

Behaviour of AISI 316L Steel Exposed to Demineralized Water

KUI – 11/2009
Received September 11, 2008
Accepted April 7, 2009

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The subject of investigation was the passivation of AISI 316L austenitic stainless steel. The effectiveness of various passivation media was tested by means of the potentiodynamic polarization technique. Potentiodynamic polarization was carried out in demineralized water before and after passivation treatment. Comparative analysis of the potentiodynamic curves for different passivation media showed that the best protection of the steel surface was provided by a HNO₃ solution, $\varphi = 6.0\%$, containing CuSO₄ · 5H₂O, $w = 2.0\%$. The satisfactory protective properties were found to agree with the high value of the pitting potential.

Key words: *Stainless steel, passivation, pitting corrosion, inhibitors*

Introduction

Various metals are used as construction materials for water purification and distribution systems. Predominantly, these are stainless steels because of the extremely disadvantageous operating conditions to which those systems are exposed, such as high temperature (up to $\vartheta = 90\text{ }^\circ\text{C}$), frequent change of temperature (from ambient to $\vartheta = 90\text{ }^\circ\text{C}$), and high concentrations of dissolved oxygen (up to $\gamma = 8\text{ mg dm}^{-3}$). In real-life operating conditions, corrosion causes dissolution of the surface layers of the construction material, enhances roughness and porosity of the surface, and accounts for uneven distribution of the alloying elements. The increased chromium and nickel contents can improve corrosion resistance, and addition of the other elements (most commonly molybdenum in AISI 316L) can enhance it further.^{1,2}

In order to diminish those effects and assure the successful corrosion-resistant performance of stainless steel, passivation must be undertaken on time.³ To determine the most effective process for surface passivation it is essential to simulate real-life passivated conditions in the laboratory and expose the metal surface to conditions identical to actual exploitation. Our investigations were therefore carried out on samples of AISI 316L stainless steel.

Experimental

Investigation of the corrosion behaviour was performed on samples of AISI 316L austenitic stainless steel as a construction material for water purification systems. The chemical composition of the steel is shown in Table 1. The selection of equipment, electrochemical reactor, auxiliary and reference electrodes, and preparation of the working electrode

followed ASTM standards.⁴ The electrochemical measurements were carried out using an EG & G PAR 273A Potentiostat/Galvanostat, a Cole-Parmer 12700–55 thermostat, and an EG&G PAR Model K0047 Corrosion Cell. A standard three-electrode corrosion cell was used. The working electrode with a $A = 1\text{ cm}^2$ surface area (disc-shaped) was made of AISI 316L steel. An Ag/AgCl/KCl (sat'd) electrode served as the reference electrode, and as a counter electrode two graphite rods were used. The reference electrode was inserted into the bridge tube, and interference of chlorides from the reference electrode was practically impossible. Therefore, all potentials will be referred to the reference electrode Ag/AgCl/KCl (its potential is 0.197 V vs. SHE). Anodic potentiodynamic curves were recorded in conformity with ASTM standards.⁵

Measurements took place in the real medium (demineralized water, $\vartheta = 80\text{ }^\circ\text{C}$) and in various passivation solutions. The chemical composition of passivation solutions, temperatures, and exposure times are shown in Table 2.

Results and discussion

Potentiodynamic polarization is the method most frequently used for assessing metal susceptibility to pitting corrosion.⁶ Before establishing the conditions for successful protection (passivation) of AISI 316L steel surface we aimed at finding out how demineralized water (real medium) affected the surface stability at the temperature of $\vartheta = 80\text{ }^\circ\text{C}$. The corrosion quantities were determined from the recorded anodic potentiodynamic curve (Fig. 1). The values of corrosion parameters are listed in Table 3. Polarization resistance, R_p , is defined as a slope of E - j curve in the range potential from -20 mV to $+20\text{ mV}$ vs. open circuit potential, E_{OC} . The corrosion current density is obtained from a Tafel Plot by extrapolating the linear portion of the curve to E_{corr} . The Tafel constants, b_a and b_c , are the slopes of the li-

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Table 1 – Chemical composition of AISI 316L steel, w/%

Tablica 1 – Kemijski sastav čelika AISI 316L, w/%

C	Si	Mn	P	S	Cr	Ni	Mo
0.023	0.35	0.71	0.033	0.007	17.49	11.27	2.09

Table 2 – Chemical composition of solutions and passivation test conditions for AISI 316L steel

Tablica 2 – Kemijski sastav otopina i uvjeti ispitivanja pasivacije čelika AISI 316L

