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Corrosion behaviour of different hot rolled steels

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Abstract

The oxidation–corrosion behaviour of hot rolled alloys was examined by electrochemical impedance spectroscopy. The corrosion behaviour of the non-oxidised alloys was first determined in order to have a reference behaviour. Then, each alloy was oxidised for 1 and 3 days at 650 °C in air and its corrosion behaviour was also determined. For all the alloys, Fe₂O₃ was formed at the scale–gas interface. However, the Fe₂O₃ crystallographic structures varied as a function of the alloy composition. Differences in the corrosion behaviour are due to the thickness, the microstructure and the porosity of the scale. The new graphite chromium iron alloy (Hi-Cr + C) have an oxidation–corrosion behaviour close to the indefinite chill double paired (ICDP) one and is therefore thought to be a good candidate to replace the ICPD alloy. In the case of the high speed steel (HSS) alloy, the oxidation–corrosion kinetics are too slow to prevent sticking problems. The Co addition decreases the corrosion–oxidation rates for the non-oxidised and oxidised samples but this effect is limited in time.

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1. Introduction

For years, the material used for hot rolling cylinders was ICDP (indefinite chill double paired) steel. More recently, new materials have been developed, for instance, the Hi chromium iron (Hi-Cr) [1–3]. This iron contains 18% chromium, and therefore has a good resistance to thermal oxidation. Nevertheless, some strip sticking problems appeared in the last stages of the rolling process. The lubrication was not sufficient, after rolling, and the strip was stuck to the roll. Studies have shown that the lubrication was due to the presence of oxide scales on the rolls. This is the reason why the sticking appeared, because with 18% Cr, this iron was not oxidised enough. The further evolution was to reduce the amount of Cr and add Mo, V and W in relatively high amounts. With only 7% chromium and 2% carbon, the high speed steel (HSS) [1–3] has a lower but still too high a resistance to oxidation. A special version of the HSS steel with a 4% Co addition was also studied and unfortunately has shown a higher oxidation resistance than the HSS steel [1]. The most recent alloy (graphite chromium iron or Hi-Cr + graphite) developed for the hot rolling rolls is an intermediate alloy between the ICDP alloys, which has a good thermal and oxidation behaviour (high C, Si and Ni contents) and the HSS alloys with a 6–8% Cr content, which allows a better wear resistance and hardness due to the presence of chromium carbides.

In this work, a comparison between the oxidation–corrosion behaviour of the new graphite chromium iron and other alloys used as hot rolling rolls is made. A new oxidation characterisation technique was used, which consists of the study of the electrochemical reactions at the metal–scale interface, with the electrochemical impedance spectroscopy (EIS) [4–14], of the oxidised samples immersed in an aggressive medium (NaCl, H₂SO₄...).

Thermodynamic calculations, XRD and optical and SEM microscope characterisations were used with the EIS results to propose an electrochemical model of the systems studied.

2. Experimental method

The iron alloy compositions tested in this work are listed in Table 1. All the samples were cut into 40 × 40 × 2 mm³ sheets, grounded to #120 and #600 SiC grit paper and cleaned with distilled water and alcohol.

Table 1
Composition of the iron alloys studied

Iron alloy	C	Si	Ni	Cr	Mo	Mn	V	W
ICDP	3.32	0.93	4.39	1.78	0.4	0.96	–	–
HSS ^a	1.8	0.6	1.5	7.0	3.5	<0.5	4	2
Hi-Cr + graphite	3.63	2.87	3.84	6.33	1.19	0.47	<0.5	–

^a Two kinds of HSS: one without Co and one with the addition of 4% Co (HSS Co).

The steel sheets were oxidised at 650 °C under air atmosphere for 1 and 3 days, taken out of the furnace and superficially cooled by a water spray to simulate the working conditions. Non-oxidised samples were also tested.

Electrochemical tests were performed at room temperature using 0.5 M NaCl electrolyte. The reference electrode was an Ag/AgCl electrode and the counter electrode was made of stainless steel.

