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EFFECTS OF CONCENTRATION OF SODIUM CHLORIDE SOLUTION ON THE PITTING CORROSION BEHAVIOR OF AISI-304L AUSTENITIC STAINLESS STEEL

The pitting corrosion behavior of the austenitic stainless steel in aqueous chloride solution was investigated using electrochemical technique. Corrosion potential (E_{corr}) measurements, potentiodynamic experiments, potential-hold experiments in the passive range, and microscopic examination were used for the evaluation of corrosion characteristics. The experimental parameters were chloride ion concentration, immersion time and anodic-hold potential. E_{corr} measurements along with microscopic examinations suggest that in or above 3.5 % NaCl at pH 2 pitting took place on the surface in absence of applied potential after 6 hour immersion. The potentiodynamic experiments revealed that E_{corr} and pitting potential (E_{pit}) decreased and current density in the passive region increased with the increase of chloride ion concentrations. A linear relationship between E_{pit} and chloride ion concentrations was found in this investigation. The analysis of the results suggests that six chloride ions are involved for the dissolution of iron ion in the pitting corrosion process of austenitic stainless steel.

Keywords: stainless steel; pitting corrosion; electrochemical technique; anodic potential.

Stainless steel finds extensive applications as a construction material in various aggressive environments such as in chemical, desalination and waste water treatment plants and in the petroleum industry due to its excellent resistance to general corrosion, adequate high temperature mechanical properties, good fabricability and weldability. The superior corrosion resistivity of stainless steel is due to a naturally formed adherent, compact and more or less flawless oxide film on the surface. In aqueous medium the passive film formed on the stainless steel is duplex in nature, consisting of a chromium-rich inner barrier oxide layer and iron-rich outer deposited hydroxide or salt layer [1-10]. Such passive films, however, are often susceptible to localized breakdown on the defect site in presence of aggressive chloride ions, causing pitting

corrosion and severe damage to the structure. The aggressiveness of chloride ions is due to their small size, high diffusivity and strong anionic nature and very high solubility of chloride salt [9-11]. So, investigation on pitting corrosion of stainless steel in chloride media is of great practical importance.

The breakdown of the passive film by chlorides with the initiation of pitting occurs at a critical potential called pitting potential, E_{pit} . This is one of the most important features that characterize the susceptibility of metals and alloys to pitting corrosion. Numerous attempts have been made to explore pitting of stainless steel [11-20]. Most of the theories believe that Cl^- penetrates and migrates through the passive films, and upon reaching the metal/film interface, results in film breakdown [17-21]. A linear relation between pitting potential and Cl^- concentration has been reported elsewhere [3,11]. Some investigators attributed the influence of inclusion like nitrogen and sulfur and their interaction with chlorides during pitting [1-3]. No quantitative study on pitting corrosion mechanism, however, has been attempted so far. Therefore, the mode of action of Cl^- , its interaction with surface passive film

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and their relations with pitting potential are worth investigation.

EXPERIMENTAL

Commercial grade AISI-304L austenitic stainless steel having composition of 10.1% nickel, 19% chromium and 0.03% carbon with dimensions $2\text{ cm} \times 4\text{ cm} \times 0.02\text{ cm}$ was used in the study. The adherent dirt of the specimen was removed by polishing with fine grain sand paper followed by rinsing with distilled water and degreasing with acetone. This was then painted with insulating plastic paint leaving $1\text{ cm} \times 1\text{ cm}$ area exposed for experiment. The base electrolyte was made up by dissolving appropriate amount of analytical grade sodium chloride in distilled water. pH was adjusted by using analytical grade H_2SO_4 and NaOH .

Electrochemical measurements were carried out with a potentiostat (Model 1186 electrochemical interface, Solartron, UK). The electrochemical cell was composed of platinum counter electrode, stainless steel working electrode and saturated Ag/AgCl electrode (SSE) as a reference electrode. Specimens were immersed in the electrolyte for 1 h before electrochemical measurement. The corrosion potential, E_{corr} , was measured with a high impedance ($10^{10}\ \Omega$) electrometer with respect to SSE. The anodic potentiodynamic measurement was carried out at a scan rate $20\text{ mV}/\text{min}$ starting from 50 mV negative to corrosion potential. In the potential hold experiment, the specimen was held at constant anodic potential and the change of current densities with time was recorded. Before and after the each experiment the samples were examined with a light microscope at required magnification.

