Effect of a plastic deformation on the electrochemical behaviors and the corrosion rates of pure iron, nickel and copper in a molar solution of sulfuric acid

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ABSTRACT

Stresses applied to ductile alloys or pure metals may induce severe plastic deformation with multiplication of defects and dislocations in their crystal networks. Such a disorder in the microstructure can influence the surface reactivity of the alloys, with consequences for their behaviour in corrosion. Here, cast pure iron, pure nickel and pure copper were elaborated by high induction melting, and some of the obtained samples were plastically deformed by compression. As-cast samples and plastically deformed samples were prepared as electrodes and tested in H_2SO_4 solution, added or not with a corrosion inhibitor, according to the Stern-Geary and Tafel methods. Polarization resistances, corrosion current densities and corrosion potentials were measured. The electrochemical characterization of the corrosion behaviour was completed by performing cyclic polarization experiments. Globally the plastic deformation improved the corrosion behaviour of iron but inversely decreased the corrosion resistance of nickel and of copper.

INTRODUCTION

When mechanically stressed metallic materials are deformed elastically and even plastically if the applied stresses are of a sufficient level. In the second case a part of the deformation is permanent, due to the multiplication and the not-reversible movement of the one-dimension crystalline defects called dislocations. After such deformation, due to tensile, compression, flexion or torsion deformations, the alloys are modified not only at the macroscopic level but also in the microscopic scale. One the one hand their strained microstructure contains a much higher density of defects and notably dislocations, and on the other hand residual stresses may still exist, even near the external surface. This may lead to a modified reactivity of the alloy, and for example to a new behaviour in corrosion when immersed in aqueous solutions containing oxidants. Typically, it is generally considered that an alloy is more reactive in a deformed condition than before, then less resistant against corrosion[1].

Numerous studies about the effects of a mechanical deformation on the corrosion behaviour of alloys were driven since at least forty years: initially about stainless steels previously cold-worked or not in solutions such as sulphuric acid[2], chlorides-containing solutions[3] or hydrochloric acids added with inhibitor[4] after cold-working, and more recently about plastically deformed/

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TABLE 1: Initial and final thickness (in mm) of the samples deformed in compression

Metal	Fe	Ni	Cu
Initial thickness (±0.02mm)	3.06	4.79	3.58
Final thickness(±0.02mm)	2.52	4.15	2.53
Resulting permanent deformation ε (%)	-17.6%	-13.4%	-29.3%

surface perpendicular to the compression direction (called « type 1»)   **surface parallel to the compression direction (called « type 2 »)**
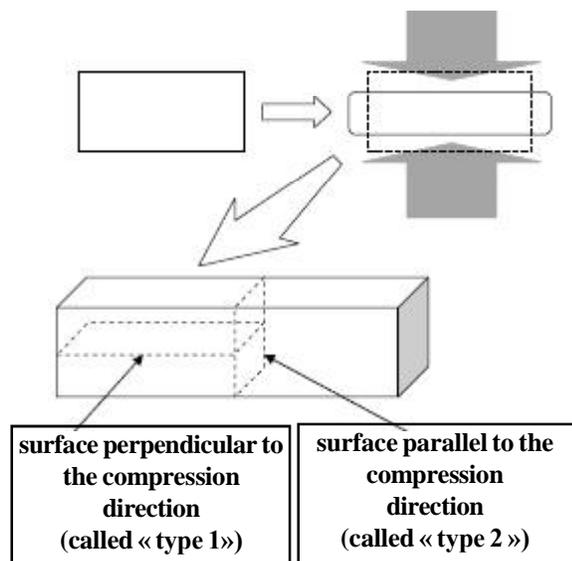
Figure 1: Scheme describing the compression deformation and the cutting performed in order to obtain the electrodes which allow determining the corrosion behaviour of the two types of surface

cold-rolled titanium-based alloys in Ringer's solution[5] or sulphuric acid[6] again, magnesium-based[7] or aluminium-based[8] alloys.

