ELSEVIER

Corrosion studies of different ferrous alloys for rolling cylinders

L. Martínez [a], C. Gómez [a], J. Lecomte-Beckers [b], F.J. Perez [a],*

[a] *Universidad Complutense de Madrid, Surface Engineering and Nanomaterials Research Group,*
Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, 28040 Madrid, Spain
[b] *Université de Liège, Dèpartement de Mètallurgie Physique, Liège, Belgium*

Abstract

The aim of this work is to study the corrosion behaviour in chloride media of a high chromium iron alloy. The influence of the surface finishing as well as the heat treatment was analysed. The technique employed for measuring the corrosion behaviour was the Electrochemical Impedance Spectroscopy, an electrochemical technique that allows the observation not only of the corrosion rates but also the changes on the corrosion mechanism of the alloy. The results showed that it is worth performing a double tempering and a having smoother surface finishing only for long exposure periods. A comparison between different oxidising conditions was also performed simulating the life in service of the hot rolling cylinders and revealed an increase in the protective properties as the oxidising time increased due to the chromium present on the alloy (18%).
© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

For years, the material used for hot rolling cylinders was Indefinite Chill Double Paired (ICDP) steel. More recently, new materials have been developed, i.e., the Hi Chromium iron (Hi–Cr) [1–3]. These alloys contains 18% Cr and, therefore, have a good resistance to thermal oxidation and good corrosion resistance. Nevertheless, some strip sticking problems appeared in the last stages of the rolling process. The lubrication was insufficient, and the strip stuck to the roll after the rolling. Certain studies have shown that the lubrication was due to the presence of oxide scales on the rolls. That is the reason why the sticking appeared, because with 18% Cr, this iron was not oxidised enough.

In this work, a study of the oxidation–corrosion behaviour of a high chromium steel with two different heat treatments was performed. In order to study the different stages of the hot rolling alloys throughout its life, different oxidising conditions were studied. Firstly, the material was studied without any further oxidation, simulating the beginning of its life. Afterwards, the samples were oxidised for 1 day at 650 °C, simulating the half of its life and finally, the samples were oxidised for 3 days at 650 °C, where the end of its life was simulated. In all these cases, the Electrochemical Impedance Spectroscopy (EIS) was used, a technique that allows the study of the electrochemical reactions at the metal–scale interface [4–7].

2. Experimental method

An iron alloy with two different heat treatments was tested in this work. The composition and heat treatments are listed in the Table 1. The samples were cut into $40 \times 40 \times 2 \text{ mm}^3$ pieces and polished with two

---

* Corresponding author. Tel.: +34 91 394 42 15; fax: +34 91 394 43 57.

E-mail address: fjperez@quim.ucm.es (F.J. Perez).

Table 1
Composition and teat treatment of the iron alloys studied

Iron alloy	C	Cr	Mo	V	Heat treatment
A: 28119	3	18	1	0.2	Quenched (from high temperature) + one-tempering
B: 28500	3	18	1	0.2	Quenched (from high temperature) + double tempering

different surface finishing: #120 and #600 SiC grit paper. The samples were cleaned with distilled water and alcohol in ultrasounds. Afterwards, additional heat treatments were carried out, where the samples were oxidised at 650 °C under air atmosphere for 1 and 3 days simulating the life in service of the alloys. Non-oxidised samples were also tested for comparison purposes.

The electrochemical tests were performed by means of Electrochemical Impedance Spectroscopy (EIS) at room temperature in a 0.5 M NaCl solution. The reference electrode was an Ag/AgCl electrode and the counter electrode was made of stainless steel. The EIS measurements were carried out at the open circuit potential with amplitude of 5 mV in a frequency range from 30 kHz to 10 mHz after the stabilisation of the open circuit potential in order to obtain accurate AC-impedance results. Different measurements were made from 0 to 168 h of immersion. All experiments were recorded with a frequency response analyser Solartron 1255 and a potentiostat EG&G 283. The impedance results were fitted into Boukamp equivalent circuit simulation programme [8].

After each experiment, the corroded specimens were slightly washed with distilled water and visually observed.

