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Influence of some minor elements on the corrosion behaviour of low alloy steels in sulfuric acid

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ABSTRACT

The corrosion behaviours of fifteen low alloy steels were studied in a molar solution of sulphuric acid, using the classical electrochemical techniques. The studied steels are all of complex compositions but they contain less than two (and often one) percents of each alloying elements. They were synthesized from pure elements by induction foundry in inert atmosphere and the characterization of corrosion was performed according to the Stern-Geary and Tafel methods. Unsurprisingly all steels were in an active state, with low polarization resistances, corrosion potentials generally near -0.2 V/HNE and current densities of corrosion just under 1 mA / cm^2. Nevertheless, some differences were seen between the corrosion parameters of some of these steels. The presence of molybdenum, niobium, tantalum and vanadium seems to lower the corrosion rate while the contrary was observed for silicon and chromium. The influences of manganese and tungsten were not well established.

KEYWORDS

Low alloy steels;
Sulphuric acid;
Corrosion;
Electrochemical
measurements.

INTRODUCTION

The low alloy steels, which contain less few percents of elements other than iron, are not so corrosion resistant than stainless steels, especially in acid solutions. If the corrosion behaviour of stainless steels has been of great interest over several tens years in more[1] or less[2] concentrated sulphuric acids, the low alloy steels were also studied in dilute[3] or concentrated[4] sulphuric acidic solutions, but the concerned works seem to be not so numerous.

The aim of this study is to characterize, using classical electrochemical techniques as measurement of polarization resistances and determination of corrosion potential and current by Tafel experiments, the corrosion behaviour of several low alloy cast steels of different compositions when immersed in a simple molar aqueous solution of sulphuric acid, with a special attention to the possible effect, beneficial or detrimental, of several elements added in small quantities to a base composition.

EXPERIMENTAL

Synthesis of the studied steels and preparation of the electrodes

Fifteen different alloys were cast, using a high frequency induction furnace (CELES), by melting the pure elements (Alfa Aesar, >99.9wt.%) together under an inert atmosphere of pure argon (300mbars). The obtained ingots (mass = about 100g) were cut, tin-soldered to a plastic-isolated copper wire, embedded in a cold resin and polished with 1200-grit paper. The area of emerging steel, which was thereafter in contact with the sulfuric solution, varied from 0.8 to 1.8 cm².

Metallographic samples were also prepared in order to examine their microstructure, using an optical microscope equipped with a digital camera, after etching with Nital 4% (96% ethanol + 4% HNO_3): immersion during 15-20 seconds at room temperature then water rinsing, ethanol rinsing and drying by hot air. The same samples also allowed controlling the obtained chemical compositions, by Wavelength Dispersion Spectrometry (using a Cameca SX50 or SX100 microprobe).

Electrochemical characterization of corrosion

The electrochemical runs were performed at room temperature, using a classical three-electrodes cell and a potensiostat / galvanostat (Princeton Applied Research, model 263A) driven by a computer (supporting the software M352 of EGG/Princeton). The electrolyte was a sulphuric solution of H_2SO_4 (concentration: 1 Mol/L), which was replaced after each {3 × Rp + 1 × Tafel} whole experiment.

The electrochemical experiments which were performed were composed of:

* three successive measurements of the polarization resistance (Rp) every about 10 minutes over a 40mV-wide range centred on the Open Circuit Potential (E_{ocp}) previously measured (from E_{ocp} – 20mV to E_{ocp} + 20mV), with a scan rate of 10mV/min,

* followed by a Tafel run, from E_{ocp} – 250mV to E_{ocp} + 250mV (scan rate: 10mV/min), with determination of the potential and current density of corrosion E_{corr} and I_{corr}, and the Tafel coefficients β_a and β_c).

RESULTS AND DISCUSSION

Chemical compositions and microstructures of the obtained alloys

The general chemical compositions of the obtained steels are given in the first columns of TABLES 1a, 1b, 2a and 2b. The cumulated contents in alloying elements are generally lower than 5wt.%, with Si contents, Mn contents, Cr contents and Mo contents varying between 0 to 0.1wt.% (Si), 0 to 1.2 (Mn), 0 to 1.4 (Cr) and 0 to 1.7 (Mo), for the elements contained in almost all steels. Additional elements can be also present in one to four steels in each case: W (0 to 1.1wt.%), V (0 to 0.9), Nb (0 to 1.7) and Ta (0 to 1.2).

