STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, Sp.Iss. 1, 2009

STUDY OF THE EFFECTS OF MINOR ELEMENTS ON THE ELECTROCHEMICAL BEHAVIOUR OF CAST LOW ALLOY STEELS IN A MOLAR SOLUTION OF SULFURIC ACID

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ABSTRACT. Fifteen low alloys steels were synthesized by induction foundry under argon atmosphere, with varied chemical compositions. In their as-cast states they were immersed in a H_2SO_4 1M solution and subjected to electrochemical measurements: polarization resistance and cyclic intensity-potential curves. All steels were logically in an active state, with low polarization resistances, low open circuit potentials and high corrosion currents. However they were all able to reach passivation for applied potentials high enough, but they fell again in the active state in the potential-decreasing part of cyclic polarization. Nevertheless, some differences were seen between the corrosion characteristics of some of these steels. The presence of niobium, tantalum and vanadium tend to lower the corrosion rate in the active state as well as they facilitate passivation. Niobium seems having a particularly strong beneficial effect on the corrosion rate of such steels both in the active state and in the passive state.

Keywords: low alloy steels, molar sulphuric acid, electrochemical behaviour, minor alloying elements

INTRODUCTION

In contrast with the stainless steels which contain at least ten percents of chromium [1], the low alloy steels, with significantly smaller contents in elements other than iron, are not resistant against corrosion, notably in acid solutions. The corrosion behaviour of stainless steels in acid solutions was extensively studied since several tens of years, for instance in aqueous solutions with more [2] or less [3] high concentrations of sulphuric acid. In contrast, works concerning corrosion of low alloy steels in such solutions, dilute [4] or concentrated [5], seem to be less frequent.

The purpose of this work is to characterize the corrosion behaviour, in a molar sulfuric acid solution, of several cast low alloy steels with various chemical compositions, by applying some of the classical electrochemical methods:

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- measurement of polarization resistance (according to the Stern Geary method) which gives first indications about the corrosion rates
- and cyclic polarization to get first estimations of the potential and current of corrosion (according to the Tafel method) but also to know the conditions of passivation and of passivation loss, as well as the level of corrosion intensity in the passive state, and to analyze the influence of each minor element on these corrosion characteristics.

RESULTS AND DISCUSSION

The obtained chemical compositions were analyzed by microprobe on mounted samples prepared from parts cut in each ingots. The results are presented in Table 1. Generally the alloys contain as least 95 wt.% Fe and the other elements are all present with low or very low contents: 0 to 0.1 of Si, 0 to 1.2 of Mn, 0 to 1.4 of Cr, 0 to 1.7 of Mo, 0 to 1.1 of W, 0 to 0.9 of V, 0 to 1.7 of Nb and 0 to 1.2 of Ta (all contents in weight percents).

Nital-etching followed by optical microscopy observation allowed evidencing the microstructures of all steels. They are generally similar to one another, and characterized by the presence of small dispersed precipitates which seem being carbides formed from carbon and the present carbides-former elements (Cr, Mo, ...). Figure 1 shows an example of the obtained microstructures.

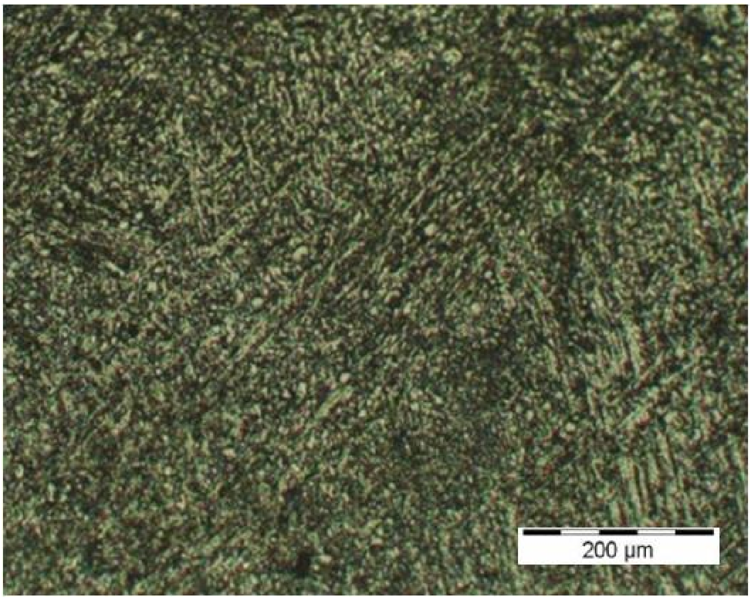

Figure 1. Example of obtained microstructure
(here: the S01r steel after Nital etching, optical microscope)