Solution Otopina	Composition Sastav	Temperature, $\vartheta/^\circ\text{C}$ Temperatura, $\vartheta/^\circ\text{C}$	Exposure time, t/s Vrijeme izloženosti, t/s
1	w(citric acid) = 10 % + w(ammonium citrate) = 25 %	80	3600
2	$\varphi(\text{HNO}_3) = 6.0\%$	60	1800
3	$\varphi(\text{HNO}_3) = 22.5\%$	60	1800
4	$\varphi(\text{HNO}_3) = 40.0\%$	40	1800
5	$\varphi(\text{HNO}_3) = 22.5\%$ + w($\text{K}_2\text{Cr}_2\text{O}_7$) = 5.0 %	60	600
6	$\varphi(\text{HNO}_3) = 22.5\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 4.0 %	60	600
7	$\varphi(\text{HNO}_3) = 12.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 4.0 %	60	600
8	$\varphi(\text{HNO}_3) = 6.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 4.0 %	60	600
9	$\varphi(\text{HNO}_3) = 6.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 2.0 %	60	600
10	$\varphi(\text{HNO}_3) = 3.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 1.0 %	60	600
11	$\varphi(\text{HNO}_3) = 6.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 2.0 %	60	3600
12	$\varphi(\text{HNO}_3) = 6.0\%$ + w($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 2.0 %	40	600

w – mass fraction

 φ – volume fraction (volume contraction has been taken into consideration)

near portion of anodic and cathodic curve respectively. The corrosion rate was calculated from j_{corr} by using the equation:

$$v_{\text{corr}} = 0.13 j_{\text{corr}}(m_{\text{eq}}) / \rho \quad (1)$$

where:

 v_{corr} – corrosion rate, mm a^{-1} m_{eq} – equivalent mass of the corroding species, g ρ – density of the corroding species, g cm^{-3} j_{corr} – corrosion current density, A cm^{-2} .

In real-life conditions, a corrosion resistant steel is expected to have achieved the corrosion potential (E_{corr}) before use. Defects on the steel surface due to long-term use will initiate porosity and cause roughness. A rough and porous structure will facilitate oxidation and dissolution of the sur-

face layers, in other words it will become more prone to pitting corrosion. The instability of the steel surface is manifested in a reduced value of pitting potential (E_p). If a timely protective treatment, i. e. passivation, is undertaken, the E_p potential will shift towards more positive values.⁶

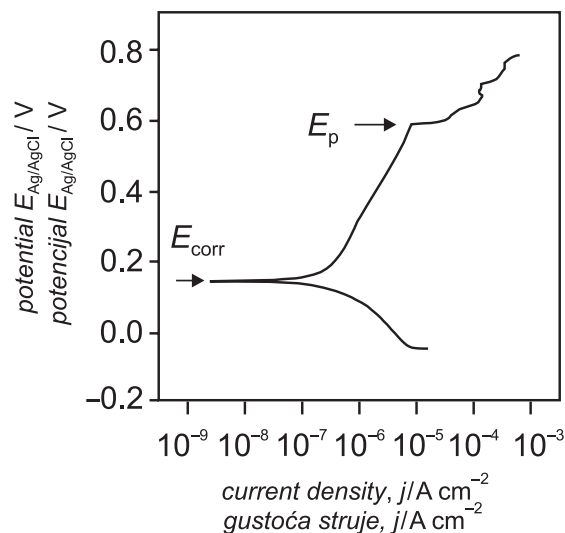
Fig. 1 – Anodic potentiodynamic curve for AISI 316L steel in demineralized water at a scan rate of $v = 5 \text{ mV s}^{-1}$ Slika 1 – Potenciodinamička krivulja čelika AISI 316L snimljena u anodnom smjeru u demineraliziranoj vodi pri brzini promjene potencijala $v = 5 \text{ mV s}^{-1}$

Table 3 – Corrosion quantities for AISI 316L steel in demineralized water

Tablica 3 – Veličine korozije čelika AISI 316L u demineraliziranoj vodi

R_p $\text{k}\Omega \text{ cm}^2$	b_a V dek^{-1}	$-b_c$ V dek^{-1}	$E_{\text{corr,Ag/AgCl/KCl}}$ V	j_{corr} $\mu\text{A cm}^{-2}$	v_{corr} mm a^{-1}	$E_{p,Ag/AgCl/KCl}$ 1.3
176	0.336	0.082	0.193	$5.310 \cdot 10^{-2}$	$5.510 \cdot 10^{-4}$	0.586

The corrosion rate (v_{corr}) of $5.5 \cdot 10^{-4} \text{ mm a}^{-1}$ denotes the average rate of surface deterioration i.e. it shows how deeply and uniformly the aggressive medium has penetrated into the steel surface structure. As well as by the penetration rate, general (uniform) corrosion can also be expressed by a mass loss occurring over the period of steel exposure to an aggressive medium. The corrosion rate of $\psi = 5.5 \cdot 10^{-4} \text{ mm a}^{-1}$ is equivalent to a mass loss of $m_{\text{loss}} = 0.044 \text{ g dm}^{-2} \text{ a}^{-1}$. It is well established that a medium having a general corrosion rate higher than $v_{\text{corr}} = 0.127 \text{ mm a}^{-1}$ i.e. having a mass loss in excess of $m_{\text{loss}} = 10.087 \text{ g dm}^{-2} \text{ a}^{-1}$ is not considered appropriate for use.⁷