The EIS measurements started after the stabilisation of the corrosion potential in order to obtain accurate ac-impedance results. Several measurements were made from 0 h to 144 h of immersion. They were carried out at the open circuit potential with an amplitude of 5 mV in the frequency range from 30 kHz to 10 mHz. All experiments were recorded with a frequency response analyser Solartron 1255 and a potentiostat EG&G 283.

After each experiment, the corroded specimens were slightly washed with distilled water and analysed by X-ray diffraction (XRD), optical and SEM microscopy. Some thermodynamic calculations were made with the HSC software to study the influence of the alloying elements on the scale formation.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

In Figs. 1–6, a comparison between each alloy is presented for different oxidation and immersion times, and different surface finishing.

Fig. 1 shows the Nyquist diagram of all the samples without oxidation after 2 h of immersion in NaCl solution. The HSS family presented a higher corrosion resistance as revealed by the larger R_{ct} values of this alloy in comparison with the rest alloys

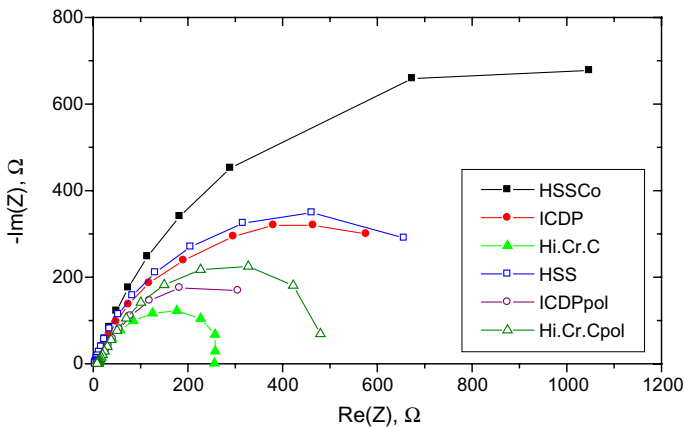


Fig. 1. Nyquist diagram obtained for the samples without oxidation, immersed for 2 h using 0.5 M NaCl solution (pol = ground to 600 grade).

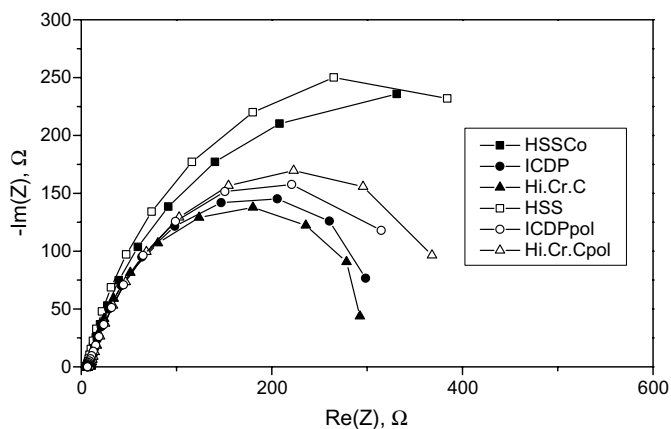


Fig. 2. Nyquist diagram obtained for the samples without oxidation, immersed for 24 h in 0.5 M NaCl solution (pol = ground to 600 grade).

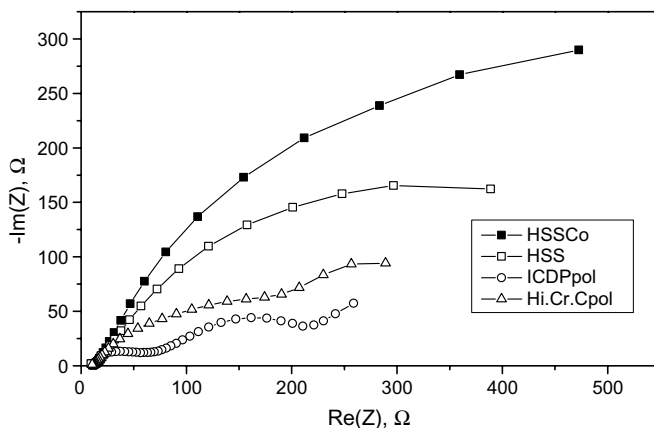


Fig. 3. Nyquist diagram obtained for the samples oxidised 1 day and immersed 2 h in 0.5 M NaCl solution (pol = ground to 600 grade).

tested. Inside this family, the Co addition promotes a higher corrosion resistance, as it acts on the surface stabilising the iron oxidation and, therefore, provide a more protective character to the alloy.

