Passivation of welded AISI 316L stainless steel

Pasivacija varjenega nerjavnega jekla AISI 316L

Mirko Gojić[1], Dražen Marijan[2], Marijan Tudja[2], Stjepan Kožuh[1]

[1]University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja 3, 44103 Sisak, Croatia;
E-mail: kozuh@simet.hr; gojic@simet.hr
[2]PLIVA Croatia, Ltd, Quality, Prilaz baruna Filipovića 25, 10000 Zagreb, Croatia;
E-mail: drazen.marijan@pliva.hr

Abstract: The paper deals with the results of passivation of welded AISI 316L austenitic stainless steel. The effectiveness of passivation in a volume fraction 6.0 % HNO_3 solution containing the mass fraction of $CuSO_4 \cdot 5H_2O$ 2.0 % was tested by potentiodynamic polarization. Polarization was carried out in demineralized water before passivation and after it. At 80 °C demineralized water induced pitting corrosion and passivation was undertaken to protect the steel surface. As a result of passivation the pitting potential decreased. The satisfactory protective properties of the passive film on steel surface were found to agree with the high value of the pitting potential. After passivation, the presence of white dotty agglomerations of copper atoms was observed on the surface in the proximity of the melted zone.

Povzetek: Članek obravnava rezultate pasivacije varjenega nerjavnega jekla AISI 313L. Učinek pasivacije v volumenski 6-odstotni raztopini HNO_3, ki vsebuje še masni delež 2 % $CuSO_4 \cdot 5H_2O$ smo preizkušali s potenciodinamično polarizacijo. Polarizacija je potekala v deminerilizirani vodi pred polarizacijo in po njej. Pri 80 °C deminerilizirana voda povzroči točkasto korozijo, pasivacija pa zagotavlja zaščito površine jekla. Posledica pasivacije je zmanjšanje potenciala za točkasto korozijo. Zadostna zaščita pasivacijskega filma plasti na površini jekla je v skladu z velikim potencialom za točkasto korozijo. Po pasivaciji pa je značilna prisotnost točkastih aglomeratov bakrovih atomov v okolici vara.

Key words: stainless steel, passivation, pitting corrosion, morphology
Ključne besede: nerjavno jeklo, pasivacija, točkasta korozija, morfologija

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INTRODUCTION

Austenitic stainless steels find important and manifold applications as construction materials in chemical and petrochemical industries, in oil and gas exploitation, shipbuilding, food and drug processing, and in water purification and distribution systems. Their chief characteristics are good resistance to corrosion and elevated temperatures, good cryogenic strength, and low magnetic permeability[1,2]. The AISI 304 and 316 austenitic stainless steels, with their low-carbon 304L and 316L grades, account for the largest fraction of the world's stainless steel production and exploitation. Welding of stainless steels causes formation of a very heterogeneous melted zone because of impurities segregated at delta ferrite/austenite interphases and because of possible presence of secondary precipitates (carbides, chi and sigma phases, etc.)[2].

Numerous investigations have shown the impairment of the corrosive and mechanical properties of the melted zone to be due in the first place to the dominant attack of corrosion at segregation sites, in dendrite nuclei, at the austenite/delta ferrite interphases, and at the interphases of the secondary precipitates present in the zone[3,4]. In certain environments and conditions, although belonging to a group of corrosion-resistant materials, austenitic stainless steels are prone to damage by corrosion, i.e. pitting corrosion.

Among various metals that are used to protect the surface of the water purification and distribution systems stainless steels come first. 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. To diminish those effects the passivation process must be carried out efficiently and on time[5]. In this work emphasis was placed on investigating the effectiveness of surface passivation of a welded joint (base metal, heat-affected zone, melted zone) because of its specific composition and microstructure.