Table 1. Chemical compositions of the obtained steels (WDS, microprobe)

Steels	**Fe**	**Si**	**Mn**	**Cr**	**Mo**	**W**	**V**	**Nb**	**Ta**
S01r	95.8 ±0.7	0.07 ±0.02	0.40 ±0.04	1.02 ±0.04	0.19 ±0.09	/	/	/	/
S02	95.6 ±1.1	0.09 ±0.02	1.22 ±0.08	1.05 ±0.04	0.29 ±0.06	/	/	/	/
S03	98.5 ±0.64	0.10 ±0.02	0.44 ±0.03	/	0.08 ±0.09	/	/	/	/
S04	97.8 ±0.2	0.09 ±0.02	0.37 ±0.04	0.96 ±0.05	/	/	/	/	/
S05	92.2 ±1.2	0.11 ±0.01	0.37 ±0.05	1.02 ±0.02	1.59 ±0.2	/	/	/	/
S06	97.2 ±0.64	0.09 ±0.01	0.11 ±0.02	1.04 ±0.06	1.66 ±0.19	/	/	/	/
S07	94.4 ±4.4	0.11 ±0.03	0.41 ±0.04	1.10 ±0.04	0.23 ±0.14	1.08 ±0.15	/	/	/
S08	95.5 ±0.5	0.09 ±0.02	0.38 ±0.06	1.03 ±0.05	0.18 ±0.09	/	/	1.73 ±0.23	/
S09	92.9 ±0.2	0.08 ±0.01	0.40 ±0.05	1.41 ±0.07	0.27 ±0.07	/	0.89 ±0.05	/	/
S10	95.5 ±0.6	0.05 ±0.03	0.41 ±0.05	1.06 ±0.06	0.17 ±0.12	/	/	/	1.19 ±0.14
S11	96.6 ±0.45	0.08 ±0.02	0.43 ±0.04	1.07 ±0.02	0.43 ±0.07	0.28 ±0.07	/	/	/
S12	96.7 ±0.7	0.10 ±0.02	0.45 ±0.07	1.08 ±0.04	0.43 ±0.07	0.12 ±0.12	0.07 ±0.02	/	/
S13	97.7 ±0.49	0.09 ±0.02	/	1.06 ±0.04	0.24 ±0.08	/	/	/	/
S14	97.6 ±0.5	/	0.43 ±0.05	1.03 ±0.05	0.24 ±0.07	/	/	/	/
S15	96.8 ±0.3	0.08 ±0.03	0.39 ±0.05	0.99 ±0.04	0.36 ±0.16	0.29 ±0.10	/	0.01 ±0.01	/

Just after immersion in the molar H_2SO_4 solution, the Stern-Geary method was used to measure successively three times the polarization resistance by applying an increase of potential from E_{ocp} – 20 mV to E_{ocp} + 20 mV at +10 mV/min, over a whole duration of about 30 minutes (E_{ocp} : open circuit potential, measured just before each Stern-Geary run). Thereafter a cyclic polarization was performed from E_{ocp} – 250 mV to 1.9 V at 5 mV/s and from 1.9 V down to E_{ocp} – 250 mV at -5 mV/s, with E_{ocp} measured just before the cyclic polarization start. The part of the obtained log(I)=f(E) curve corresponding to the [E_{ocp} – 250 mV, E_{ocp} + 250 mV] range was considered for applying the Tafel method in order to estimate both potential and current of corrosion E_{corr} and I_{corr}.

