613

IMPEDANCE MEASUREMENTS ON THE PASSIVE LAYERS OF STAINLESS DIFFERENT HEAT TREATED STEELS

Mojca Slemnik, Valter Doleček, Miran Gaberšček[*]

Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia
[*]*National Institute of Chemistry, Hajdrihova 19, 61115 Ljubljana, Slovenia*

Abstract

The behavior of differently heat-treated X20Cr13 steels in 0.1 M H_2SO_4 was studied using the electrochemical impedance spectroscopy. Impedance spectra were recorded at constant passsive potentials of 0.2, 0.4 and 0.6 V vs. SCE, respectively. At low passive potential, 0.2 V vs. SCE, impedance spectra typical for an active – passive transition were observed. The assumption has been made, that they are the result of the adsorption process, caused by bound water, which blocks the passive layer of steel and leads to corrosion rate reduction. The process is the most significant at the oil and the air-quenched, but less at the tempered steel. When more noble potentials are approached the impedance spectra become typical for passive metals and the value of resistance and capacitance differ from each other with respect to the heat treatment.

Introduction

Electrochemical impedance spectroscopy (EIS) is a well-established powerful technique for investigating electrochemical and corrosion systems. This technique has been successfully used for the study of corrosion-resistive systems such as organic coatings,[1,2] concrete,[3] systems containing inhibitors,[4] and is one of the principal methods for investigating interfacial reaction mechanisms, particularly anodic dissolution and passivation of metals.[5]

From a theoretical point of view, the impedance is also one of most relevant quantities that can be measured in electrochemistry and corrosion.

Many corrosion processes are controlled kinetically by the charge transfer at the interface and/or by the transport of a reactant to, or a product from the surface and have a profound effect on the rates of corrosion of metals. Both processes have been studied extensively using EIS.[6] The analysis of mechanisms for corrosion of iron and other metals in aqueous solutions and also the identification of the elementary steps involved in active dissolution, active – passive transitions and passivation of metals have been studied with EIS.[7]

For stainless steels, a dynamic model of the passive film and the role of bound water incorporated into the film, was proposed.[8] The resistance of the passive film on stainless steels was found to depend on the potential and the time of film formation, film thickness and the change of composition. Nevertheless, the structure and the composition of the film depend also on the method of surface preparation.[9]

In our former work, stainless steel X20Cr13 was exposed to various heat treatments: quenched on air, quenched in oil and quenched in oil and tempered. After the passivation, the measurements of electrochemical noise on the passive layers have been made with the purpose to determine the influence of the heat treatments on corrosion resistance of steels.[10]

In the present work, electrochemical impedance spectroscopy measurements have been made at same conditions: differently heat-treated steels were passivated under potentiostatic conditions and then the impedance spectra were measured. The values of passive layers resistance, R_{pl}, and interfacial capacitance, C_i, were determined by the extrapolation as proposed by other workers[11] using standard software, until the computer-generated plots closely matched the experimental data. The comparison of simulation parameters between steels has been made to assign the corrosion resistance on the basis of heat treatment.

Experimental method

The material tested was a 13 − chromium stainless steel labeled as X20Cr13 made in Steel Works Ravne, Slovenia.

The samples with 10 mm diameter and 3 mm thickness were treated under the following conditions:

annealed 20 minutes at 1000 °C, quenched on air

annealed 20 minutes at 1000 °C, quenched in oil

annealed 20 minutes at 1000 °C, quenched in oil and tempered 1 h at 250 °C.

The test samples were mechanically polished with 400, 800 and 1000 abrasive papers and fine polished with diamond pastes almost to a mirror quality. The degreasing was performed in acetone.

The measurements were made in a standard Tacussel glass cell with the specimen as a working electrode, the platinum auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The cell was filled with 300 ml of 0.1 M H_2SO_4 solution. The measurements were performed at room temperature. Impedance measurements were made with a Solarton 1287 Electrochemical Interface and a 1250 Frequency response analyzer and the data were collected using ZPlot. R and C data were estimated and interpreted using a fit circle technique made with ZWiew software. Both softwares were developed by Scribner Associates, Inc. An example of a fit circle technique is shown in Fig. 1. For samples passivated at 0.2 V/SCE a fit circle was made only on the first slightly indicated semicircle, which represents the R of passivated surface (R_{pl}).

Measurements were performed in a frequency range from 60 kHz down to 0.001 Hz. The amplitude of excitation voltage was 30 mV.

