

THE ELECTROCHEMICAL STUDY OF DUPLEX STAINLESS STEEL IN CHLORIDE SOLUTIONS

ELEKTROKEMIJSKE RAZISKAVE DUPEKSNEGA NERJAVNEGA JEKLA V KLORIDNIH RAZTOPINAH

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The evolution of the passive film formed on duplex stainless steel 2205 in a chloride solution was studied using cyclic voltammetry and potentiodynamic measurements. The anodic peaks in cyclic voltammograms at -0.6 V, 0 V and 1.1 V were identified with the formation of $\text{Fe}(\text{OH})_2$, FeOOH and the transpassive oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ and $\text{Ni}(\text{II})$ to $\text{Ni}(\text{IV})$, respectively. The reduction peaks at 0.3 V, -0.6 V and -0.8 V are attributed to valence transitions in solid state associated with the chromium and iron in the oxide, respectively. None of the current peaks detected in the voltammetric curves can be attributed to the Mo species alone.

Keywords: duplex stainless steel, potentiostatic, cyclic voltammetry, passive films

Raziskovali smo tvorbo pasivne plasti na površini dupleksnega nerjavnega jekla 2205 v kloridnih raztopinah s ciklično voltmetrijo in potenciodinamsko polarizacijo. Anodne vrhove v cikličnih voltamogramih pri potencialih $-0,6$ V, 0 V in $1,1$ V pripisujemo tvorbi $\text{Fe}(\text{OH})_2$, FeOOH in transpasivni oksidaciji $\text{Cr}(\text{III})$ v $\text{Cr}(\text{VI})$ in $\text{Ni}(\text{II})$ v $\text{Ni}(\text{IV})$. Pojav katodnih vrhov je povezan z redukcijo kromovih in železovih oksidov znotraj trdne faze. Nobenega od opaženih vrhov ne pripisujemo Mo.

Ključne besede: dupleksno nerjavno jeklo, potenciostatske meritve, ciklična voltmetrija, pasivna plast

1 INTRODUCTION

Duplex stainless steels (DSSs) are widely used as structural materials in the oil and gas industries as well as for special applications in chemical, waste-water and marine-plant engineering, where a high mechanical strength and good corrosion resistance are required. The combination of ferrite and austenite phases in the volume ratio of about 1:1 results in a beneficial influence on the corrosion characteristics in various aqueous environments¹. The high Cr content together with high Mo and N contents gives rise to a high pitting-corrosion resistance in chloride solutions. The chromium adds to the overall resistance through a passivation process with forming a complex spinel-type passive film $(\text{Fe}, \text{Ni})\text{O}(\text{Fe}, \text{Cr})_2\text{O}_3$ ². Molybdenum increases the stability of the passive film and, therefore, the ability of the stainless steel to resist the localised corrosion, including pitting and crevice corrosion, particularly in environments containing chloride ions². The presence of approximately 50 % (by volume) of ferrite phase results in an increase in the strength compared with austenitic stainless steels^{3,4}.

Various electrochemical techniques have been used to study the corrosion behaviour of duplex stainless steels⁵⁻⁸. Souto et al.⁵ studied the passivation and the resistance to pitting corrosion of duplex stainless steel in neutral and alkaline buffered solutions, with and without chloride ions. The presence of NaCl enhanced the metal's electrodisolution through the passive layer. The

interpretation of the results was based on the presence of Cr and Ni in the alloy. Debala et al.⁶ showed that the corrosion resistance of superduplex stainless steel increased during annealing at heat-treatment temperatures lower than 1300 °C due to the improvement in the corrosion resistance of ferrite, which grows rich in Ni with temperature. Ahmad et al.⁷ studied the corrosion resistance of duplex stainless steel in sea water. It was found that 2205 duplex stainless steel showed good corrosion resistance in chlorinated and unchlorinated sea water at 25 °C, but at 50 °C it failed to resist. Torres et al.⁸ investigated 2205 duplex stainless steel in a chloride solution after various heat-treatments. The results showed that the simulated sensitisation had an adverse influence on the corrosion resistance, indicating that the corrosion rates increased by increasing the sensitisation temperatures.

In the present work 2205 duplex stainless steel is studied in various sodium chloride solutions. The study was conducted using the electrochemical techniques of cyclic voltammetry and potentiodynamic measurements.

2 EXPERIMENTAL

Duplex 2205 stainless steel was investigated. Its composition was confirmed by analytical chemical methods, as shown in **Table 1**.