Susceptibility to pitting corrosion of AISI 316L steel was established on the basis of the pitting potentials, Table 3. The more positive E_p potential i.e. the greater the $E_p - E_{\text{corr}}$ difference, the higher the resistance of steel to the initiation of localized attack. From Fig. 1 it is evident that the anodic E_p value was too low and the $E_p - E_{\text{corr}} = 0.393 \text{ V}$ difference

consequently too small for the surface to be protected from possible pitting corrosion. It was therefore essential to protect the surface by passivation treatment. The effectiveness of individual passivation solutions was assessed by conducting potentiodynamic polarization measurements on AISI 316L in demineralized water following surface passivation (Figs. 2–5). The characteristic pitting quantities for AISI 316L steel in demineralized water after passivation are given in Table 4.

Comparison of the shapes of potentiodynamic curves and the corresponding E_p and E_{corr} values showed that a solution of $w = 10\%$ citric acid and $w = 25\%$ ammonium citrate (solution 1, Fig. 2a) was not an efficacious medium for passivation of AISI 316L steel exposed to demineralized water. A decrease in the E_p value (from 0.586 to 0.480 V) following passivation was taken as evidence of enhanced susceptibility to pitting corrosion. In earlier experiments the solution

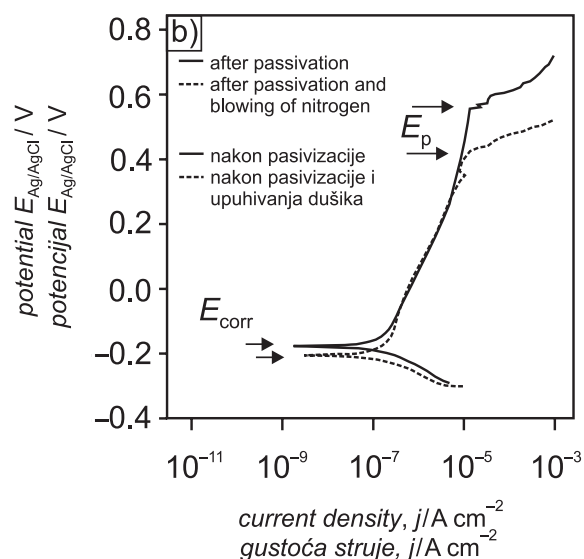
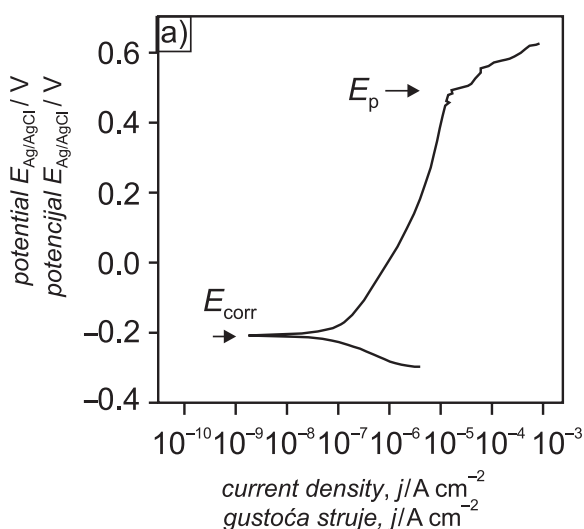


Fig. 2 – Anodic potentiodynamic curves for AISI 316L steel in demineralized water after passivation in solution 1 (a), in solution 2 (b) at a scan rate of $\nu = 5 \text{ mV s}^{-1}$

Slika 2 – Potenciodinamičke krivulje čelika AISI 316L snimljene u anodnom smjeru u demineraliziranoj vodi nakon pasivizacije u otopini 1 (a) i 2 (b) pri brzini promjene potencijala $\nu = 5 \text{ mV s}^{-1}$

of citric acid and ammonia yielded satisfactory results only as a chemical cleaning medium but not one for passivation. Irrespective of concentration, this solution is known to be a weaker oxidizing medium than nitric or phosphorus acids.⁸ By a weak oxidative action it causes oxidation only of the first few layers of iron, chromium, molybdenum and nickel. The resulting passive film is sufficiently stable ($\delta = 5\text{--}50 \text{ nm}$) to protect the steel surface from uniform dissolution (general corrosion) but not from pitting corrosion.⁹ The solution of citric acid and ammonia has therefore been exempt from use as a passivation medium.

