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Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1130

Zastita Materijala 65 (2)
273 - 278 (2024)

Investigation of properties of epoxy coating on X80 steel under cathodic polarization conditions

ABSTRACT

The effect of cathodic polarization on the properties of the protective epoxy coating on X80 steel samples under cyclic changes in temperature from 20 to 75 ^{o}C over a period ~3.5 months was investigated. It is shown that in a 3% NaCl solution, with decreasing polarization potential from -1.05 to -0.85 V, the disbondment radius of the epoxy coating decreased by ~3.48 times (from 10.8 to 3.1 mm). At -0.75 V and in the absence of polarization, disbondment of the coating from the steel don't observed. By potential -0.75 V coating retains its protective properties according to the transient specific electrical resistance indicator, and its aging is slowed down.
Keywords: *epoxy coating, X80 steel, cathodic polarization, protective potential, cathodic disbondment, transient specific electrical resistance, coating degradation*

1. INTRODUCTION

Polyurethane and epoxy coatings, which are used in oil and gas pipelines, have high resistance to cathodic disbondment, and according to DSTU 4219 with amendment No. 1 [1], they are classified as class B (very reinforced) and are recommended for use in areas with a potentially high probability of corrosion cracking. Under such conditions, using polarizing potentials more negative than -850 mV is not recommended to minimize coating disbondment [2]. In addition, important characteristics of coatings are their resistance to the development of defects over time and their preservation of transient electrical resistance values [3].

Cathodic polarization affects the properties of the environment around the pipe under the disbonded coating, which contributes to the degradation of the coating matrix and its disbondment. It is believed that the causes of disbondment are the dissolution of iron oxides at the metal/coating interface [4, 5], the formation and accumulation of hydroxide ions, which increases the pH of the medium to 14, crevice corrosion due to the cathodic reduction of hydrogen [6], the state of the surface [7], the presence of soluble salts on the surface [8], the level of the cathodic polarization potential, and the size of the gap between the exfoliated coating and the steel [9], which affects the change in corrosion and electrochemical conditions on the surface of the pipe near the area of disbondment.

To increase the resistance of coatings against cathodic disbondment, the use of inhibitors in the environment (for example, thiourea) [10], nanostructured films [11, 12], the addition of zinc filler in epoxy compositions [13], lowering the level of cathodic polarization, etc., is proposed.

This investigation aimed to determine the influence of the cathodic polarization level on the protective properties of modern epoxy coatings applied to the surface of X80 steel, as well as the changes in the solution's properties under the influence of polarization and its effect on steel.

2. MATERIALS AND METHODS

A two-component epoxy coating, amine-approved (further - the coating), which does not contain solvents, with a dry residue of (98±2) %, intended for application to the outer surface of pipelines, was used in this work. The coating was applied in one layer on X80 pipe steel specimens with dimensions of 100 mm ×100 mm ×20 mm after sandblasting. The chemical composition of the X80 steel is listed in Table 1.

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Paper received: 12. 12. 2023.
Paper accepted: 21. 12. 2023.
Paper is available on the website: www.idk.org.rs/journal

Table 1. Chemical composition Chemical composition of X80 steel

Tabela 1. Hemijski sastav Hemijski sastav čelika X80

Element	C	Mn	V	Nb	Ti	Cu	Mo	Cr
Wt. %	0.06	1.635	0.036	0.040	0.015	0.07	0.012	0.03

All defined indicators of physical, mechanical and protective properties of the coating corresponds to the requirements of DSTU 4219 [1]. Particularly, the thickness of the coating in the initial state was 2 mm, the dielectric continuity – $17.5 \cdot 10^3$ V (according to DSTU 4219 the dielectric constant must be equal not less than $5 \cdot 10^3$ V/(mm of the thickness of the coating)), the transient specific electrical resistance from $1.2 \cdot 10^{10}$ to $1.5 \cdot 10^{10}$ Ohm·m^2. Cathodic disbondment of the coating was studied in 3% NaCl according to [1] in the range of protective polarization potentials from -0.75 to -1.05 V relative to the silver chloride reference electrode (which is corresponds to the range from -0.85 to -1.15 V relative to the copper sulfate reference electrode). A polarization potential of -1.05 V was maintained using a magnesium anode, and other potentials (-0.75 and -0.85 V) were set using a multi-channel potentiostatic device using a laboratory stand with a clamping electrochemical cell. A defect with a diameter of 6 mm was artificially created in the epoxy coating. Polarization potentials were adjusted using the device. Potentials were measured by a voltmeter with an accuracy of 0.08%, and polarization currents using an ammeter.