EIS measurements were carried out after a 10-min polarization at a given potential. Passivation potentials were chosen in the passive region of the classical polarization curve for X20Cr13.[12]
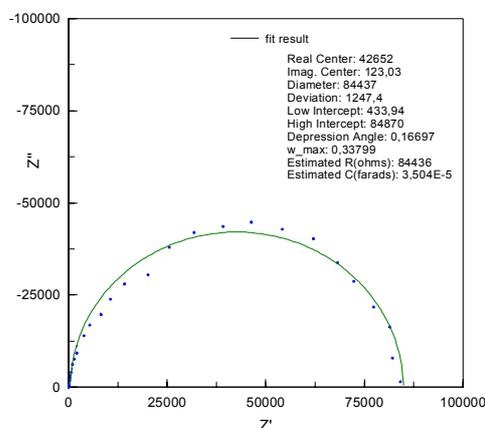

Fig.1.: A fit circle made for the impedance spectra for the air – quenched X20Cr13 passivated in 0.1 M H_2SO_4 at 0.6 V / SCE

Results and discussion

Annealed X20Cr13 steel contains alloying elements, which reduce the carbon diffusion and increase corrosion resistance. Quenching of steel prevents carbon diffusion, increases hardness, but leads to brittleness. Therefore, the steel has to be tempered before use. Tempering reduces the tension and increases the toughness, but on the other hand, causes the carbon to precipitate, leading to pitting corrosion. Passivation

means that under appropriate conditions, the surface of a metal is covered with a protective (usually oxide) film, which also includes bound water incorporated into the layer, but yet the bonds of water groups to the metal are relatively weak.[8]

Typical complex - plane impedance spectra for studied materials at 0.2 V/SCE, 0.4 V/SCE and 0.6 V/SCE are presented in Figs. 2, 5, and 6.

The high-frequency portions of the measured spectra always had typical semicircular shapes of complex - plane plots, whereas at low frequencies the plots deviated from these semicircles. At the lowest passive potential measured, 0.2 V/SCE (Fig. 2), the low-frequency ends are turning upwards and also to the left, more significantly so for the oil and air-quenched and less for the tempered steel. Such impedance spectra are typical for systems undergoing an active – passive transition.

The sudden transition of metal / solution interface from a state of active dissolution to the passive state is phenomenon of a great scientific and technological interest. This transition has been attributed to the formation of either a monolayer (or less) of absorbed oxygen on the surface, or to the coverage of surface by a three – dimensional corrosion product film. In either case, the reactive metal is shielded from the aqueous environment and the current drops sharply to a low value that is determined by the movement of ions or vacancies across the film. In the complex plane impedance diagram the high frequency arm of the impedance is typical of a resistive / capacitive system, but the impedance locus terminates in a negative differential resistance as $\omega \rightarrow 0$. At higher potentials, the high – frequency locus is again dominated by an apparent resistive / capacitive response, but the low – frequency arm is not observed to terminate at the real axis, in this case because of the very high value for the polarization resistance. The origin of the negative resistance can be accounted for theoretically in terms of an increasing coverage of the surface by an absorbed intermediate as the potential is increased. Thus, the low – frequency loop exhibited is due to relaxations involving this surface species.[7]

In our case, for the oil and air-quenched steel, the adsorption process may refer to a strong incorporation of water molecules into the passive film.

In our article[10] in which electrochemical noise measurements were used to detect the amount and the form of bound water incorporated into the passive film, a conclusion