EXPERIMENTAL

Investigation of corrosion behaviour was performed on a weld joint from AISI 316L austenitic stainless steel which formed part of a water purification and distribution system. The chemical composition of the steel is given in Table 1. The choice of measuring equipment, electrochemical reactor, and auxilliary and reference electrodes, and the preparation of the working electrode were made in conformity with ASTM standards[6,7]. The equipment for electrochemical measurements consisted of an EG&G PAR 273 A potentiostat/galvanostat, a Cole-Parmer 12700-55 thermostat, and an EG&G Corrosion Cell System, Model K47 electrochemical reactor. A standard three-electrode corrosion cell was used. A disc-shaped working electrode (A = 1 cm^2) was prepared from the AISI 316L weld joint. Welding was performed under a protective argon flow. The weld included the melted zone, the heat-affected zone, and the painted fraction of the base metal. An Ag/AgCl electrode served as the

reference electrode, and the counter electrode was a roller-shaped graphite electrode. Anodic potentiodynamic polarization curves were recorded in conformity with ASTM standards.

Table 1. Chemical composition of AISI 316L steel in mass fractions, w/%
Tabela 1. Kemična sestava jekla AISI 316L v masnih deležih, 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

Electrochemical measurements were carried out in a real medium (demineralized water, 80 °C) and the passivating in volume fraction 6.0 % HNO_3 solution containing the mass fraction of $CuSO_4 \cdot 5H_2O$ 2.0%.
In addition to electrochemical measurements, a comparative examination of the surface of welded and non-welded AISI 316L steel samples was performed with a Jeol JSM-5800 scanning electron microscope and an Oxford ISIS-302 chemical analyser. The welded sample was examined without prior mechanical treatment, whereas the non-welded one was polished with a 1000 grit abrasive paper in Al_2O_3 (0.5 µm) solution. The non-welded surface was machined to conform to ASTM criteria, to facilitate detection of defects due to passivation, and to make electrochemical measurements easier to conduct. For chemical cleaning the mass fraction 2 % of citric acid solution with 5 % the mass fraction of ammonia (1800 s, 80 °C) was used. Passivation was carried out at 60 °C in the volume fraction 6.0 % of HNO_3 solution containing the mass fraction of $CuSO_4 \cdot 5H_2O$ 2 % for 3400 s.

RESULTS AND DISCUSSION

Electrochemical measurements combined with surface analysis facilitated assessment of the surface condition of the AISI 316L steel weld. With the two methods the modifications produced by chemical cleaning and passivation could be followed simultaneously. In this way it was possible to establish a link between the corrosion parameters (R_p, E_{CORR}, j_{CORR} and E_p) and the morphological features of the surface.

Electrochemical measurements
Before testing the capability for passivation of the 6.0 % HNO_3 solution containing the mass fraction of $CuSO_4 \cdot 5H_2O$ 2 % with the help of a potentiodynamic polarization curve we first investigated how demineralized water (real medium), at 80 °C, affected the surface stability of the AISI 316L steel weld (Figure 1). We then determined the corrosive properties of the steel in demineralized water after passivation (Figure 2) and in the passivation solution (Figure 3). The general and pitting corrosion parameters as read from the potentiodynamic polarization curves are listed in Table 2. In practice, to be considered 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 roughness. A rough and porous structure will facilitate oxidation and dissolution of the surface layers, in other words it will become more susceptible to pitting corrosion. The instability of the steel surface will produce as a result a lower pitting potential (E_p). By undertaking a timely protective treatment i.e.
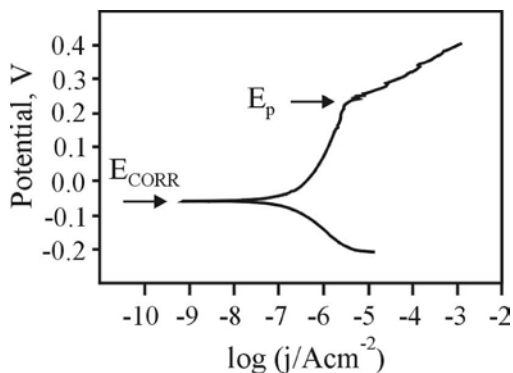
Figure 1. Anodic potentiodynamic polarization curve for AISI 316L steel weld in demineralized water before passivation, at the potential scan rate of 5 mV s^{-1}
Slika 1. Krivulja anodne potenciometrične polarizacije zvara jekla AISI 316L v demineirilizirani vodi pred pasivacijo pri hitrosti menjave potenciala 5 mV s^{-1}
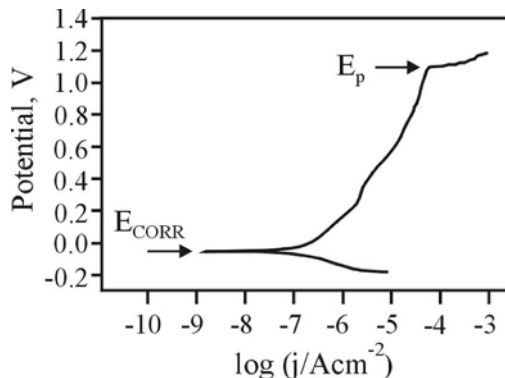
Figure 2. Anodic potentiodynamic polarization curve for AISI 316L steel weld in demineralized water after passivation, at the potential scan rate of 5 mV s^{-1}
Slika 2. Krivulja anodne potenciometrične polarizacije zvara jekla AISI 316L v deminerilizirani vodi po pasivaciji pri hitrosti menjave potenciala 5 mV s^{-1}