RESULTS AND DISCUSSION

Figure 1 shows that the corrosion potential (E_{corr}) of the austenitic stainless steel steadily decreased with immersion time in 4.5% NaCl (0.77 M) solution at pH 2. Microscopic observation of the surface after 6 h immersion in this condition showed a stable pit on the surface (Figure 2). The average size and number of the pits were 0.05 mm in diameter and 5 cm^2 surface respectively. In 3.5% (0.60 M) NaCl solution, E_{corr} increased up to 4 h. Afterwards, it suddenly decreased steeply indicating stable pit formation. Microscopic examination of the surface at this stage showed a shallow pit on the surface (Figure 2e). In all other cases (2.5, 1.5 and 0.5% NaCl), E_{corr} increased with time up to a certain period and remained steady afterwards. Microscopic examination did not show any pit on the surface (Figures 2b-2d). This reveals no pitting corrosion in these conditions.

Figure 3 shows the anodic potentiodynamic behavior of austenitic stainless steel in aqueous media containing different amount of chloride ion after one hour immersion at pH 2. The scan rate was $20\text{ mV}/\text{min}$. A steady increase of current with potential in 4.5% NaCl indicates active corrosion. In 3.5% NaCl solution current increased steeply after 0.2 V vs. SSE indicating passivation breakdown at this point. Passivation breakdown potential shifted towards more positive potentials with the decrease of chloride concentration. Microscopic examination of surface after anodic sweep showed pits on the surface (Figures 4a-4d). Therefore, the steep increase of current density is due to surface breakdown by pitting corrosion. Extended passive region (potential region with low current density) was observed in solu-

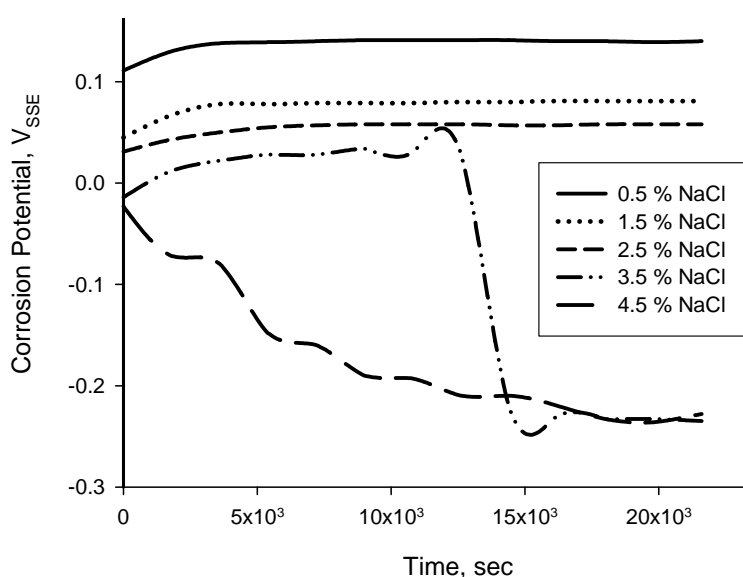


Figure 1. Effect of soaking time on corrosion potential in chloride media of pH 2.

tion having low concentration of the chloride ion. This is due to shifting of the pitting potential toward the anodic direction with the decrease of chloride ion concentration.