The ICDP and Hi-Cr + graphite (Hi-Cr + C) alloys presented similar behaviours with the smoother surface finishing (SiC#600). However, the samples with a rougher finishing (SiC#120) presented different behaviours. On the other hand, the ICDP showed a good corrosion resistance, close to the HSS resistance values, whereas the rougher Hi-Cr + C presented a higher corrosion rate among all the tested samples.

Fig. 2 shows the Nyquist diagram of the same samples after 24 h of immersion. At this time, a certain decrease of the R_{ct} values was observed in comparison with the

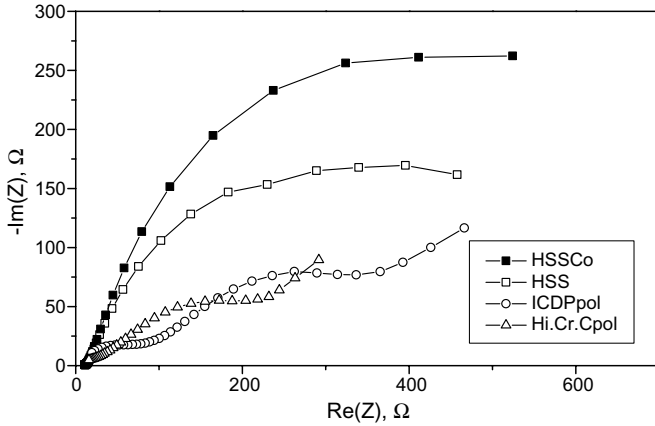


Fig. 4. Nyquist diagram obtained for the samples oxidised for 1 day and immersed for 24 h in 0.5 M NaCl solution (pol = ground to 600 grade).

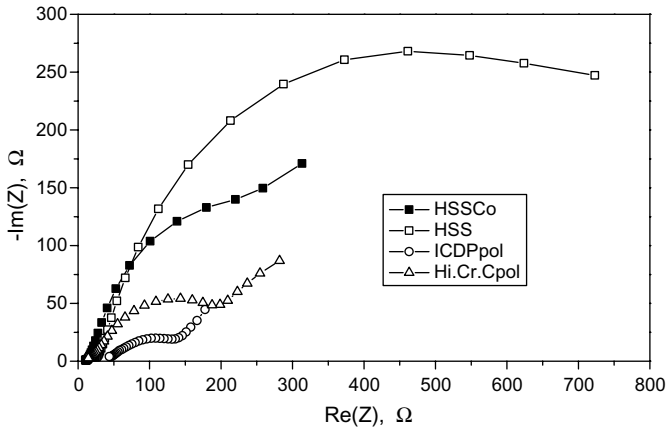


Fig. 5. Nyquist diagram obtained for the samples oxidised for 3 days and immersed for 2 h in 0.5 M NaCl solution.

2 h spectra, except in the Hi-Cr + C non ground sample, the one that presented a higher corrosion rate for lower immersion periods, and now show a slight increase (50 Ω) in its R_{ct} . The most significant decrease of R_{ct} is shown by the HSS Co alloy, where a decrease of about 50% was noticed. Nevertheless, this sample continued showing a better behaviour than the other samples. The Co effect seems to be limited in time. This element acts as an iron oxide stabiliser, but once the oxide is formed on the material's surface, the effect of this element does not seem as important as for lower immersion periods. The same tendency was observed in both ICDP and Hi-Cr + C alloys and surface finishing, with similar R_{ct} . After 24 h in contact with the solution, the ground samples presented a higher corrosion resistance than the non

