Comparsion of the corrosion behavior of AISI 304, AISI 316L and duplex steel in chloride solution

ABSTRACT

The corrosion behavior of stainless steels (AISI 304, AISI 316L and duplex steel) in NaCl solution was investigated using open circuit potential measurements, cyclic polarization and linear sweep voltammetry measurements. After cyclic polarization measurements electrode surfaces was investigated by light microscope.

Duplex steel have the most noble open circuit potential, the lowest corrosion current density and the largest width of the passive region indicates its highest corrosion resistance. Also, compared to other samples, duplex steel shows the possibility of self-healing of oxide film.

Increasing the concentration of Cl− ion, the depassivation potential becomes more negative for all investigated samples. If the potential scan rate increases depassivation potential becomes more positive, meaning that a certain time (induction time) is needed for the pitting occurs after the actual depassivation potential is established. Depassivation potential and pitting corrosion nucleation time of investigated samples increase in order: AISI 304 < AISI 316L < duplex steel.

Light microscopy investigations of samples reveal pits on the surface of AISI 304 and AISI 316L steel while duplex steel surface is almost clear of any corrosion damage.

Keywords: corrosion, stainless steel, polarization, light microscopy.

1. INTRODUCTION

Stainless steels are important construction materials which are often used when high mechanical properties, weldability and good corrosion resistance are imperative [1-4].

Although stainless steels possess excellent resistance to general corrosion, they are susceptible to the localized corrosion attack such as pitting corrosion in chloride containing environment [5-7]. Corrosion resistance of stainless steels are related to the formation of an insoluble, relatively uncreative chromium oxide-hydroxide enriched passive surface film that forms naturally in the presence of oxygen (self-passivation), whose thickness is in the range from 1 to 10 nm [7-10]. Corrosion resistance of the passive film is determinate by the alloy composition and environmental conditions, to which stainless steels are exposed.

High content of Cr in the stainless steels leads to the formation of a complex spinel-type passive film (Fe,Ni)O(Fe,Cr)2O3 responsible for its high corrosion resistance [8,11,12]. Manganese has been traditionally considered as austenite former and is often added to increase nitrogen solubility [13]. Nevertheless, its addition is usually accompanied by reduction of pitting corrosion resistance, associated with the formation of manganese sulphide inclusions [14]. There is a certain correlation between resistance to pitting corrosion and the size of MnS inclusions: reducing the size of the inclusions leads to increase resistance to pitting corrosion [15]. Molybdenum is considered as one of the principal alloying elements in stainless steel which enhances the pitting corrosion resistance and expands the passive region of stainless steel [12,16].

The most corrosion damages of stainless steels occur in neutral to acidic solutions containing chloride ions. Chlorides are the most common cause of local destruction processes because they are strong acid anions, and many metal cations possess significant solubility in chloride solutions. In addition, chlorides are relatively small anions
with a high diffusion power which impedes passivation [17]. Pitting corrosion is considered to be an autocatalytic process - once when pit is formed and the corrosion process is initially localized in the pit area, there is a significant change in the medium within the pit which becomes impoverished by cathode reactants (e.g. oxygen) and enriched with metal cations and chlorides. Inside the pit the pH value is reduced. The resulting chloride medium is very aggressive, prevents repassivation and encourages further growth of the pits [18].

The purpose of this study is to compare the corrosion behavior of duplex stainless steel with AISI 304 and AISI 316L stainless steels through electrochemical polarization studies in NaCl solution.

Table 1. Chemical composition of investigated stainless steels

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical composition, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304</td>
<td>19.05% Cr, 10.00% Ni, 1.30% Mn, 0.52% Si, 0.04% C, 0.05% N, 0.02% S, 69.00% Fe</td>
</tr>
<tr>
<td>AISI 316L</td>
<td>16.64% Cr, 10.68% Ni, 2.53% Mo, 0.47% Si, 0.002% C, 0.024% Nb, 0.009% S, 0.0045% P, 69.60% Fe</td>
</tr>
<tr>
<td>duplex steel</td>
<td>22.21% Cr, 5.47% Ni, 3.14% Mo, 1.52% Mn, 0.33% Si, 0.26% Cu, 0.012% C, 0.035% V, 0.012%, Nb, 67.00% Fe</td>
</tr>
</tbody>
</table>

Corrosion behavior of stainless steels was investigated with different electrochemical methods such as open circuit potential (\(E_{oc}\)), cyclic polarization and linear sweep voltammetry measurements in NaCl solutions at 20 °C. Electrochemical experiments were performed using a potentiostat PAR M273A. A three-electrode cell was used for measurements; the working electrode was test samples whereas the counter and the reference electrode was platinum sheet and saturated calomel electrode.