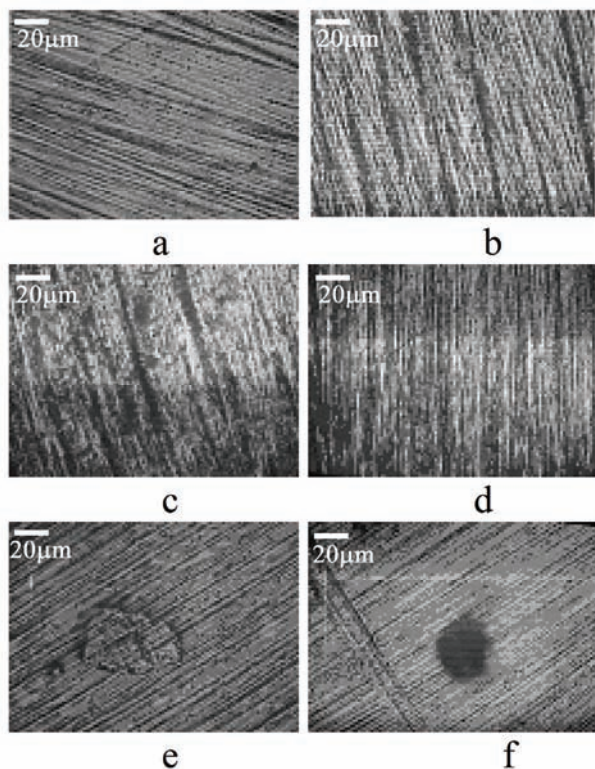


Figure 2. Surface morphology of AISI-304L austenitic stainless steel without soaking (a), 6 h soaking in 0.5% (b), 1.5% (c), 2.5% (d), 3.5% (e) and 4.5% (f) NaCl solutions of pH 2.

Figure 5 shows the effect of time on the current density at 200 mV anodic potential in chloride solution at pH 2. The current density increased with time in 2.5% and higher chloride containing media, and decreased rapidly and afterwards remained constant in all other cases of low chloride concentrations. The increase of current density with time is an indication of corrosion due to passivation breakdown by pit initiation. Absence of current density leveling off reveals continued pit initiation and propagation during this period. Therefore, higher amount of chloride ion has an effect on the pit initiation and propagation. At lower concentrations, the chloride ion is unable to initiate pit and the current levels off to the lower value within 5 min. The steep decrease of current to lower values is mostly due to dissipation away of initial non-faradaic current.

Figure 6 shows that pit initiation time at 0.2 V vs. SSE anodic potential is dependent on chloride ion concentration. Higher the chloride concentration less is the pit initiation time (induction time). If the concentration of chloride ion is higher, surface accumulation of chloride ion for pit initiation is faster. Induction time is also dependent on the anodic-hold potential in the passive region, as shown in Figure 7. More positive the hold potential in the passive range less is the pit initiation time. The rate of migration of the chloride ion to the defect site is higher at more anodic-hold potential. This supports the fact that higher is the anodic hold potential less is the induction time.

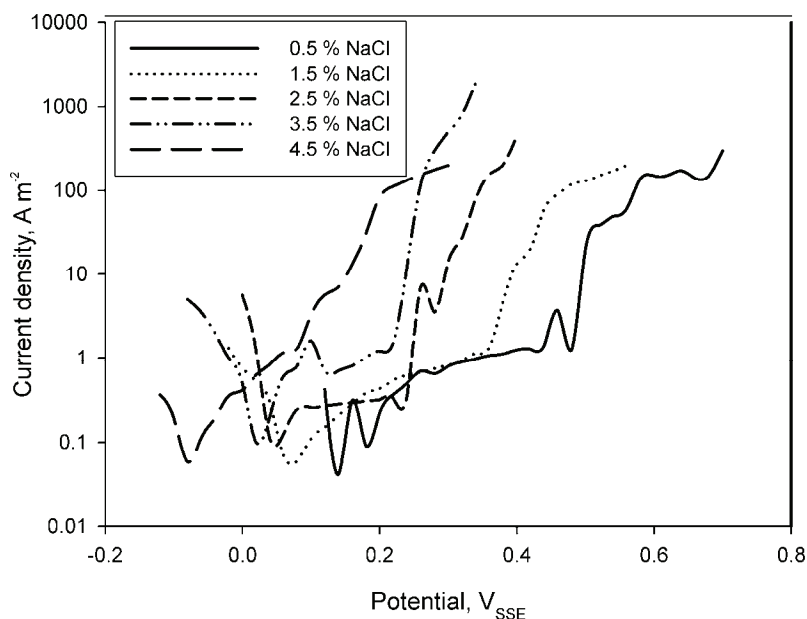


Figure 3. Effect of concentration of sodium chloride solution of pH 2 on the behavior of potentiodynamic anodic polarization of AISI-304L austenitic stainless steel.