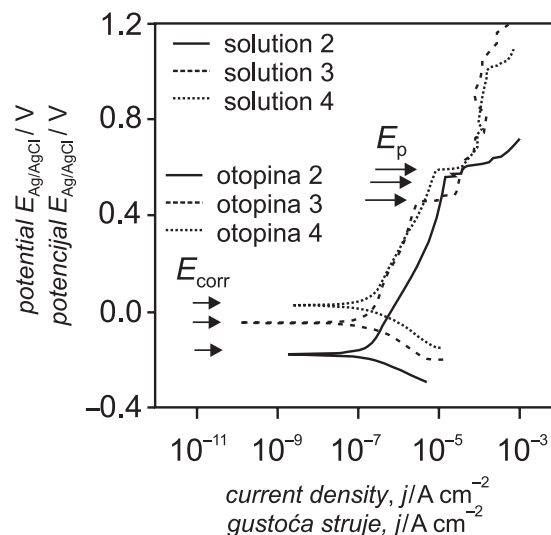


Fig. 3 – Anodic potentiodynamic curves for AISI 316L steel in demineralized water after passivation in solutions 2–4 at a scan rate of $\nu = 5 \text{ mV s}^{-1}$

Slika 3 – Potenciodinamičke krivulje čelika AISI 316L snimljene u anodnom smjeru u demineraliziranoj vodi nakon pasivizacije u otopinama 2–4 pri brzini promjene potencijala $\nu = 5 \text{ mV s}^{-1}$

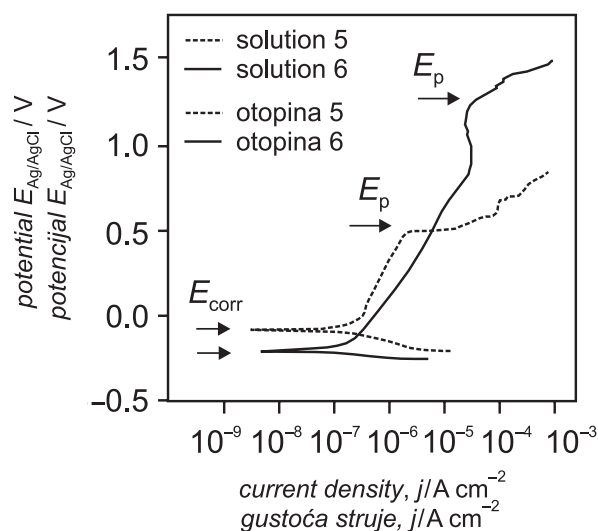


Fig. 4 – Anodic potentiodynamic curves for AISI 316L steel in demineralized water after passivation in solutions 5 and 6 at a scan rate of $\nu = 5 \text{ mV s}^{-1}$

Slika 4 – Potenciodinamičke krivulje čelika AISI 316L snimljene u anodnom smjeru u demineraliziranoj vodi nakon pasivizacije u otopinama 5 i 6 pri brzini promjene potencijala $\nu = 5 \text{ mV s}^{-1}$

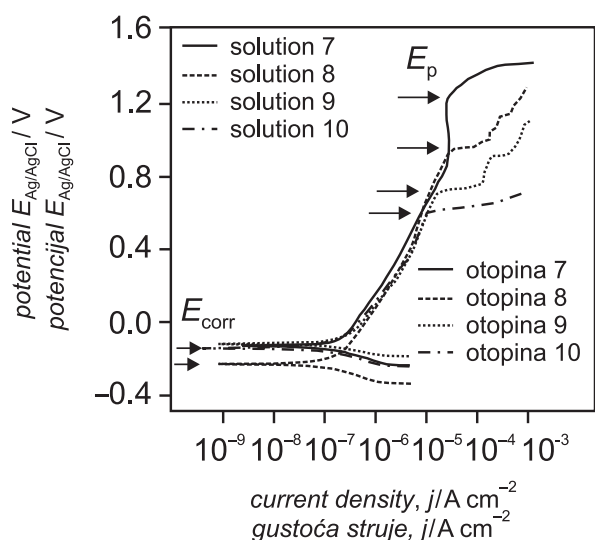


Fig. 5 – Anodic potentiodynamic curves for AISI 316L steel in demineralized water after passivation in solutions 7–10 at a scan rate of $v = 5 \text{ mV s}^{-1}$

Slika 5 – Potenciodinamičke krivulje čelika AISI 316L snimljene u anodnom smjeru u demineraliziranoj vodi nakon pasivizacije u otopinama 7–10 pri brzini promjene potencijala $v = 5 \text{ mV s}^{-1}$

Table 4 – Pitting quantities for AISI 316L steel in demineralized water after passivation

Tablica 4 – Veličine jamičaste korozije čelika AISI 316L izloženog demineraliziranoj vodi nakon pasivizacije

