

The passivation treatment of stainless steel surface studied by Electrochemical Impedance Spectroscopy

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ABSTRACT

The properties of oxide films formed on ferritic, austenitic Cr-Ni and austenitic Mn-Ni stainless steel's surface after passivation procedure for 30, 60 and 120 min in aqueous solution containing nitric acid were investigated by means of electrochemical impedance spectroscopy (EIS). For all studied stainless steel grades an optimal passivation time was 60 min when taking into account, both the surface roughness increase and the EIS parameters describing the resistance and capacitance character of the formed oxide layer of double-layer nature.

1. INTRODUCTION

Stainless structures play an important role in different processing equipment (piping, processing tanks, etc.), where corrosion resistance is a crucial factor. Stainless are the primary construction material in the chemical industry, pulp and paper industry, petrochemical and pharmaceutical industry as well food processing and architectural applications, both load-bearing and decorative. This is due to their high durability, versatile application and outstanding price-quality ratio comparing more corrosion resistant, but also more expensive nickel and titanium alloys. It is therefore an increasing interest of basic mechanical testing and design methodology development of different stainless steel members under loading conditions i.e. tubular members, hollow sections columns and many other (Kiyamaz et al. 2014, Dai et al. 2010, Kiyamaz 2009).

Stainless steel structure corrosion resistance is strictly related to its surface conditions regarding both surface roughness as well as properties of the formed passive layer. The surface roughness plays an important role in keeping the stainless steel surface free of corrosion signs. The lowest surface roughness the better its corrosion resistance what is connected with easier surface cleaning and harder sticking

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of dirt and chlorides to the surface involved in the local corrosion phenomena (pitting, crevices, etc.). The passivity phenomenon is extremely important, since it is the basic mechanism in the corrosion resistance of stainless steels. It involves the formation of a very fine barrier layer at the alloy surface (passive layer) of the order of few nm thick, which reduces the corrosion rate to negligible levels. This film forms in the presence of oxidising agents, and are protective in that it has the ability to self-heal in a variety of environments. This passive layer or film adheres strongly to the metal substrate and prevents virtually all contact between the alloy and the aggressive species in the surrounding medium.

The research focused on the explanation of the passive layer structure and its structural-functional description of the stainless steels ongoing for many years and are the subject of numerous studies (Freire et al. 2010, Kim and Young 2013, Boissy et al. 2015). According to the one of accepted theories the passive layer formed on the stainless steel show the nature of a semiconductor. Despite this, their exact electrical structure is not fully explained. It is assumed that the passive layer has a “double-layer” structure proposed originally by Okamoto (c 1973), wherein the inner layer is mainly formed of chromium oxides and has the characteristics of the semiconductor p-type of the barrier characteristics for diffusing ions, while the outside layer is thinner, and more hydrated, rich in iron oxides and corrosion products, and has the characteristics of the semiconductor n-type.

The passivity of the stainless steel structures is achieved by post manufacturing chemical surface treatment, where during contact with oxidising acid (like nitric acid) the thickness of the oxide layer is effectively increased. The chemical surface treatment usually is composed of degreasing, where organic contaminations are eliminated, the pickling process (using strong acids able to dissolve stainless steel surface) when embedded iron particles are dissolved and the passivation process promoting formation of the passive film on a fresh surface. The process of surface passivation is controlled by contact time of passivation solution with the surface that depend on the chemical composition of the stainless steel, i.e. more alloyed stainless steel grades demand longer treatment. For these reasons, the determination of passive layer stability and the identification and explanation of the mechanisms which determine its destruction at the stainless steel alloys is in particular interest. In summary, the interpretation and understanding of the passive layer formation during the passivation process and its growth is greatly facilitated by considering the underlying electrochemistry. In particular, it shows that the basic chemical composition of the alloys is an essential factor determining the corrosion resistance (passivation behaviour) and the processing history (surface finish) can also interact with the propensity to corrosion or passivation.