was made, that at 0.2 V/SCE the current fluctuations were the highest for all samples resulting from the highest amount and strongest dynamics of bound water on the steel but, in general, they did not change markedly with respect to the heat treatment. With impedance measurements, this difference becomes more distinctive since the spectra differ from each other: the oil and air-quenched steels show a strong adsorption effect, visible as an upward and left turn of curves in Fig. 2. The fact is, that in these two samples the bound water is considered to be incorporated with relatively weak bonds but in high amount into the thin passive layers in a form of M–OH$_2$ or M–OH.[10]
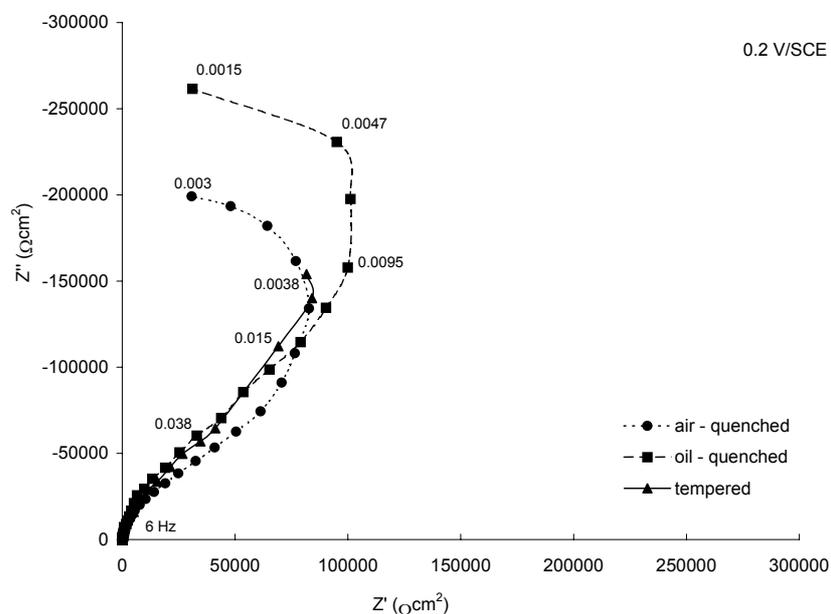

Fig.2.: Impedance spectra for X20Cr13 passivated in 0.1 M H$_2$SO$_4$ at 0.2 V / SCE

For the tempered steel this effect is less pronounced, since the upward and left turn of the curve is only slightly indicated. It seems that this sample has less adsorbed water in the passive layer at this potential or this adsorbed layer is less stable. (Fig. 2)

In Fig. 3, the resistance at the lowest passivating potential of 0.2V /SCE shows high values for all samples. It can be assumed that the adsorbed water somehow blocks the passive layer.
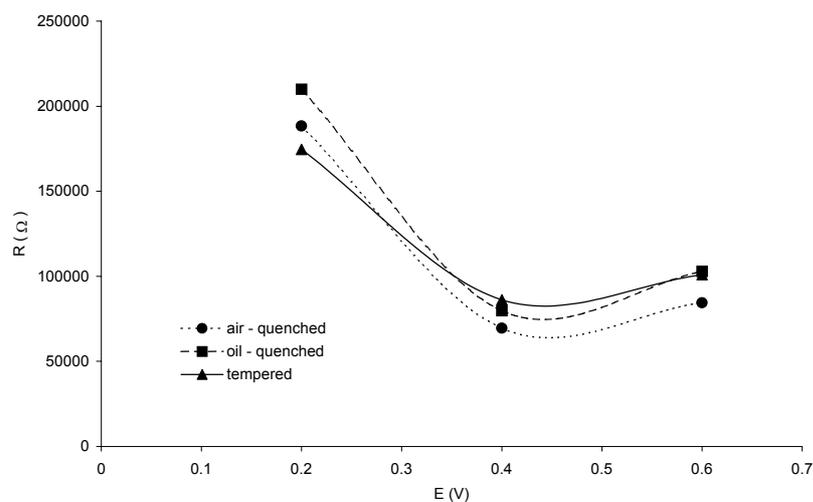
Fig.3.: Passive layer resistance, R_{pl}, for X20Cr13passivated in 0.1 M H_2SO_4 at different potentials

Such a blockade decreases the current density and increases the resistance of the layer, whereas the C_i remains at the highest value, (Fig. 4).
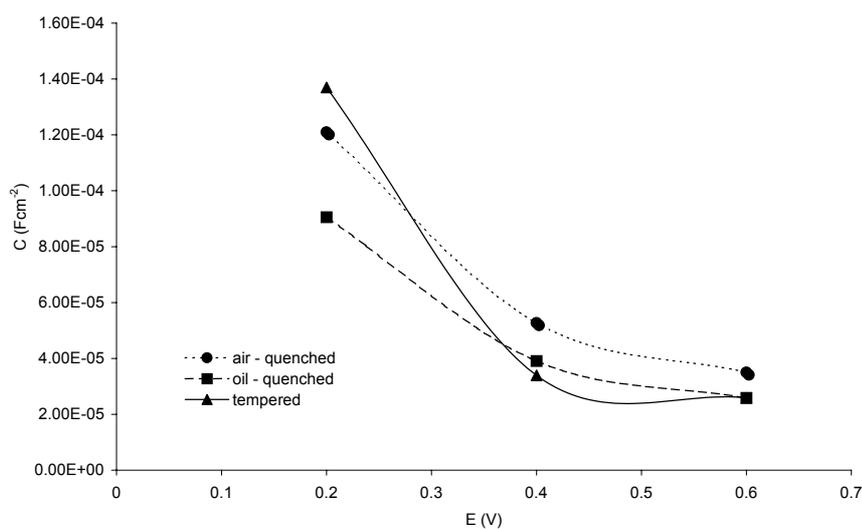