Observed using optical microscope after Nital-etching their microstructures are generally similar to one another, with dispersion of very small precipitates which are probably carbides formed from carbon and the present carbides-former elements (Cr, Mo, ...). Figure 1 shows two examples of the obtained microstructures.

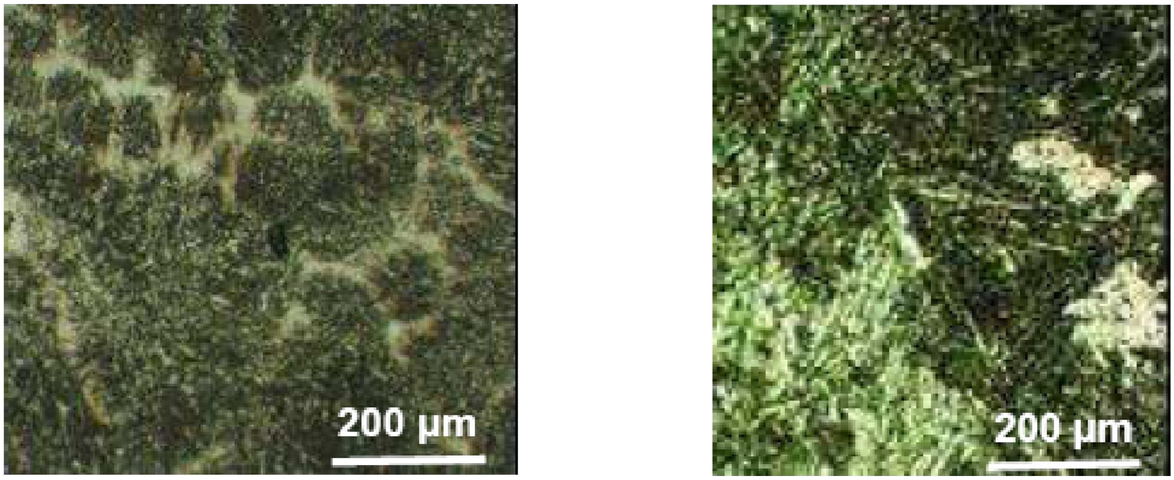

Figure 1: Examples of microstructures (Nital etching): steel 2 (left hand) and steel 7 (right hand)

Results obtained according to the stern-geary method

The polarization resistances which were measured (three per alloy) are presented in TABLE 1a and TABLE 1b, which allow comparing directly the steels which differ from one another about only one element. In TABLE 1a, in which the other steels are compared with the reference steel (“STEEL01”), one can see that some of the elements seem being beneficial for the polarization resistance, even if they are present in small or very small quantities, while other elements have the inverse effect:

TABLE 1a : Values obtained for the three successive polarization resistances; comparison between the reference steel (STEEL01) and two (or three) steels different from the first one about a single element

Si	Si	Mn	Cr	Mo	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
steel14	/	0.43	1.03	0.24	36.7	38.0	36.9
STEEL01	0.07	0.40	1.02	0.19	29.2	27.2	25.6

Mn	Si	Mn	Cr	Mo	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
steel13	0.09	/	1.06	0.24	30.1	30.2	27.1
STEEL01	0.07	0.40	1.02	0.19	29.2	27.2	25.6
steel02	0.09	1.22	1.05	0.29	24.6	25.0	24.7

Cr	Si	Mn	Cr	Mo	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
steel03	0.10	0.44	/	0.08	35.0	32.1	28.1
STEEL01	0.07	0.40	1.02	0.19	29.2	27.2	25.6

Mo	Si	Mn	Cr	Mo	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
steel04	0.09	0.37	0.96	/	31.4	21.2	19.2
STEEL01	0.07	0.40	1.02	0.19	29.2	27.2	25.6
steel05	0.11	0.37	1.02	1.59	29.0	26.6	25.8