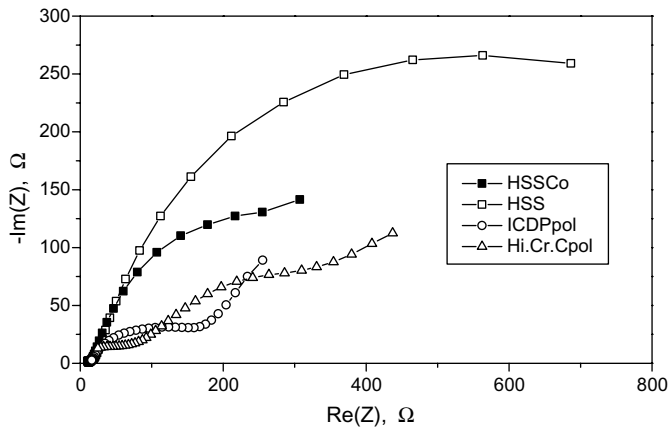


Fig. 6. Nyquist diagram obtained for the samples oxidised for 3 days and immersed for 24 h in 0.5 M NaCl solution (pol = ground to 600 grade).

ground ones. This could mean that with the smoother surface finishing, a fewer number of defects were placed on the surface of the material and, therefore, a better response is achieved. From now on, only the response of the ground samples will be plotted so as to simplify the discussion.

There is only one reaction controlling the corrosion process of all samples, as revealed by the one time-constant mechanism. This reaction is the homogeneous corrosion of the surface in contact with the solution. The higher corrosion resistance of the HSS alloys is due to a higher amount of alloying elements such as Cr and Mo that promote the formation of an oxide layer on the surface of the material.

Figs. 3 and 4 shows the Nyquist diagram of the samples oxidised for 1 day at 650 °C and different immersion times in the chloride solution. A decrease in the corrosion resistance in comparison to the non-oxidised samples was found in all the specimens.

After 2 h of immersion (Fig. 3), as occurred in the non-oxidising conditions, the HSS with Co presented the slowest corrosion rate, followed by the HSS without Co. Differences between both spectra are smaller than those shown by the same samples without oxidation (Fig. 1). The HSS alloys not only have smaller corrosion rates than the other materials, but also a different corrosion mechanism. This could be explained in terms of the number of time-constants of each spectrum. HSS alloys showed a single time-constant, as occurred in all the non-oxidised samples (Figs. 1 and 2), whereas Hi-Cr + C showed two time-constants and ICDP a three time-constant mechanism.

The one time-constant mechanism of the HSS alloys revealed homogeneous corrosion process where differences on the impedance values were due to a superficial oxide layer present in the surface of the material. The two time-constants of the Hi-Cr + C could be due to an incomplete oxidation of the surface samples and, therefore, the presence of heterogeneities on the surface. Finally, in the case of ICDP alloys, where a faster corrosion rate was obtained, some damaged parts could have

reached the bulk, leading the rough material to be in contact with the solution which could explain the apparition of the third time-constant. In all cases, differences in the R_{ct} values in comparison with Figs. 1 and 2 were due to the different oxides present on the surface.

After 24 h of immersion (Fig. 4), the HSS with Co continued showing better behaviour, increasing differences with the other HSS and showing the same shape as at 2 h of immersion. In contrast with this behaviour, the apparition of a third time-constant is found in the Hi-Cr + C spectrum. It seems that now the rough material is being corroded by the solution. This third time-constant could have appeared at 2 h in the high frequency range, but it was not distinguishable. The ICDP alloy shows the same corrosion mechanism but with a certain increase of the impedance values, which means a certain recovery of its behaviour.

Figs. 5 and 6 show the Nyquist diagrams of the samples oxidised for 3 days at 650 °C and different immersion times in the chloride solution. The impedance values are of the same level as the ones found after 1 day oxidation with the exception of the HSS without Co, where an increase in the corrosion resistance was observed.

Fig. 5 shows the impedance spectra of the oxidised samples after 2 h of immersion. This oxidising conditions leads to major changes in HSS alloy spectra. In this case, the one which has the slower corrosion rate is the HSS without Co, followed by the HSS with Co. The oxidation for 3 days produces the apparition of a new time-constant in the low frequency range of the HSS Co, which is not clear enough to distinguish whether it is due to a new corrosion process or due to a certain diffusion through the oxide layer on the surface. Therefore, the Co addition, which is beneficial for short oxidation times does not seem to promote the same changes as the other HSS alloy blocking an increase in the corrosion resistance.