The main purpose of the paper was to evaluate duration of passivation treatment on formed oxide layer properties by electrochemical impedance spectroscopy (EIS) of several stainless steel grades of varied chemical composition and surface finish.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The stainless steels of chemical composition presented in Table 1 after surface chemical treatment described below have been studied by means of electrochemical

impedance spectroscopy (EIS) to evaluate passive layer properties. The test samples having different surface finish, so different initial surface roughness were employed. The research was carried on the 1.5 mm sheets with standard mill finish, cold rolled 2B for 1.4301, polished P120 grit size for YU4 (J4) grade and cold rolled 2R (BA – bright annealed) in the case of 1.4016 grade. The different surface finish of studied grades was introduced in order to evaluate the relationship between initial surface finish and passivation process. The Pitting Resistance Equivalent Number PREN was calculated according to the formula: $PREN = \%Cr + 3.3 \times (\%Mo) + 16 \times (\%N)$ for studied steels (Table 1). The PREN number is related to the pitting corrosion resistance of the stainless steel, the higher PREN the highest corrosion resistance. It should be noted, that the PREN is referring only to the chemical composition of an alloy not to its thermal or processing history.

Table 1. Chemical composition of studied stainless steels

Designation EN / UNS / trade name	PREN	Chemical composition, wt. %							
		C	Si	Mn	Cr	Ni	Mo	Cu	N
1.4016 / UNS S43000 / -	16.2	0.068	0.65	0.82	16.21	-	-	-	-
- / UNS S20430 / YU4	16.0	0.063	0.76	7.59	15.27	4.03	-	1.61	0.045
1.4301 / UNS S30400 / -	19.5	0.053	0.29	1.22	18.47	8.10	-	-	0.063

The samples of dimension 5x10 were prepared to surface treatment. The chemical surface treatment was composed of the following steps: degreasing, pickling and passivation using dedicated chemical solutions, where for degreasing PROSOLV 541 was applied, for pickling process the PROCAP INOX and for passivation the PROCIV 300 solution provided by Chimimeca Polska S.A. company. After each step of surface chemical treatment samples surface was rinsed in tap water in order to clean remained traces of used chemicals. The final passivation step was performed for different times 30, 60 and 120 min (Table 2) to validate passivation.

Table 2. The chemical surface treatment process

Process	Degreasing	Pickling	Passivation
Solution trade name:	PROSOLV 541	PROCAP INOX	PROCIV 300
Main chemical components	HNO ₃ , HF, Alcohol	HNO ₃ , HF	HNO ₃
Process duration, min	30	60	30, 60, 120

The surface roughness were controlled after the chemical surface treatment measuring R_a and R_z parameters. The Profilometer Surtronic 25 of Taylor Hobson Precision was applied, where L_t - length of travel was set to 4.0 mm and L_c - Cutoff length to 0.8 mm.

The electrochemical impedance spectroscopy (EIS) was applied to determine the electrical characteristics of passivated stainless steel surface in 1M NaCl solution. This was done by recording changes in the resistance and impedance at variable frequency range from 100 kHz to 0,01 Hz by the signal of 10mV. Based on registered results the Bode and Nyquist relationship was determined. Basing on collected EIS impedance parameters the resistance of formed oxide layer was discussed.

3. RESULTS AND DISCUSSION

Surface roughness play a decisive role in the corrosion resistance of stainless steel alloys. The higher roughness the contaminations and chlorides can easier stick to the surface and initiate corrosion phenomena. The strong decrease in corrosion resistance takes place when the surface roughness increases above $R_a = 0.5 \mu\text{m}$, so the smoother, more mirror-like finish shows higher corrosion resistance. The influence of passivation time on the surface roughness was studied by means of arithmetic average roughness parameter R_a (Fig. 2) and mean roughness depth R_z (Fig. 3).