The research was carried out under cyclic temperature changes from 20 to 75 °C, close to the maximum operating temperature of the coating. One cycle continued for 24 h (1 day): at a temperature of 75 °C – 12 h; at a temperature of 20 °C – 12 h. On weekends, the specimens were kept at a temperature of 20 °C. The total duration of the cover study was 3.5 months, of which 29 days were spent at elevated temperatures. According to the results of previous studies, at a temperature of 20 °C, disbondment of the coating was not observed, therefore, the duration of exposure at this temperature was not taken into account.

After the research, the disbondment radius was determined according to [1], the dielectric continuity was determined using a spark gap detector DKI-1, and the transient resistivity of the coating was determined using a teraohmmeter E6-13.

In the solutions before and after the coating study, electrical conductivity and pH were measured by standard methods, redox potential by potentiometry using platinum and silver chloride electrodes.

The density of the limiting diffusion current j_{O_2} was determined from the cathodic polarization curves, which were recorded on a PI-50.1.1 potentiostat with a sweep speed of $1 \cdot 10^{-3}$ V/sec in 3% NaCl after tests of the coating in that solutions without polarization and under polarization.

The residual corrosion rate i_{res} in mm/year in the coating defect was counted according to the method [1] by the formula:

$$i_{res} = i_{cor} \cdot 10^{\frac{E_{pol} - E_{cor}}{b_a}} \quad (1)$$

Where i_{cor} is corrosion rate of metal in the studied environment, determined by the polarization resistance method in a 3% NaCl solution, equal to 0.101 mm/year [14];

E_{pol} – polarization potential, V;

E_{cor} – corrosion potential, V;

b_a – Tafel slope of the anodic polarization curve, equal to 0.06 V [15].

3. RESULTS AND DISCUSSION

When the potential decreases from -1.05 to -0.75 V, the polarization current naturally decreases by almost 3 orders of magnitude (Fig. 1).

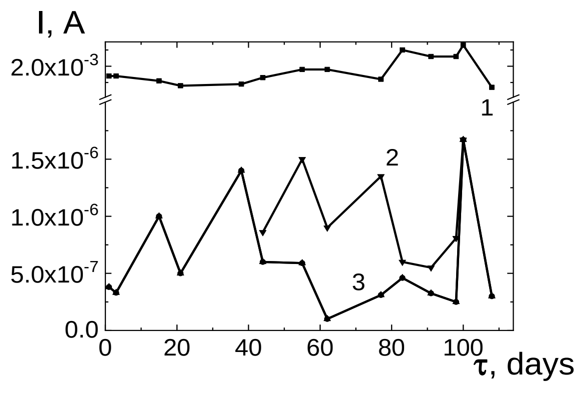

Figure 1. Change of polarization currents in time at the potential -1.05 V (1), -0.85 V (2), and -0.75 V (3)

Slika 1. Promena polarizacionih struja u vremenu na potencijalu -1.05 V (1), -0.85 V (2) i -0.75 V (3).

This type of current change corresponds to a decrease in the disbondment radius (Fig. 2). At a potential of -1.05 V, the disbondment radius was 10.8 mm (Fig. 2, b). The disbondment nature of the coating was adhesive, so coating disbonding was not detected. When the potential decreases from -1.05 to -0.85 V, the disbondment radius of the coating decreased by nearly 3.48 times (from 10.8 to 3.1 mm). When the potential was further reduced to -0.75 V and when polarization was not applied, coating disbondment from the steel was not observed (Fig. 2, c-e).