The experiments were carried out in 0.9 %, 2 % and 3.5 % solutions of sodium chloride. All the chemicals were from Merck, Darmstadt, Germany.

Table 1: The composition of 2205 duplex stainless steel (w/%)**Tabela 1:** Sestava dupleksnega nerjavnega jekla 2205 (w/%)

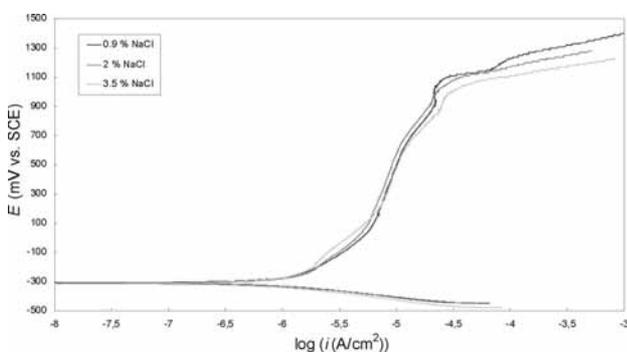
| Material | Cr | Ni | Mn | Si | P | S | C | Mo |
|-------------|-------|------|------|------|-------|-------|------|------|
| duplex 2205 | 22.74 | 5.74 | 1.37 | 0.38 | 0.032 | 0.001 | 0.03 | 2.57 |

The test specimens were cut into discs of 15 mm diameter. The specimens were grounded with SiC emery paper down to 1000 grit prior to the electrochemical studies, and then rinsed with distilled water. The specimens were then embedded in a Teflon PAR holder and employed as a working electrode. The reference electrode was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter electrode was a high-purity graphite rod.

The cyclic voltammetry and potentiodynamic measurements were recorded using an EG&G PAR PC-controlled potentiostat/galvanostat Model 263 with M252 and Softcorr computer programs. In the case of potentiodynamic measurements the specimens were immersed in the solution 1 h prior to the measurement in order to stabilize the surface at the open-circuit potential. The potentiodynamic curves were recorded, starting at 250 mV more negative than the open-circuit potential. The potential was then increased, using a scan rate of 1 mV s⁻¹, until the transpassive region was reached. In cyclic voltammetry a scan rate of 20 mV s⁻¹ was used, unless stated otherwise.

3 RESULTS

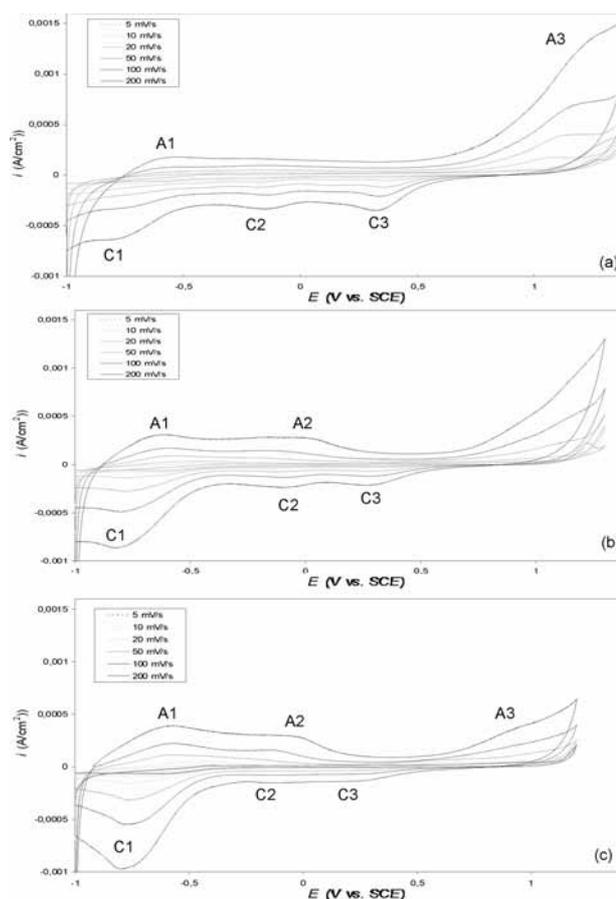
Figure 1 shows the potentiodynamic curves for 2205 DSS in mass fractions 0.9 %, 2.0 % and 3.5 % of sodium chloride solutions. After 1 h of stabilization at the open-circuit potential, the corrosion potential (E_{corr}) for 2205 DSS in all three solutions was approximately of -0.300 V. Following the Tafel region, the alloy exhibited passive behaviour. The extent of the passive range slightly decreased with the increasing chloride concentration. The passive range is limited by the breakdown potential (E_b), which corresponds to the oxidation of water and the transpassive oxidation of metal species.