The lowest initial surface roughness of ferritic stainless steel grade 1.4016 of 2R finish (mirror-like finish) was increased during passivation. The surface roughness parameters after passivation for 30 min were following $R_a = 0.02 \mu\text{m}$ and $R_z = 0.17 \mu\text{m}$ and were practically the same like after 60 min, while after passivation for 120 min they highly increased, where $R_a = 1.2 \mu\text{m}$ and $R_z = 7.63 \mu\text{m}$. The passivation for 120 min results to be too long for this grade increasing significantly surface roughness what can be explained by the excessive local non uniform build-up of a passive layer.

The surface roughness defined by R_a parameter of chromium-nickel austenitic stainless steel 1.4301 of a mill finish 2B not changed significantly during passivation between 30 and 120 min ($R_a = 0.17\text{-}0.15 \mu\text{m}$), while the R_z parameter describing the mean roughness depth increased during passivation for 30 and 60 min ($R_z = 1.4$ and $1.46 \mu\text{m}$, respectively), but for 120 min it was slightly decreased ($R_z = 1.24 \mu\text{m}$). The build-up of a passive layer seems to stop after 120 min, what can be associated to the compacting of formed oxide layer than its growth and thickening.

The manganese-nickel austenitic stainless steel of YU4/UNS S20430 grade having polished surface, during tested passivation treatments clearly increased both surface roughness parameters R_a and R_z , where R_a increased from $1.38 \mu\text{m}$ for 30 min. to $2.06 \mu\text{m}$ for 120 min and R_z from 9.4 to $13.1 \mu\text{m}$, respectively. This austenitic Cr-Mn-Ni grade shows similar behaviour when prolonged passivated like the ferritic 1.4016 grade (Figs. 2 and 3).

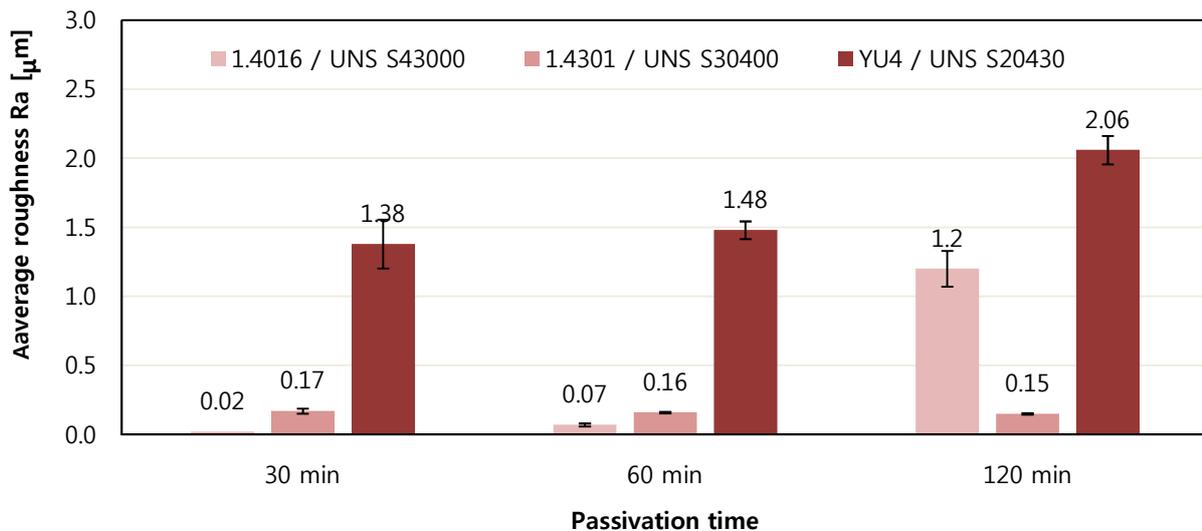


Fig. 2 The influence of passivation time on the average roughness R_a of studied stainless steel surfaces having different initial surface finish

