KOROZIONA OTPORNOST 1.4713 VATROSTALNOG FERITNOG ČELIKA U 0.5M NITRATNOJ KISELINI

CORROSION RESISTANCE OF 1.4713 FERRITIC HEAT-RESISTANT STEEL IN 0.5M NITRIC ACID

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U ovom radu su predstavljena eksperimentalna istraživanja korozionog ponašanja i otpornosti feritnog (EN 1.4713/X10CrAlSi7) čelika u azotnoj kiselini koncentracije 0,50 mol·dm^{-3}. Korozione karakteristike ovog čelika ispitane su sledećim elektrohemijskim metodama: potencijal otvorenog kola (POK), ekstrapolacija polarizacione krive u Tafelovom regionu i metoda linearnog polarizacionog otpora (LPO). Pored toga, korišćena je metoda gubitka mase (u trajanju od 10 dana) i upoređena je sa metodama polarizacije. Rezultati merenja pokazali su izvrsno međusobno slaganje elektrohemijskih metoda, sa razlikama u određenoj korozionoj struji u okviru ± 10%. Metoda gubitka mase pokazala je oko polovine vrednosti brzine korozije u odnosu na ove elektrohemijske metode. Iako izgleda kao značajna razlika, može se smatrati dobrim rezultatom, jer je to uobičajena razlika između ovih metoda; jer one određuju brzinu korozije u različito vreme izlaganja uzoraka u korozivnom okruženju. Opšti zaključak je da ispitivani nerđajući čelik otporan na visoke temperature ne pruža visoku otpornost na koroziju u 0,5M rastvoru azotne kiseline. Ovo istraživanje je izvedeno uzimajući u obzir procenu pogodnosti materijala za opremu za obnovljive izvore energije, poput baklji za odlagalište gasa (LGF) i dodatnu opremu tog sistema. Iako čelik 1.4713 ima dobre mehaničke i toplotne karakteristike, za upotrebu u takvim radnim uslovima potrebna je dodatna zaštita od korozije.

Ključne reči: *feritni čelilk; nitratna kiselina; korozija; baklja deponijskog gasa.*

Experimental research of corrosion behavior and resistance of ferritic (EN 1.4713/X10CrAlSi7) steel in nitric acid with the concentration of 0.50 mol·dm^{-3} is presented in this paper. The corrosion characteristics of the steel were tested using the following electrochemical methods: open circuit potential (OCP), extrapolation of the polarization curve in the Tafel region, and linear polarization resistance (LPR). Additionally, the weight-loss method (with a duration of 10 days) was used and compared with the polarization methods. The measurement results have shown excellent agreement between electrochemical methods with the differences in determining corrosion current within ±10%. Although it looks like a significant difference, it can be considered a good result since that is the usual difference between these methods because they determine the corrosion rates at different times of the samples exposal in corrosion environment. The general conclusion is that examined heat-resistant stainless steel does not provide high corrosion resistance in the 0.5M nitric acid. This research was performed considering assessing the suitability of the material for renewable energy equipment like landfill gas flares (LGF) and additional equipment for that system. Although the 1.4713 steel has good mechanical and thermal characteristics, it requires additional corrosion protection for use in such working conditions.

Key words: *Ferritic steel; Nitric Acid; Corrosion; Landfill gas flare.*

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1 Introduction

Stainless steels (SSs) are commonly classified by their structure. The main five types of the SSs are: austenitic, ferritic, martensitic, duplex (ferritic-austenitic; containing both phases), and precipitation hardened. Austenitic steels are famous for their corrosion resistance in various environments, although some ferritic steels are also very stable in many aggressive environments, particularly those with high chromium content. Consequently, they are applied in different industries: automotive, chemical, metallurgy, food, and civil engineering. Additionally, they are used in high-tech applications, like aerospace, machine-tool, and nuclear [1-4].