passivation, the E_p potential will be shifted towards more positive values.

The values of general corrosion parameters measured in demineralized water demonstrated that general corrosion did not cause any major damage to the surface of the AISI 316L steel weld. The general corrosion rate of 4.530 · 10^{-3} mm a^{-1} was taken to represent the average rate of deterioration of the weld surface. As well as from the rate, general corrosion could be assessed from the mass loss occurring over the period of steel exposure to demineralized water. Equivalent to the general corrosion rate of 4.530 · 10^{-3} mm a^{-1} was a mass loss of 0.036 g dm^{-2} a^{-1}. It is well established that a medium having a general corrosion rate exceeding 0.127 mm a^{-1}, or a mass loss in excess of 10.087 g dm^{-2} a^{-1}, is not considered appropriate for use[8] he low values of general corrosion parameters were proof that general corrosion was not

the reason why the surface of the welded AISI 316L steel needed to be passivated (Table 2). The chief reason for passivation was the onset of pitting corrosion. The pitting potential (E_p) at the steel surface was 0.228 V (Figure 1, Table 2). From Figure 1 it is evident that the E_p value was too low and the $E_p – E_{CORR}$ difference too small for the weld surface to resist pitting corrosion. The susceptibility to pitting corrosion of AISI 316L steel was the main reason why it was necessary to protect the steel surface by passivation.

The passivation effectiveness of the volume fraction 6.0 % HNO$_3$ solution containing the mass fraction of CuSO$_4$·5H$_2$O 2.0 % was evaluated using the parameters from the potentiodynamic polarization curve recorded in demineralized water after passivation (Figure 2, Table 2). The values of general corrosion parameters after passivation indicated that the corrosion
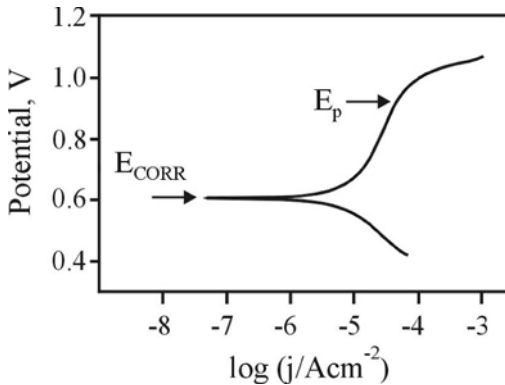
Figure 3. Anodic potentiodynamic polarization curve for AISI 316L steel weld in passivation solution, at the potential scan rate of 5 mV s^{-1}
Slika 3. Krivulja anodne potenciometrične polarizacije zvara jekla AISI 316L v raztopini za pasivacijo pri hitrosti menjave potenciala 5 mV s^{-1}