3. Results and discussion

Fig. 1 shows the surface aspect of all the tested samples after the electrochemical tests. The comparison revealed that depending on the oxidising conditions, different surfaces were found. To begin with, the general aspect of the surfaces was different before the electrochemical tests depending on the pre-oxidising conditions. The samples without oxidation presented the typical aspect of a metallic surface, whereas the samples oxidised for one day presented a darker surface where certain oxidation have taken place. The samples oxidised for three days presented rust in their surfaces. In this case, the rust formation was more important in the A alloy than in the B alloy.

After the electrochemical tests, in general terms, for the same oxidation treatment, the smoother surface finishing (#600) presented a better surface aspect at the end of the experiments. In addition, the A alloy presented a slightly better surface condition after the electrochemical tests than the B alloy.

Depending on the oxidising conditions prior to the electrochemical tests, a different morphology of the

corrosion could be distinguished. The non-oxidised samples presented signs of a generalised corrosion process with the whole corroded area, although small pits throughout the surfaces were also observed with an homogeneous distribution. In the samples oxidised for 1 day, the localised corrosion is clearer than in the non-oxidised samples, although certain differences could be established: firstly, a smaller pits density than in the non-oxidised samples was observed; secondly, it seems that once a pit was nucleated, it grew faster than in the non-oxidised sample as revealed the bigger pit's size; to finish with, in this case the pit's distribution is not homogeneous. It must be borne in mind that pit is a random process. After the oxidation process, a Cr-rich oxide scale started growing, even though this formation did not seem enough to cover the whole surface and protect it. As a consequence, less pit nucleation events took place in the oxidised samples, although they grew faster that in the non-oxidised samples.

Finally, the samples oxidised for 3 days presented rust in their surfaces that might proportion protection to the alloys, as less quantity of pits were found. Only in the case of the B alloy, where the lower amount of rust was formed, more evidences of localised corrosion were found.

In Figs. 2–5, a comparison between the corrosion behaviour of each alloy is presented for different oxidation and immersion times, and different surface finishing.

In Fig. 2 shows the Nyquist diagram of the samples without oxidation after 2 h (Fig. 2(a)) and 24 h (Fig. 2(b)) of immersion. At the beginning of the experiment (Fig. 2(a)), all the samples shows a capacitive loop that represented one time-constant on the impedance spectra and, in consequence, one reaction on the electrode/electrolyte interface responsible for the corrosion behaviour of each sample. The diameter of the capacitive loops informed about the corrosion resistance of each sample as it represented the charge transfer resistance (R_t) of the alloy [9]. However, the depression of the semicircle could represent heterogeneities on the corroding surfaces and, therefore, an additional time-constant in the impedance spectra.

The results showed that The samples with the #120 surface finishing presented a better corrosion behaviour in comparison to the same samples with a smoother surface finishing (#600), as revealed the bigger capacitive loops of the Nyquist diagram that represented a higher charge transfer resistance (R_t). At this time, the double

