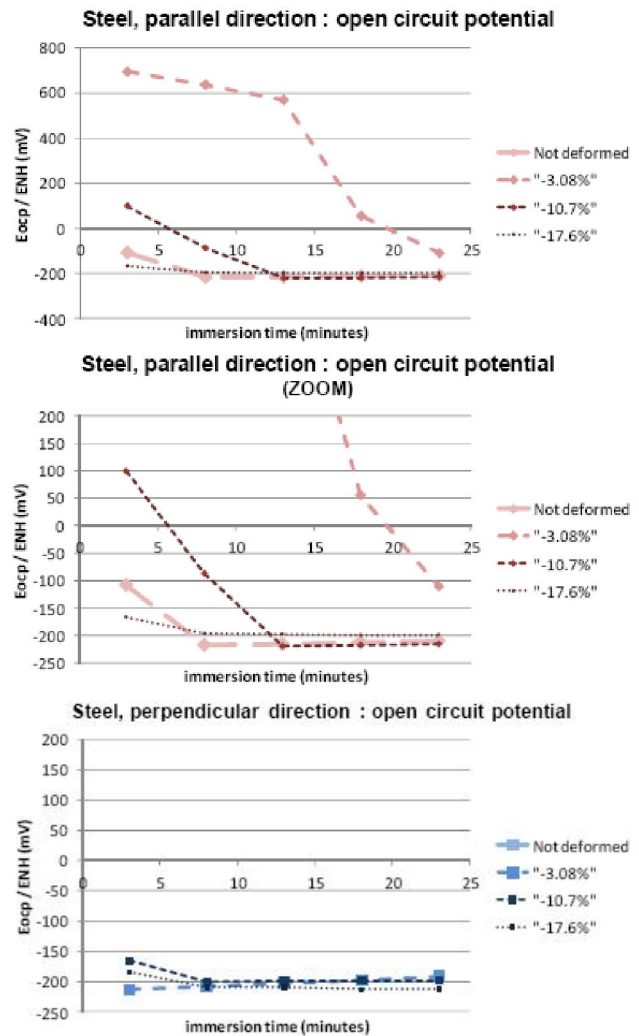


Figure 4 : Evolution of the open circuit potential with time for the four deformation states and the two orientations in the case of the FeNiCr steel

Figure 4. For the parallel orientation as well as for the perpendicular orientation, there is no clear dependence of the E_{ocp} on the deformation rate since the results are too scattered, even if the evolution with time is a rapid then slower decrease in most cases. Some very high values were observed (existing at immersion and either kept or lost before the experiment end), which let think to a more or less passive state in some cases (SD¶llel: initial high E_{ocp} but which falls after, AC/not de-formed&perpendicular: always high E_{ocp}). It seems that the tendency to passive may exist for the not-deformed or slightly deformed (-3.08%) for this Cr-rich alloy despite the acidity of the solution while a too deformed state does not allow such tendency.

The values versus time of the polarization resistance for all the FeNiCr samples are listed in TABLE 5 and

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TABLE 5 : Evolution of the polarization resistance versus time and versus the plastic deformation rate, for the two surface orientations, in the case of the FeNiCr alloy

FENICR Temps(min)	PARA/AC Rp Ohm.cm ²	PARA/SD Rp Ohm.cm ²	PARA/MD Rp Ohm.cm ²	PARA/HD Rp Ohm.cm ²
3	143	699	106	9
8	43	6683	396	45
13	84	3627	78	53
18	103	88	89	55
23	122	1086	96	61

FENICR Temps(min)	PERP/AC Rp Ohm.cm ²	PERP/SD Rp Ohm.cm ²	PERP/MD Rp Ohm.cm ²	PERP/HD Rp Ohm.cm ²
3	203	12	8	4
8	194	59	90	43
13	189	110	118	47
18	180	108	136	48
23	183	110	144	48

plotted in Figure 5. If they are rather variable for the parallel surface orientation they present a clearer dependence on immersion duration (increase with time) as well as on the plastic deformation rate (decrease with the deformation amount). There is logically a general correspondence of high values of Rp and of the high values of E_{ocp} .