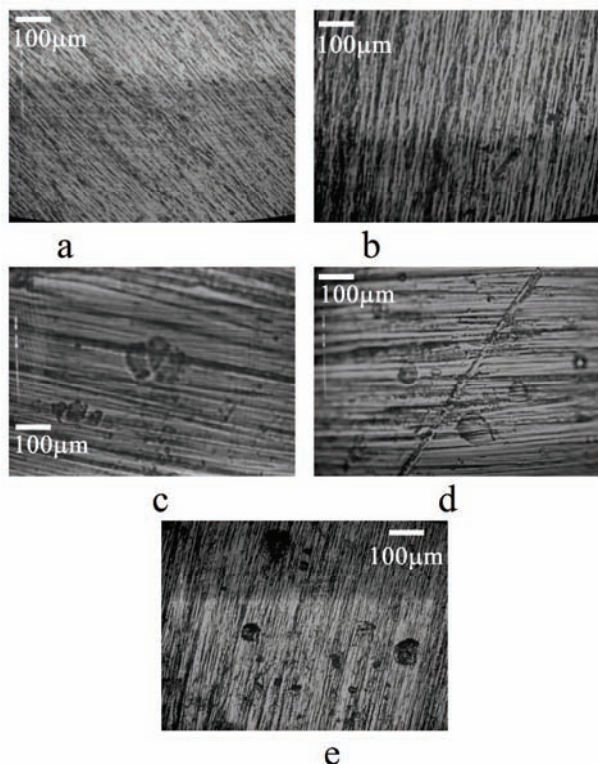


Figure 4. Surface morphology of AISI-304L austenitic stainless steel after potentiodynamic anodic polarization test; in a) 0.5%, b) 1.5%, c) 2.5%, d) 3.5% and e) 4.5% NaCl solution at pH 2 after 1 h immersion.

As stated earlier, in aqueous media the outer layer of passive film consists of hydrated Fe_2O_3 ($FeOOH$) and ferrous hydroxide $[Fe(OH)_2]$ or salt film

[22-28]. It has been reported that the surface pH of a non buffered solution is 4 units greater than the bulk solution [29]. Additionally, at the applied anodic potential, H^+ is repelled away from the surface making the anode area basic. This explains the stability of the surface oxide film even at bulk pH 2. It has been proposed that chloride ions do not enter into the oxide film, but are chemisorbed onto the oxide surface aiding oxide dissolution *via* the formation of chloride complexes at film/solution interface [30-33].

At the applied anodic potential ferrous ions are produced at the metal/passive oxide interface. These are migrated through passive film to the oxide-solution interface and forms ferrous hydroxide [25,26]. Applied anodic potential stimulates the migration of the chloride ion preferably to the defect sites of the surface. Sufficient accumulation of Cl^- in these defects leads pitting. With increase of bulk chloride ion concentration the pitting potential shifts toward more negative value undermining the role of anodic potential. Thus, either applied anodic potential or increased concentration of chloride ion is necessary for the pitting of stainless steel. It is convenient to state that the breakdown of passive film at pitting potential and film dissolution below the pitting potential are deferent phenomena.

At the potential in the passive region, the observed constant current density is due to the conversion of $Fe(OH)_2$ to more stable $FeOOH$ according to the reaction [20]:

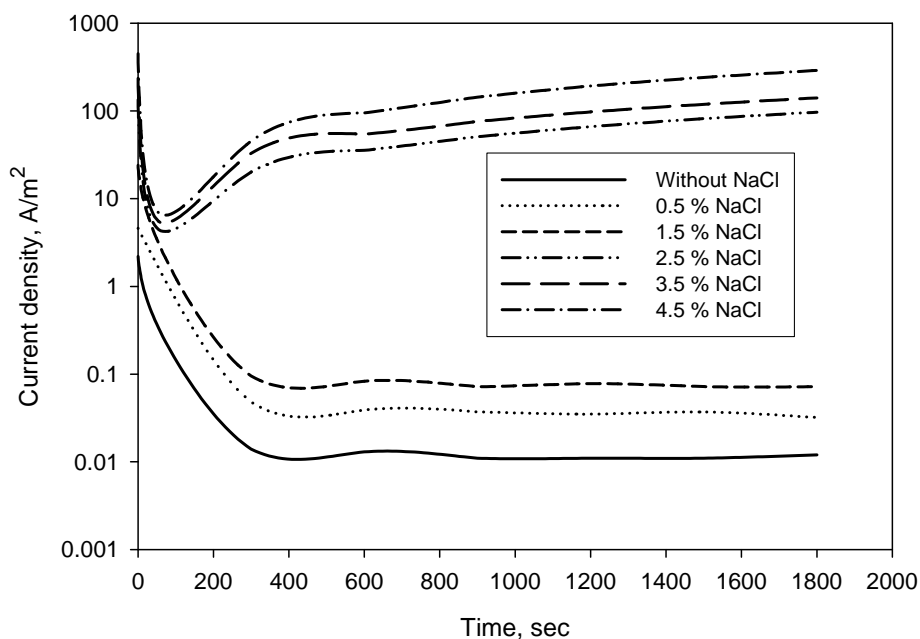
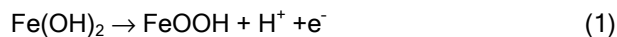