Just after immersing the tested electrode in the 0.5 mol dm\(^{-3}\) NaCl solution, the resulting open circuit potential was measured through the period of 45 min. After that, cyclic polarization measurements were performed in potential range of -0.2 V vs. \(E_{oc}\) to 0.6 V (i.e. to 1.2 V for duplex steel) with the scan rate of 0.1 mV s\(^{-1}\).

Linear sweep voltammetry measurements were performed in different concentrations of NaCl solution (0.01, 0.05, 0.1, 0.5 and 1 mol dm\(^{-3}\)) and with different scan rates (1, 5, 10, 50 and 100 mV s\(^{-1}\)).

After cyclic polarization measurements the surface of electrodes was investigated using light microscope MXFMS-BD, Ningbo Sunny Instruments co. with the magnification of 50 times.

2. EXPERIMENTAL

The chemical composition of the investigated samples was shown in Table 1.

The electrical contact for the electrochemical measurements was achieved by soldering the stainless steel samples with the copper wire and then isolated them with acrylic resin leaving only one side exposed to the test solution. Prior to each measurement the electrode surface (0.5 cm\(^2\)) was ground successively with different grades of SiC paper down to 1200 grit. After that, the samples were ultrasonically cleaned in ethanol and deionized water and immersed in electrolyte solution.

3. RESULT AND DISCUSSION

Figure 1 presents the evolution of open circuit potential as a function of time for AISI 304, AISI 316L and duplex stainless steel in a 0.5 mol dm\(^{-3}\) NaCl solution. The open circuit potential (\(E_{oc}\)) reflect the composite results of the electrochemical reactions which take place at the electrode/solution interface. From the Figure 1 it is clearly visible that the most noble \(E_{oc}\) was observed for the duplex steel, while AISI 304 and AISI 316L exhibit similar \(E_{oc}\) values. Moreover, the values of \(E_{oc}\) for duplex steel and AISI 316L steel increases gradually towards a nobler direction during the immersion which indicate the formation and thickening of the protective passive film on their surfaces. The values of \(E_{oc}\) for AISI 304 steel slowly decrease with time which indicates the poorer protective properties of its oxide film compared to the AISI 316L and duplex steel.

The general corrosion behavior of AISI 304, AISI 316L and duplex stainless steel in 0.5 mol dm\(^{-3}\) NaCl solution was investigated by recording the cyclic polarization curves in wide potential range. The purpose of these measurements was to evaluate the possibility of passivation and repassivation of tested samples and determination of corrosion current density (\(i_{corr}\)) and corrosion potential (\(E_{corr}\)).
Comparsion of the corrosion behavior of AISI 304, AISI 316L...
In this investigation special attention is dedicated to the depassivation of AISI 304, AISI 316L and duplex steel, therefore for each sample, polarization curves were recorded in different chloride ion concentrations (from 0.01 to 1 mol dm$^{-3}$) with scan rate of 1 mV s$^{-1}$. Results of investigation for duplex stainless steel are shown in Figure 4.

By anodic polarization of duplex steel, after passing the passive potential range the depassivation potential ($E_{dp}$) for duplex steel becomes more negative. Furthermore, parallel with the displacement of $E_{dp}$ towards the negative values, more steeper slopes of the linear part of the curve are observed, in the potentials range responsible for propagation of the pit, i.e., with potentials more positive than depassivation potential. The linear part of the curve ($dE/di$) defines the polarization resistance ($R_p$) of the corrosion process [20]. Many authors have explained this ohmic control by the presence of a thin, stable salt layer formed of an oversaturated solution present inside the pits, which gives some form of passivity [21]. Similar results were obtained for other investigated steel samples.