The obtained values all show that the steels were all in the active state. All these first results, which thus concern the corrosion parameters for the active state, are presented in Table 2 (successive polarization resistances Rp1, Rp2 and Rp3, potentials and currents of corrosion E_{corr} and I_{corr}, anodic and cathodic Tafel coefficients b_a and b_c).

Table 2. Effect of the minor elements on the corrosion parameters in the active state (Stern-Geary + Tafel in the E-increasing part of the cyclic polarization curves)

steels	Stern-Geary	Tafel (cyclic polarization curve, part E ↑)			
	Rp1–Rp2–Rp3 ((Ω × cm^2)	E_{corr}/NHE (mV)	I_{corr} (mA/cm^2)	b_a (mV/dec)	b_c (mV/dec)
S01r (reference steel)					
S01r	25.6 – 25.0 – 23.2	-228	0.95	66	148
Effect of Cr (comparison with **S01r: 1.02 wt.% Cr**)					
S03: 0.00Cr	24.3 – 23.6 – 21.6	-228	1.19	72	145
Effect of Si (comparison with **S01r: 0.07 wt.% Si**)					
S14: 0.00Si	31.0 – 30.8 – 28.8	-231	1.00	76	185
Effect of Mo (comparison with **S01r: 0.19 wt.% Mo**)					
S04: 0.00Mo	24.4 – 23.1 – 21.9	-243	0.90	67	157
S05: 1.59Mo	25.1 – 22.3 – 21.1	-205	0.88	55	159
Effect of Nb (comparison with **S01r: 0.00 wt.% Nb**)					
S08: 1.73Nb	30.7 – 62.2 – 71.5	-265	0.21	50	177
Effect of Ta (comparison with **S01r: 0.00 wt.% Ta**)					
S10: 1.19Ta	29.2 – 25.6 – 25.6	-232	0.68	66	169
Effect of V (comparison with **S01r: 0.00 wt.% V**)					
S09: 0.89V	24.6 – 24.7 – 24.0	-239	0.82	80	172
Effect of Mn (comparison with **S01r: 0.40 wt.% Mn**)					
S13: 0.00Mn	28.3 – 26.4 – 25.0	-232	1.17	74	177
S02: 1.22Mn	17.4 – 19.2 – 17.7	-236	1.47	79	189
Effect of Mn (comparison between the alloys bellow only)					
S06: 0.11Mn	24.3 – 22.1 – 20.1	-204	1.02	56	165
S05: 0.37Mn	25.1 – 22.3 – 21.1	-205	0.88	55	159
Effect of W (comparison with **S01r: 0.00 wt.% W**)					
S07: 1.08W	20.2 – 19.0 – 17.7	-215	1.70	81	214
Effect of W (comparison between the alloys bellow only)					
S12: 0.12W	23.0 – 19.9 – 19.5	-219	0.70	67	144
S11: 0.28W	24.6 – 22.9 – 17.2	-215	0.84	64	146
S15: 0.29W	23.0 – 21.4 – 19.5	-220	1.25	68	180

By comparing directly the steels with the S01r steel (which plays the role of reference steel in many cases) which significantly differ from the latter one concerning only one element, or simply some of the steels to each other when only one element is significantly different between them, it appears that:

* the Rp values tend to increase and the I_{corr} values tend to decrease when the following elements are present or when their contents are higher: Cr, Nb (effect especially strong), Ta and V
* the Rp values tend to decrease and the I_{corr} values to increase when W and even Si are present or when their content are higher,
* while no systematic evolution of Rp and I_{corr} can be noted for the changes in the contents of Mo and Mn.

One can remark the absence of real correlation between the corrosion rate and the E_{corr} values. The latter are all between -0.3 V and -0.2 V, as is to say between the standard potentials of the Fe^{2+}/Fe^0 and H^+/H_2 systems. The anodic and cathodic Tafel coefficients b_a and b_c are also generally consistent with the reactions $Fe^0 \rightarrow Fe^{2+} + 2e$ and $H^+ \rightarrow ½ H_2 + e$ since they are more or less close to 59 mV/decade and 118 mV/decade, respectively.

The parameters corresponding to the passive state were measured on the cyclic polarization curves, an example of which is given in Figure 2.