Figure 5. Effects of concentration of sodium chloride solution of pH 2 and an applied potential of $0.2 V_{SSE}$ on the behavior of time versus anodic current density of AISI-304L austenitic stainless steel.

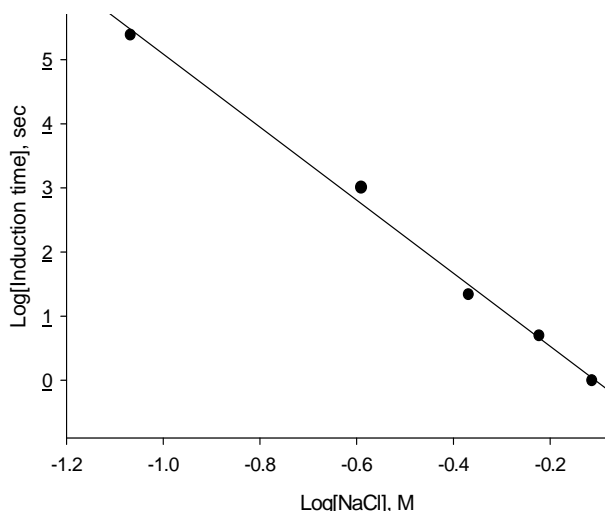


Figure 6. Relationship of concentration of sodium chloride solution of pH 2 and induction time at an applied potential of 0.2 V_{SSE} of AISI-304L austenitic stainless steel.

◇ 0.5 percent □ 1.5 percent △ 2.5 percent × 3.5 percent

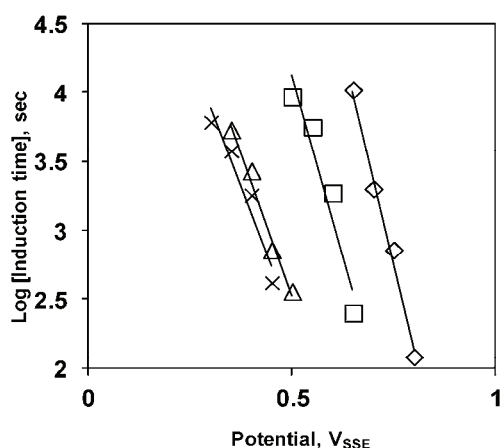
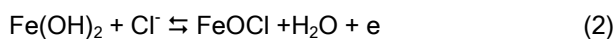


Figure 7. Relationship of anodic potential and induction time in different concentration of sodium chloride solution of pH 2.

In the presence of chloride ion increased passive current density may be due to conversion of Fe(OH)₂ to highly soluble FeOCl according to the reaction [21]:



From the pitting potential, E_{pit} vs. chloride concentrations plots, shown in Figure 8, it is clear that E_{pit} decreases linearly with logarithmic value of chloride ion concentration. This suggests the following equation for chloride ion dependency of pitting potential:

$$E_{\text{pit}} = a - b \log [\text{Cl}^-] \quad (3)$$

where E_{pit} is the pitting potential, and a and b are constants. The values of a and b obtained from Figure 8 are 0.089 V/mol and 0.35 V, respectively. The value

of b for iron-base alloys lies between 0.04 and 0.68 as reported elsewhere [34].