The ICDP alloy continued showing a lower corrosion resistance, although certain changes have taken place. After 3 days of oxidation, it is not possible to notice the third time-constant which appeared after one day oxidation probably because a thicker scale was formed and the bulk is not reached. This alloy has the lowest chromium content of the three alloys tested and this could be one of the main causes for the lower corrosion resistance. In addition, longer oxidising conditions lead to a higher amount of rust on the surface, which makes the diffusion of the corrosion products difficult. In these conditions, the response of the material is conditioned by the diffusion of these products and the apparition of another time-constant is impeded.

The Hi-Cr + C alloys presented no significant differences with the increasing oxidising conditions, but the two time-constants are more clearly defined than for one oxidation day. This effect cannot be clearly defined and, further investigations in this direction will be made.

After 24 h of immersion (Fig. 6), the HSS and ICDP alloys have a similar tendency than at 2 h of immersion. However, in the Hi-Cr + C spectrum, as occurs after 1 day oxidation, another time-constant appeared.

In conclusion, the HSS family presents the higher corrosion resistance of the tested alloys. The addition of Cobalt to this alloy promotes a more protective character for short oxidising conditions. However, after 3 days of oxidation, the

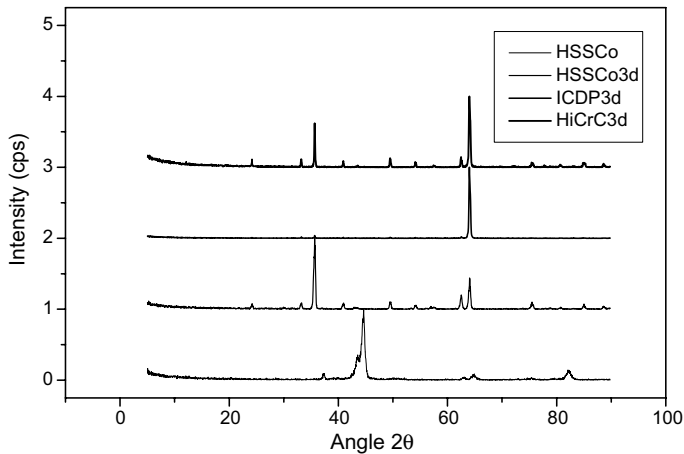


Fig. 7. XRD spectra of the alloys oxidised for 3 days and a non-oxidised HSS Co samples. Only the Fe_2O_3 is detected in outer scale. The intensity variation of the α and γ phases is clearly seen for different alloys.

Co addition does not seem to have a beneficial effect in the corrosion protection of this alloy. On the other hand, the ICDP alloy presented a lower corrosion protection due to a lower amount of protective alloying elements such as chromium.

3.2. X-ray diffraction (XRD)

The XRD spectra of all the alloys are shown in Fig. 7. In all cases, Fe_2O_3 were formed but the relative intensity of the peaks varies from one alloy to another. This could mean a higher amount of oxide in the case of the HSS alloy and a lower content in the ICDP. However, the presence of Cr in the oxide cannot be ruled out in the case of HSS, where a higher amount of Cr is present in the alloy, because the relative angles of both compounds have nearly the same and a slight shift was found in the case of this alloy.

4. Conclusions

- The HSS family presents the best corrosion behaviour under all oxidising conditions tested in this work, due to a higher amount of alloying elements such as Cr or Mo.
- The addition of cobalt hot rolled steels has only effect during the first steps of the lifetime of the rolling cylinder, when it acts as an iron stabiliser and increase the protective properties of the alloy. Once the oxide is formed, no additional effect was found and for longer oxidising conditions the alloy without Co presented better protective properties.

- Hi-Cr + C alloy also presents a better corrosion resistance than ICDP alloys, although much lower than HSS alloys. The higher Cr content is probably responsible for this improvement.
- Therefore, both HSS and Hi-Cr + C families are a good alternative for hot rolling cylinders in terms of corrosion resistance, even though HSS is found much more protective.

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