NON-OXIDISED
A# 120

1 DAY OXIDATION
A# 120

3 DAYS OXIDATION
A# 120

A# 600

A# 600

A# 600

B# 120

B# 120
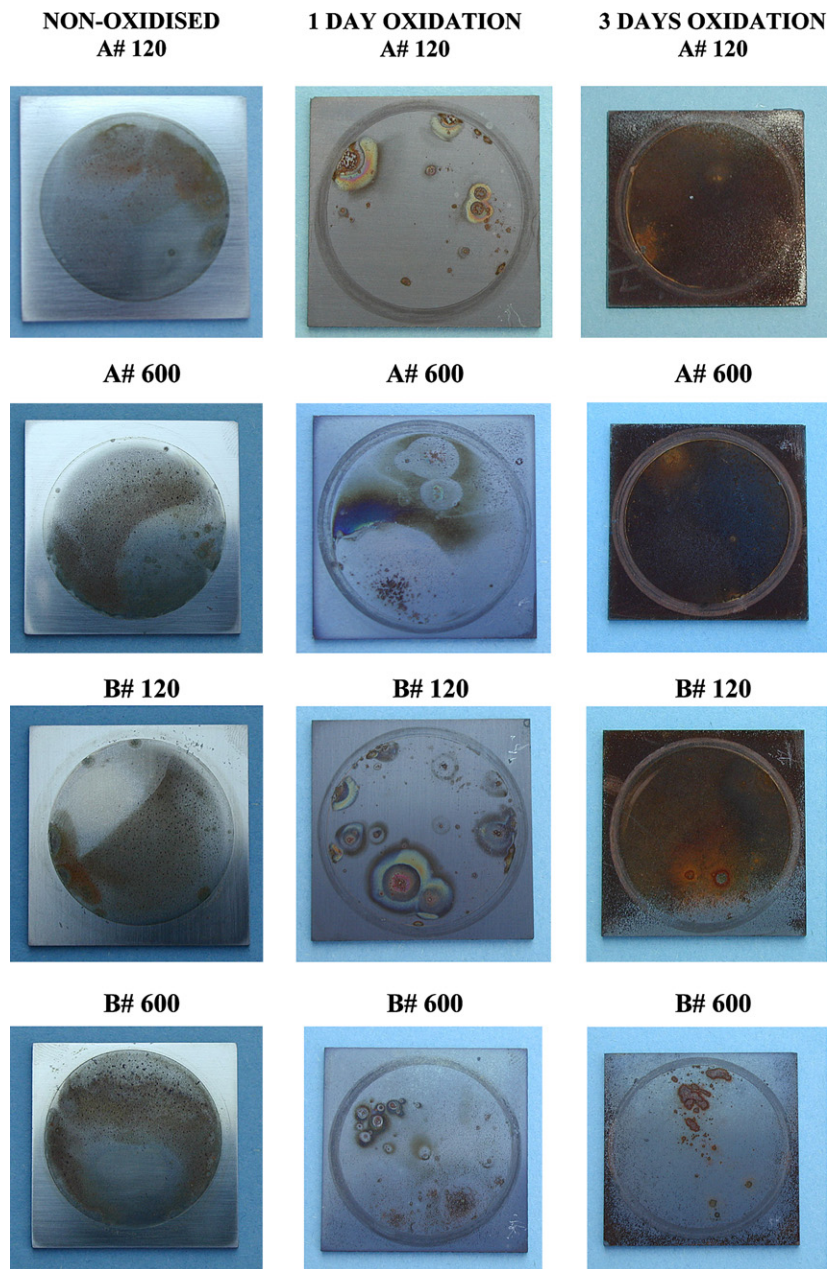
B# 120

B# 600

B# 600

B# 600

Fig. 1. Superficial aspect of the samples after the electrochemical tests.

tempering (B alloy) presented a better corrosion behaviour than the single tempering (A alloy). Therefore, the B alloy with the rougher surface finishing showed the better protective properties.

After 24 h in contact with the solution (Fig. 2(b)), capacitive loops were also observed in each sample. However, the smaller size in comparison to the 2 h spectra revealed a decrease in the R_t values and, therefore, in the corrosion resistance. The B alloy with the #120 surface finishing, which presented the best corrosion behaviour at lower immersion periods, showed after 24 h an important decrease in the corrosion resistance. On the contrary, the A alloy with the same finishing kept simi-

lar values in comparison to the 2 h spectra and presented the best corrosion behaviour till the end of the experiment. Afterwards, both A and B alloys with the smoother surface finishing presented similar behaviours, intermediate between the A and B alloy with the rougher finishing, showing that there is no need to do a double tempering in order to increase the protective properties. In this conditions, the A alloy with the #120 surface finishing presented the better corrosion behaviour if no further oxidation treatment took place.