Following the type of alloy, the chemical composition and the manufacturing mode of which is often too complex to deduce well established general rules in reality, several effects of the plastic deformation on the corrosion behaviour can be found, sometimes in the opposite directions. The aim of this work is to study the influence of an uniaxial plastic deformation on the corrosion behaviour in a simple sulphuric acid solution (H_2SO_4 2N) in the case of three pure metals (Fe, Ni and Cu), elaborated following a known procedure (casting) and subjected or not to a simple compression inducing a permanent deformation.

EXPERIMENTAL

Preparation of the electrodes

Three ingots were synthesized by melting of pure elements (Fe, Ni or Cu, purity higher than 99.9wt.%,

Alfa Aesar) in a High Frequency (300kHz) induction furnace (CELES), under an inert atmosphere of 300 millibars of pure argon. The initial charges (about 100g in each case) were melt in the water-cooled copper crucible of the furnace, maintained about five minutes at high temperature (liquid state in levitation due to the magnetic field), then cooled and solidified. The ingots were cut in order to obtain two parallelepipeds (about $7 \times 7 \times 4$ mm^3), near the centre of the ingot. For each studied metal, one of the two samples was plastically deformed by uniaxial compression (initial thickness and thickness after compression given in TABLE 1) while the second one was not mechanically stressed. The deformed sample was cut in two parts according to the scheme presented in figure 1, in order to obtain two surfaces, one perpendicular to the compression axis, and the other one parallel to the compression axis.

Each sample was tin-soldered to a gained copper wire, embedded in a cold resin (Araldite Escil CY230) + hardener (Escil HY956) mixture, polished with a 800-grit SiC paper then shortly polished a second time with a 1200-grit paper (a new one for each sample).

The electrochemical experiments were performed with a three electrodes-cell filled with about 100cm^3 of a solution of sulphuric acid H_2SO_4 2N (and, in the case of the iron electrodes also with the same solution but added with an inhibitor: H_2SO_4 2N + 0.1wt.% allylthiourea) for which pH is equal to 0. The three electrodes were a Saturated Calomel Electrode (SCE) for the reference in potential, a graphite rod for the counter electrode, and, for the working electrode, the embedded and polished metal which was studied. The potensiostat which was used is a VersaStat from EG&G Princeton Applied Research, driven by the M352 software of EG and G via a Compaq Prolinea computer.

The electrochemical measurements done

The iron electrodes and the nickel electrodes underwent several types of experiments in the sulphuric acid solution:

- Preliminary measurement of the actual free potential E(I=0), linear polarization between E(I=0) - 20mV up to E(I=0) + 20mV at 10mV min^{-1} (this whole sequence repeated three times successively, for a total duration of about 20 minutes) ; thereafter a TAFEL-type experiment performed by linear polarization from E(I=0) - 250mV up to E(I=0) + 250mV at 1mV s^{-1}.
- Preliminary measurement of the actual free potential

E(I=0), then a cyclic polarization constituted by an increase in potential from E(I=0) - 250mV up to +1.9V at +5mV min⁻¹ followed by a decrease in potential from +1.9V down to the initial value (i.e. E(I=0) - 250mV)

The copper electrodes only underwent the first experiment (three linear polarization through the small interval in potential, followed by the Tafel experiment) while the iron electrodes underwent the same first experiment (linear polarization then Tafel) in the sulphuric acid solution added with the inhibitor.

The first experiment allowed seeing how the potential and the polarization resistance evolved during the first twenty minutes of immersion while the Tafel experiments permitted the determination of the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}), with in addition estimation of the cathodic and anodic Tafel coefficients (β_a and β_c).

The second experiment allowed seeing the conditions of passivation, transpassivation and depassivation:
- For the intensities: the critical current of passivation and the average anodic current in the passivation plateau
- For the potential: the potential of passivation, the potential of transpassivation, the potential of oxidation of the solvent and the potential of depassivation.