The EN 1.4713 steel belongs to a ferritic type of steel and is classified in the group of EN 1.47xx stainless heat resistant steels. One of the main features of this type of steel is that they contain chromium, aluminum, and silica. Among them, the examined steel has the lowest Cr concentration (7±1%) and the lowest heat resistance and corrosion resistance [5]. Chromium directly influences the corrosion behavior of the SSs; the higher Cr concentration leads to better characteristics [6].

Ferritic steels are known for their high corrosion resistance in alkaline solutions [7-9]. They are also resistant to oxidation at high temperatures (approx. 800 °C or more if Cr content is 18% or more) by the formation of the oxide layers at the surface [10, 11]. The use of artificial intelligence for optimization between main alloying elements in ferritic steels was applied and published recently [12]. Nevertheless, ferritic SSs are far more susceptible to corrosion in sulfuric acid solutions [2, 13, 14]. Because of that, it is important to improve the corrosion resistance of the ferritic steels in acidic environments. Various methods can accomplish it. The most popular are the following two: producing oxides on their surfaces by annealing at high temperatures in air, oxygenated air, or pure oxygen atmosphere and with various coatings.

In this paper, the aim was to investigate the influence of the heat-treatment and alumina coating on corrosion resistance of the 1.4713 steel in nitric acid with a concentration of 0.5 $mol\cdot dm^{-3}$. In that goal, different corrosion determining methods (OCP, LPR, Tafel extrapolation, weight-loss method) were used and mutually compared.

2 Experimental

Examined base material was commercial 1.4713 EN steel obtained from the local supplier. The elemental composition of 1.4713 steel was determined by the use of ICP-OES. Iron and chromium are the metals with the highest content, and thus the XRF method for their analysis was used. The SpectroBlue (Spectro Analytical Instruments, Germany) was used for ICP-OES and Niton XL3t-950 (ThermoFisher Scientific, USA) for XRF analysis.

Content of Fe was performed just as control and is not given in the composition. The elemental composition of 1.4713 steel was (in wt. %):

C 0.105, Si 0.725, Mn 0.674, P 0.026, S 0.008, Cr 6.62, Al 0.850, Fe balance.

Samples of the untreated 1.4713 EN steel, heat-treated steel at 800 °C, and with alumina/titania coatings were used for electrochemical (EH) measurements. The heat-treated sample was annealed at 800 °C in the air for a period of 2 h. Alumina/titania coating has 2.2% of TiO_2 and Al_2O_3 as balance. The thickness of the coating was 0.5 mm with the base of AlNi5 (0.1 mm thick). This coating was applied on the surface by a plasma spray system (METCO 3M). A mixture of argon and hydrogen was used as plasma gas. The main spraying parameters were: arc current 550 A, voltage 62 V, with the argon flow rate of 2.88 $m^3\cdot h^{-1}$.

The active surface of samples for electrochemical analysis was 2.0 cm^2. EH measurements were performed in HNO_3 with a concentration of 0.5M (p.a. Merck, Germany). Before electrochemical experiments, the sample of untreated steel was ground with SiC emery papers, and then polished with 3 μm diamond paste, washed in distilled water, and degreased with absolute ethanol (99.8% p.a. Zorka, Serbia). The weight loss measurements were performed by weighing the cleaned coupons before and after immersion in 0.5M HNO_3 solutions for 240 h. After every 24 h, the coupons were retrieved, treated as outlined in ASTM G1-72, dried in acetone, and reweighed.

The electrochemical corrosion tests were conducted in a standard thermostatic three-electrode cell consisting of a platinum sheet as the counter electrode, sample as working electrode, and a saturated calomel electrode (SCE) as the counter electrode. The working temperature for these measurements was 25±1 °C. The EH measurements were performed using a Gamry Interface 1000 potentiostat/galvanostat. The open circuit potential (OCP) has been recorded for 3600 s. Potentiodynamic polarization measurements were performed in the potential range of −0.2 to 0.2 V versus open circuit potential (OCP) at the scan rate of 1 $mV\cdot s^{-1}$. Linear polarization resistance (LRP) was performed at potential ±20 mV from the OCP at the scan rate of 0.1667 $mV\cdot s^{-1}$ according to the ASTM G3-89(2010) standard. For the weight-loss method, an analytical balance with 0.1 mg precision was used.