For the theoretical interpretation of the results, in some cases, the impedance of an electrochemical system is equivalent to an electrical circuit composed by passive
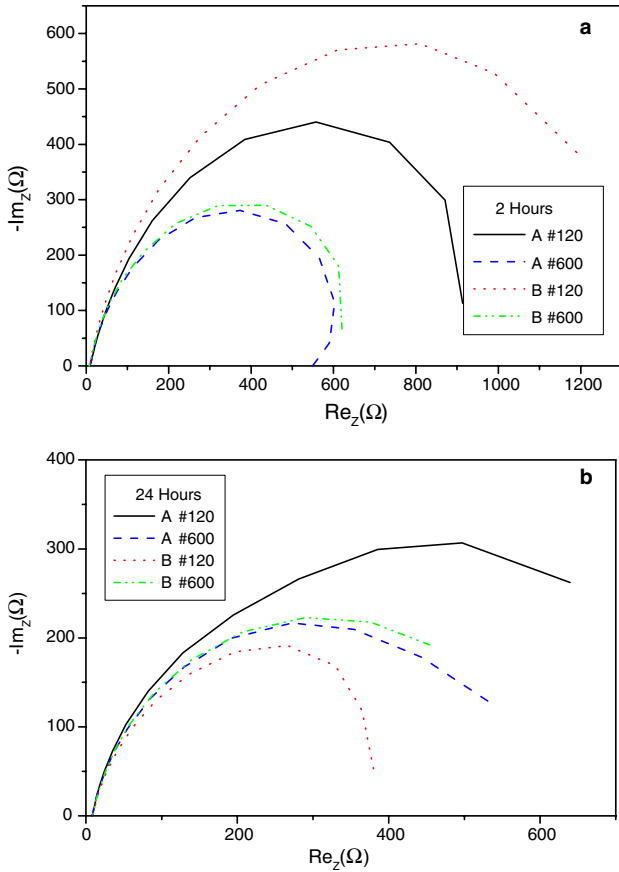
Fig. 2. Nyquist diagram for the non-oxidised samples after: (a) 2 h and (b) 24 h of immersion in 0.5 M NaCl solution.
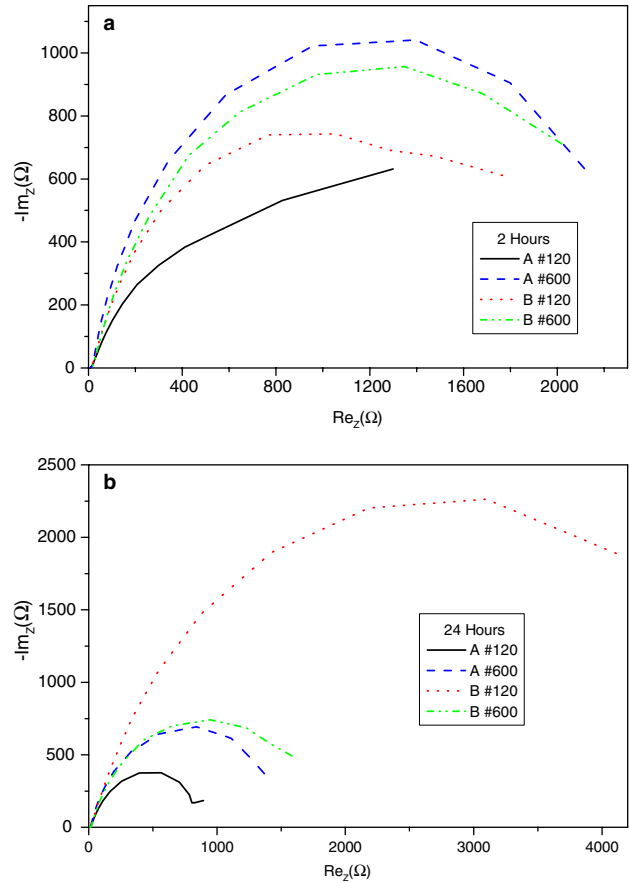

Fig. 4. Nyquist diagram for the samples oxidised for 1 day after: (a) 2 h and (b) 24 h of immersion in 0.5 M NaCl solution.
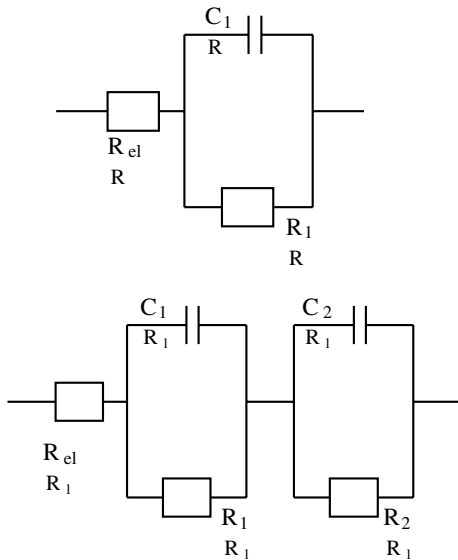

Fig. 3. Equivalent circuits purposed for the impedance tests.