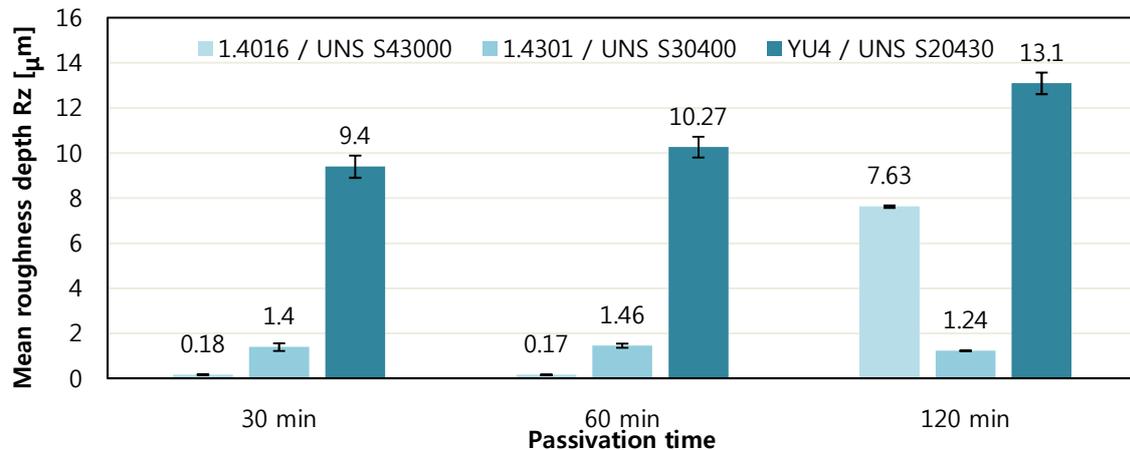


Fig. 3 The influence of passivation time on the mean roughness depth R_z of studied stainless steel surfaces having different initial surface finish

The results of impedance measurements carried out in a wide frequency range provide information related to the tested corrosion system and occurring therein electrochemical processes. Interpretation of electrochemical impedance measurements involves the use of electrode-equivalent circuits (EEC). The individual elements of EECs correspond to electrochemical properties of the tested corrosion system and allow to determine the corrosion parameters, including charge transfer impedance. The EEC circuit used to fit the experimental data is presented in Fig. 4.

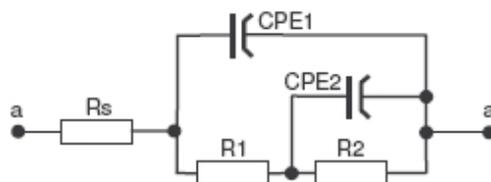


Fig. 4 The equivalent electrical circuit used to fit the impedance data

The equivalent circuit corresponds to double-layer structure of passive film formed on the stainless steel surface. Element R_s corresponds to the electrolyte resistance i.e. 3% NaCl solution, while element R_2 is the resistance and CPE_2 is the capacitance of the inner compact passive film (oxide layer). The R_1 and CPE_1 elements correspond to the resistance and capacitance respectively, of the outer porous film (hydroxide layer) of the double-layer structured passive film. For this reason the R_1 parameter can be correlated with the resistance of the electrolyte present in the porous film (Blanco et al. 2006). The modelling impedance of a more complex systems involves application of the constant phase elements (CPE). The CPE element has a fixed phase shift angle, where its impedance is described by the expression: $Z_{Cpe} = 1/Y_0 (j\omega)^n$, where Y_0 and n are the parameters related to the shift phase angle. The n parameter describes the corrosion process on the surface and the smaller n value the more heterogeneous the process. The parameter n reach values in the range from -1 to 1, where a value of -1 is

characteristic for an inductance and a value of 1 corresponds to a capacitor and a value of 0 corresponds to a resistor (McDonald and Kenan 1987). In the present study the n_1 parameter related to outer porous hydroxide layer was included in the range characteristic to capacitor 0.8-0.9, while the n_2 related to the inner compact oxide layer shows more resistance characteristic, n_2 varied from 0.4 to 0.8. The thickness of the oxide layer can also be correlated to EIS parameters, basing on capacitances response (CPE_1 , CPE_2 and their sum) where the film thickness is inversely proportional to the capacitances (Feng et al. 2015).