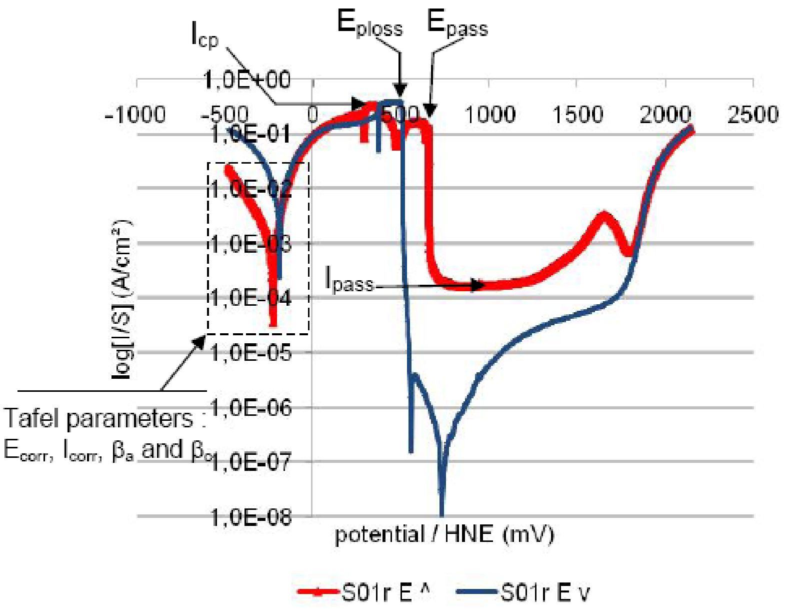

Figure 2. The whole cyclic polarization curve for the reference steel S01r, with visualization of the parameters of interest

The corrosion parameters which were of interest are:

- for the potential-increasing part of the cyclic polarization curve: the critical current of passivation I_{cp} and the potential of passivation E_{pass} (which both characterize the level of difficulty to reach the passive state) and the average corrosion current in the passivation plateau I_{pass} (corrosion rate in the passive state),
- for the potential-decreasing part of the curve: the potential of passivation loss E_{ploss} (characterizing the stability of the passive state when the potential is lowering).

All the measured values are given in Table 3, which also allows either comparing directly the steels with the reference S01r steel when they differ from this one about only one element, or directly steels to each other when one element is different between them (cases of Mn and W again).

Concerning the conditions for reaching the passive state it appears that:

* the I_{cp} and E_{pass} values tend to decrease when the following elements are present or when their contents are higher: Nb, Ta and W; in contrast it is not so clear for vanadium,
*the I_{cp} and E_{pass} values tend to increase when Cr, Si and Mo is present or when their contents are higher; Mn seems also to have the same effect.

Concerning the corrosion rates in the passive state one can notice that:

* unsurprisingly the corrosion current is significantly lowered by passivation (about ten times lower than in the active state) but most of the alloying elements led to higher values of critical current of passivation Icp (Si, Mn, W but also Ta and V),
* three elements (Cr, Mo and Nb) lower I_{cp}.

The protective layer formed by passivation is unfortunately lost in all cases when the applied potential decreases. However this generally occurs at lower potentials when the alloying elements are added or when their contents are higher. Indeed, Cr, Nb, Ta, V and W all led to lower E_{ploss} values while no systematic effect was observed in the case of Mo and Mn. Si is the single element which appeared to deteriorate the stability of the passive state.

The differences discussed before between steels about the corrosion potential and current, and the characteristics of passivation, can be graphically illustrated by Figure 3 and Figure 4, in which the potential-increasing parts of the cyclic polarization of some of the studied steels are superposed with the S01r reference steel one.