elements [10,11]. In each electrode, the charge separation in the alloy/electrolyte interface can be represented by a capacitance and the difficult for the charge transfer (R_1) that reflects the electron movement in the corrosion process can be represented as a resistance [12]. Finally, the electrolyte resistance is represented by an additional resistance R_{el}. These three elements form the circuit purposed by Randles [13], the simplest equivalent circuit that represents a corroding surface. This circuit has been widely used to explain several electrochemical systems [11] and is one of the equivalent circuits purposed in this work (Fig. 3(a)). The addition of new elements allows the representation of more complex processes. In this case, the possible presence of two time-constants was represented by another group of resistance and capacitor in parallel between them and in series with the other components of the circuit (Fig. 3(b)). This equivalent circuit represents to a double layer in contact with the solution. The combination of the passive elements of this equivalent circuit can describe other equivalent circuits with a physical meaning able to represent other corroding systems with an analogue response.

For the fitting, Constant Phase Elements (CPE) instead of capacitors were used. This parameter is usually employed to represent real corroding surfaces, as it considered the deviations from ideality [14].

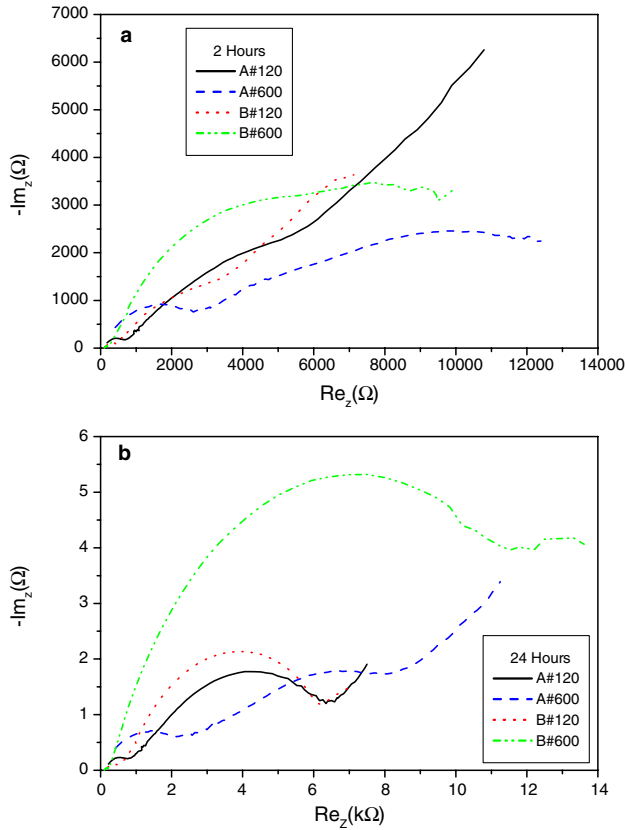$$Z_{CPE} = Y_o(j\omega)^{-n}, \tag{1}$$

Fig. 5. Nyquist diagram for the samples oxidised for 3 days after: (a) 2 h and (b) 24 h of immersion in 0.5 M NaCl solution.

where Y_o is the admittance and n is an empirical exponent related to the surface roughness [15,16]. When $n = 1$, the CPE acts as an ideal capacitor.

Table 2 shows the parameters employed for the fitting with the Boukamp simulation program of the non-oxidised samples using both equivalent circuits. The values obtained shown that, at the beginning of the experiments (2 h), the samples presented a better fitting into a one time-constant equivalent circuit (Fig. 3(a)) due to the small values of the parameters of the second time-constant. Therefore, these results confirmed that despite the depression of the capacitive loops, the two time-constant mechanism was ruled out and there is only one reaction controlling the corrosion process.

Table 2
Equivalent circuit for the samples without oxidation

Alloy	Time (h)	R_{el} ($\Omega\,cm^2$)	R_1 ($\Omega\,cm^2$)	CPE$_1$	
				Y_{01} ($s^n/\Omega\,cm^2$)	n_1
A#120	2	8.7	1.1E+3	2.5E−3	0.81
Non-oxidised	24	8.1	7.8E+2	5.2E−3	0.83
A#600	2	9.1	7.2E+2	1.7E−3	0.84
Non-oxidised	24	7.7	5.8E+2	5.2E−3	0.83
B#120	2	7.64	1.5E+3	2.25E−3	0.82
Non-oxidised	24	8.33	4.5E+2	4.87E−3	0.82
B#600	2	7.3	7.6E+2	3.31E−3	0.82
Non-oxidised	24	8.33	5.9E+2	4.88E−3	0.83