3 Results and Discussion

Measurements of the open circuit potential for untreated, heat-treated, and alumina/titania coated samples are shown in figure 1.

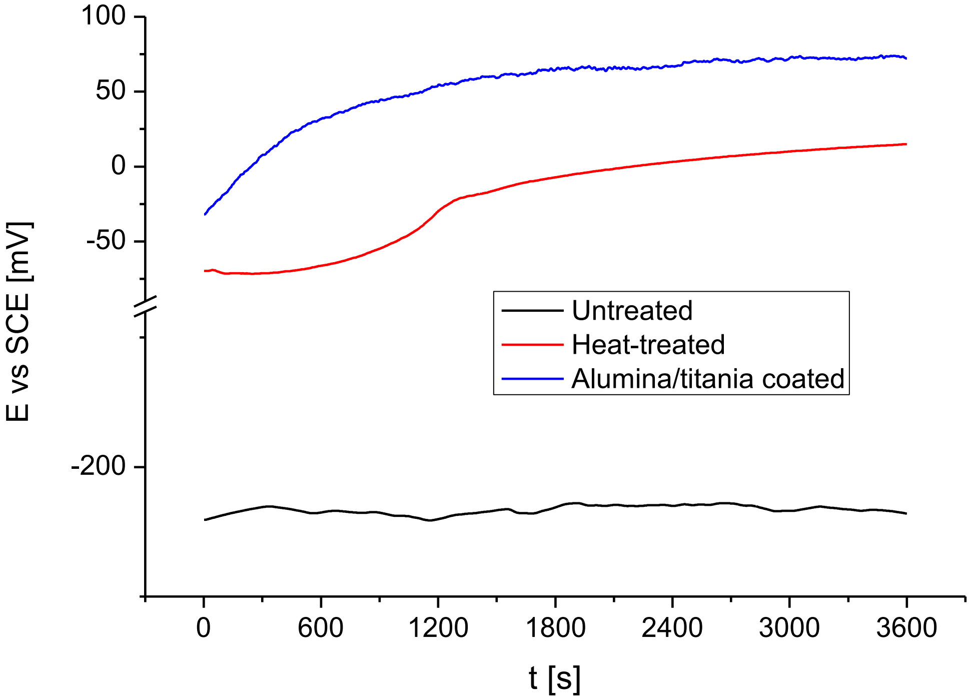

Figure 1 OCP for 1.4713 ferritic steel: untreated, heat-treated and with coating, in 0.5M HNO_3

The OCP value of the untreated sample was very stable. The differences within the measurement interval were only ± 3 mV which is almost within the limits of the OCP stability criteria (usually ± 1 mV in 5 minutes). This means reaching the absolute value of this parameter relatively quickly but with a tendency of minor but constant variations. These variations are typical for processes where a protective (passivation) layer is created on the surface of a metal (alloy) which is damaged over time by a dynamic construction process and decomposition of a passive film on the surface. The nitric acid concentration is obviously insufficient for forming a stable, protective layer, which is why this lower concentration (approx. 3%) was chosen because passivation is typical for 10-50% HNO_3. The value of -209.0 mV vs. SCE is also 92 mV more positive than the equilibrium hydrogen reduction reaction, which additionally indicates the formation of an oxide film on the surface (oxygen reduction reaction, at least as one of the reactions in the system if not dominant).