Table 3. Effect of the minor elements on the corrosion parameters concerning the passive state (in the E-increasing part of the polarization curve: critical current of passivation I_{cp}, potential of passivation E_{pass} and average corrosion current in the passive state I_{pass}; in the E-decreasing part of the cyclic polarization curve: potential of passivation loss E_{ploss})

steels	E-increasing part of the cyclic polarization curve			E-decreas. part
	I_{cp} (mA/cm²)	E_{pass}/NHE (mV)	I_{pass} (µA/cm²)	E_{ploss}/NHE (mV)
S01r (reference steel)				
S01r	339	+666	177	+546
Effect of Cr (comparison with **S01r: 1.02 wt.% Cr**)				
S03: 0.00Cr	223	+640	192	+570
Effect of Si (comparison with **S01r: 0.07 wt.% Si**)				
S14: 0.00Si	280	+577	147	+511
Effect of Mo (comparison with **S01r: 0.19 wt.% Mo**)				
S04: 0.00Mo	281	+572	215	+510
S05: 1.59Mo	> 285	+939	413	+507
Effect of Nb (comparison with **S01r: 0.00 wt.% Nb**)				
S08: 1.73Nb	277	+551	133	+509
Effect of Ta (comparison with **S01r: 0.00 wt.% Ta**)				
S10: 1.19Ta	271	+587	193	+511
Effect of V (comparison with **S01r: 0.00 wt.% V**)				
S09: 0.89V	378	+600	270	+520
Effect of Mn (comparison with **S01r: 0.40 wt.% Mn**)				
S13: 0.00Mn	266	+578	176	+508
S02: 1.22Mn	181	+762	390	+538
Effect of Mn (comparison between the alloys bellow only)				
S06: 0.11Mn	386	+570	166	+526
S05: 0.37Mn	> 285	+939	413	+507
Effect of W (comparison with **S01r: 0.00 wt.% W**)				
S07: 1.08W	244	+641	214	+517
Effect of W (comparison between the alloys bellow only)				
S12: 0.12W	373	+664	169	+516
S11: 0.28W	276	+574	187	+530
S15: 0.29W	399	+558	188	+512

For example in Figure 3 one find again the increase in passivation potential (1) due to silicon or the increase in anodic current in the passive state (2) due to tungsten. But one see also, for the alloys containing Cr while it is absent for the Cr-free S03 steel) the enlargement of the peak (3) preceding the solvent's oxidation due to the small quantity of chromium which previously led to a $Cr^{III}(OH)_3$ layer partly covering the steel surface and which thereafter suffers new oxidation in $Cr^{VI}O_7^{2-}$ species by transpassivation.