Fig.4.: Interfacial capacitance C_i, for X20Cr13 passivated in 0.1 M H_2SO_4 at different potentials

Binding of water molecules into the passive layer of steel at a low passive potential is a dynamic process: the adsorbed layer frequently disrupts and restores itself. The conclusion has been made, that the value of C_i is criteria for the dynamics of the process and the R_{pl} for the blockade of passive layer of steel. C_i has the highest value for the tempered steel, where the dynamics of adsorption is obviously the largest, but the blockade of passive layer of steel is less significant, since the value of R_{pl} for the tempered steel is the lowest at that potential. Blocking the passive layer with adsorbed

species is most expressed in the case of oil-quenched steel, which also has the highest value of R_{pl}, whereas this sample shows the most significant adsorption part of a semicircle.
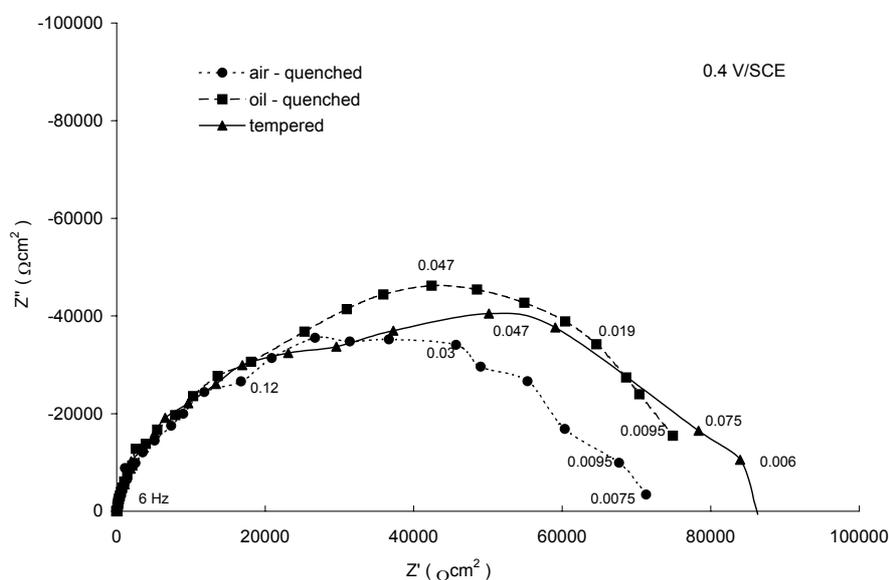

Fig.5.: Impedance spectra for X20Cr13 passivated in 0.1 M H_2SO_4 at 0.4 V / SCE

The increase in the potential increases the thickness of the passive film, changes the content of elements (Fe, Cr) and decreases the amount of bound water, which forms

M-O-M and M-OH-M bridges.[8] Such a structure decreases the number of active sites in metallic dissolution. This happens approximately at 0.4 V/SCE and at this potential the low-frequency tail is expected to turn downwards, so that the part of the impedance spectrum which represents the adsorption, disappears. Indeed, the spectra shown in Fig.5 have the expected shape, thus confirming the proposed mechanism. Moreover, at 0.4 V/SCE, the capacitance drops to values between 20 and 40 μFcm^{-2} (Fig. 4), typical for the double layer capacitance rather than for a capacitance due to dynamic adsorption process. This fact further confirms the proposed mechanism.

At the more noble potential of 0.6 V/SCE, semicircles preserve the same shape confirming the same mechanism as that for 0.4 V/SCE, i.e., typical for passivated metals, but have highest value of resistance of passive layers, (Fig. 6). At this potential, the number of active sites depends on the structure of steel, its passive film and the bridge formation of bound water.[10] A comparison between all three samples shows that