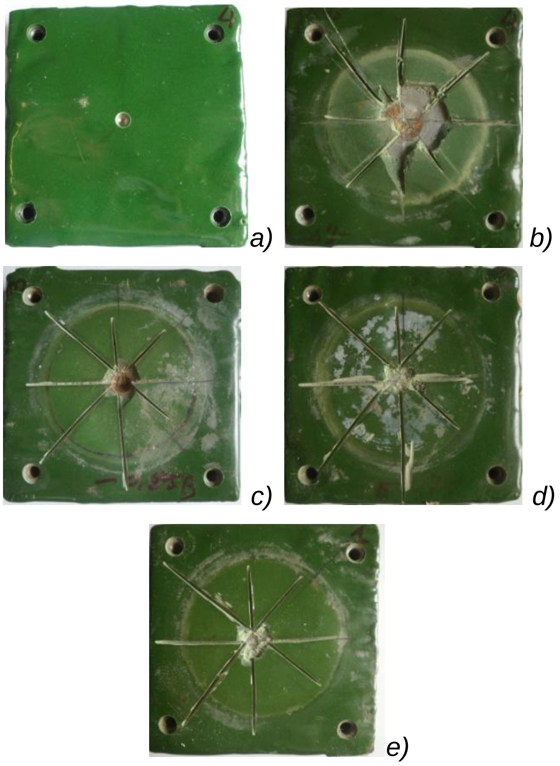

Figure 2. The appearance of the epoxy coating in the area of the artificial defect in the initial state (a) and after tests for cathodic disbondment in a solution of 3% NaCl with cyclic temperature changes for 3,5 months and determination of the disbondment radius: b – for polarization -1.05 V; c – with a polarization of -0.85 V; d – at polarization -0.75 V; e – without polarization

Slika 2. Izgled epoksidnog premaza u predelu veštačkog defekta u početnom stanju (a) i nakon ispitivanja katodnog odvajanja u rastvoru 3% NaCl uz ciklične promene temperature tokom 3,5 meseca i određivanje odvajanja. poluprečnik: b – za polarizaciju -1,05 V; c – sa polarizacijom od -0,85 V; d – pri polarizaciji -0,75 V; e – bez polarizacije.

Change of the cover properties depending on polarization potential, namely disbondment radius, and transient electrical resistivity are shown in Fig. 3, changes in the properties of a 3% NaCl solution after testing the cathodic disbondment coating at different potential are presented in Fig. 4. Coating aging was evaluated by the change in transient electrical resistance. It was established that the transient electrical resistance increased from $2.06\cdot10^6$ Ohm·m^2 after coating testing at a potential of -1.05 V to $8.42\cdot10^6$ Ohm·m^2 after coating disbondment investigation at a potential of -0.75 V and up to $1.45\cdot10^7$ Ohm·m^2 when coating disbondment was tested without polarization (Fig. 3). Such values of transient electrical resistance correspond to normalized indicator for a new coating of a highly reinforced type according to [1] ($1\cdot10^7$ Ohm·m^2 after exposure to a 3% NaCl solution for 100 days at a temperature of 20 ^{o}C). The dielectric integrity of the coating was changed only in cells in which the coating was tested at polarization -1.05 V, and its value was $12.5\cdot10^3$ V, while in the initial state, it was $17.5\cdot10^3$ V. A change in the color of the solution was also noted, which is obviously associated with coating degradation.

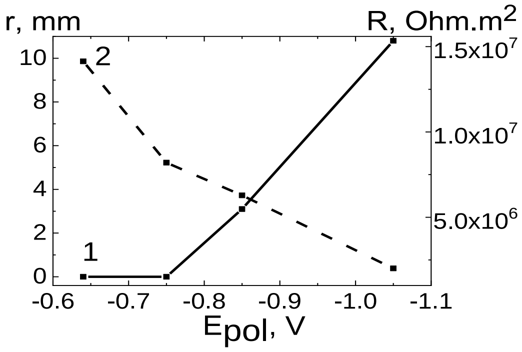

Figure 3. Change of the cover properties depending on polarization potential: 1 – disbondment radius; 2 – transient electrical resistivity

Slika 3. Promena svojstava poklopca u zavisnosti od polarizacionog potencijala: 1 – radijus odvajanja; 2 – prolazna električna otpornost

An increase in the pH of the solutions in which the coating disbondment was studied under potentials -0.75, -0.85, and -1.05 V, respectively, from 7.0 (in the initial state) to 12.2 was established. A decrease in the redox potential from 0.518 V (in the initial state) to 0.313 V was noted (Fig. 4).

Therefore, the properties of the solution changed from moderately oxidizing (from 0.5 to 0.6 V) to weakly reducing (from 0.3 to 0.4 V). In addition, the electrical conductivity of the solution (in Sm/cm) varies non-monotonically in the rows $1.1\cdot10^{-2}$ (before the tests) → $1.23\cdot10^{-2}$ (after coating disbondment tests at E_{cor}) → $4.30\cdot10^{-2}$ (after coating disbondment tests at -0.75 V) → $4.14\cdot10^{-2}$ (after coating disbondment tests at -0.85 V) → $7.82\cdot10^{-2}$ (after coating disbondment tests at -1.05 V). It is obvious that such changes in the solution due to cathodic polarization can lead to a change in the corrosion rate of steel.