**Figure 1:** Polarisation curves recorded for 2205 duplex stainless steel in chloride solutions of three different concentrations

Slika 1: Polarizacijske krivulje dupleksnega nerjavnega jekla 2205 v raztopinah natrijevega klorida z različnimi koncentracijami

The breakdown potential for 2205 DSS in a 0.9 % chloride solution was approximately 1.10 V, and this moved towards more negative values with an increasing chloride concentration, i.e., to 1.03 V and 1.00 V, respectively.

The cyclic voltammograms of 2205 DSS recorded in three different chloride solutions make it possible to compare the current peaks and the corresponding electrochemical processes taking place on the material investigated as well as the influence of the potential scan rate (ν) (**Figure 2**). The cyclic voltammograms were recorded at different scan rates in the potential range from -1 V to 1.2 V, 1.3 V and 1.4 V in 3.5 %, 2 % and 0.9 % NaCl, respectively. As can be seen, the main characteristics of the cyclic voltammograms are similar, with minor deviations in all three chloride solutions. In

**Figure 2:** Cyclic voltammograms recorded for 2205 duplex stainless steel with an increasing scan rate in (a) 0.9 % NaCl, (b) 2 % NaCl and (c) 3.5 % NaCl

Slika 2: Ciklični voltamogrami dupleksnega nerjavnega jekla 2205 pri različnih hitrostih spreminjanja potenciala s časom v: (a) 0.9 % NaCl, (b) 2 % NaCl in (c) 3.5 % NaCl

the presence of the 0.9 % NaCl, five peaks are observed (**Figure 2a**). The first anodic peak A1 at a potential -0.6 V can be ascribed to the electro-formation of Fe(II) hydroxide upon the Cr(III)-containing passivating layer, existing on the electrode at such negative potentials⁵. It is followed by the region with a constant current density, up to 0.5 V. Another peak in the anodic cycle A3 is observed in the transpassive region at a potential of 1.1 V, and this is associated with the oxidation of Cr(III) to Cr(VI)⁹. The Ni(II) species formed during the passivation process might have been oxidised to Ni(IV) oxide (NiO₂) in this potential range, too. In the reduction cycle in the potential range of peak C3 at 0.3 V Cr(VI) is reduced to Cr(III) and the iron oxide-hydroxide layer is largely reduced to Fe(II) in the potential range of peak C2, which is furthermore reduced in the potential range of peak C1 at -0.8 V⁹. In the presence of 2 % and 3.5 % NaCl another peak A2 at a potential range of 0 V is observed that corresponds to the conversion of the Fe(OH)₂ constituent to Fe(III) oxy-hydroxide FeOOH⁵ (**Figure 2b and c**).

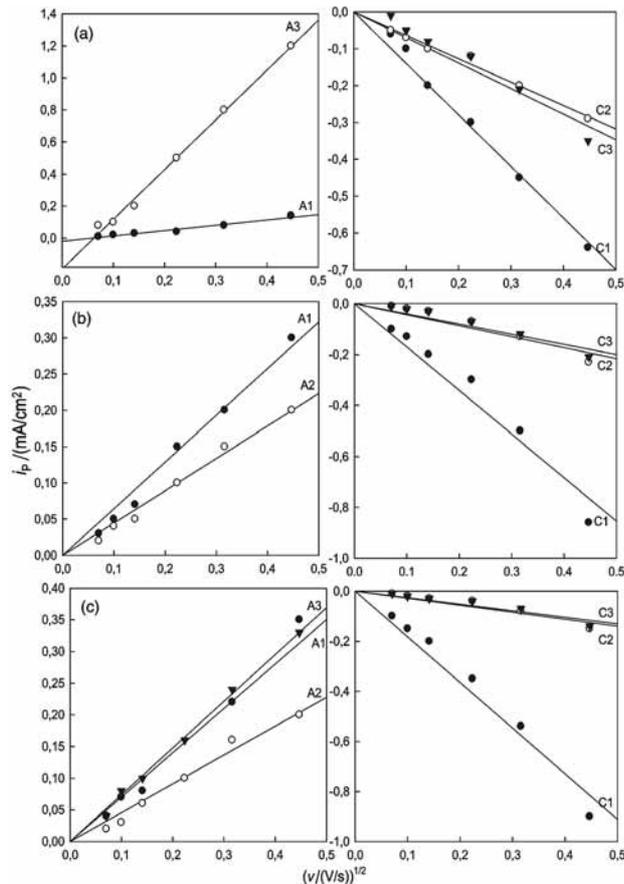


Figure 3: Calculated values of the peak current densities as a function of $\nu^{1/2}$ for 2205 duplex stainless steel in (a) 0.9 % NaCl, (b) 2 % NaCl and (c) 3.5 % NaCl