second semicircles differ with respect to the heat treatment of steel: the highest impedance value has been found for the oil-quenched sample, although the tempered steel has a very similar value. The air-quenched steel shows significantly lower impedance, (Figs. 5, 6), also the lowest passive layer resistance (Fig. 3) and the highest capacitance value (Fig. 4) which indicates the poorest passivation of this sample at chosen potentials.
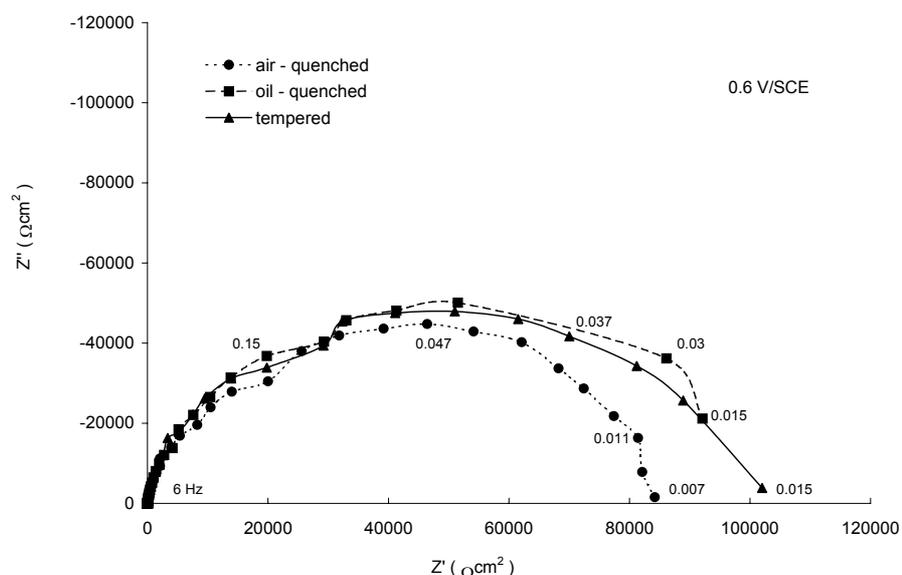

Fig.6.: Impedance spectra for X20Cr13 passivated in 0.1 M H_2SO_4 at 0.6 V / SCE

References

1. F. Mansfield, L. T. Han, C. C. Lee, C. Chen, G. Zhang, H. Xiao *Corrosion Science* **1997**, *39*, 255–279.
2. F. Mansfield *Models in Chemistry* **1995**, *132* (4), 619–631.
3. C. Andrae, L. Soler, X. R. Novoa *Materials Science Forum* **1995**, *192-194*, 843–856.
4. R. D. Armstrong, M. F. Bell, J. P. Hlomes *Corrosion Science* **1979**, *19*, 297–304.
5. I. Epelboin, C. Gabrielli, M. Keddam *Corrosion Science* **1975**, *15*, 155–165.
6. D. D. Macdonald *Techniques for Characterization of Electrodes and Electrochemical Processes* **1991**, 515–580.
7. M. Keddam, O. R. Mattos, H. Takenouti *J. Electrochem. Soc*. **1981**, *128*, 257-266; M. Keddam, J. F. Lizee, C. Pallotta, H. Takenouti *J. Electrochem. Soc* **1984**, *131*, 2016–2024.
8. G. Okamoto *Corrosion Science* **1973**, *13*, 471–489.
9. K. Doss, A. R. Brooks, C. R. Clayton *Proc. Int. Congr. Met. Corros. NRC*, Canada, Toronto, **1984,** *1*, 138–142.
10. M. Slemnik, A. Petek, V. Doleček *Werkst. Korros*. **1995**, *46*, 13–17.
11. K. Hladky, L. M. Callow, J. L. Dawson *Br. Corros*. *J.* **1980**, *15*, 20–27.
12. M. Slemnik, M.Sc. Thesis, Ljubljana, Slovenia, **1994**.

Povzetek

Merili smo impedanco na različno toplotno obdelanih jeklih X20Cr13 v 0.1 M H_2SO_4, pri konstantnih napetostih pasiviranja 0.2 V, 0.4 V in 0.6 V/NKE. Pri nizki pasivni napetosti 0.2 V/NKE opazimo obliko impedančnih krivulj, ki so sicer tipične za aktivno – pasivni prehod, zato predpostavljamo, da se pri tej napetosti pojavi proces adsorpcije, ki blokira pasivno površino jekla in znižuje korozijsko hitrost, kar se pokaže v relativno visoki vrednosti upornosti pasivnih plasti. Adsorpcijski proces, ki ga pripisujemo vezani vodi v pasivni plasti je izrazit pri jeklu, kaljenem v olju in na zraku, manj pa za popuščano jeklo. Pri bolj pozitivnih pasivnih napetostih postanejo impedančni diagrami tipični za pasivirane kovine, vrednosti upornosti in kapacitivnosti pa se med seboj razlikujejo glede na toplotno obdelavo jekel.