Solution for passivation Otopina za pasivizaciju	E_p / V vs. Ag / AgCl / KCl	E_{corr} / V vs. Ag / AgCl / KCl	$(E_p - E_{\text{corr}})$ / V vs. Ag / AgCl / KCl
1	0.480	-0.210	0.690
2	0.556	-0.173	0.729
3	0.454	-0.048	0.502
4	0.582	-0.022	0.604
5	0.502	-0.075	0.577
6	1.218	-0.200	1.418
7	1.240	-0.146	1.386
8	0.935	-0.243	1.178
9	0.711	-0.131	0.842
10	0.585	-0.156	0.741
11	1.076	-0.161	1.237
12	0.580	-0.140	0.720

The passivation efficiency of a $\varphi = 6.0\%$ HNO_3 solution was tested before and after nitrogen sparging ($w = 99.999\%$, 15000 Pa) for 45 min. The purpose of sparging was to diminish oxygen concentration in demineralized water because of a possible major effect on pitting corrosion.¹⁰ However, the onset of pitting corrosion on the surface of AISI 316L steel proved to be only negligibly dependent on dissolved oxygen (Fig. 2b). The $\varphi = 6.0\%$ HNO_3 solution therefore did not prove to be a convenient passivation medium because it failed to induce a shift in the pitting po-

tential towards more positive values as compared to the potential recorded on the nonpassivated surface.

Our investigation of passivation treatment and of susceptibility to pitting corrosion also concerned the effect of nitric acid as passivation medium (Fig. 3). The potentiodynamic curves clearly show that the AISI 316L steel surface failed to be protected regardless of the selected acid concentration. The pitting potential that corresponded to that of the nonpassivated surface (0.586 V) was reached only after passivation in $\varphi = 40.0\%$ HNO_3 (0.582 V) (Table 4). Although nitric acid is a stronger oxidizing reagent than citric acid, it is more often used for the protection of steel surface from general corrosion and less often for protection against pitting corrosion.^{11–13} The ineffectiveness of nitric acid to provide protection against pitting corrosion stems from its inability to form a stable passive oxide film on the surface. As a result of dissolution of iron, chromium, molybdenum, and nickel atoms there is an increase in the number of possible pitting initiation sites.¹⁴ As a strong oxidizing reagent nitric acid, irrespective of concentration or oxygen content, does not make a solution that can be conveniently used for passivation.

By addition of an inhibitor to the passivation solution the corrosion resistance of the passive film can be improved.^{15,16} Fig. 4 shows the potentiodynamic curves for AISI 316L steel recorded in demineralized water after passivation in solutions containing corrosion inhibitors ($\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The pitting potential values indicate that the solution containing the inhibitor $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ had a much greater capability for passivation than the one that contained $\text{K}_2\text{Cr}_2\text{O}_7$. After addition of the $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor the surface stability remained unmodified because of the strong oxidative action of $\text{Cr}_2\text{O}_7^{2-}$ which caused uncontrolled dissolution of all atoms on the steel surface and thus prevented the formation of a protective passive film. The passivation capability of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ containing solution was manifested in a higher value of the pitting potential (1.218 V) as well as in a wider $E_p - E_{\text{corr}}$ range (1.418 V). In the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ containing solution there was a shift in the pitting potential, by 0.84 V, towards more positive values as compared to the solution containing the $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor. The reason for the shift in the potential towards more positive values lay in the formation of a more resistant passive oxide film on the steel surface. The addition of copper sulphate as corrosion inhibitor made it possible to control dissolution of the first surface layers of iron, nickel, and manganese. After their initial selective dissolution the metal surface was enriched with undissolved chromium and molybdenum atoms. In the passivation solution these underwent oxidation to the first stable oxidation state (+3), and formed hard soluble Cr_2O_3 and Mo_2O_3 layers¹⁷. The chromium and molybdenum oxides and hydroxides formed a compact protective layer which was sufficiently stable to protect the AISI 316L steel surface against the harmful effect of pitting corrosion.^{18,19}

Based on the satisfactory results of passivation treatment obtained with a $\varphi = 22.5\%$ HNO_3 solution containing $w = 4.0\%$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ we further investigated the effect of nitric acid concentration, copper sulfate concentration, temperature, and exposure time on passivation (Fig. 5). We found that the protection of AISI 316L steel by passivation could

be achieved with a HNO_3 solution, $\varphi = 12.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 4.0\%$, or with a HNO_3 , $\varphi = 6.0\%$, solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 4.0\%$. Analysis of the pitting potential values showed that neither the HNO_3 solution, $\varphi = 6.0\%$, with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 4.0\%$ ($E_p = 0.711\text{ V}$) nor the HNO_3 , $\varphi = 3.0\%$ solution with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 10\%$ ($E_p = 0.585\text{ V}$) were capable forming a corrosion-resistant passive film on the AISI 316L steel surface.

