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# CORROSION RESISTANCE OF SOME STAINLESS STEELS IN CHLORIDE SOLUTIONS

The present work compares corrosion behaviour of four types of S30403, S31603, S32615 austenitic and S32404 austenitic-ferritic stainless steels in chloride solutions (1%, 3% NaCl) and in Ringer solution, at 37°C temperature. Corrosion resistance was determined by potentiodynamic polarization measurements and a thirty day immersion test conducted in Ringer solution. The immersion test was performed in term of biomedical application. These alloy were spontaneously passivated in all electrolytes, wherein S30403, S31603 and S32404 undergo pitting corrosion. Only S32615 containing 5.5% Si shows resistance to pitting corrosion.

*Keywords:* stainless steel, chemical composition, corrosion, Ringer solution

## 1. Introduction

Conventional austenitic stainless steels (SS) 304 and 316 are used as construction materials for a wide range of technological applications. The main applications are in the chemical, petrochemical and seawater processing industries. These steels also are widely used as a materials in biomedical applications. The sufficient corrosion resistance, good mechanical properties and reasonable cost are the contributing factors for their applications as outstay structural material. However these alloys are subjected to localized corrosion in the presence of chloride ions. Based on the fact that Cr and Mo have a synergetic effect in enhancing the pitting resistance of steel in chloride solutions (especially in seawater), high alloy stainless steels (containing 6%Mo) are used [1,2].

Beside chromium and molybdenum, addition of Si may also increase pitting corrosion resistance of chromium-nickel steels [3]; particularly at higher concentration of Si in these alloys [4]. However, the corrosion behaviour of these steels in chloride solution is not fully understood.

Currently, austenitic-ferritic stainless steels (DSS), are replacing the austenitic ones, due to their good balance between the mechanical properties, the corrosion resistance and the economic advantages [1,5,6].

The comparative research of electrochemical behaviour of 2205 DSS and AISI 316 stainless steels in chloride solution 0,9M NaCl [7], and marine environment [8] indicates, that the 2205 DSS is more resistance to pitting corrosion then the AISI 316 stainless steel due to wider passivation range. However, the corrosion properties of duplex stainless steels have not been investigated extensively.

The aim of the present study is a comparison of corrosion behaviour of conventional SS (304 and 316), austenitic-ferritic 324 (duplex) and high alloy (containing 5%Si) stainless steel (326) in chloride solutions (1%, 3% NaCl and Ringer solution) in terms of their suitability for industrial technology and biomedical application.

## 2. Experimental part

Three grades of austenitic stainless steels S30403 (304), S31603 (316), S32615 (326) and one duplex S32404 (324) were investigated. The chemical composition (Table 1) of steels was determined by means of an atomic emission spectrometer (SpektromaxX).

Corrosion resistance was determined on the basis of potentiodynamic polarization measurements in aqueous solution of chloride (Ringer solution,1% NaCl and 3% NaCl) at 37°C (in respect of biomedical and industrial applications). The test specimens were cut into discs of 7 mm diameter. Before electrochemical treatment specimens were polished with abrasive paper with the gradation from 200 to 1200. Specimens were then embedded in a Teflon holder and employed as a working electrode.

Active surface of the samples was washed with acetone and were immersed in electrolites. The polarization was performed with the potentiokinetic technique (LSV) at a scan rate (dE/dt) of 0.1 V/min., in a classical tri-electrode system (0.25 L volume). The counter electrode was a platinum plate, and as a reference electrode Ag/AgCl one was used. After 1h of stabilization at the open circuit potential, the corrosion potential of the samples were