**Table 3. Results of the analysis of anodic polarization curves for investigated stainless steels in a function of the concentration of NaCl solution ($v = 1$ mV s$^{-1}$)**

<table>
<thead>
<tr>
<th>$c$ / mol dm$^{-3}$</th>
<th>AISI 304</th>
<th>AISI 316L</th>
<th>duplex steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{dp}$ / V</td>
<td>$R_p$ / $\Omega$ cm$^2$</td>
<td>$E_{dp}$ / V</td>
</tr>
<tr>
<td>0.01</td>
<td>0.099</td>
<td>225.988</td>
<td>0.485</td>
</tr>
<tr>
<td>0.05</td>
<td>0.045</td>
<td>59.746</td>
<td>0.424</td>
</tr>
<tr>
<td>0.10</td>
<td>0.042</td>
<td>22.462</td>
<td>0.381</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.044</td>
<td>5.875</td>
<td>0.359</td>
</tr>
<tr>
<td>1.00</td>
<td>-0.083</td>
<td>2.786</td>
<td>0.335</td>
</tr>
</tbody>
</table>
By analyzing the polarization curves $E_{dp}$ and $R_p$ was determined, and the obtained values in the function of chloride concentration for all examined samples are given in Table 3. Increasing the concentration of Cl\(^-\) ion, the $E_{dp}$ becomes more negative for all investigated samples, while the $R_p$ decreases considerably. Depassivation potential shift to the negative side greatly, which depends on the composition of the sample. Thus, the negative displacement potential of AISI 304 is $\approx 180$ mV, for AISI 316L $\approx 150$ mV and for duplex steel $\approx 120$ mV.

Graphical representation of dependence of $E_{dp}$ on log $c$, can be described by the empirical equation:

$$E_{dp} = A + B \log c_{Cl^-}.$$  

The constants $A$ and $B$ can be determined from the section and slope of the linear part of $E_{dp}$ - log $c$ dependence (Figure 5) and the obtained values are given in Table 4. Values of the empirical parameters $A$ and $B$ for the investigated steel samples are very well matched with the data given in the literature, and this constant depends on the electrolyte temperature [22,23].

Table 4. Values of parameters $A$ and $B$ for investigated stainless steels in different concentration of NaCl solution ($v = 1$ mV s\(^{-1}\))

<table>
<thead>
<tr>
<th>Steel</th>
<th>$A$/V</th>
<th>$B$/V mol(^{-1}) dm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304</td>
<td>-0.071</td>
<td>-0.090</td>
</tr>
<tr>
<td>AISI 316</td>
<td>0.330</td>
<td>-0.073</td>
</tr>
<tr>
<td>Duplex steel</td>
<td>1.164</td>
<td>-0.063</td>
</tr>
</tbody>
</table>

Figure 6. Anodic polarization curves for duplex stainless steel in 0.5 mol dm\(^{-3}\) NaCl solution in a function of the potential scan rate

Figure 6 and Table 5 show the influence of the potential scan rate on depassivation of stainless steel in 0.5 mol dm\(^{-3}\) NaCl. It can be noticed that the $E_{dp}$ of all investigated samples becomes more positive if the potential change in the positive direction is achieved faster (this shift for AISI 304 is 110 mV, for AISI 316L 160 mV and for duplex steel 200 mV), which means that for evaluation of pitting it takes a certain amount of time (induction time) after the actual depassivation potential is established [21].

Table 5. Results of the analysis of anodic polarization curves for investigated stainless steels in 0.5 mol dm\(^{-3}\) NaCl solution in a function of potential scan rate

<table>
<thead>
<tr>
<th>$v$/mV s(^{-1})</th>
<th>AISI 304</th>
<th>AISI 316L</th>
<th>Duplex steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{dp}$/V</td>
<td>$R_p$/Ω cm(^2)</td>
<td>$E_{dp}$/V</td>
</tr>
<tr>
<td>1</td>
<td>-0.045</td>
<td>5.875</td>
<td>0.359</td>
</tr>
<tr>
<td>5</td>
<td>0.014</td>
<td>6.540</td>
<td>0.443</td>
</tr>
<tr>
<td>10</td>
<td>0.035</td>
<td>5.192</td>
<td>0.514</td>
</tr>
<tr>
<td>50</td>
<td>0.058</td>
<td>4.528</td>
<td>0.514</td>
</tr>
<tr>
<td>100</td>
<td>0.069</td>
<td>6.110</td>
<td>0.518</td>
</tr>
</tbody>
</table>

Slika 6. Ovisnost potencijala depasivacije nerezljivog čelika u 0.5 mol dm\(^{-3}\) otopini NaCl od koncentracije (v = 1 mV s\(^{-1}\))