Fig. 6 shows the relationship between the effectiveness of the passivation solution on one hand, and exposure time and solution temperature on the other. From the potentiodynamic curves it is evident that a prolongation of exposure time from 600 to 3600 s caused a 0.365 V shift in the pitting potential towards more positive values (Fig. 6a, Table 4). The result of prolonged exposure was the formation of a passive oxide film which was resistant to pitting corrosion. Increase in the temperature of the passivation solution also had a positive effect on the effectiveness of the passivation treatment. The pitting potential was higher by 0.131 V at 60 °C than at 40 °C (Fig. 6b, Table 4).

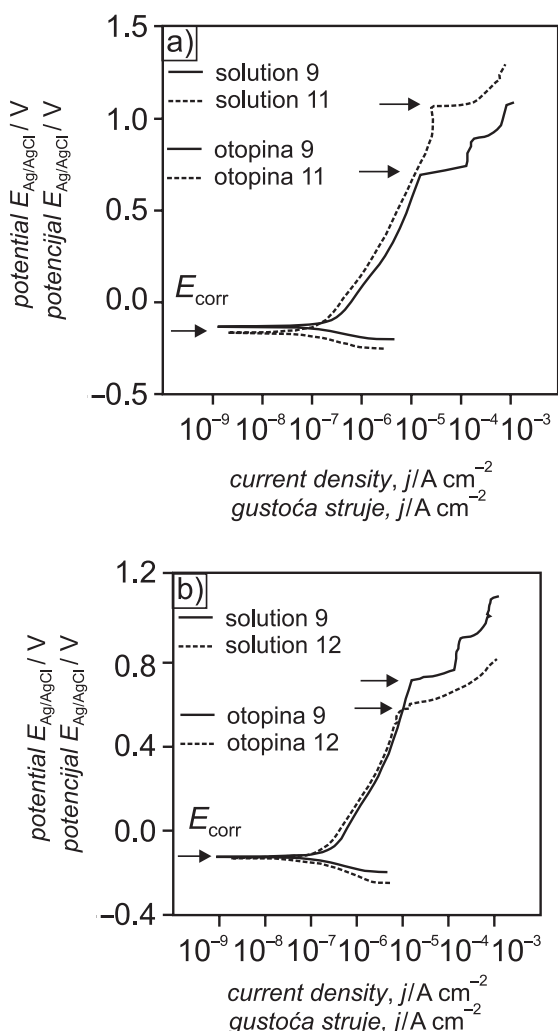


Fig. 6 – The effect of immersion time (a) and temperature (b) on the shape of anodic potentiodynamic curves of AISI 316L steel in demineralized water at a scan rate of $\nu = 5\text{ mV s}^{-1}$

Slika 6 – Utjecaj vremena (a) i temperature (b) na oblik potenciodinamičke krivulje čelika AISI 316L u demineraliziranoj vodi pri brzini promjene potencijala $\nu = 5\text{ mV s}^{-1}$

From the shape of the cyclic voltammogram, i.e. from the characteristic peaks of the current of oxidation/reduction processes recorded at a certain potential, it is possible to make a qualitative and quantitative characterization of the metal surface.²⁰ The cyclic voltammograms of the nonpassivated and passivated AISI 316L steel surfaces immersed in sodium hydroxide solution (Fig. 7) were therefore recorded. The solution ($c = 1\text{ mol dm}^{-3}$) was chosen for its nonaggressive surface action, i. e. for the fact that in the course of cyclic voltammogram recording there was no dissolution of the steel surface. The anodic potential region between -400 mV and 480 mV was found to correspond to the process of surface chromium oxidation. By integration of the surface below the anodic voltammogram the surface charge density was obtained which related to the reaction involving oxidation only of surface chromium and molybdenum atoms.²¹ For the nonpassivated surface the measured charge density was $\tau = 2.580\text{ mC cm}^{-2}$, and for the passivated one it was $\tau = 4.362\text{ mC cm}^{-2}$. A 70% increase was especially significant considering that the total chromium and molybdenum mass fraction of AISI 316L steel was about $w = 20\%$.

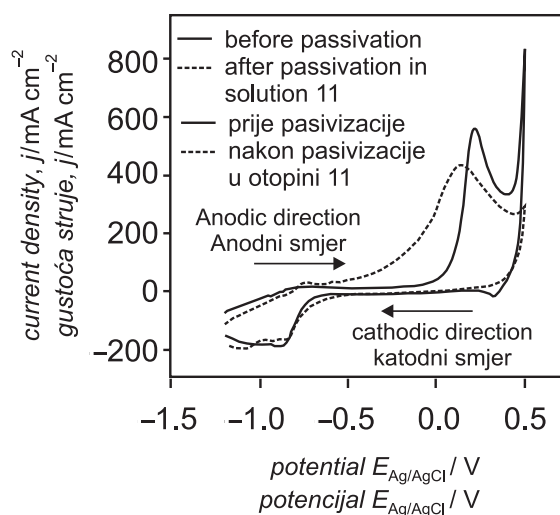


Fig. 7 – Cyclic voltammograms for nonpassivated and passivated AISI 316L steel surfaces recorded in sodium hydroxide solution ($c = 1\text{ mol dm}^{-3}$) at a scan rate of $\nu = 50\text{ mV s}^{-1}$