RESULTS

Free immersion and Tafel experiment of iron in H_2SO_4 without or with presence of allylthiourea

The three Tafel curves obtained for the electrode of as-cast iron and for the two electrodes of iron plastically deformed in compression are given in figure 2 while several numerical characteristics of these curves, as well as other results recorded during the about twenty minutes preceding each Tafel experiment, are given together in TABLE 2. Between immersion and Tafel experiment, the free potential E(I=0)ᵢ sometimes slightly increases (not deformed Fe, thereafter called "Fe0"), remains almost constant (deformed Fe with orientation 1, "Fe1") or on the contrary slightly decreases (deformed Fe with orientation 2, "Fe2"). Thus there is no significant variation of the free potential, and furthermore the potential just before Tafel experiment does not significantly depend on the mechanical state of iron. In contrast the polarization resistance (Rpᵢ with i=1, 2 then 3) systematically increases during these twenty

TABLE 2: Iron electrodes-results of linear polarizations and Tafel experiments

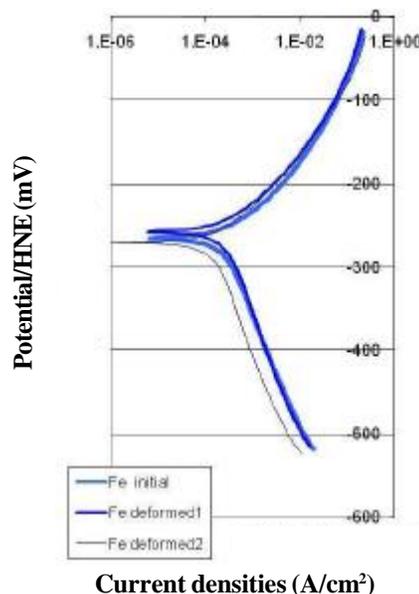| Electrode	Initial Fe (not deformed, "Fe0")	Compressed Fe	
		Orientation 1 ("Fe1")	Orientation 2 ("Fe2")
E(I=0)₁ (mV/HNE)	-283	-264	-268
Rp₁ (Ω cm²)	29	23	32
E(I=0)₂ (mV/HNE)	-276	-263	-272
Rp₂ (? cm²)	64	54	83
E(I=0)₃ (mV/HNE)	-270	-263	-272
Rp₃ (Ωcm²)	67	60	98
Tafel			
β_a (mV/decade)	55	59	54
β_c (mV/decade)	166	175	191
E_{corr} (mV/HNE)	-265	-257	-271
I_{corr} (μA cm⁻²)	274	285	170

Figure 2: Superposition of the Tafel curves obtained for the three iron electrodes

minutes before Tafel experiment, up to a value which is significantly higher for Fe2 than for Fe0 and Fe1. This means that the resistance against corrosion should be slightly higher for the Fe2 than for the two others. This is effectively obtained by applying the Tafel method since the corrosion current (more precisely density of corrosion current) I_{corr} of Fe2 is significantly lower than the two other electrodes. The E_{corr} values deduced from the Tafel curves are still close to one another, and the values of the anodic (β_a) and cathodic (β_c) Tafel coefficients are respectively conform to the anodic reaction $Fe \rightarrow Fe^{2+} + 2\,e$, and also to the cathodic reaction $H^+ + 1\,e \rightarrow 1/2\,H_2$ even it can be thought that β_c is a little

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TABLE 3: Iron electrodes (+ inhibitor) - results of linear polarizations and Tafel experiments

Electrode	Initial Fe (not deformed, "Fe0")	Compressed Fe	
		Orientation 1 ("Fe1")	Orientation 2 ("Fe2")
$E(I=0)_1$ (mV/HNE)	-308	-296	-305
Rp_1 (Ω cm²)	67	88	99
$E(I=0)_2$ (mV/HNE)	-290	-289	-280
Rp_2 (Ω cm²)	111	120	not recorded
$E(I=0)_3$ (mV/HNE)	-277	-282	-266
Rp_3 (Ω cm²)	169	157	327
Tafel			
β_a (mV/decade)	71	68	60
β_c (mV/decade)	155	172	143
E_{corr} (mV/HNE)	-260	-274	-258
I_{corr} (μA cm⁻²)	83	127	49

TABLE 4: Nickel electrodes - results of linear polarizations and Tafel experiments