Table 5. Rezultati analize anodnih polarizacijskih krivulja za ispitivane uzorke nerezljivog čelika u 0.5 mol dm\(^{-3}\) NaCl otopini u funkciji brzine promjene potencijala

<table>
<thead>
<tr>
<th>$v$/mV s(^{-1})</th>
<th>AISI 304</th>
<th>AISI 316L</th>
<th>Duplex steel</th>
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<tbody>
<tr>
<td></td>
<td>$E_{dp}$/V</td>
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<td>6.110</td>
<td>0.518</td>
</tr>
</tbody>
</table>
As shown in Table 5, irrespective of the $E_{dp}$ shift towards more positive values, the rate of potential changes does not affect the value of polarization resistance. At all observed scan rates, similar values of $R_p$ were obtained, whose value however depends on the composition of the examined sample and grows in order: AISI 304 < AISI 316L < duplex steel.

The parameters $A$ and $B$ of the investigated samples increase in order: AISI 304 < AISI 316L < duplex steel. Namely, in the same order the depassivation potential becomes more positive, and the nucleation time of pitting corrosion increases. This behavior is the result of physical and chemical properties of the oxide films formed on the surface of tested samples.

Properties of the oxide films which form on the surface of stainless steels primarily depend on the chemical composition of the base metal, i.e. the content of the individual alloying elements in the investigated samples (Table 1). If the alloying element facilitates passivation of the steel, the properties of the oxide film will be better (higher resistance and thickness, more compact structure), which will ultimately increase the corrosion resistance of the metal in the aggressive media.

The role of alloying elements on metal passivation can be explained by the model proposed by Marcus [24]. The model is based on two fundamental properties of metals, such as:

- strength of the oxygen (or OH) chemisorption bond, $\Delta M-O$, (reflected by the value of the heat of oxygen adsorption, $\Delta H_{ads(ox)}$) and
- the facility of conversion from the oxygen (or OH) monolayer to a 3D oxide in which a critical factor is disruption of the metal-metal bonds (reflected by metal-metal bond energy, $\Delta M-M$) [24].

Passivation usually begins by adsorption of oxygen or OH from the water solution, followed by nucleation and oxide growth. Obviously, metals with high heat of oxygen adsorption are easily passivated. However, it is less apparent and less recognizable that the passive film formation requires additional activation energy for conversion of chemisorbed layer into 3D oxide, and that this process inevitably leads to a metal-metal interruption. Therefore the lower the energy required to disrupt metal-metal bonds, the lower the activation energy barrier for the conversion into 3D oxide [24]. The metals which adsorbs oxygen (or OH) strongly and on which metal-metal bonds are easily broken will be very suitable for the passive oxide film growth. Hence, alloying elements with high energy adsorption of oxygen, and low metal-metal bonds energy, reinforce the passivation of the base metal. However, the easy metal-metal bond disruption will also accelerate metal dissolution. Therefore, fine balancing between the effect of metal-metal bonding energy and the effect of oxygen adsorption heat is crucial in design of alloys which can passivate.
Based on such considerations, it is possible to divide alloying elements on passivity promoters and dissolution moderators or blockers. In order to make these ideas clearer, the diagram $\Delta H_{\text{ads(ox)}} - \varepsilon_{M-M}$ (Figure 8) is constructed on the basis of Marcus consideration \cite{24}.

![Diagram of passivity promoters and dissolution moderators](image)

**Figure 8.** Passivity promoters and dissolution moderators according to the synergy between the $\Delta H_{\text{ads(ox)}}$ and $\varepsilon_{M-M}$ \cite{24}

Different metal groups can be seen on the diagram. In the upper left area of the diagram, are placed metals with high $\Delta H_{\text{ads(ox)}}$ and a relatively low $\varepsilon_{M-M}$: Cr, Al, Ti. This area of the diagram corresponds to passivity promoters, i.e. the alloying elements that facilitate passivation of the metal.