Slika 7 – Ciklički voltamogrami nepasivizirane i pasivizirane površine čelika AISI 316L snimljeni u otopini NaOH ($c = 1\text{ mol dm}^{-3}$) pri brzini promjene potencijala $\nu = 50\text{ mV s}^{-1}$

Comparative analysis of the effectiveness of the selected passivation solutions showed that the HNO_3 solution, $\varphi = 6.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 2.0\%$, in which AISI 316L steel was kept for $t = 3600$ seconds at $\vartheta = 60\text{ °C}$, was the most suitable solution for surface protection by passivation. By passivation in that solution the effect of pitting corrosion was reduced to a minimum. To assess the influence of the passivation solution on the general and pitting corrosion parameters a potentiodynamic curve was recorded for AISI 316L steel immersed in a HNO_3 solution, $\varphi = 6.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 2.0\%$ (3600 s, 60 °C) (Fig. 8). The quantities obtained are listed in Table 5.

Comparison of the results of general corrosion measurement in a selected passivation medium (Table 5) and those

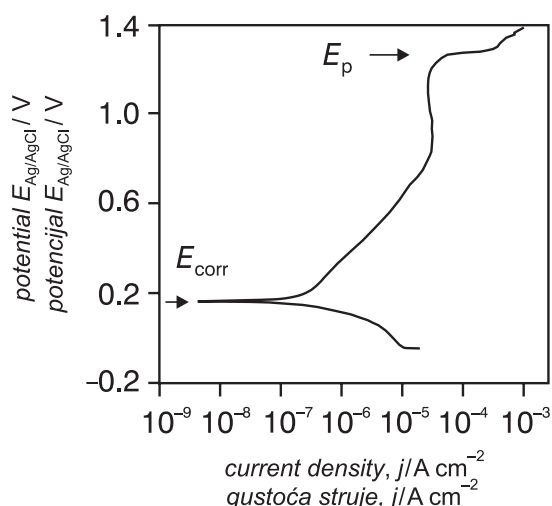


Fig. 8 – Anodic potentiodynamic curve for AISI 316L steel in HNO_3 solution, $\varphi = 6.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\varphi = 2.0\%$ (3600 s, 60°C) at a scan rate of $\nu = 5 \text{ mV s}^{-1}$

Slika 8 – Potenciodinamička krivulja čelika AISI 316L snimljena u anodnom smjeru u otopini $\varphi = 6,0\%$ $\text{HNO}_3 + \varphi = 2,0\%$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3600 s, 60°C) pri brzini promjene potencijala $\nu = 5 \text{ mV s}^{-1}$

Table 5 – Corrosion quantities for AISI 316L steel in $\varphi = 6.0\%$ HNO_3 solution containing $w = 2.0\%$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3600 s, 60°C)

Tablica 5 – Veličine korozije čelika AISI 316L u otopini $\varphi = 6,0\%$ $\text{HNO}_3 + w = 2,0\%$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3600 s, 60°C)

R_p $\text{k}\Omega \text{ cm}^2$	b_a V dek^{-1}	$-b_c$ V dek^{-1}	$\frac{E_{\text{corr,Ag/AgCl/KCl}}}{V}$	j_{corr} $\mu\text{A cm}^{-2}$	ν_{corr} mm a^{-1}	$\frac{E_p, \text{Ag/AgCl/KCl}}{1.3}$
141	0.382	0.360	0.193	0.433	4.5310^{-3}	1.3

obtained in demineralized water (Table 3) showed the passivation solution to have been more aggressive. The solution selected for passivation had to be aggressive in order to provide a sufficiently efficacious protection against pitting corrosion to the steel surface. However, in addition to protecting the steel surface against pitting corrosion the behaviour of the passivation solution was not as aggressive as to cause steel dissolution i.e. general steel corrosion. The measured corrosion rate ($\nu = 4.53 \cdot 10^{-3} \text{ mm a}^{-1}$) was not considered to present a risk, as only a rate higher than $\nu = 0.127 \text{ mm a}^{-1}$ was taken to be hazardous to the steel surface. A relatively high value of the pitting potential ($E_p \sim 1.3 \text{ V}$) proved that the choice of passivation solution had been correct and that using a solution as passivation medium which was bound to cause pitting corrosion would have been pointless.

Conclusion

From the results of potentiodynamic polarization measurements on AISI 316L steel in demineralized water and in different passivation solutions it may be concluded that

– Demineralized water at 80°C caused damage to the steel surface.