rate decreased (from $4.530 \cdot 10^{-3}$ mm a^{-1} to $1.204 \cdot 10^{-3}$ mm a^{-1}), i.e. that general corrosion resistance increased. The pitting potential at the passivated surface was higher (1.098 V) than the one at the nonpassivated surface (0.228 V). A rise in the E_p value led to a higher $E_p - E_{CORR}$ value (from 0.287 V to 1.063 V). The E_p and $E_p - E_{CORR}$ values indicated that the chosen passivation treatment provided effective protection against pitting corrosion to the AISI 316L

steel surface exposed to demineralized water. However, unless the steel surface was thoroughly rinsed with demineralized water there was a risk of galvanic corrosion[9]. Galvanic corrosion occurs when two dissimilar metals, immersed in a corrosive medium, come in direct contact and form a galvanic couple. The greater the difference between standard electrode potentials (E^0) of individual metals in the couple the more pronounced galvanic corrosion. After passivation, the residual copper atoms ($E^0 = 0.337$ V) absorbed on the steel surface may have formed microcouples with the steel constituents, iron ($E^0 = -0.037$ V), nickel ($E^0 = -0.250$ V), and chromium ($E^0 = -0.744$ V), and thus may have induced galvanic corrosion. To prevent this from hapenning it was essential that the steel surface be thoroughly rinsed after passivation.

Taking the volume fraction 6.0 % HNO$_3$ solution with the mass fraction of CuSO$_4$·5H$_2$O 2.0 % to be an efficacious protective agent against pitting corrosion, it was important to determine general and pitting corrosion parameters for the situation where the steel was exposed solely to the passivation solution. Analysis

Table 2. General and pitting corrosion parameters of AISI 316L steel weld in demineralized water before and after passivation, and in passivation solution
Tabela 2. Parametri splošne in točkaste korozije zvara jekla AISI 316L v deminerilizirani vodi pred pasivacijo in po njej ter v raztopini za pasivacijo

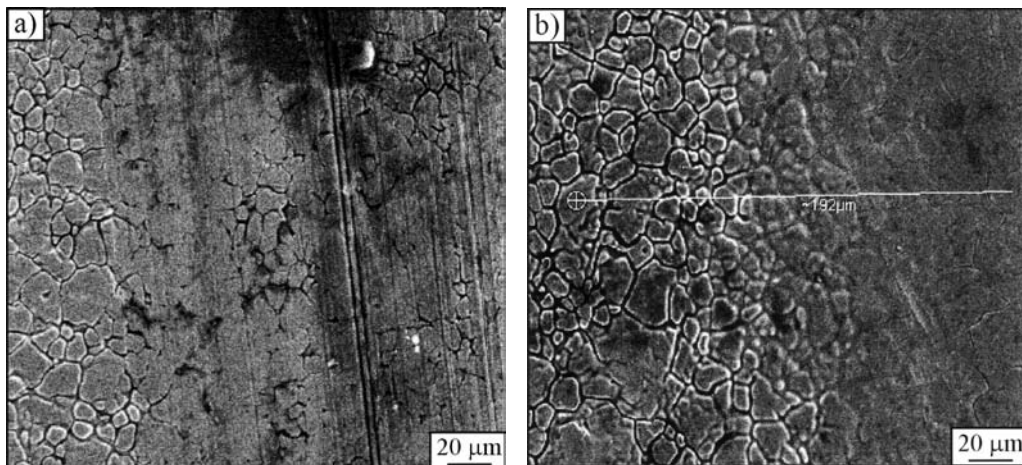| Solution	$R_p/$ kΩ	$b_a/$ dek^{-1}/V	$-b_c/$ dek^{-1}/V	$E_{CORR}/$ V	$j_{CORR}/$ (μA cm^2)	$v_{CORR}/$ mm a^{-1}	$E_p/$ V
Demineralized water	0.251	0.312	0.152	-0.059	0.430	$4.530 \cdot 10^{-3}$	0.228
Demineralized water after passivation	0.406	0.354	0.153	0.035	0.148	$1.204 \cdot 10^{-3}$	1.098
Passivation solution	0.010	0.387	0.296	0.643	4.74	0.049	0.900