In the upper right-hand region of the diagram are metals with high $\varepsilon_{M-M}$ and high $\Delta H_{\text{ads(ox)}}$: Mo, Nb, Ta and W. The high value of $\varepsilon_{M-M}$ indicates the difficulty to break metal-metal bonds, so these elements can be dissolution moderators or blockers. Furthermore, the metals of this group also have a high amount of $\Delta H_{\text{ads(ox)}}$ so they do not lose the ability of passivation. They may participate in passivation and be incorporated in surface oxide film. Based on the ideas presented, it is interesting to compare the influence of key alloying elements such as Cr, Mo and Nb on the passivation of stainless steels, whose content in the tested samples mostly increases in order: AISI 304 < AISI 316L < duplex steel. The specific roles of Cr and Mo (or Nb) can be well understood in the framework of the proposed model. Namely, the behavior of these elements in the initial stage of steel passivation is very different. Although the heat of oxygen adsorption on Cr, Mo and Nb is similar, the Cr-Cr bond energy is much lower than that of Mo-Mo and Nb-Nb \cite{24}. A large amount of energy released during the adsorption of oxygen is able to easily disrupt Cr-Cr bonds, thus causing oxide nucleation much before completion of the adsorbed monolayer.

On the other hand, the Mo and Nb further improves the corrosion resistance of the stainless steels, especially in solution containing Cl in which pitting is a common occurrence. Namely, the high Mo-Mo and Nb-Nb bond strength causes a lowering of the dissolution rate by increasing the activation energy barrier for the disruption of metal-metal bonds on the surface \cite{24}. This effect of alloying elements in the iron base ultimately results in the corrosion resistance of the tested samples growing in the same order, i.e. AISI 304 < AISI 316L < duplex steel. The content of the other elements in the individual samples also favors the increase of corrosion resistance according to sequence discussed.
4. CONCLUSIONS

In this paper, corrosion behavior of different types of stainless steels (AISI 304, AISI 316L and duplex steel) was studied in NaCl solution. From the analysis of the obtained results can be concluded as follows:

- Anodic polarization of all samples in NaCl solution results in the destruction of the natural oxide film and the occurrence of local activation of the surface with the creation of small pits. The damages of oxide film on duplex steel have tendency of self-healing.
- As the concentration of aggressive ions increases, the depassivation potential of all investigated stainless steel samples becomes more negative, while the polarization resistance of the corrosion process decreases considerably.
- If the change of potentials in the positive direction is realized faster, depassivation potential becomes more positive, meaning that a certain time (induction time) is needed for the pitting occurs after the actual depassivation potential is established.
- The potential scan rate does not affect the value of polarization resistance.
- Corrosion resistance of investigated stainless steels is following the order: AISI 304 < AISI 316L < duplex steel. Namely, the depassivation potential and pitting corrosion induction time of the examined samples increase in the same way.
- A key role in the corrosion resistance of the alloyed alloys has alloying elements such as Cr, Mo and Nb. Cr belongs to the elements which promote the passivation, while Mo and Nb in a group which prevents the dissolution of the metal.

5. REFERENCES

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IZVOD

USPOREDBA KOROZIJSKOG PONAŠANJA AISI 304, AISI 316L I DUPLEX ČELIKA U OTOPINI KLORIDA

Korozijsko ponašanje različitih vrsta nehrđajućeg čelika (AISI 304, AISI 316L te duplex čelika) u NaCl otolini ispitano je mjerenjem potencijala otvorenog strujnog kruga te primjenom cikličke i linearnе polarizacije. Nakon mjerenja cikličkom polarizacijom površine elektroda snimljene su svjetlosnim mikroskopom. Duplexs čelik pokazuje najpozitivniju vrijednost potencijala otvorenog strujnog kruga, najmanju gustoću korozijske struje i najšire područje pasivacije, što ukazuje na njegovu najveću korozijsku otpornost. Također, u usporedbi s drugim ispitivanim uzorcima, duplex čelik ima sposobnost obnavljanja površinskog oksidnog filma.

S porastom koncentracije kloridnih iona potencijal depasivacije svih ispitivanih uzoraka čelika postaje negativniji. Nadalje, ukoliko se promjena potencijala u pozitivnom smjeru ostvaruje brže, potencijal depasivacije postaje pozitivniji, što znači da je za pojavu pittinga potrebno izvjesno vrijeme (indukcijsko vrijeme) nakon što se uspostavi stvaram potencijal depasivacije. Potencijal depasivacije i vrijeme nukleacije pitting korozije ispitivanih uzoraka raste redom: AISI304 < AISI 316L < duplex čelik. Ispitivanjem uzoraka svjetlosnim mikroskopom uočena su oštećenja na površini AISI 304 i AISI 316L dok je površina duplex čelika gotovo neoštećena korozijom.

Ključne riječi: korozija, nehrđajući čelik, polarizacija, svjetlosna mikroskopija.

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