– Aqueous solution containing $w = 5\%$ citric acid and $w = 25\%$ ammonia did not act as an efficacious medium for passivation of steel surface. Nitric acid solution likewise failed to produce a protective effect, irrespective of concentration and oxygen content.

– Nitric acid solution failed as passivation medium because it did not raise the pitting potential to a more positive value in comparison with the potential measured on the nonpassivated surface. The steel surface failed to be protected regardless of the nitric acid concentration used.

– The pitting potential indicated that the solution containing the inhibitor $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($E_p = 1.218 \text{ V}$) had a much greater capability for passivation than the solution containing $\text{K}_2\text{Cr}_2\text{O}_7$ ($E_p = 0.502 \text{ V}$).

– Protection of the steel surface was provided by passivation in HNO_3 , $\varphi = 12.0\%$, solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 4.0\%$, and in HNO_3 , $\varphi = 6.0\%$, solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 4.0\%$.

– Prolongation of exposure time in HNO_3 solution, $\varphi = 6.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 2.0\%$, from 600 to 3600 s caused a shift in the pitting potential by 0.365 V to more positive values. Increase in temperature also had a positive effect on passivation.

– Analysis of effectiveness of the selected passivation solutions showed that AISI 316L steel surface was best protected by the HNO_3 solution, $\varphi = 6.0\%$, containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 2.0\%$, with the exposure time of 3600 seconds and temperature of 60°C .

– A relatively high value of the pitting potential ($E_p \approx 1.3 \text{ V}$) measured in the HNO_3 solution, $\varphi = 6.0\%$, with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w = 2.0\%$ (3600 s, 60°C) was taken to prove that the choice of passivation solution had been correct.

List of symbols

Popis simbola

- A – surface area, cm^2
– površina, cm^2
- b – slope of the curve, V dek^{-1}
– nagib krivulje, V dek^{-1}
- c – concentration, mol dm^{-3}
– koncentracija, mol dm^{-3}
- E_{corr} – corrosion potential, V
– korozijski potencijal, V
- E_p – pitting potential, V
– potencijal početka jamičaste korozije, V
- j_{corr} – current density, mA cm^{-2}
– gustoća struje, mA cm^{-2}
- m_{eq} – equivalent mass, g
– ekvivalentna masa, g
- m_{loss} – mass loss, g
– gubitak mase, g
- R_p – polarization resistance, cm^2
– polarizacijski otpor, cm^2
- t – time, s
– vrijeme, s

- v_{corr} – corrosion rate, mm a^{-1}
– brzina korozije, mm a^{-1}
- w – mass fraction, %
– maseni udjel, %
- γ – mass concentration, mg dm^{-3}
– masena koncentracija, mg dm^{-3}
- δ – thickness of layer, nm
– debljina sloja, nm
- ϑ – Celsius temperature, $^{\circ}\text{C}$
– Celsiusova temperatura, $^{\circ}\text{C}$
- ν – scan rate, mV s^{-1}
– brzina promjene potencijala, mV s^{-1}
- ρ – density, g cm^{-3}
– gustoća, g cm^{-3}
- τ – charge density, mC cm^{-3}
– gustoća naboja, mC cm^{-3}
- φ – volume fraction, %
– volumni udjel, %

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SAŽETAK**Ponašanje čelika AISI 316L izloženog demineraliziranoj vodi**M. Gojić,^a D. Marijan,^b S. Kožuh^a i T. Sorić^c

Predmet istraživanja rada bila je pasivizacija austenitnog nehrđajućeg čelika AISI 316L. Djelotvornost različitih sredstava za pasivizaciju ispitivana je potenciodinamičkom polarizacijom. Potenciodinamička polarizacija provedena je u demineraliziranoj vodi prije i nakon pasivizacije. Uočeno je da demineralizirana voda pri 80 °C prouzroči oštećenje površine čelika. Vodena otopina limunske kiseline, $w(\text{limunske kiseline}) = 5\%$, i amonijaka, $w(\text{amonijaka}) = 25\%$, ne djeluje povoljno kao sredstvo za pasivizaciju. Dobivene vrijednosti potencijala početka jamičaste korozije upućuju na to da otopina koja sadrži $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ kao inhibitor korozije ima znatno veću sposobnost pasivizacije nego otopina koja sadrži $\text{K}_2\text{Cr}_2\text{O}_7$. Usporedna analiza potenciodinamičkih krivulja snimljenih u različitim sredstvima za pasivizaciju pokazala je da se najbolja zaštita površine čelika postiže s otopinom HNO_3 , $w = 6,0\%$, i $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $w(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 2,0\%$. Zadovoljavajuća zaštitna svojstva podudaraju se s visokom vrijednošću potencijala početka jamičaste korozije.

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Prispjelo 11. rujna 2008.
Prihvaćeno 7. travnja 2009.