Figure 4. SEM micrograph of the initial surface of AISI 316L steel base metal (a) and weld joint (b)
Slika 4. Mikrografiji začetne površine jekla AISI 316L (osnovni material) (a) in zvarnega spoja (b)
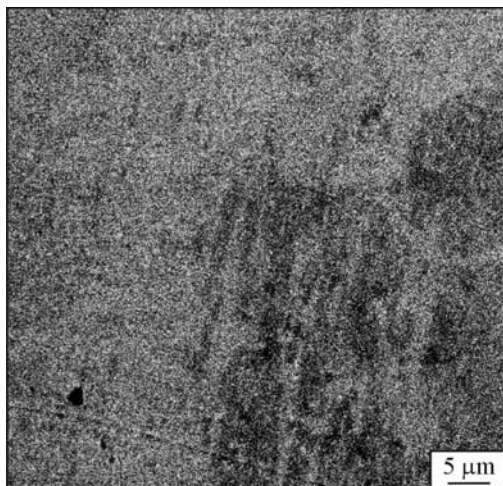

Figure 5. SEM micrograph of the surface of AISI 316L steel after polishing
Slika 5. Mikrografija polirane površine jekla AISI 316L; SEM

of the results obtained from the potentiodynamic polarization curve recorded in the passivation solution demonstrated that the passivation solution was more aggressive than demineralized water (Figure 3, Table 2). The aggressiveness of the passivation solution was as expected because, were it not so, the protection against pitting corrosion provided by the solution would not have been effective. However, the adverse effect of the passivation solution was still not strong enough to cause the steel surface to dissolve, i.e. to induce general corrosion (Table 2). A general corrosion rate of over 0.127 mm a^{-1} was considered to be hazardous to the steel surface[10]. The pitting potential value (0.900 V) was taken to prove that the passivation medium was well chosen.

Of the methods used for protecting the steel surface none has proved capable of completely stopping the process of corrosion. By efficient and timely protection of the steel surface only the rate of corrosion can be diminished. It is therefore essential to repeat the protective passivation treatment after a certain period. How often passivation needs repeating will depend on a number of fac-
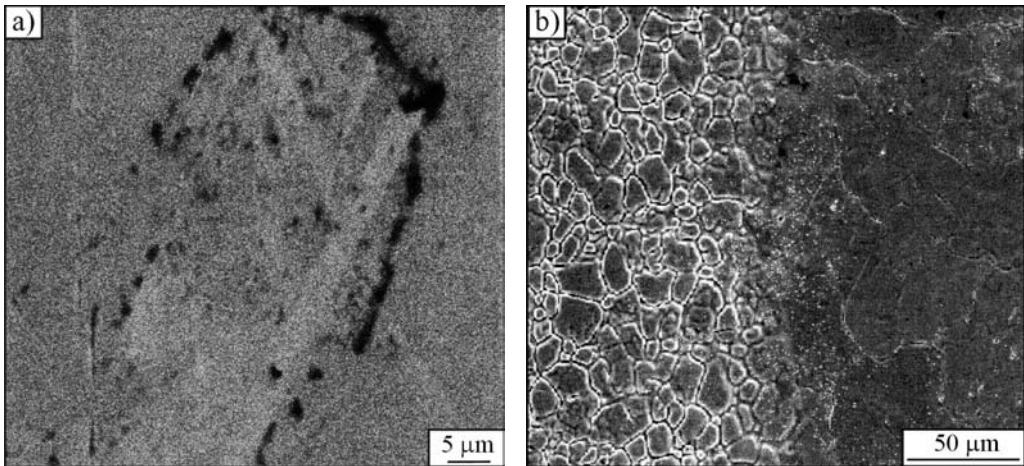
Figure 6. SEM micrograph of the surface of AISI 316L steel base metal (a) and weld joint (b) after passivation
Slika 6. Mikrografija pasiviranih površin jekla AISI 316L (osnovni material) (a) in zvarnega spoja (b); SEM

tors: operating conditions of the water purification and distribution system, type and frequency of welding, temperatures of the media present in the system, temperature stresses during exploitation, oxygen content in the system, reduced oxygen values, etc[11]. Assessment of the steel surface condition will therefore require not only laboratory studies but also real-life investigations in water distribution systems[12].