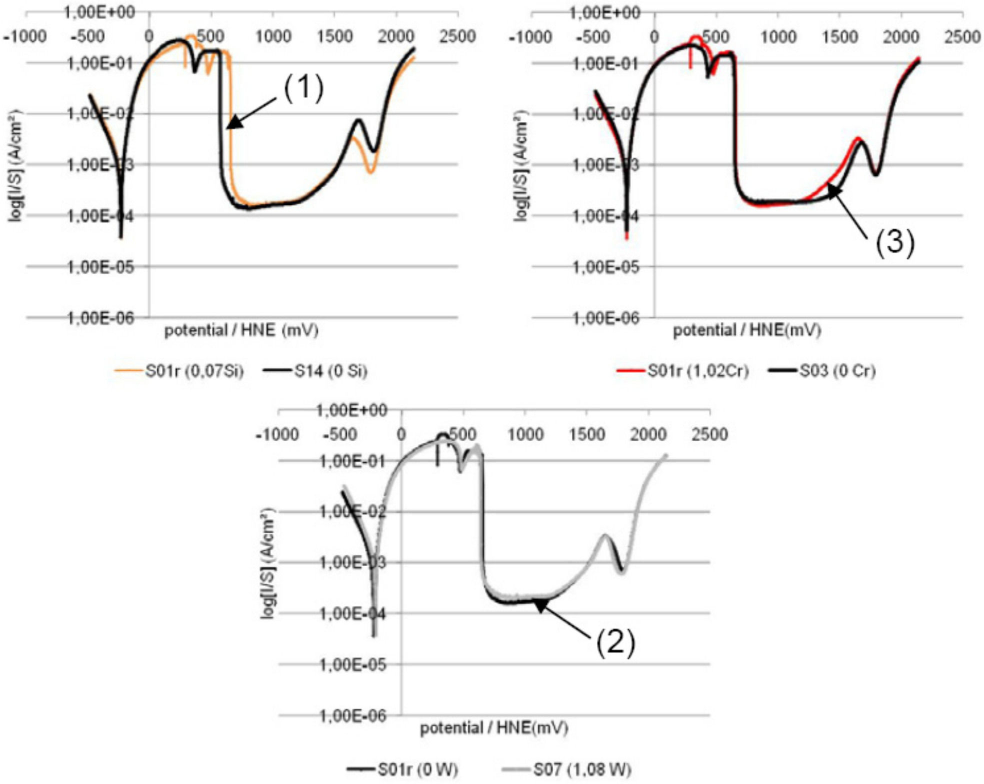

Figure 3. Effects of silicon, tungsten and chromium on the E-increasing parts of the polarization curves (steels S14, S03 and S07 compared to the reference steel S01r)

In Figure 4, one find again the tendency of tantalum (4), vanadium (5) and niobium (6) to decrease the passivation potential, but a new observation is the progressive second decrease in anodic current (following the first sudden part of decrease) which delays over several hundreds mV the reaching of the minimum passivation current (7). In the curve corresponding to the S09 steel, there is an additional small peak near 1000 mV (8) which may correspond to the re-oxidation of $V^{IV}O^{++}$ (coming from the vanadium initially present in the steel) in $V^{V}O_2^{+}$ in the solution [6].

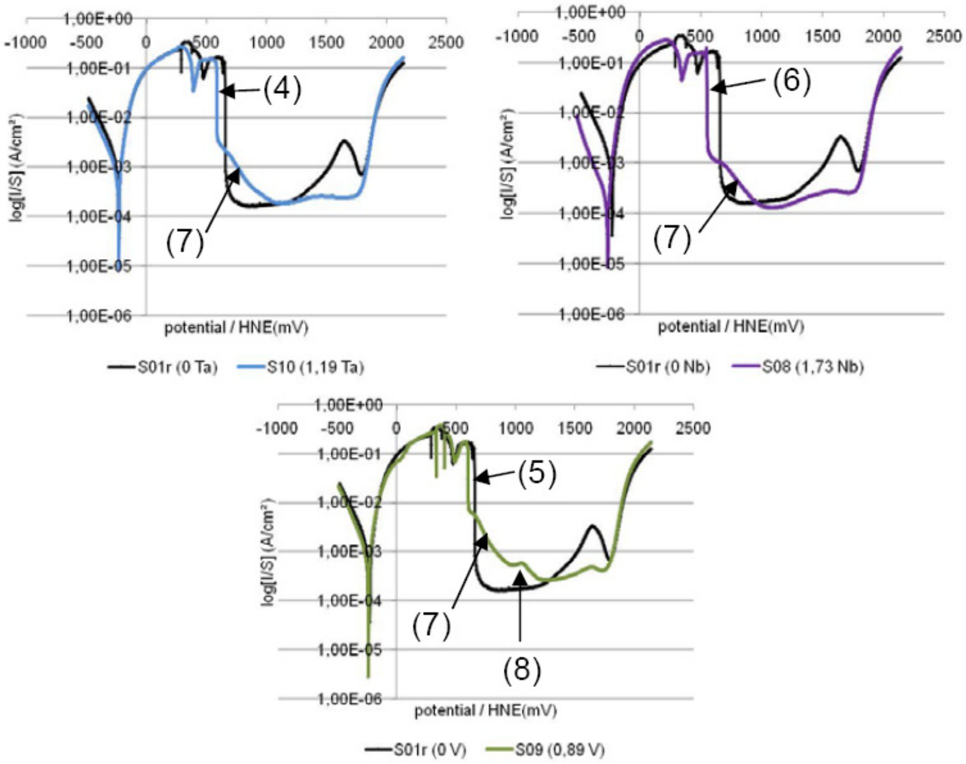

Figure 4. Effect of tantalum, niobium and vanadium on the E-increasing parts of the polarization curves (steels S10, S08 and S09 compared to the reference S01r)