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Chemical composition of steels

| Steel grade | Content [% mass.]/[% at.] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Fe | Cr | Ni | Mn | Si | Mo | Cu | S | P | C |
| 304 | 71.34/<br>70.43 | 18.13/<br>19.30 | 8.05/<br>7.52 | 1.35/<br>1.35 | 0.34/<br>0.67 | 0.31/<br>0.18 | 0.40/<br>0.35 | 0.03/<br>0.045 | 0.03/<br>0.057 | 0.021/<br>0.097 |
| 316 | 69.11/<br>68.74 | 16.54/<br>17.67 | 10.10/<br>9.51 | 1.60/<br>1.62 | 0.55/<br>1.09 | 2.02/<br>1.17 | — | 0.03/<br>0.052 | 0.03/<br>0.054 | 0.02/<br>0.093 |
| 324 | 66.01/<br>64.46 | 20.40/<br>22.45 | 7.50/<br>7.27 | 1.60/<br>1.66 | 0.59/<br>1.21 | 2.33/<br>1.39 | 1.52/<br>1.38 | 0.03/<br>0.059 | 0.02/<br>0.037 | 0.03/<br>0.14 |
| 326 | 51.83/<br>49.07 | 18.50/<br>18.85 | 21.00/<br>18.87 | 1.90/<br>1.83 | 5.50/<br>10.41 | 1.20/<br>0.66 | — | 0.03/<br>0.051 | 0.03/<br>0.043 | 0.07/<br>0.31 |

measured. The potentiodynamic curves start at 200 mV below the open circuit potential.

Investigation metal release were performed using the immersion test in Ringer's solution (8.6 g/L NaCl, 0.3 g/L KCl, 0.48 g/L CaCl$_2$). Samples prepared for measurements were placed into the vessels with 100 mL of fluid. Immersion experiment were performed for the 30 days using water bath at 37°C temperature. After the exposure test all samples were cleaned in pure water and dried in ambient conditions and kept in polymer containers for further studies. Chemical analysis (Fe, Cr, Ni, Mn, Si, Mo, Cu) of corrosive medium was performed using Inductively Coupled Plasma Mass Spectrometry (Elan6100).

## 3. Result and discussion

### 3.1. Electrochemical polarization measurements

The anodic polarization curves of the examined steels, in Ringer's solution, 1% and 3%, are presented in Fig. 1a,b,c. The course of the curves confirms the passivation properties of natural oxide film, present on all steel types. The electrochemical passivation parameters, determining the durability of the passive layer, depend on the type of steel-mainly on the presence of alloy additions, such as Mo and Si.
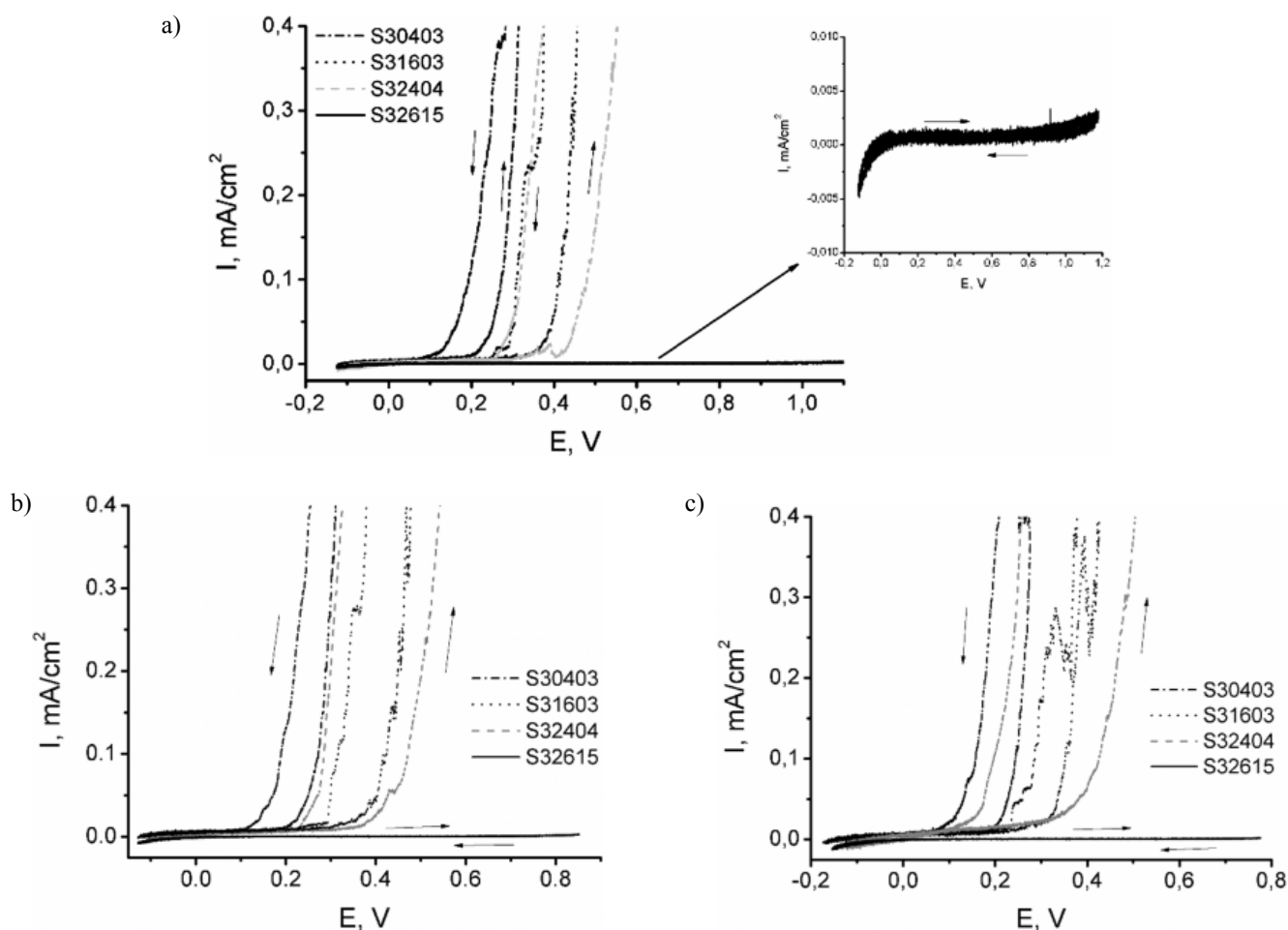