The Nyquist plots of EIS data (Fig. 5) shows changes in slope of the impedance Z curve of passivated surfaces. The general trend of increasing impedance with passivation time can be visible indicating thickening of the passive layer and passivation of the surface. The Nyquist plots of studied stainless steels for different passivation times shows similar characteristic for individual grades, but in the case of ferritic stainless steel 1.4016 (Fig. 5a) and manganese-nickel austenitic grade YU4 (Fig. 5c) the difference in the curve run is most noticeable.

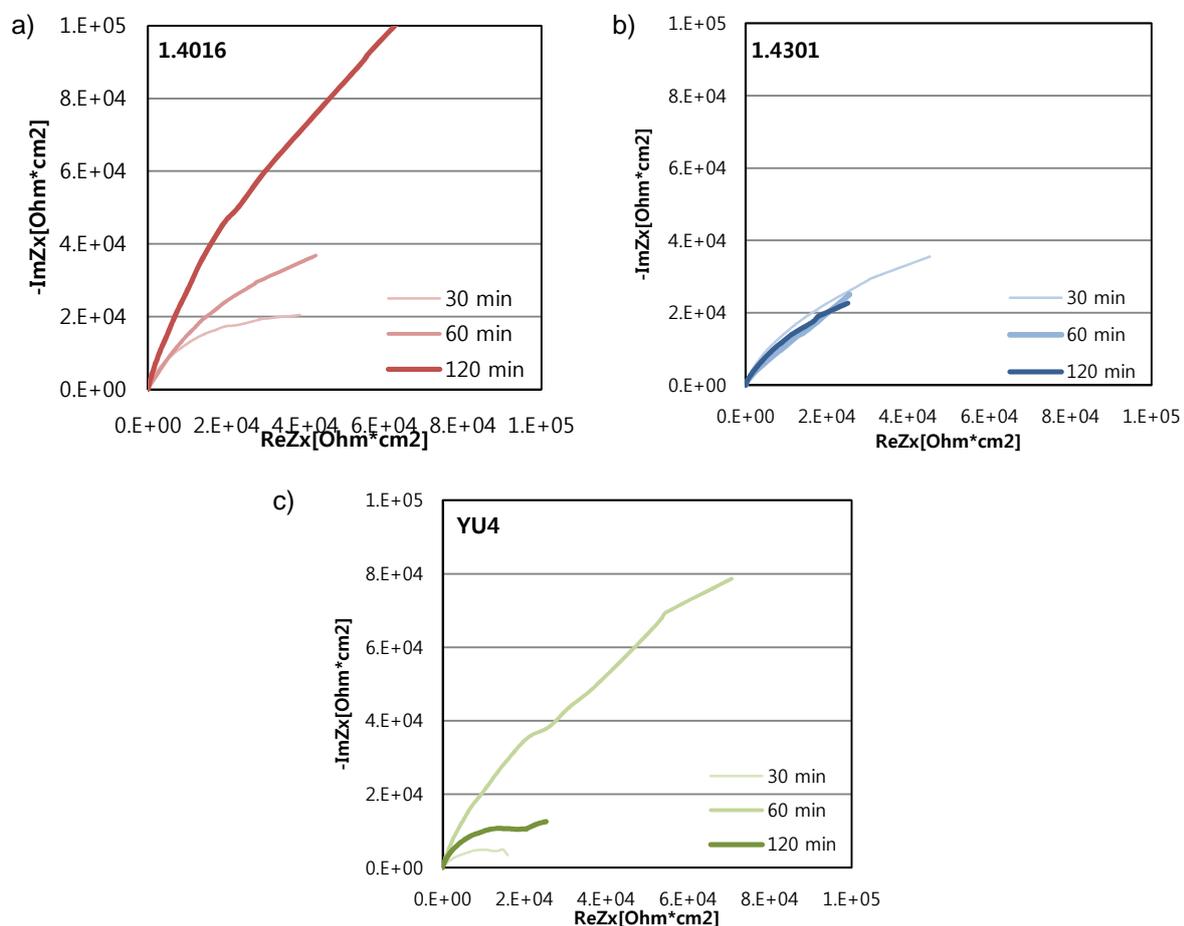


Fig. 5. The Nyquist plot of EIS data of a) ferritic 1.4016, b) austenitic 1.4301, c) austenitic YU4 stainless steels