The effects of minor elements on the corrosion behaviour of steels in such acid solutions were previously studied in numerous works when these alloys were stainless steels, but more rarely when they were low alloy steels. Indeed, the latter were more studied in other aqueous solutions, such as sea water (e.g. [7]) or underground water (e.g. [8]). Therefore comparisons with earlier results are difficult to do. Nevertheless one can remind that it was previously found that niobium and tungsten were beneficial (as found here for Nb but not for W) to the corrosion resistance in dilute sulphuric acid solutions [4], but in the case of an austenitic stainless steel. It was also reported that sufficiently high amounts in molybdenum or chromium led to improvements in corrosion resistance for some Cr-rich steels and nickel-base alloys in sulphuric acid solutions with various concentrations [9,10] (this was the case only for Cr here). Contrarily to what was observed here, it was formerly found that silicon favors corrosion resistance, but again in the case of stainless steel able to passivate [11] for which Si decreased the passive current density.

CONCLUSIONS

The low alloy steels studied here are unsurprisingly not resistant against corrosion in a molar sulphuric solution since they logically remain in the active state if simply immersed. However they are able to passivate if a sufficiently high potential is applied. Nevertheless the presence of minor elements may slightly modify (and even significantly in the case of niobium) their corrosion potential and intensity, as well as the easiness of their passivation, their corrosion rate in the passive state and the stability in potential of the latter. To finish, one may underline the beneficial effect of niobium on all corrosion characteristics in the active state as in the passive state.

EXPERIMENTAL SECTION

All the alloys were cast using a high frequency induction furnace (CELES), by melting pure elements (Alfa Aesar, >99.9 wt.%) together under 300 mbars). Fusion and solidification were achieved in the water-cooled copper crucible of the furnace. The obtained ingots, which weighed about 100 g, were cut, tin-soldered to a plastic-isolated copper wire, and embedded in a cold resin before polishing with 1200-grit paper. The areas of steel in contact with the electrolyte were comprised between about 1 and 2 cm².

The microstructures of the steels were observed by optical microscopy after etching by Nital 4% (96% ethanol + 4% HNO_3 and their chemical compositions controlled by Wavelength Dispersion Spectrometry using a Cameca SX50 or SX100 microprobe.

The electrochemical experiments were performed using a classical three-electrodes cell containing the H_2SO_4 1M solution and a Princeton Applied Research potensiostat (model 263A) driven by the software M352 of EGG/Princeton. The electrolyte was replaced after each {3 × Rp + 1 × cyclic polarization} whole experiment.

The electrochemical experiments performed were composed of:

* the measurement of three successive polarization resistances (Rp) from E_{ocp} – 20 mV to E_{ocp} + 20 mV at 10 mV/min,

* a cyclic polarization run, from E_{ocp} – 250 mV to 1.9 V at 10 mV/min, then from 1.9 V down to E_{ocp} – 250 mV at -10 mV/min.

REFERENCES

1. G. Murry, "Aide-mémoire Métallurgie", Dunod, Paris, **2004**, chapter 12.
2. B.T. Ellison, W.R. Schmeal, *Journal of the Electrochemical Society*, **1978**, *125*, 524.
3. U. Quaranta Cabral, L. Sathler, *Metal ABM*, **1973**, *29*, 91.
4. K. Osozawa, Y. Fukase, K. Yokota, *Corrosion Eng.*, **1971**, *20*, 11.

5. M.B. Ives, J.R. Kish, J.R. Rodda, *Materials Science Forum*, **1995**, *185-188*, 887.
6. D.F. Shriver, P.W. Atkins, C.H. Langford, “Inorganic Chemistry”, Oxford University Press, Oxford, **1990**.
7. E. Dajoux, S. Malard, Y. Lefèvre, D. Kervadec, O. Gil, *Matériaux et Techniques*, **2005**, *93*, 69.
8. C. Bataillon, C. Musy, M. Roy, *J. Phys. IV France*, **2001**, 11, Pr1-267.
9. M. A. A. Tullmin, F. P. A. Robinson, *Corrosion*, **1988**, *44*, 664.
10. N. Sridhar, *Materials Performance*, **1988**, *27*, 40.
11. K. Hio, Y. Hosoi, M. Tsutsui, M. Okabe, *Journal of the Japan Institute of Metals*, **1999**, *63*, 1248.