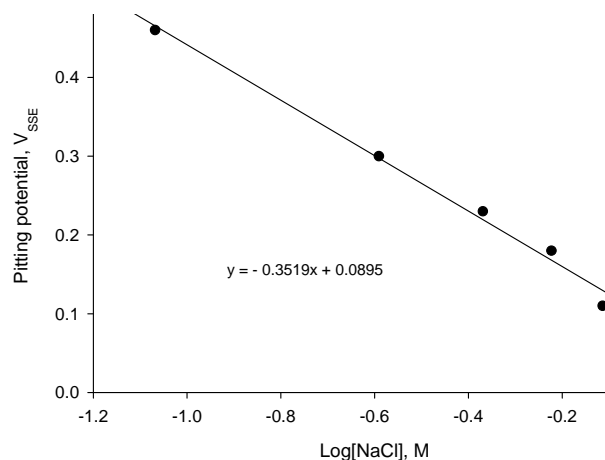


Figure 8. Effects of concentration of sodium chloride solution of pH 2 on the pitting potential of AISI-304L austenitic stainless steel.

Stirrup *et al.* [35] proposed the following equation for the dependency of chloride ion for passive metal at pitting potential:

$$E = E^0 - 2.303nRT/(n_1F) \log [\text{Cl}^-] \quad (4)$$

where n and n_1 are the number of chloride ions and number of electron transfer involved; and R , T and F are the gas constant, absolute temperature and Faraday constant, respectively. Putting the values of R , T and F , Eq. (4) can be written as:

$$E_{\text{corr}} = E^0 - (0.059 n/n_1) \log [\text{Cl}^-] \quad (5)$$

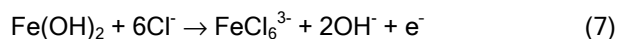
Comparing Eqs. (3) and (5) one can obtain:

$$b = (0.059 n/n_1) = 0.35 \quad (6)$$

Since the electrochemical reaction is the conversion of ferrous to ferric ion according to the reaction (2), therefore putting $n_1 = 1$ in Eq. (6) one can obtain:

$$(0.059 n) = 0.35 \text{ or } n = 5.93$$

This reveals that six chloride ions are involved for the dissolution of one surface Fe(OH)₂ during pitting process of austenitic stainless steel in the chloride media according to the following reaction:



Therefore, pit initiation or induction time is the time required for the accumulation of six chloride ions for each Fe²⁺. Accumulation of higher number of chlorides in the defect (pit initiation site) is easier when chloride ion concentration and anodic potential are higher.

CONCLUSIONS

1. The susceptibility of pitting corrosion of austenitic stainless steel increases with the increase of chloride ion concentration in acidic chloride media.
2. The pitting potential (E_{pit}) decreases with the increase of chloride ion concentration.
3. Induction time decreases with the increase of chloride concentration and anodic hold-potential in the passive region.

Six chloride ions are involved for dissolution of one surface $Fe(OH)_2$ at the defect site during the pitting process of the austenitic stainless steel in chloride media.

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NAUČNI RAD

UTICAJ KONCENTRACIJE NATRIJUM-HLORIDA NA TAČKASTU KOROZIJU AUSTENITNOG NERĐAJUĆEG ČELIKA AISI 304L

Ispitivana je tačkasta korozija kod austenitnog nerđajućeg čelika u vodenom rastvoru hlorida korišćenjem elektrohemijske metode. Za određivanje karakteristika korozije korišćeni su: merenje korozionog potencijala, potenciodinamički eksperimenti, eksperimenti u području potencijala pasivizacije i mikroskopska ispitivanja. Kao eksperimentalni parametri su korišćeni koncentracija hloridnih jona, vreme uranjanja i anodni potencijal. Merenje korozionog potencijala zajedno sa mikroskopskim ispitivanjima ukazuju na to da se tačkasta korozija javlja na površini u odsustvu primenjenog potencijala posle 6 sati potapanja u rastvor NaCl koncentracije od ili iznad 3,5% pri pH 2. Potenciodinamička ispitivanja pokazuju da se korozioni potencijal i potencijal tačkaste korozije smanjuju, dok se gustina struje u oblasti pasivizacije povećava sa porastom koncentracije hloridnih jona. Utvrđena je linearna zavisnost između potencijala tačkaste korozije i koncentracije hloridnih jona. Analiza rezultata ukazuje na to da je šest hloridnih jona uključeno u proces rastvaranja jona gvožđa prilikom tačkaste korozije austenitnog nerđajućeg čelika.

Ključne reči: nerđajući čelik; tačkasta korozija; elektrohemijske metode; anodni potencijal.