The result of EIS data fitted to the equivalent circuit (Fig. 4) for studied stainless steels after surface passivation for 30, 60 and 120 min are reported in Table 3 and presented as the Bode plot in Figure 6.

Table 3. Equivalent circuit parameters of studied stainless steel surface passivated for different times

Grade	Passivation time, min	R_1 , Ohm*cm ²	CPE_1 , S/cm ²	R_2 , Ohm*cm ²	CPE_2 , S/cm ²	R_1+R_2 [Ohm*cm ²]	CPE_1+CPE_2
1.4016	30	1.52E+04	5.80E-05	5.85E+04	6.90E-05	7.37E+04	1.27E-04
	60	3.67E+04	3.90E-05	1.26E+05	6.00E-05	1.62E+05	9.90E-05
	120	1.43E+05	4.20E-05	4.10E+05	2.30E-05	5.53E+05	6.50E-05
1.4301	30	6.23E+03	4.50E-05	2.32E+05	4.50E-05	2.32E+05	9.00E-05
	60	7.32E+03	7.00E-05	3.40E+05	9.70E-05	3.40E+05	1.67E-04
	120	9.78E+03	1.14E-04	6.24E+04	1.10E-04	6.24E+04	2.24E-04
YU4	30	2.37E+02	1.70E-05	2.08E+05	8.30E-05	2.08E+05	1.00E-04
	60	2.36E+04	3.80E-05	3.30E+15	2.20E-05	3.30E+15	6.00E-05
	120	1.90E+04	6.40E-05	2.59E+12	2.70E-04	2.59E+12	3.34E-04