Except for a small number of cases for which a passivation of the surface may be suspected, it appeared that the values of polarization resistance were generally not much higher than the ones measured for the simple iron samples, despite the presence of both nickel and chromium. This was also the case above for the open circuit potential in many cases.

Cyclic polarization runs (FeNiCr steel only)

The aim of the cyclic polarization curves over the considered potentials range is to measure again the corrosion potential, study the possibility of passivation (existence of a low corrosion intensity plateau), value the difficulty of reaching this passive state (passivation potential, critical current for passivation), knowing the corrosion rate in the passive state and to see if the passive state is stable and can be kept when the applied potential decreases down to the open circuit potential or lower. It appeared that, in all cases the passivation exists and was obtained rather easily. It was not lost in the potential-decreasing part of the curve and a new

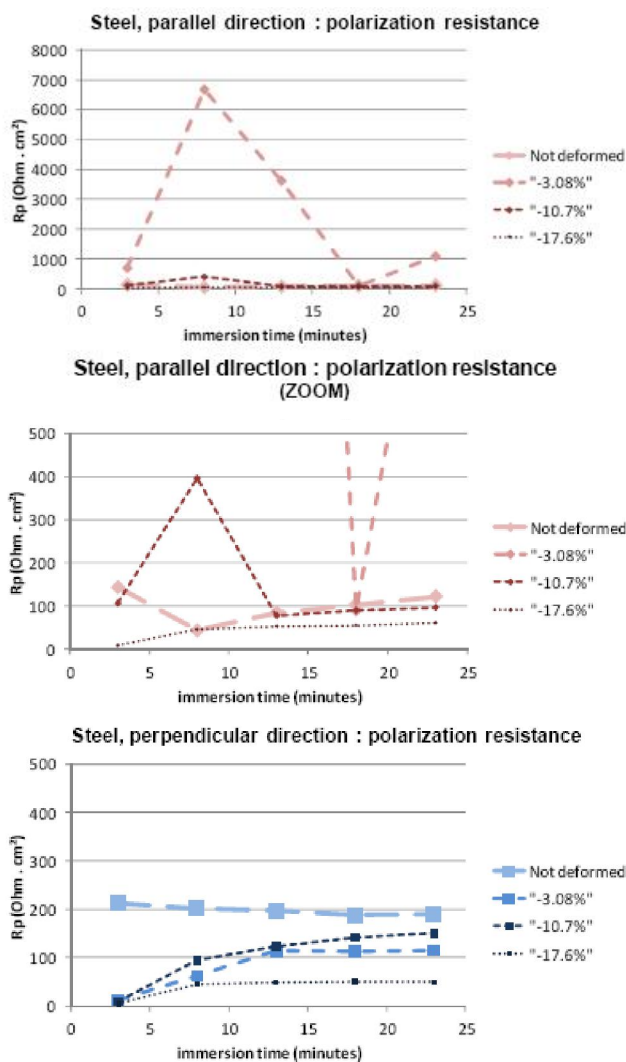


Figure 5 : Evolution of the polarization resistance with time for the four deformation states and the two orientations in the case of the FeNiCr steel

much higher corrosion potential (Cr^{VI}/Cr^{III}) was obtained.

The determined characteristics of the cyclic polarization curves obtained for the FeNiCr electrodes are presented in TABLE 6.