Fig. 1. LSV polarization curves of the 304, 316, 324; 326 in: a) Ringer solution; b) 1%NaCl; c) 3%NaCl

The passive area, in the case of classic steels, is limited by the breakdown potential (Ep, Fig. 2) and the repassivation potential (Fig. 1a-c). The values of Ep, and also the width of the passive range, decrease together with the increase of the Cl⁻ ion concentration. The highest values of the Ep potential and the lack of an anodic loop on the return curve in all the examined solutions, and thus the highest local corrosion resistance are exhibited by steel (326) with a silicon addition. The least durable one is steel 304. This is proven by the values of the anodic current density ($I_a$, Fig. 3), the breakdown potential (Fig. 2) and the repassivation potential (Fig. 1a-c). The corrosion potential (Table 2) of the austenitic steel 304 lies in the vicinity of the repassivation potential and points to the possibility of the occurrence of pitting corrosion, especially after a long exposure time.

TABLE 2

Corrosion potential of steels

| Alloy Solution | Ek [V] | | | |
|---|---|---|---|---|
| | S30403 | S31603 | S32404 | S32615 |
| RR | 0.096 | 0.106 | 0.086 | 0.101 |
| 1%NaCl | 0.095 | 0.103 | 0.105 | 0.099 |
| 3%NaCl | 0.076 | 0.085 | 0.085 | 0.109 |