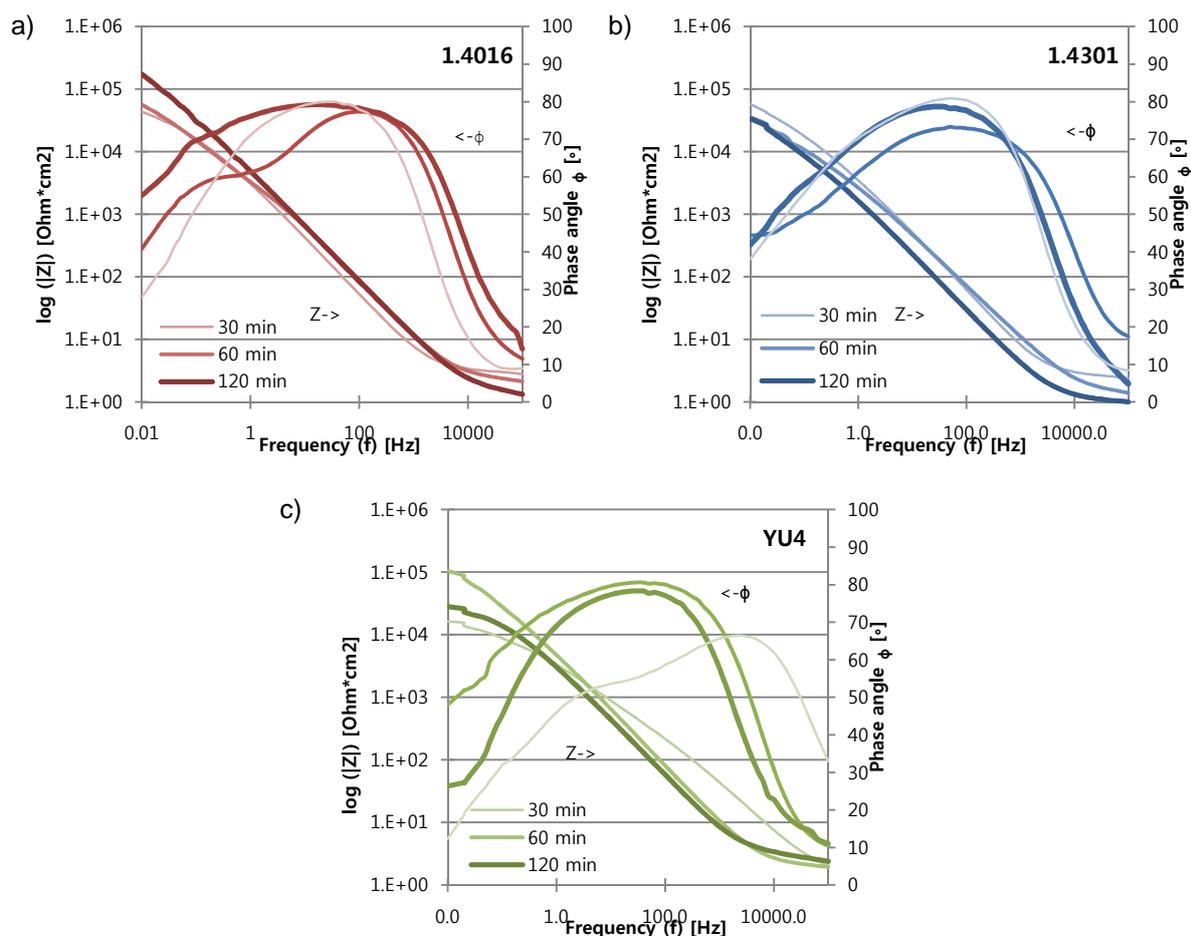


Fig. 6. The Bode phase-angle plot of fitted EIS data of a) ferritic 1.4016, b) austenitic 1.4301, c) austenitic YU4 stainless steels

The EIS Bode phase angle plots (Fig. 6) shows a high phase angles over a large frequency range, that is typical of passive materials, likely due to the presence of a passive layer on the stainless steel surface. The Bode plots shows the typical capacitive like behaviour, where the phase angle maximums are smaller than 80° what can be interpreted as a deviation from ideal capacitor behaviour (Luo et al. 2011). The similar Bode plot characteristic results have been reported in literature for passivated stainless steels (Luo et al. 2011, Blanco et al. 2006). The Bode plot analysis confirms the resistive nature of studied surfaces, as evidenced by the phase angle value close to 0 and almost constant value of $\log Z$ in the high frequency range. Moreover, the Bode phase angle plots for studied stainless steel are characterized by a well defined phase angle maximum with its peak at approximately 100Hz. However, for austenitic stainless steel YU4 passivated for 30 min the phase angle located in the 10kHz range presents a slight upward curvature and the second peak start to be visible and the phase angle (ϕ) in the high frequency range is higher than 30° (Fig. 6c).

Analysing ECC circuit parameters of studied stainless steel passivated for different times (Table 3) in the case of ferritic stainless steel 1.4016 the resistances (R_1 , R_2) of both constituent layers in a double-layer system were uniformly increased with passivation time, where R_1 increased from $1.52 \cdot 10^4$ to $1.43 \cdot 10^5$ Ohm \cdot cm 2 and R_2 from $5.85 \cdot 10^4$ to $4.1 \cdot 10^5$ Ohm \cdot cm 2 , while the capacitances CPE_1 , CPE_2 where decreased. The CPE_1 decreased from $5.8 \cdot 10^{-5}$ to $4.2 \cdot 10^{-5}$ S/cm 2 ; while the CPE_2 from $6.9 \cdot 10^{-5}$ to $2.3 \cdot 10^{-5}$ S/cm 2 . On this basis, it can be concluded that the passive layer on ferritic stainless steel surface 1.4016 become thicker and more resistant when increasing passivation time from 30 to 120 min. Closer look at the EIS data reveal that passivation for 120 min for this grade seems to be optimal, because the outer porous film of double-layer system is still resistant (electrolyte present in the film porosity stabilize) and its thickness too (stable CPE_2 parameter), while the inner compact passive film become thicker– the CPE_2 decrease and more resistant than for 60 min – higher resistances R_2 and R_1+R_2 .