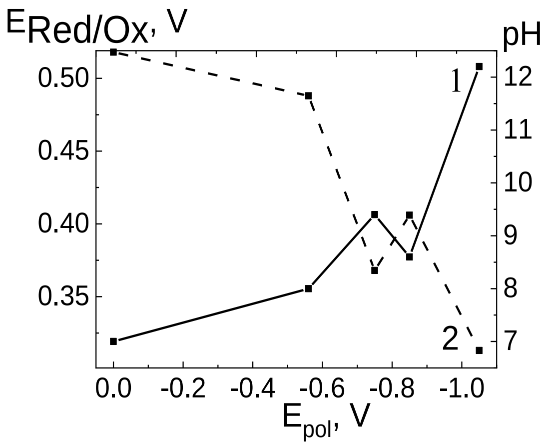

Figure 4. Changes in the properties of a 3% NaCl solution after testing the coating by the cathodic disbondment method at different potentials: 1 – pH; 2 – Red Ox potential

Slika 4. Promene svojstava 3% rastvora NaCl nakon ispitivanja prevlake metodom katodnog odvajanja pri različitim potencijalima: 1 – pH; 2 – Red Ox Potencijal

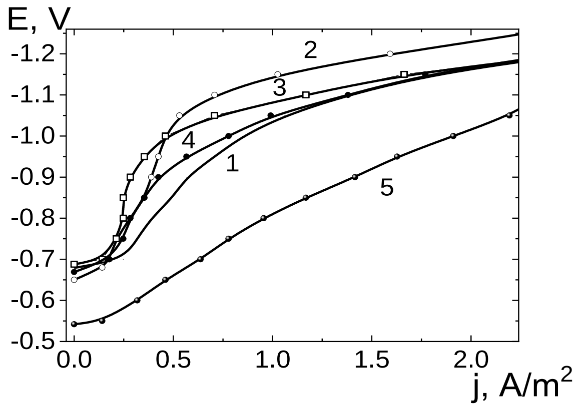

Figure 5. Cathodic polarization curves of X80 steel in a solution of 3% NaCl after testing the coating by the cathodic disbondment method at different potentials: 1 – initial state; 2 – E_{cor}; 3 – -0.75 V; 4 – -0.85 V; 5 – -1.05 V

Slika 5. Krive katodne polarizacije čelika Ks80 u rastvoru 3% NaCl nakon ispitivanja prevlake metodom katodnog odvajanja pri različitim potencijalima: 1 – početno stanje; 2 – E_{cor}; 3 – -0,75 V; 4 – -0.85 V; 5 – -1.05 V.

The corrosion resistance of X80 pipe steel in solutions (with different pH) after coating tests were evaluated by the limiting diffusion current, as well as other related characteristics such as the ratio of the cathodic protection current to the limiting diffusion current j_{cp}/j_o and the residual corrosion rate. In Fig. 5 the cathodic polarization curves of this steel in solutipons with different pH after coating degradation tests are shown, from which the limiting diffusion current was determined. Electrochemical corrosion of steel in f 3% NaCl solution occurs with diffusion control (curves 1-4) and mixed control (curve 5). From the analysis of the nature of the curves, it was established that in the original solution, the limiting diffusion current on the steel was equal to 0.47 A/m^2. In the solutions after coating disbondment testing at potentials of -0.75 and -0.85 V, the limiting diffusion current density of oxygen was, respectively, 0.28 and 0.26 A/m². In the solution, in which coating disbondment tests were carried out at potential of -1.05 V, the absence of the limiting diffusion current was explained by a change in the properties of the solution under the action of cathodic polarization of the steel (Fig. 4), presumably due to the reduction of compounds with the participation of iron ions (oxides, hydroxides, and hydroxyl chlorides) and degradation of the coating. From the analysis of the obtained results, it follows that the susceptibility of steel to uniform corrosion in the corresponding solution after disbondment of the coating is lower the higher the level of polarization.