Slika 3: Izračunane vrednosti višine vrhov gostote toka v odvisnosti od $\nu^{1/2}$ za duplexno nerjavno jekli 2205 v: (a) 0.9 % NaCl, (b) 2 % NaCl in (c) 3.5 % NaCl

Figure 3 shows the calculated values of the peak current densities as a function of $\nu^{1/2}$. In the presence of 0.9 % NaCl it is clear that the current densities of the anodic peaks A1 and A3 increase with increasing sweep rate. The plot of peak current densities vs. $\nu^{1/2}$ gives straight lines with slopes of 0.27 for peak A1 and 2.70 for peak A3. The line of peak A1 passes through the origin, while that of peak A3 meets the current axis at a negative current value. These results suggest that the oxidation process within the potential range of peak A1 is mainly diffusion controlled according to Delahay's equation¹⁰, while that which occurred in the potential range of peak A3 is a mixed controlled process. The straight lines of the cathodic peak current densities i_p vs. $\nu^{1/2}$ originate at the origin in accordance with Delahay's equation¹⁰ and have slopes of -1.40 , -0.63 and -0.69 , respectively. In the presence of 2 % and 3.5 % NaCl the straight lines of the anodic and cathodic peak current densities i_p vs. $\nu^{1/2}$ originate at the origin in accordance with Delahay's equation¹⁰ and are therefore mainly diffusion-controlled processes.

4 DISCUSSION

The corrosion-passivation processes of a duplex stainless steel polarised in neutral chloride solutions were investigated by using electrochemical techniques. Increasing the chloride concentration causes the surface films to become less stable and eventually film breakdown may occur. In this case, the potential range for passivity is subsequently reduced, and further growth of the oxide film is hindered as the metal electro-dissolution becomes the dominant electrochemical process⁵. Pit initiation appears to be related to both a loss in the protective characteristics of the passive layer, which increases as the applied potential moves in the positive direction, and to the presence of aggressive chloride ions in the electrolyte⁵. The passivity of stainless steels arises from the high corrosion resistance exhibited by the Cr(III) oxide-hydroxides present in the passivating layers. The role of the alloyed chromium in enhancing the passivity of stainless steels is frequently explained in terms of a percolation model of passivation⁵. It is assumed that chromium forms insoluble Cr₂O₃, and a continuous network of Cr-O-Cr-O is then produced, which prevents the dissolution of iron.

Though nickel additions have been claimed to benefit the corrosion resistance of ferritic steels where nickel is frequently present, some investigations with superferritic alloys without nickel suggested superior characteristics of the latter⁵. Therefore, Ni(II) must be regarded as less effective than Cr(III) in anchoring the water molecules and the hydroxyl ions, which are directly bounded to the metal ions forming complex species. In this way, chloride ions can migrate through the passivating layer by replacing the water and hydroxyl groups, accumulate

in the metal-oxide interface and cause localised corrosion.

Molybdenum increases the stability of the passive film and, therefore, the ability of the stainless steel to resist the localised corrosion, including pitting and crevice corrosion, particularly in environments containing chloride ions². This induced modification in the film can explain the increasing Cr³⁺/Cr⁶⁺ process in the voltammograms for DSS, which indicates the better corrosion characteristics of molybdenum-containing alloys.

5 CONCLUSIONS

An electrochemical study of the passive film generated in a chloride-containing medium on DSS 2205 was performed, and the results were analysed. Cyclic voltammograms obtained in the chloride solution showed characteristic peaks. The anodic peaks at -0.6 V, 0 V and 1.1 V were identified with the formation of Fe(OH)₂, FeOOH and the transpassive oxidation of Cr(III) to Cr(VI) and Ni(II) to Ni(IV), respectively. The reduction peaks at 0.3 V, -0.6 V and -0.8 V are attributed to valence transitions, occurring in the solid state, associated with the chromium and iron in the oxide, respectively.

None of the current peaks detected in the voltammetric curves can be attributed to the Mo species

alone, which indicates that molybdenum mainly enhances the effect of other passivating species, i.e., Cr, more than acting directly in the passivating process in chloride media. This conclusion explains the improved corrosion resistance of duplex stainless steels.

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