Electrode	Initial Ni (not deformed, "Ni0")	Compressed Ni	
		Orientation 1 ("Ni1")	Orientation 2 ("Ni2")
$E(I=0)_1$ (mV/HNE)	-56	-41	-28
Rp_1 (Ω cm²)	448	1070	248
$E(I=0)_2$ (mV/HNE)	-52	-32	-28
Rp_2 (Ω cm²)	683	483	411
$E(I=0)_3$ mV/HNE)	-48	-32	-25
Rp_3 (Ω cm²)	765	549	462
Tafel			
β_a (mV/decade)	66	56	51
β_c (mV/decade)	138	212	249
E_{corr} (mV/HNE)	-53	-29	-15
I_{corr} (μA cm⁻²)	19	23	31

too high. In fact, the main differences existing between the three Tafel curves concern the cathodic straight line of Tafel obtained for Fe2 which seems being moved towards lower densities of current, by comparison with the two other cathodic straight lines, what is responsible to the lower value of I_{corr} obtained for Fe2.

When allylthiourea is added to the sulphuric solution, the free potential is not modified (Figure 3, TABLE 3) but the polarization resistances are logically higher, for the three electrodes (Rp3: ×2.5, ×2.6 and ×3.3 for respectively Fe0, Fe1 and Fe2). I_{corr} is also lowered (divided by almost 3 for the three electrodes). One can notice that the three cathodic Tafel straight lines are almost the same while the difference, which is here between Fe0+Fe2 and Fe1, is now due to a shift of the anodic Tafel straight line of Fe1 alone towards higher intensities by comparison to Fe0 (whereas Fe2 remains close to Fe0). The E_{corr} values deduced from the Tafel curves are still close to one another, and the values of
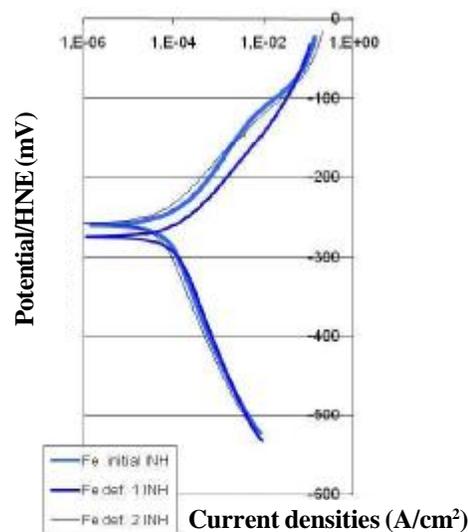

Figure 3: Tafel curves obtained for the three iron electrodes in presence of allylthiourea
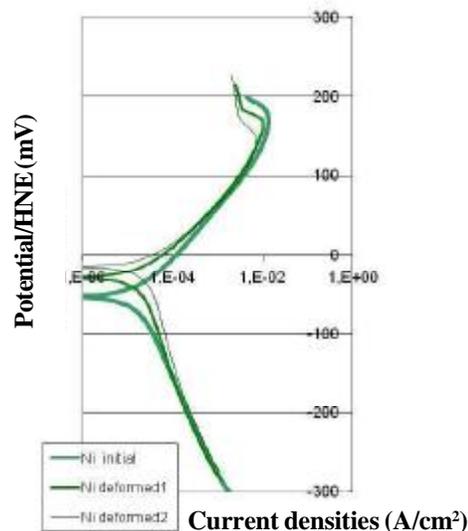

Figure 4: Tafel curves obtained for the three nickel electrodes in presence of allylthiourea

the anodic (β_a) and cathodic (β_c) Tafel coefficients are respectively conform to the anodic reaction Fe $\rightarrow$ Fe²⁺ + 2 e, and also to the cathodic reaction H⁺ + 1 e $\rightarrow$ ½ H₂ even it can be thought that β_c is a little too high

Free immersion and Tafel experiment of nickel in H₂SO₄ (Figure 4 and TABLE 4)

The free potentials of nickel recorded just before the Tafel experiments are all logically higher than for iron, and the polarization resistances are also greatly higher. The free potential slightly increases with time and tends to be slightly higher for the "Ni2" (deformed Ni, orientation 2) and "Ni1" (deformed Ni, orientation