W	Si	Mn	Cr	Mo	W	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
STEEL01	0.07	0.40	1.02	0.19	/	29.2	27.2	25.6
steel07	0.11	0.41	1.10	0.23	1.08	25.7	22.8	21.4

V	Si	Mn	Cr	Mo	V	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
STEEL01	0.07	0.40	1.02	0.19	/	29.2	27.2	25.6
steel09	0.08	0.40	1.41	0.27	0.89	39.3	34.5	34.1

Nb	Si	Mn	Cr	Mo	Nb	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
STEEL01	0.07	0.40	1.02	0.19	/	29.2	27.2	25.6
steel08	0.09	0.38	1.03	0.18	1.73	73.3	84.0	96.5

Ta	Si	Mn	Cr	Mo	Ta	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
STEEL01	0.07	0.40	1.02	0.19	/	29.2	27.2	25.6
steel10	0.05	0.41	1.06	0.17	1.19	43.0	34.3	33.7

TABLE 1b: Values obtained for the three successive polarization resistances; comparison between two (or three) steels different from one another about a single element

Mn	Si	Mn	Cr	Mo	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$)
steel06	0.09	0.11	1.04	1.66	35.5	31.8	29.7
steel05	0.11	0.37	1.02	1.59	29.0	26.6	25.8

W	Si	Mn	Cr	Mo	W	V	Rp_1 ($\Omega \times cm^2$)	Rp_2 ($\Omega \times cm^2$)	Rp_3 ($\Omega \times cm^2$
steel12	0.10	0.45	1.08	0.43	0.12	0.07	26.4	23.9	23.0
steel11	0.08	0.43	1.07	0.43	0.28	/	28.1	26.1	24.8
steel15	0.08	0.39	0.99	0.36	0.29	/	28.5	27.2	26.5

- V, Nb, Ta, and Mo lead to an increase in polarization resistance,
- Si, Cr and Mn (TABLES 1a and 1b) lower the polarization resistance,

while the effect of W is not well established since its presence lowers the polarization resistance in TABLE 1a while the inverse effect is observed in TABLE 1b.

Results obtained according to the Tafel method

The results of the Tafel calculations are given in TABLE 2a and TABLE 2b, with a presentation which here too facilitates the direct comparison between the steels different from one another about only one element. As above, one can see in TABLE 2a, where the other steels are compared with the reference STEEL01, that there are some elements which lead to lowered corrosion rates, while there are other elements which have the inverse effect:

- V, Nb, Ta and Mo lower the density of corrosion current,
- Si and Cr lead to an increase in corrosion current,

while the effects of Mn and of W are variable, as it can be seen in TABLE 2a and TABLE 2b.

Some of the Tafel curves are displayed in the graphs presented in Figure 2 and Figure 3. In each graph of Figure 2 the Tafel curve for the reference STEEL01 is plotted together with the one of the other steel which is different from this one about the content in vanadium, niobium or tantalum (elements beneficial for a slower corrosion), while each graph of Figure 3 contains the Tafel curve of STEEL01 plotted together with the one of the other steel which differs from the latter one about the content in silicon or in chromium (elements tending to enhance corrosion), and also in tungsten (which has not a very established role in this point of view).

TABLE 2a: Values obtained for the potentials and currents of corrosion; comparison between the reference steel (STEEL01) and two (or three) steels different from the first one about a single element

Si	Si	Mn	Cr	Mo	E_{corr} / HNE (mV)	I_{corr} (µA/cm²)	β_a (mV/dec)	β_c (mV/dec)
steel14	/	0.43	1.03	0.24	-219	471	62	157
STEEL01	0.07	0.40	1.02	0.19	-211	668	62	170
Mn	**Si**	**Mn**	**Cr**	**Mo**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec)**
steel13	0.09	/	1.06	0.24	-211	618	61	147
STEEL01	0.07	0.40	1.02	0.19	-211	668	62	170
steel02	0.09	1.22	1.05	0.29	-218	574	57	169
Cr	**Si**	**Mn**	**Cr**	**Mo**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec)**
steel03	0.10	0.44	/	0.08	-213	642	63	154
STEEL01	0.07	0.40	1.02	0.19	-211	668	62	170
Mo	**Si**	**Mn**	**Cr**	**Mo**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec)**
steel04	0.09	0.37	0.96	/	-214	892	62	187
STEEL01	0.07	0.40	1.02	0.19	-211	668	62	170
steel05	0.11	0.37	1.02	1.59	-189	528	47	141