Surface analysis
Analysis of surface morphology of the AISI 316L base metal and weld joint was carried out before and after polishing, and also after passivation (Figures 4–6). Initially, the base metal surface showed the presence of grooves as well as of impurities, cracks, and dimples (Figure 4a). In the weld two zones could be distinguished: the melted zone and the zone adjacent to the melted zone (Figure 4b). The melted zone morphology was characterized by an even and compact struc-

ture (Figure 4b, right). The adjacent zone, contrariwise, exhibited cracks and grain boundaries (Figure 4b, left). Despite morphological differences, a quantitative linear analysis demonstrated equal proportions of individual elements in the two zones (Figure 7). Chemical cleaning helped reduce the cracks' width and achieve a more uniform structure of the welded surface.

The polished surface of AISI 316L steel was characterized by a smooth and uniform structure (Figure 5). After polishing there were no signs of cracks or impurities on the steel surface. The passivated surface of the base metal exhibited an irregular distribution of indentations (with a maximum diameter of up to 5µm) (Figure 6a). Quantitative linear analysis showed the chemical composition of the steel surface inside and outside indentations (dimples) to be identical (Figure 8). The appearance of dimples was the result of dissolution of unstable surface sulphur in the acidic me-
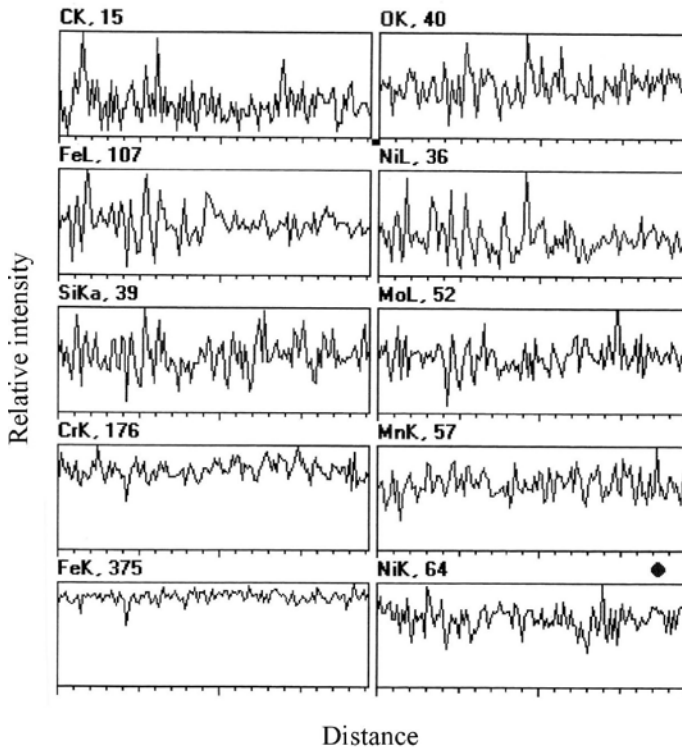
Figure 7. Quantitative linear analysis of the initial surface of AISI 316L steel weld joint
Slika 7. Kvantitativna kemična črtna analiza na začetni površini zvara jekla AISI 316L; EDXS

dium, i.e. in the passivation medium.