The increase of passivation time of chromium-nickel austenitic stainless steel 1.4301 resulted in a slight increase of resistance R_1 (values remain at the same level of 10^3) describing outer porous hydroxide layer that becomes more stable, dense and less porous. Meanwhile, the R_2 resistance of the inner compact oxide layer was slightly increased - one order of magnitude when the passivation time was extended from 30 to 60 min, but when passivation lasted 120 min it was decreased of one order of magnitude from $3.4 \cdot 10^5$ to $6.24 \cdot 10^4$ Ohm \cdot cm 2 . The capacitances CPE_1 and CPE_2 were both increased by extending passivation treatment time, meaning thinning of the present hydroxide and oxide layers. The passivation treatment for 120 min deteriorates resistance of the inner compact passive layer even if its thickness related to the capacitance increase.

The EIS measurements of austenitic manganese rich stainless steel YU4 were characterised by most non-heterogeneous values and the bigger scatter of registered values during EIS data collection. The passivation for 60 min increased both resistance's value (R_1 , R_2) and capacitances were decreased showing improvement of formed passive layer, but the long-lasting passivation for 120 min slightly decreased both resistance and capacitor properties of formed passive layer. It should be noted that prolonging passivation from 30 to 60 min greatly increased resistance of the inner compact oxide layer of 10 orders of magnitude (R_2 changed from $2.08 \cdot 10^5$ to $3.30 \cdot 10^{15}$

Ohm*cm²), while passivation for 120 min revealed decrease of 3 orders of magnitude. In the same time the inner compact passive film thickness that is inversely proportional to the CPE_2 parameter, slightly increased – the value of CPE_2 parameter decreased of one order of magnitude. However, such a large increase in the value of resistance requires more detailed studies and is difficult to explain in the present stage of the research. High manganese austenitic stainless steel have been reported to show lower corrosion resistance than low Mn stainless steels (chromium-nickel alloys) due to the negative influence of Mn addition on the passive layer properties due to formation of manganese sulphide inclusions and preferential development on this sites of the pitting corrosion attack (Fong-Yuan Ma 2012). Analysing registered EIS results for manganese-nickel stainless steel grade YU4 the passivation time of 60 min it seems to be the best due to highest resistance parameters.

3. CONCLUSIONS

On the basis of performed studies on the influence of passivation time on electrochemical impedance spectroscopy EIS characteristic of different stainless steel grades with varied surface finish the following conclusion can be made:

- The extended passivation time increases the surface roughness of studied grades, especially after 120 min of passivation, where highly polished finish (2R type) of ferritic stainless steel revealed the highest increase of surface roughness parameters (R_a and R_z). In the case of polished austenitic manganese-nickel grade YU4 the surface roughness increased proportionally to passivation time. The surface roughness of austenitic chromium-nickel grade 1.4301 of 2B finish was not influenced by the passivation treatment.
- The passive layer of studied stainless steels follows the Okamoto double-layer model where formed layer is composed of outer porous film - hydroxide layer (described by R_1 and CPE_1 parameter) and the inner compact passive film – the oxide layer (described by R_2 and CPE_2).
- During the passivation process the resistance parameters have been increased showing improvement of corrosion resistance of the formed layers and their thickening correlated to the capacitances of the system.
- For all studied stainless steel grades an optimal passivation time seems to be 60 min, when taking into account, both the surface roughness and the EIS parameters of the formed passive layer of double-layer nature. Prolonged passivation time to 120 min start to negatively influence on the recorded EIS parameters resulting in deteriorated characteristic of the inner compact passive layer even when its thickness was increased.

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