W	Si	Mn	Cr	Mo	W	E_{corr} / HNE (mV)	I_{corr} (µA/cm²)	β_a (mV/dec)	β_c (mV/dec
STEEL01	0.07	0.40	1.02	0.19	/	-211	668	62	170
steel07	0.11	0.41	1.10	0.23	1.08	-199	863	62	171
V	**Si**	**Mn**	**Cr**	**Mo**	**V**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec**
STEEL01	0.07	0.40	1.02	0.19	/	-211	668	62	170
steel09	0.08	0.40	1.41	0.27	0.89	-217	496	59	173
Nb	**Si**	**Mn**	**Cr**	**Mo**	**Nb**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec**
STEEL01	0.07	0.40	1.02	0.19	/	-211	668	62	170
steel08	0.09	0.38	1.03	0.18	1.73	-240	201	56	231
Ta	**Si**	**Mn**	**Cr**	**Mo**	**Ta**	**E_{corr} / HNE (mV)**	**I_{corr} (µA/cm²)**	**β_a (mV/dec)**	**β_c (mV/dec**
STEEL01	0.07	0.40	1.02	0.19	/	-211	668	62	170
steel10	0.05	0.41	1.06	0.17	1.19	-211	463	57	178

TABLE 2b: Values obtained for the three successive polarization resistances; comparison between two (or three) steels different from one another about a single element

Mn	Si	Mn	Cr	Mo	E_{corr} / HNE (mV)	I_{corr} (µA/cm²)	β_a (mV/dec)	β_c (mV/dec)
steel06	0.09	0.11	1.04	1.66	-185	561	52	157
steel05	0.11	0.37	1.02	1.59	-189	528	47	141

W	Si	Mn	Cr	Mo	W	V	E_{corr} / HNE (mV)	I_{corr} (µA/cm²)	β_a (mV/dec)	β_c (mV/dec)
steel12	0.10	0.45	1.08	0.43	0.12	0.07	-203	859	68	177
steel11	0.08	0.43	1.07	0.43	0.28	/	-201	734	61	167
steel15	0.08	0.39	0.99	0.36	0.29	/	-203	672	59	165