The samples finished with #120, which presented the better corrosion resistance, showed the higher R_1 values as it was extrapolated before. In addition, both samples presented the smaller Y_0 values that revealed higher dielectric properties of the electrode interface. All the samples presented n values higher than 0.8 that represented a leaky capacitor [15,17]; that is to say, the samples presented a capacitive behaviour, although the n value revealed the presence of heterogeneities on the surfaces [15,18] that might be responsible for the imperfections of the loop.

After 24 h, the impedance spectra presented a better fitting into the Randles equivalent circuit. Once again, the small values of the R_2 (two magnitude orders smaller) revealed that there is a better fitting with a one time-constant mechanism. Therefore, although the non-perfect capacitive loops could mean other corrosion reactions that also controlled the process, they did it in a smaller amount in comparison with the main reaction. Moreover, the imperfections in the capacitive loops could be due to preferential dissolution in certain places, as at the end of the experiments the visual observation of the samples revealed the presence of a number of small pits throughout the surface.

As it was mentioned before, an extrapolation of these results could be made at the beginning of the life in service of the hot rolling cylinders. Therefore, in the first stages of the life in service, the one-tempering rougher surface performed the best in corrosion terms and it is not worth doing a double tempering or having a smoother surface finishing.

For an extrapolation of the half of the life in service of the hot rolling cylinders, in Fig. 4 are shown the Nyquist diagram of the samples oxidised for 1 day at 650 °C and different immersion times. After 2 h of immersion (Fig. 4(a)), all the samples show a capacitive loop, as occurred in Fig. 2(a) and (b). However, in general terms, the bigger R_t values, as well as an increase of approximately 0.1 V in the corrosion potential, revealed a higher corrosion resistance in comparison with the non-oxidised samples. The oxidising treatment generated an oxide layer, as shown in Fig. 1, that proportioned additional protection to the alloys. The presence of an 18%Cr in the alloy allowed the possibility of the formation of a Cr-rich layer on the surface that increased the corrosion resistance of both A and B alloys. However, this oxide layer formed did not cover homogeneously the surface sample and, as a consequence, another time-constant could be noticed from the beginning of the experiment. However, this additional time-constant took place in the high frequency range and, therefore, it is difficult to see them in the Nyquist plot.

In this case, in contrast with the results obtained for the non-oxidised samples after 2 h of immersion, the A and B alloys with the smoother finishing presented a better corrosion behaviour after 2 h (Fig. 4(a)) than the rougher surface finishing with no significant differences

between them. The rougher finishing not only presented smaller R_t values but also showed the presence of a second time-constant in the impedance spectra. This additional time-constant is not clear in the smoother surfaces. The A#120 alloy, now presented the smaller R_t values and, therefore, the higher corrosion rate. The smoother finishing probably enable a more homogeneous formation of the oxide scale than the rougher finishing. As a consequence, the presence of an additional time-constant is less evident and a bigger capacitive loop was achieved, showing higher protective properties.

After 24 h of immersion, an important change took place. The B#120 alloy showed a big increase in its protective properties and presented the better corrosion behaviour until the end of the experiments. The other samples, as occurred in the non-oxidised alloys (Fig. 2(b)), a decrease in the R_t values was observed in comparison to the 2 h spectra (Fig. 4(a)) and, therefore, presented higher corrosion rates. In these conditions, after 24 h the double tempering provides the alloy with a better corrosion resistance. While in the B alloy the better protective conditions were presented by the rougher surface finishing, in the A alloy the smoother finishing proportioned an increase in the corrosion resistance. Furthermore, only in the rougher A alloy the presence of the beginning of an additional time-constant was observed. In the other cases the presence of more than one time-constant was not clear, as only a depressed capacitive loop was registered as in the non-oxidised samples.