1) electrodes than for the Ni0 one (as-cast Ni). This order is kept for the corrosion potentials determined thereafter during the Tafel experiments. In contrast, the polarization values follow the inversed order (higher for Ni0 than for Ni1 and higher for Ni1 than for Ni2), whereas the corrosion current determined during the Tafel experiments is lower for Ni0 than for Ni1 and, above all, than Ni2. These differences between the I_{corr} and E_{corr} values issued from the Tafel method are seemingly attributed to variations of slope among the anodic parts of the curves as well as among their cathodic parts. In the case of nickel too the values of the Tafel coefficients β_a and β_c (which is a little higher for the deformed nickel than for the as-cast one) respectively correspond to Ni $\rightarrow$ Ni^{2+} + 2 e and H$^+$ + 1 e $\rightarrow$ ½ H$_2$. One can also notice a start of passivation at the end of all the three Tafel curves (near the highest potentials), with seemingly lowered critical current of passivation for the deformed nickel (especially Ni2) than for as-cast nickel (Ni0).

Free immersion and Tafel experiment of copper in H$_2$SO$_4$ (Figure 5 and TABLE 5)

The free potential before Tafel experiment decreases and is higher for the Cu2 (deformed Cu, orientation 2) electrode than for the two others, Cu1 (deformed Cu, orientation 1) and Cu0 (as-cast Cu). This decrease in potential is faster for Cu0 and Cu1 than for Cu2, and this is more obvious when the E_{corr} values determined thereafter by the Tafel method are added to enrich the comparisons. The polarisation resistances increase rapidly and the last value is the highest for Cu1, followed by the one for Cu0 and finally Cu2. The Tafel experiments, which lead to a value of E_{corr} especially high for Cu2, also show that the corrosion currents are higher for the two electrodes of deformed copper (Cu1 and especially Cu2) than for the not deformed one (Cu0). This is due to a special position of the cathodic Tafel straight line for Cu2 which is significantly shifted towards higher current densities. The exploitation of the files using the software was more difficult than for the Fe or Ni electrodes, which did not permit the determination of the Tafel coefficients. Nevertheless it appeared that the anodic one (β_a) tended to be near 40mV/decade or little more (i.e. representative of the Cu $\rightarrow$ Cu^{2+} + 2 e anodic reaction). The cathodic Tafel's coefficient (β_c) was comprised between 55 and 230mV/decade, and seemed being close to the first value for the highest

TABLE 5: Copper electrodes - results of linear polarizations and Tafel experiments

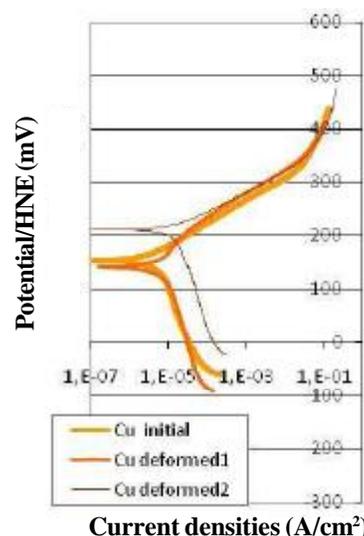| Electrode	Initial Cu(not deforme, "Cu0")	Compressed Cu	
		Orientation 1 ("Cu1")	Orientation 2 ("Cu2")
E(I=0)$_1$ (mV/HNE)	+219	+227	+236
Rp$_1$ (Ω cm²)	67	16	162
E(I=0)$_2$ (mV/HNE)	+196	+207	+231
Rp$_2$ (Ωcm²)	398	247	259
E(I=0)$_3$ (mV/HNE)	+187	+192	+227
Rp$_3$ (Ωcm²)	685	1373	338
Tafel			
E$_{corr}$ (mV/HNE)	+153	+143	+216
I$_{corr}$ (µA cm^{-2})	3	8	16

Figure 5: Tafel curves obtained for the three copper electrodes in presence of allylthiourea

parts of the cathodic potential interval and to the second value in their lowest parts. This can be seen more clearly in figure 5 in the cathodic part of the Tafel curve of Cu2 which appears constituted by two successive linear parts with two different slopes. Since copper is the noblest of the three metals, Cu0, Cu1 and Cu2 were able to be freely oxidized only by dissolved O$_2$ (which is reduced according to ½ O$_2$ + H$^+$ + 2 e $\rightarrow$ OH$^-$; $\beta_c \approx$ 60mV/decade) while reduction of H$^+$ may appear in case of polarization at lower potentials).