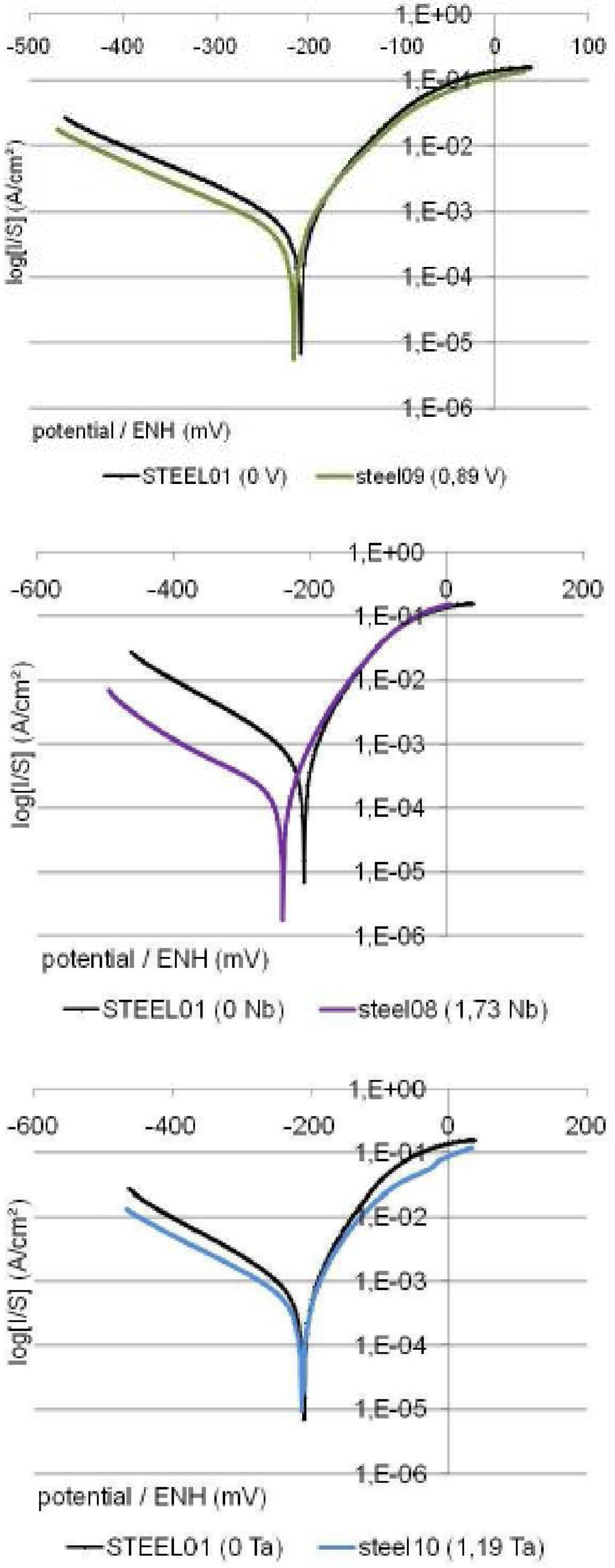

Figure 2 : Tafel curves concerning the elements which improve the corrosion resistance