The fitting of the impedance spectra into equivalent circuits (Table 3) shows that, after 2 h in the corrosive media, the samples presented a better fitting into a double layer equivalent circuit (Fig. 3(b)). This could mean that the chromium oxide layer formed with the oxidation treatment is not homogeneous enough to cover the whole surface and, therefore, two different regions

of the surface in contact with the solution could be distinguished. A comparison with the values obtained in the fitting of the non-oxidised samples (Table 2) revealed a higher resistance (R_1) of the samples oxidised for one day, verifying the increase in the protective properties. In addition, a decrease in the Y_0 values revealed higher dielectric properties of the oxidised surfaces that also proportioned additional protection to the alloys. The fact that the second time-constant is not clearly defined in the impedance spectra makes that certain values are not accurate – for instance, $n < 0.5$. Therefore, the values obtained for the fitting with the equivalent circuit of Fig. 3(a) were also included.

After 24 h of immersion, the samples also fitted into a two time-constant equivalent circuit (Fig. 3(b)). In this case, as occurs in the non-oxidised samples, at 24 h the surface of the samples were covered with oxidation products. In general, a decrease in both resistance values was observed in comparison to the 2 h fitting. Only in the case of the B#120 alloy, the sample that presented the better corrosion behaviour, an increase in the resistance was observed.

The extrapolation of these results revealed that at the half of the life of the rolling cylinders, a double tempering proportioned additional protection to the alloy. In addition, the rougher surface finishing proportioned the better protective conditions of this double tempered alloy.

For an extrapolation of the end of the life in service, the Fig. 5(a) and (b) show the Nyquist diagrams of the samples oxidised for 3 days at 650 °C. After 2 h of immersion (Fig. 5(a)), three time constants could be noticed in each spectrum. As a consequence, there are three reactions controlling the corrosion mechanism of the samples oxidised for three days. The reason for this behaviour could be attributed to the presence of rust in the surface of the samples. Fig. 1 showed the presence

Table 3
Equivalent circuit for the samples oxidised for 1 day at 650 °C

Alloy	Circuit	Time (h)	R_{el} ($\Omega\,cm^2$)	R_1 ($\Omega\,cm^2$)	CPE$_1$		R_2 ($\Omega\,cm^2$)	CPE$_2$	
					Y_{01} ($s^n/\Omega\,cm^2$)	n_1		Y_{02} ($s^n/\Omega\,cm^2$)	n_2
A#120	a	2	9.37	2.08E+3	1.99E−3	0.65			
Oxidised	b	2	7.1	1.6E+3	1.8E−3	0.7	5.5	8.1E−4	0.56
1 day	a	24	9.86	1.08E+3	1.37E−3	0.74			
650 °C	b	24	5	1.45E+3	3.2E−2	0.17	8.8E2	1.2E−3	0.86
A#600	a	2	8.7	2.98E+3	1.7E−3	0.79			
Oxidised	b	2	3.1	2.4E+3	1.6E−3	0.9	1E2	2.8E−2	0.16
1 day	a	24	8.68	2.06E+3	2.03E−3	0.77			
650 °C	b	24	1.5	1.5E+3	1.9E−3	0.89	68.9	2.6E−2	0.16
B#120	a	2	9.42	2.56E+3	1.46E−3	0.75			
Oxidised	b	2	7	2E+3	1.34E−3	0.82	13.7	8.7E−3	0.37
1 day	a	24	9.45	7.39E+3	1.02E−3	0.76			
650 °C	b	24	6.48	5.7E+3	1E−3	0.84	7.36E3	2.12E−2	0.27
B#600	a	2	11.2	3.05E+3	1.62E−3	0.74			
Oxidised	b	2	5.2	2.4E+3	1.52E−3	0.84	32.4	1.45E−2	0.22
1 day	a	24	11.3	2.77E+3	1.77E−3	0.73			
650 °C	b	24	5.5	1.8E+3	1.5E−3	0.85	25.3	9.8E−3	0.26

of an heterogeneous layer of rust on the surface. In this case, the longer-term oxidation allowed the generation of a thicker oxide layer. The Cr present in the alloy proportioned protection to the alloys, and higher R_t values were registered in comparison to lower oxidation times. As a consequence, one of the reactions that controlled the corrosion mechanism could be due to the rust; another to the oxidised part of the surface without rust and the third reaction could be due to the localised corrosion sites. Therefore, it is difficult to compare the results obtained with lower oxidised samples. However, a further increase in their protective properties was achieved. The R_t values of all the samples increased several magnitude orders due to the apparition of additional time-constants in their spectra that revealed a more complex corrosion mechanism. The #120 surface finishing presented a better corrosion behaviour than the smoother #600 and, once again, the double tempering is not worthy because no big differences were found.