The passivation process is known to reduce not only localized sulphur concentration in AISI 316L steel but also its total concentration thus increasing steel resistance to pitting corrosion[10]. Increase in the pitting resistance of the weld following passivation was established by analysis of the parameters obtained by potentiodynamic measurements (Table 2). The passivated surface in the close proximity of the melted zone exhibited white dotty agglomerations and slightly less pronounced grain boundaries in comparison with the nonpassivated

surface. The structure was granular, with grains having a smooth surface. Surface analysis showed the granular agglomerations to consist of copper atoms (Figure 9). Quantitative linear analysis of the steel surface following passivation failed to show a major difference in the content of individual elements between the melted zone and the adjacent zone (Figure 10). It may therefore be concluded that the passivation medium "attacked" the steel weld surface in a uniform manner. As a result of passivation all steel constituents formed oxides without prior dissolution. On the other hand, had
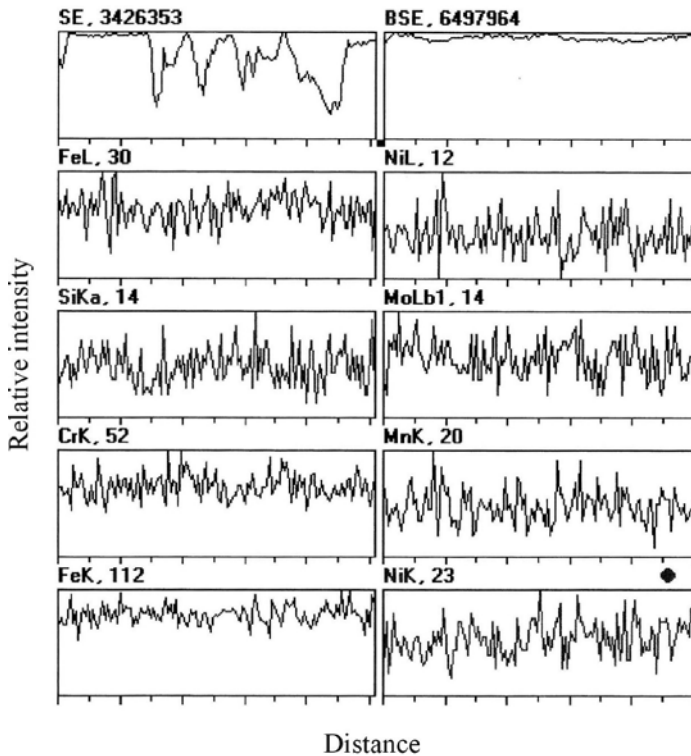
Figure 8. Quantitative linear analysis of the passivated surface of AISI 316L steel base metal
Slika 8. Kvantitativna kemična črtna analiza pasivirane površine jekla AISI 316L (osnovni material); EDXS
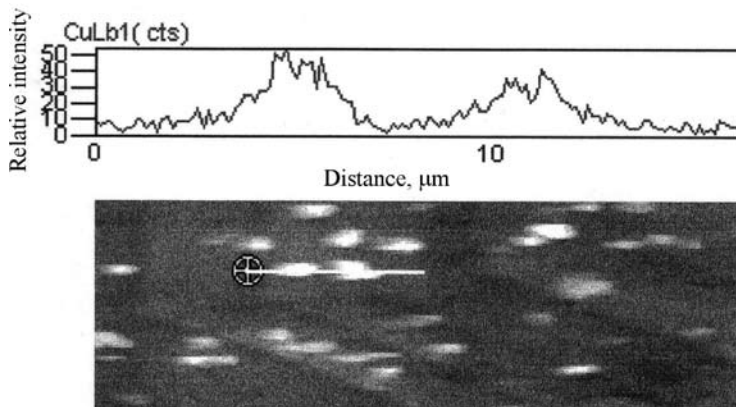