The increase of the concentration of Cl⁻ ions (from 0.15 M to 0.55 M) marks a slight increase of the current density ($i_a$) in the passive area, in the case of classic SS (304, 316) and the 324 DSS. The values of $i_a$ are within the range from 3 to 7 μA/cm². As regards the density of the anodic current, in the case of the 326 alloy, it does not depend on the Cl⁻ ion concentration. The value of $i_a$, in a wide passive area up to 0.8 V and in all the media, is a few times lower than the current density for the remaining types of steel and it equals about 1 μA/cm² (Fig. 1a-c and Fig. 3).
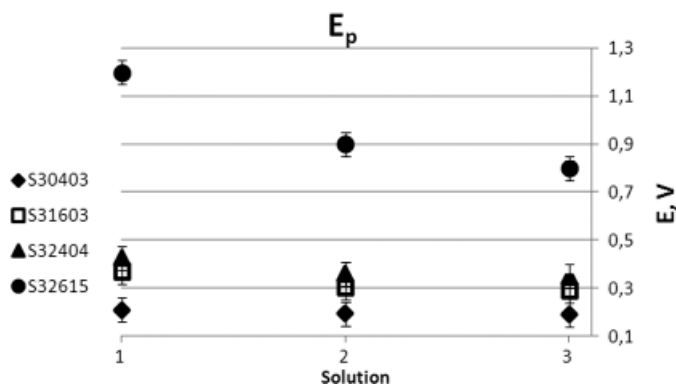
Fig. 2. Value of breakdown potential of the S30403, S31603, S32404, S32615 in: 1 – Ringer solutions, 2 – 1%NaCl, 3 – 3%NaCl

The behaviour of 316 and the 324 steel in chloride solutions is in agreement with previous works by other authors [2,9,10]. Only S326 steel (containing 5.5% of silicon), as it was mentioned before, exhibits a high corrosion resistance (also pitting), in all the examined media.
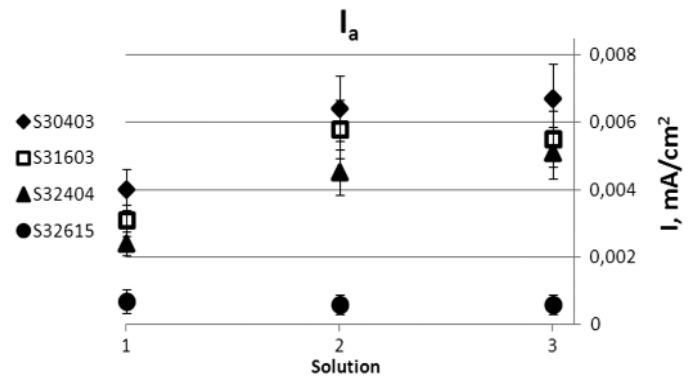
Fig. 3. Anodic current density in the passive range (of 0V) of the S30403, S31603, S32404, S32615 in: 1 – Ringer solutions, 2 – 1%NaCl, 3 – 3%NaCl

### 3.2. Immersion test

All the tested types of steel, with the natural oxide film, were exposed to Ringer's solution. The metal concentrations (Fe, Cr, Ni, Mn, Si, Cu) passing into the solution are presented in Table 3.

TABLE 3

Chemical analysis of the corrosive medium determined by ICP MS technique

| Alloy Element | Concentration [mg/ dm³] | | | |
|---|---|---|---|---|
| | S30403 | S31603 | S32404 | S32615 |
| Fe | 0.465 | 0.194 | 0.014 | <0.002 |
| Cr | 0.0031 | 0.0047 | 0.0028 | 0.0027 |
| Ni | 0.0003 | 0.0002 | 0.0003 | 0.0002 |
| Mn | 0.114 | 0.055 | 0.023 | 0.003 |
| Cu | 0.0073 | <0.0001 | 0.0093 | <0.0001 |
| Si | <0.1 | <0.1 | <0.1 | <0.1 |

The corrosion indicators for the particular metal released into the solution (Fig. 4) were calculated from the results of the chemical analysis of the corrosive medium (Tab. 3).

The static immersion tests indicate, that in the corrosion process of the examined alloys, mainly iron and manganese pass into the solution. The highest amounts of iron and manganese are released in the case of 304 steel, and the smallest amounts-in the case of 326 steel. The concentration of Fe and Mn in Ringer's solution decreases in the following order: 304 > 316 > 324 > 326, similarly to the anodic current density on the polarization curves (Fig. 1a, Fig. 3).