Cyclic polarization experiments for the iron and nickel electrodes in H$_2$SO$_4$

Cyclic polarizations were performed in order to specify the conditions of reaching of the passive states (potential of passivation E$_p$, critical anodic current of passivation I$_{cp}$), and to examine the efficiency of the protection of the deformed or not metal by the passiva-

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TABLE 6: Iron electrodes-results of cyclic polarizations

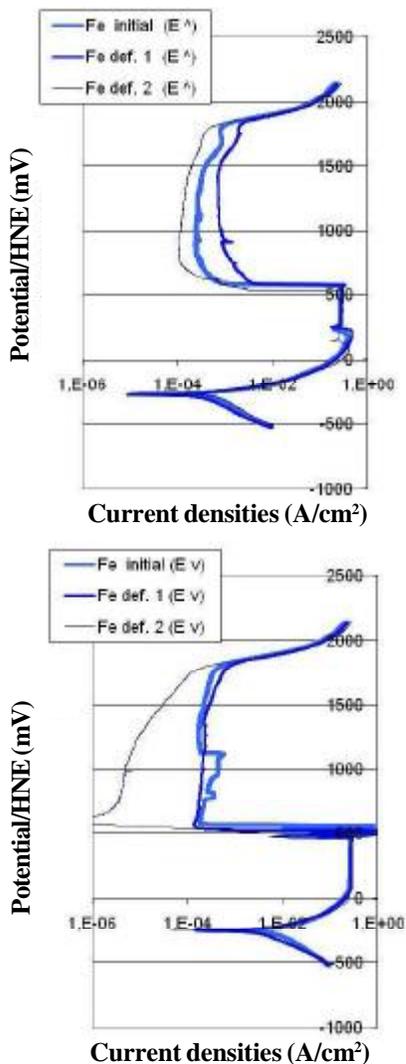| Electrode	Initial Fe (not deformed, "Fe0")	Compressed Fe	
		Orientation 1 ("Fe1")	Orientation 2 ("Fe2")
E_p (mV/HNE)	+583	+572	+534
E_{dp} (mV/HNE)	+573	+531	+510
Current densities			
I_{cp} (mA cm^{-2})	374	463	403
I_{pass} (µA cm^{-2})	265	724	127

Figure 6: The superposed potential-increasing parts (left hand) and the potential-decreasing parts (right hand) of the cyclic polarization curves obtained for the three iron electrodes
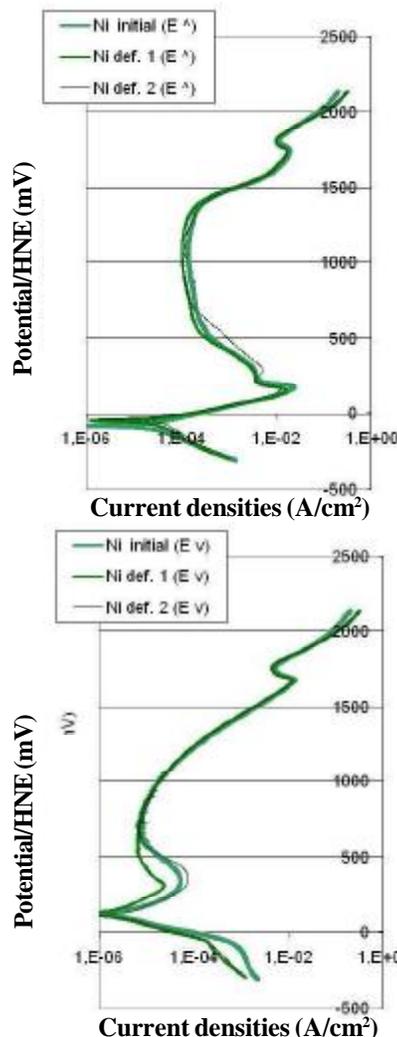