Figure 9. Quantitative linear analysis of small agglomerations on the surface of AISI 316L steel weld joint
Slika 9. Kvantitativna kemična črtna analiza drobnih aglomeratov na površini zvara jekla AISI 316L; EDXS
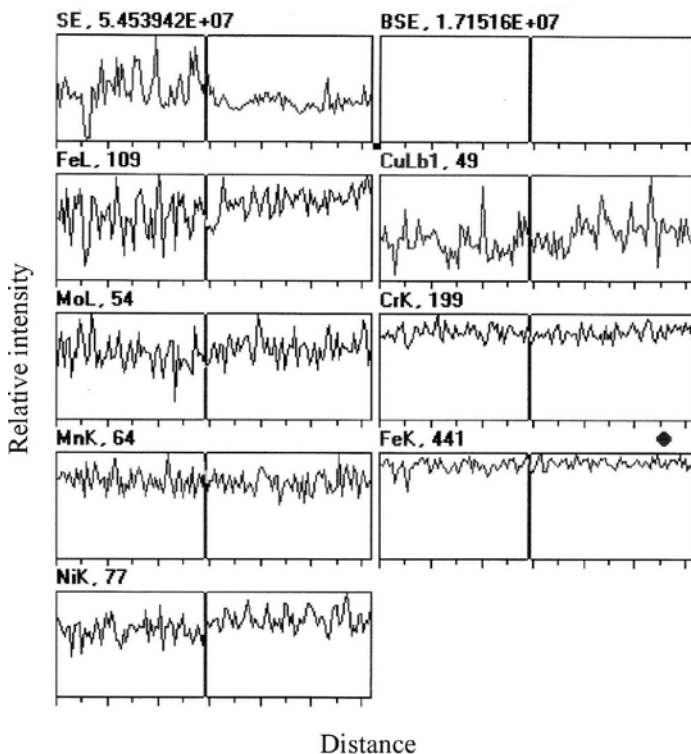
Figure 10. Quantitative linear analysis of the passivated surface of AISI 316L steel weld joint

Slika 10. Kvantitativna kemična črtna analiza pasivirane površine zvara jekla AISI 316L; EDXS

dissolution taken place before oxidation of surface atoms, quantitative analysis would have shown an uneven distribution of the alloying elements. The uniform surface composition of the steel weld, by warranting invariable ratios of chromium and iron mass fractions, proved to be a measure of effectiveness of passivation treatment[13,14].

Roughness measurements (R_a) are often used for testing the efficacy of passivation media. The postpassivation roughness values were 1.6 μm for the melted zone, 0.37 μm for the painted zone, and 0.25 μm for the base metal. The painted area of the passivated surface adjacent to the melted zone exhibited a highest level of roughness, being the site of highest exposure to the negative effect of heat input during welding. By failing to enhance surface roughness, passivation helped prevent a possible drop in surface stability of AISI 316L steel.

CONCLUSIONS

From the results of potentiodynamic measurements and surface analysis of the AISI 316L steel weld exposed to demineralized water it may be concluded that:

- General corrosion did not cause a major damage to the steel surface.
- At 80 °C demineralized water caused damage to the steel surface inducing pitting corrosion so that passivation treatment in the volume fraction 6.0 % HNO_3 solution containing the mass fraction of $CuSO_4 \cdot 5H_2O$ 2.0 % was undertaken.
- After passivation the general corrosion rate diminished (from $4.530 \cdot 10^{-3}$ mm a^{-1} to $1.204 \cdot 10^{-3}$ mm a^{-1}), and general corrosion resistance increased.
- The pitting potential at the passivated steel surface (1.098 V) was more positive than the one at the nonpassivated surface (0.228 V). A rise in the pitting potential was accompanied by increase in $E_p - E_{CORR}$ value (from 0.287 V to 1.063 V) indicating that the chosen passivation treatment provided efficacious protection against pitting corrosion.
- The passivation solution was more aggressive than demineralized water. The noted aggressivity was insufficient to cause dissolution of the steel surface.
- After passivation the steel surface needed to be thoroughly rinsed with demineralized water to prevent adsorption of copper atoms on the welded surface and possible occurrence of galvanic corrosion.
- After passivation the surface adjacent to the melted zone exhibited white dotty agglomerations. Analysis showed the agglomerations to consist of copper atoms.
- The painted portion of the passivated surface adjacent to the melting zone was characterized by the highest level of roughness, being the site of the most pronounced negative effect of heat input during welding.

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