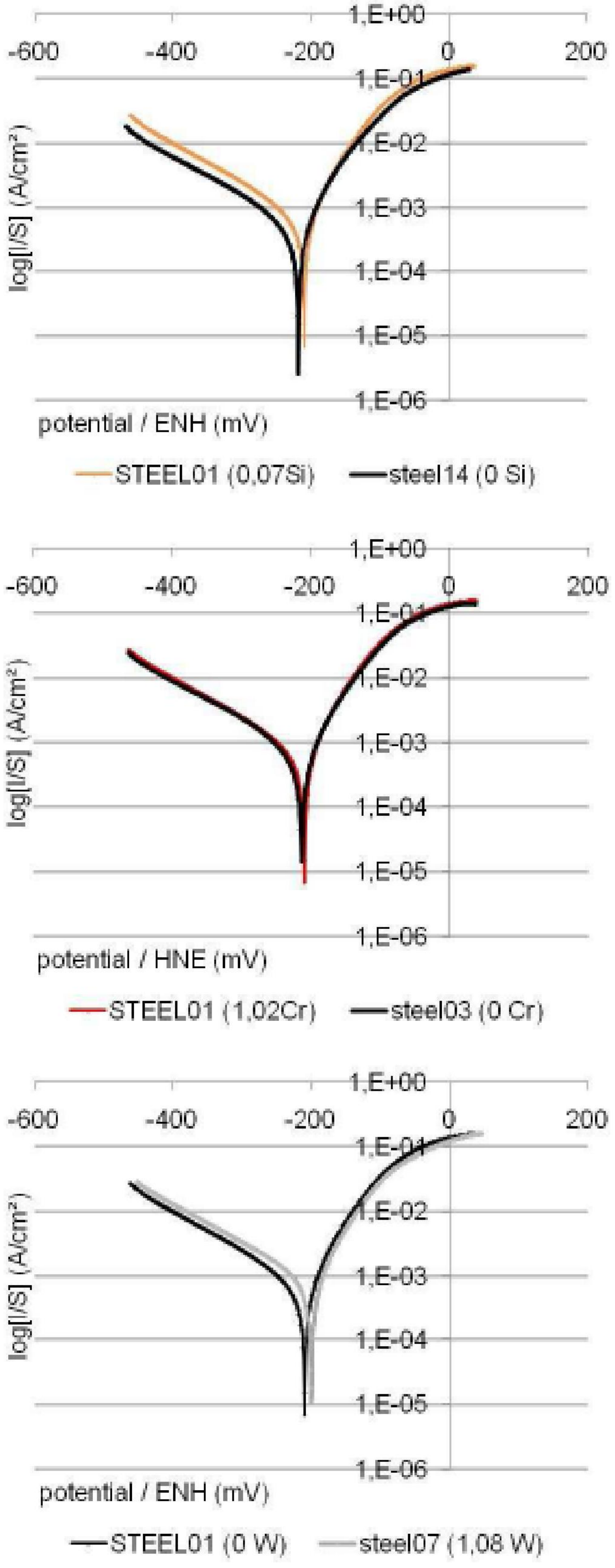

Figure 3 : Tafel curves concerning the elements which deteriorate the corrosion resistance

General commentaries

The steels considered in this study, which contain very low alloying elements, notably chromium, do not display behaviours similar to real stainless steels in which notably the chromium and nickel contents are significantly higher (e.g. more than ten weight percents). If such Cr-rich alloys tend to easily passivate, even in acidic solutions, the present alloys remain obviously in the active state, without any tendency to begin passivating, even at the end of the Tafel experiments (when the imposed potential is the highest). Thus the polarization resistances are only of several tens $\Omega \times cm^2$, the corrosion potential logically remains between the Fe^{2+}/Fe and H^+/H_2 standard potentials, and the corrosion densities of current are not far from one mA / cm^2. The anodic and cathodic Tafel coefficients, which are either close to, or at least not far from, 60mV / decade and 120mV / decade respectively, well correspond to the anodic reaction Fe -> Fe^{2+} + 2e and cathodic reaction H^+ + 1 e -> ½ H_2.

Nevertheless, if the presence of the alloying elements does not promote passivation one observed that some of them allowed a small decrease in corrosion rate. Indeed, 1wt.% of vanadium, 1.7wt.% of niobium or 1.2wt.% of tantalum led to higher polarization resistances (especially in the case of niobium: Rp are multiplied by a factor between 2 and 4) and lower corrosion currents (here too especially in the case of niobium: I_{corr} is decreased three times).

In contrast, chromium and silicon, which are known to favour a good resistance against corrosion by leading to a protective oxide or hydroxide layer (i.e. when passivation is possible), tend to slightly accelerate corrosion in the active state.

It was previously found that niobium (and tungsten) were beneficial to the corrosion resistance in dilute sulphuric acidic solutions[3], but in the case of an austenitic stainless steel. It was also observed, for such Cr-rich steel or nickel-base alloys, that sufficiently high amounts in molybdenum or chromium led to improvements in corrosion resistance in sulphuric acid solutions with various concentrations[5,6]. Instead accelerating corrosion, it was formerly found that silicon favours corrosion resistance, contrarily with what was observed here, but again in the case of stainless steel able to passivate[7] (Si decreases the passive current density). Thus, comparisons with earlier works are not very easy to do since the great majority of steels studied in corrosion in sulphuric acid solutions are Cr-rich (and sometimes simultaneously Ni-rich) stainless steels. Low alloy steels studied in corrosion are more often characterized in immersion in other aqueous solutions, such as sea water[8] or underground water[9].

CONCLUSIONS

Low alloy steels, which do not passivate in these conditions, are logically not suitable for contact with sulphuric acid since their corrosion rates are high, even if the solution is not concentrated. However, the presence of 1 to 2wt.% of elements as vanadium, niobium or tantalum can lead to a moderate or significant increase in polarization resistance or decrease in the corrosion current. In contrast, the presence of elements known to improve the corrosion resistance when passivation is possible, chromium and silicon, tends to accelerate corrosion for such steels in the active state.

Thus, in such sulphuric solution, these results seem showing that it would be better for a low alloy steel to contain 1 or 2 wt.% of niobium (for example) rather than the same contents in chromium. To ensure a real protection against corrosion the content in chromium ought to be higher, in order to allow the steel to behave as a real stainless one (passivation).

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