The amount of the released iron and manganese, in the case of S316 steel, is about 2 times lower than that of 304 steel. In the case of the 324 DSS and 326 SS amount of released Fe and Mn is one and two orders of magnitude lower than of 304 SS respectively. It should be emphasized that the chromium and nickel concentration in the corrosive medium for the same type of steel, 304 and 316, as well as the duplex cast steel, are lower by one, two and three orders of magnitude, respectively, as compared to the iron concentration. This confirms the selective dissolution of iron in these alloys and the enrichment of the alloy surface

in chromium (the passivising component) [11,12]. Only in the case of S326 steel (containing 5.5% of Si), the concentrations of Fe, Cr and Mn are at a similar level (0.002 ±0.001mg/dm$^3$). These values prove a high corrosion resistance of the alloy and point to a different structure of the passive layer [13] as well as a different passivation mechanism. So far, the structure of the passive layer and the mechanism of alloy's passivation for the 326 SS have not been recognized. The obtained experimental results indicate that, beside chromium and molybdenum, the presence of silicon in the alloy can significantly increase its corrosion resistance, also in chloride solutions.
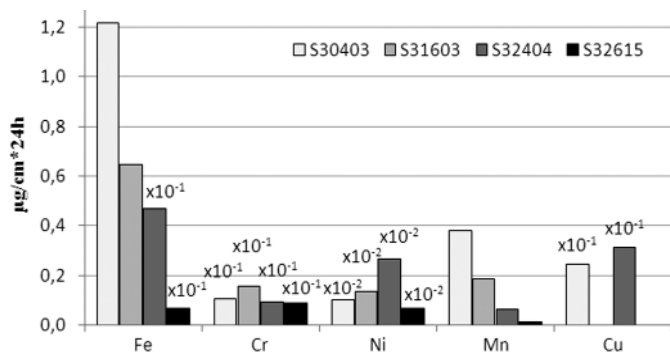


Fig. 4. Release rates of alloy constituents (Fe, Cr, Ni, Mn, Cu) from examined alloys

The obtained release rate of Fe, Cr, Ni and Mn from classic steels S304 and S316 as well as duplex 324 are comparable with the results in similar environments reported by other authors [14,15]. For 326 steel, there is no respective literature data. The release rates of Fe, Cr and Ni, released from 326 SS, are similar to those for the Co-Cr-Mo-Ni-Fe alloy (0.03 µg/cm*24 h, 0.01 µg/cm*24 h, 0.01 µg/cm*24 h), while the release rate of Mn (0.01 µg/cm*24 h) from 326 corresponds to the rate of its release from the Cr-Ni-Mn alloy [14].

## 4. Summary

The result of electrochemical polarization measurements and the static immersion test confirmed a higher corrosion resistance of the austenitic-ferritic 324 steel compared to austenitic 304 and 316 SS, and shows that the highest resistance is exhibited by the austenitic 326 SS in aqueous chloride solutions.

The static immersion test shows that 304, 316, as well as 324 steels, undergo selective dissolution. Mainly iron and manganese pass into the corrosive medium. The 324 DSS exhibits a resistance close to that of 316 SS, while the amount of the passing iron is lower by one order of magnitude.

The highest-resistant steel 326 SS (containing 5.5% Si), does not undergo selective dissolution in Ringers's medium. The amount of the metals (Fe, Cr, Mn) passing into the corrosion medium is practically at the same, very low, level (0.002, 0.3 µg/cm*24 h). Moreover 326 SS shows local corrosion resistance.

As has been shown by the previous studies [16,17], nickel slightly increases the pitting corrosion resistance. From this it can be concluded that the high resistance of steel 326 is mainly connected with the presence of silicon in the alloy. Up till now, steels containing about 5% Si have been used only in highly-oxidizing environments (concentrated sulfuric or nitric acid) [18,19], where the silicon has been built into the structure of the passive layer. The structure of the passive layer in steel 326 in aqueous chloride solutions has not been recognized so far.

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