After 24 h of immersion (Fig. 5(b)), the samples oxidised for 3 days presented a better definition of the time-constants and an increase of the R_t values in comparison to the 2 h spectra (Fig. 5(a)). This corrosion behaviour could be explained by the rust on the surface that prevents corrosion.

As occurred with the 1 day oxidised samples, the double tempered sample presented a better behaviour. However, in this case the best behaviour was achieved in the case of the #600 surface finishing.

In this case, the fitting with the equivalent circuit was not included due to the problems found in the 1 day oxidised samples and due to the complexity of the spectra obtained.

An extrapolation of the life in service revealed that, at the end of the life in service, this kind of alloys increased the protective properties. The Cr content allowed the formation of an oxide scale in the surface that increased the corrosion resistance and prevented corrosion. The increasing oxidation time also allowed a thicker oxide on the surface that proportioned further protection.

However, this oxide formation also promoted a modification of the corrosion mechanism. The EIS spectra evidenced the presence of additional TC in the oxidised samples. This fact, together with the visual observation of the samples after the electrochemical analysis (Fig. 1) revealed a tendency towards suffering a localised corrosion process. This kind of corrosion is typical of materials that presented protective layers such as coatings or passive layers. In this case, the layer is not homogeneous and penetration of the electrolyte might occur. Therefore, the presence of more than OTC represented the general surface on contact with the corrosive media and the defective corroding regions. A redistribution of the circuit elements could represent several corrosion processes.

4. Conclusions

- It is not necessary to obtain a smoother surface finishing (#600) because with #120 finishing, similar results were obtained.
- A double tempering also revealed a similar behaviour as the single tempering. Only after a long-term oxidation, the sample with the double tempering and the smoother surface finishing showed the best behaviour.
- As the oxidation time increase, the corrosion resistance is also increased due to the formation of a Chromium oxide layer on the surface, which improve the protective properties of the alloy in contact with the aggressive media. Therefore, the higher corrosion resistance properties were achieved after 3 days at 650 °C.

References

[1] Lee S, Kim DH, Ryu JH, Shin K. Met Mat Trans A 1997;28: 2595.
[2] Jin W, Choi JY, Lee YY. ISIJ Int 1998;38:739.
[3] Lecomte-Beckers J, Terziev L, Breyer JP, Delcour N. Rev Metall-Cahiers d'informations Tech 1999;96:1401.
[4] Tato W, Landolt D. J Electrochem Soc 1998;145-12:4173.
[5] Jütner K. Electrochim Acta 1990;35:1501.
[6] Bouzek K. Corros Sci 1999;41:2113.
[7] Kendig M, Mansfeld F. In: 6th International congress on metallic corrosion, vol. 3, Toronto, Canada, June; 1984. p. 74.
[8] Bernard A. Boukamp. Equivalent circuit 3.96. University of Twente (1988/89).
[9] Basics of Electrochemical Impedance Spectroscopy (EIS)". EG&G Princeton Applied Research; 1989.
[10] Ross Macdonald J, editor. Impedance spectroscopy. Emphasizing solid materials and systems. Wiley; 1987.
[11] Hladky K, Callow LM, Dawson JL. Br Corros J 1980;15:20.
[12] Brett Christopher MA, Oliveira Brett Ana María. Elecrochemistry: principles, methods and applications. Oxford University Press; 2000.
[13] Randles JEB. Discuss Faraday Soc 1947;1:11.
[14] Martini Emilse MA, Muller Induvirges L. Corros Sci 2000;42: 443.
[15] Liu C, Bi Q, Leyland A, Matthews A. Corros Sci 2003:1243.
[16] Yoo Ji-Hong, Ahn Seung-Ho, Kim Jung-Gu, Lee Sang-Yul. Surf Coat Technol 2002;157:47.
[17] Li Moucheng, Luo Suzhen, Zeng Chaoliu, Shen Jianian, Lin Haichao, Cao Chu'nan. Corros Sci 2004;46:1369.
[18] Ismali Kh, Jayaraman A, Wood TK, Earthman JC. Electrochim Acta 1999;44:4685.