It appears that:

- the corrosion potentials (E_{corr}) on the E-increasing parts of the curves do not show clear evolution with the deformation rate and there is no clear dependence on the surface orientation
- the critical passivation current ($I_{crit\ pass}$) is quite variable and there is no clear dependence on the orientation
- the passivation potential (E_{pass}), despite it varies, does not show any established dependence neither

TABLE 6 : Evolution of different characteristics of the cyclic polarization curves versus the deformation rate and the surface orientation for the FeNiCr samples

		Surface parallel to axis		Surface perpendicular to axis	
		$E_{\text{corr}} \uparrow$ (mV/ENH)	$E'_{\text{corr}} \downarrow$ (mV/ENH)	$E_{\text{corr}} \uparrow$ (mV/ENH)	$E'_{\text{corr}} \downarrow$ (mV/ENH)
FeNiCr alloy	AC	-193	+942	/	/
	SD	-147	+906	-188	+939
	MD	-208	+901	-191	+762
	HD	-191	+798	-197	+804
		Surface parallel to axis		Surface perpendicular to axis	
		$E_{\text{pass}} \uparrow$ (mV/ENH)	$E_{\text{depass}} \downarrow$ (mV/ENH)	$E_{\text{pass}} \uparrow$ (mV/ENH)	$E_{\text{depass}} \downarrow$ (mV/ENH)
FeNiCr alloy	AC	+7.5	N/A	/	/
	SD	+43.5	N/A	-31.5	N/A
	MD	+0.5	N/A	+37.5	N/A
	HD	+39.5	N/A	+13.5	N/A
		Surface parallel to axis		Surface perpendicular to axis	
		$I_{\text{crit pass}} \uparrow$ (mA/cm ²)	$I_{\text{pass min}} \uparrow$ (μ A/cm ²)	$I_{\text{crit pass}} \uparrow$ (mA/cm ²)	$I_{\text{pass min}} \uparrow$ (μ A/cm ²)
FeNiCr alloy	AC	1135	31.8	/	/
	SD	154	14.8	1856	43.9
	MD	795	27.7	943	39.6
	HD	2218	42.1	1528	35.1

- on the deformation rate, nor on the orientation
- the corrosion current in the passive state ($I_{\text{pass min}} \uparrow$) tends to increase with the deformation rate for the parallel orientation and to decrease for the perpendicular orientation; in contrast there is also no systematic difference between the two orientations
- the new potential ($E'_{\text{corr}} \downarrow$) tends to decrease for the parallel orientation when the sample is more deformed but the variation is not monotone for the other surface orientation; no real order exists between the two orientations

General commentaries

Despite that the elaboration mode and the sample preparation were conceived and carefully realized, it appeared that there are globally no clear dependence of the different electrochemical parameters characterizing the corrosion behaviour, for the active state, for the change-over of the active state to the passive state, and finally for the passive state. This can be maybe due first to a dependence on the plastic deformation rate and on the orientation with respect to the deformation axis which possibly lead to variations of the same order

of magnitude as the lack of reproducibility, and second, especially concerning the possible effect of orientation, that the elaboration procedure, characterized by a radial growth towards the future sample axis during solidification may induce itself effects on the orientation-dependence of plastic deformation and then on the corrosion behaviour, or even directly on the orientation dependence of this corrosion behaviour, as suggested by the differences sometimes noted for the two orientations for the not deformed samples. Nevertheless a small number of potentially interesting observations were done, concerning for example the effect of both the plastic deformation rate and the orientation on the polarization resistance and open circuit potential during the first 25 minutes following immersion, or the tendency to passive in case of no or low deformation by comparison to higher deformed states.

CONCLUSIONS

The plastic deformation, as well as the orientation with respect to the deformation axis, do have an effect on the corrosion behaviour of the two studied iron-

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based cast alloys. The different parameters obviously were changed for deformation rate change or for orientation change but the possible superposition with probable dependence of the microstructural texture issued from the solidification process have led to difficulties for the highlighting and interpretation of the resulting effects of the two parameters, hardening \times geometry studied, this showing that it could be better to prepare samples in equi-axed zones in ingots.

This work, which continues previous studies {plastic deformation \leftrightarrow corrosion} realized in the same electrolytic media for pure metals deformed in compression^[9] or carbon steels deformed in traction^[10], will be followed by final investigations^[11,12] concerning a ferrito-pearlitic steel.

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