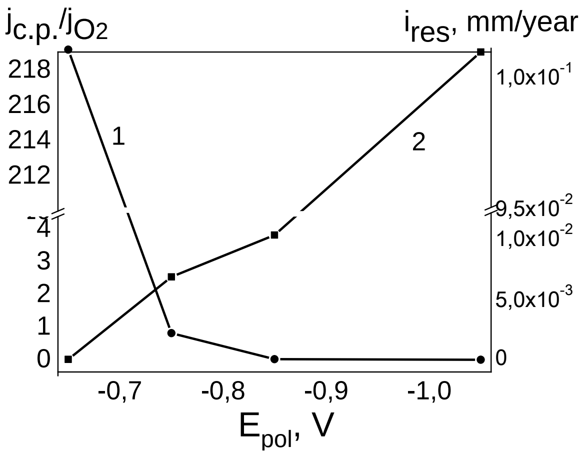

Figure 6. Change in the ratio j_{cp}/j_o at potential -1.05 V (1) after testing coating on cathodic disbondment in cells and residual corrosion rate of X80 steel (2) in 3% NaCl solution at different polarization potentials

Slika 6. Promena odnosa j_{cp}/j_o od potencijala -1.05 V (1) nakon ispitivanja prevlake na katodno odvajanje u ćelijama i zaostale brzine korozije čelika X80 (2) u 3% rastvoru NaCl pri različitim potencijalima polarizacije

It was previously established [14] that the analysis of the relationship between cathodic protection current, limiting diffusion current $j_{c.p.}/j_{O_2}$, and the residual corrosion rate makes it possible to assess the protection state of the coating defect and the corrosion resistance of the steel. Calculating these ratios $j_{c.p.}/j_{O_2}$ at a potential of -1.05 V from the polarization curves (Fig. 5) for X80 steel in the corresponding solutions, it was found that the ratio in the solution after polarization of the steel at a potential of -1.05 V is higher than 4, which indicates the possibility of steel hydrogenating. Residual corrosion rate values calculated according to [1], Fig. 6, (curve 2), showed that in all tested solutions, a technically sufficient protective effect, for which the residual corrosion rate is less than 0.01 mm/year, is achieved at a potential of -0.75 V. That is, if the values of the protective potentials are exceeded by the absolute value of -0.75 V, it is possible to accelerate the degradation of the epoxy coating in the defect area, and the probability of hydrogenation of X80 steel will increase with time, which can create favorable conditions for the development of stress-corrosion cracking.

4. CONCLUSIONS

It was established that the protective properties of the epoxy coating applied to X80 steel in a solution of 3% NaCl for 3.5 months with a cyclic temperature change from 20 to 75 ^oC, which simulates a temperature close to the maximum operating temperature, with a decrease in the absolute value of the polarization potential from -1.05 to -0.75 V relative to the silver chloride reference electrode, are preserved: the disbondment radius decreases from 10.8 to 0 mm, and the transient resistivity of the coating is from $2.03 \cdot 10^6$ to $8.42 \cdot 10^6$ Ohm·m^2. Polarization potentials that are less negative than -0.85 V help minimize cathodic exfoliation.

Acknowledgment

The work was carried out with the support of the National Academy of Sciences of Ukraine (state registration number 0118U100537)

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IZVOD

ISTRAŽIVANJE SVOJSTVA EPOKSI PREMAZA NA ČELIKU X80 U USLOVIMA KATODNE POLARIZACIJE

Ispitivan je uticaj katodne polarizacije na svojstva zaštitnog epoksidnog premaza na uzorcima čelika X80 pri cikličnim promenama temperature od 20 do 75°C u periodu ~3,5 meseca. Pokazano je da se u 3% rastvoru NaCl, sa smanjenjem potencijala polarizacije sa -1,05 na -0,85 V, radijus odvajanja epoksidnog premaza smanjio za ~3,48 puta (sa 10,8 na 3,1 mm). Na -0,75 V i u odsustvu polarizacije, odvajanje prevlake od čelika nije primećeno. Potencijal -0,75 V premaz zadržava zaštitna svojstva prema prolaznom specifičnom indikatoru električnog otpora, a njegovo starenje se usporava.

Ključne reči: *epoksidni premaz, X80 čelik, katodna polarizacija, zaštitni potencijal, katodno odvajanje, prolazni specifični električni otpor, degradacija premaza*

Naučni rad
Rad primljen: 12.12.2023.
Rad prihvaćen: 21.12.2023.
Rad je dostupan na sajtu: www.idk.org.rs/casopis