Figure 7: The superposed potential-increasing parts (left hand) and the potential-decreasing parts (right hand) of the cyclic polarization curves obtained for the three nickel electrodes

TABLE 7: Nickel electrodes-results of cyclic polarizations

Electrode	Initial Ni (not deformed, "Ni0")	Compressed Ni	
		Orientation 1 ("Ni1")	Orientation 2 ("Ni2")
E_p (mV/HNE)	+683	+691	+769
E_{dp} (mV/HNE)	+570	+502	+602
Current densities			
I_{cp} (mA cm^{-2})	23	17	12
I_{pass} (µA cm^{-2})	159	112	115

tion layer (average current of corrosion in the passive state I_{pass}). The stability of the passive state was characterized by the determination of the potential of loss of the passive state E_{dp} in the potential-decreasing part of the experiment. This was done only for the three iron electrodes in the sulphuric solution without inhibitor (Figure 6 and TABLE 6) and for the three nickel electrodes (Figure 7, TABLE 7).

In the case of iron, the critical currents of passivation are all around 400 mA cm^{-2} but I_{cp} tends to be slightly higher for the electrodes of deformed iron than

for the as-cast iron one. Passivation of Fe2 occurs for a lower potential than for the other electrodes and the corrosion current in the passive state is also lower for Fe2 than for Fe0 and Fe1. When the potential decreases, the passive state seems being more stable for Fe2 and Fe1 than for Fe0 since depassivation occurs for lower potential for the deformed iron electrodes.

Concerning the nickel electrodes, the critical current of passivation is lower for the Ni2 electrode than for the two other ones but the establishment of the passive state, which seems more progressive than for the iron alloys, is achieved for a higher potential Ep. The corrosion current in the passive state is lower for the deformed nickel electrodes Ni1 and Ni2 than for the as-cast nickel one and, in the potential-decreasing part of the curve, the loss of the passive state, which is also itself more progressive than iron, is started earlier (for higher potentials) for Ni0 and Ni2 than for Ni1.

DISCUSSION

The plastic deformation by compression obviously induces changes in the electrochemical behaviour of iron. More precisely this seems lead generally to an improvement of its resistance against corrosion in the active state by the sulphuric solution since the polarization resistance Rp increases and the corrosion current I_{corr} decreases (as for stainless steel 304 in NaCl solution[9]), especially for the second orientation: Fe2 (the order between as-cast iron and deformed iron tends to be inversed if one considers the first orientation: Fe1). These differences remain when the inhibitor allylthiourea is added in the sulphuric solution. Reaching the passivation plateau seems being a little more difficult for the deformed iron than for as-cast iron but the passive state seems more stable and characterized by a lower corrosion current, especially in the case of Fe2.

The situation appears inversed in the case of nickel since, in the active state, the values of Rp and of I_{corr} tend demonstrating a better behaviour in corrosion in the active state for the as-cast nickel than for the deformed nickel, as formerly reported in another study of polycrystalline Ni in a sulphuric solution[10]. In the passive state, the deformed nickel can be more resistant against corrosion, notably in the case of Ni2 for which passivation seems easier to achieve and the corrosion current I_{pass} is the lower.

About copper, which is the noblest metal of this study, it can be corroded essentially in presence of dissolved oxygen in such solution, and its corrosion in active state is logically greatly lower than for Ni and for Fe. The polarization resistance are the greatest and the corrosion currents the lowest. In its case too, the plastic deformation by compression induces a decrease in corrosion resistance in the active state.

CONCLUSIONS

Plastic deformations, obtained by cold-working during an elaboration step, or resulting from mechanical stresses in service, modify alloys or pure metals in their microstructure by creating new defects as dislocations, especially in metals with cubic structure as bcc iron, fcc nickel and fcc copper. These ones can modify the reactivity of surface, either for the anodic reaction kinetic, or for the cathodic one, with in addition a possible influence of the orientation of the external surface with respect to the direction of the uniaxial deformation. This can modify their electrochemical behaviour, for example in situation of corrosion as here in sulphuric acid, sometimes in the good way as for pure iron, or with detrimental effect for pure nickel or pure copper.

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