For the oxidized (thermally treated) sample, an OCP curve with a time of the usual shape was obtained, which is characteristical for many metals and alloys in various corrosive environments. One of the characteristics is that the POK is not completely stabilized even after a full 60 minutes, which was not expected considering that an oxide layer has already formed on the surface. The curve can be interpreted as the process of ion adsorption or formation of (protective) oxides, in this case on damaged surfaces, during the measurement, and considering the previous one, it is probably an ion adsorption. This value is (significantly) higher than the hydrogen reduction potential (even at such a low pH value); it is +256 mV in relation to the Standard Hydrogen Electrode, i.e., close to 300 mV higher than the equilibrium hydrogen evolution potential at pH = 0.5 (as for the tested HNO_3 concentration). Such a positive value of OCP indicates a certain corrosion resistance, i.e., protection with the already created passive layer during annealing. Absolute value of +15 mV was higher than untreated sample for 224 mV meaning much higher corrosion resistance.

The shape of the OCP-1 curve is similar to that of the oxidized sample, except that the OCP stabilization in 60 minutes was completed in this case. The shape of the curve indicates that the corrosion rate is low and that the reaction (corrosion reactions) slows down during the measurement, probably by the creation of an oxide layer on the surface. The voltage oscillations in the image result from the fact that the free surface is not recorded, as for samples without coating. The obtained OCP value was +72.19 mV. Such a high value indicates high corrosion resistance. It is significantly higher than the hydrogen reduction potential, approximately 350 mV for this reaction at pH = 0.5. Compared to the untreated sample, it is almost 300 mV more positive and about 60 mV higher than that obtained for the annealed sample indicating higher corrosion resistance.

The linear polarization resistance electrochemical (LRP) method was used to determine the corrosion current density of the samples. Polarization resistance (R_p) is by definition slope on the diagram electrode potential vs. corrosion current density, for the small variations of the potential from equilibrium state (OCP), and with slow change of the potential. Then the corrosion current can be obtained by using the Stern–Geary equation [15]. Corrosion parameters for all three samples are shown in Table 1.

Table 1 Corrosion paramethers for the examined samples in 0.5M HNO_3 by the use of LPR method

EN 1.4713 steel	R_p, $\Omega\cdot cm^2$	$j_{corr.}$, $mA\cdot cm^{-2}$	Corrosion rate (CR), $mm\cdot year^{-1}$	$E_{corr.}$, mV vs. SCE
Untreated	16.35	1.638	18.95	-208.6
Heat-treated at 800 °C	57.73	0.301	3.48	+18.9
With Al_2O_3/TiO_2 coating	780.3	0.044	0.51	+73.7

From Table 1, it can be concluded that the corrosion rate of the tested untreated steel in the examined acid solution is high, with close to 20 $mm\cdot year^{-1}$, and that the material is not stable in the observed environment and technically unusable.

In the annealed sample, the corrosion current density is an order of magnitude lower in the same medium compared to the polished untreated sample. The value of 301 $\mu A\cdot cm^{-2}$ is still not a low value for $j_{corr.}$ in the absolute sense. Still, it can be argued that the corrosion resistance is significantly improved over the standard material (oxidation coating has a significant protective role) with the heat treatment.

The polarization resistance of the coated sample reaches almost kΩ level and is by far the highest of all measurements. Here, the current was two orders of magnitude (37 times) lower compared to the untreated sample. In relation to the annealed sample, this was approximately seven times lower value. This is still not a low value for current that material can be classified as corrosion-resistant, but it can be stated that it has been significantly improved over the standard and even heat-treated material.

Figure 2 shows the polarization measurement in Tafel region for the untreated sample.

Parameters from the Tafel extrapolation were:

Anodic Tafel slope (β_A): 145.5 mV/dec
Cathodic Tafel slope (β_C): 106.8 mV/dec
Corrosion potential: –209,0 mV vs. SCE
$j_{corr.} = 2.00\ mA\cdot cm^{-2}$
CR = 23.2 $mm\cdot year^{-1}$ (912 mpy or 498 $g\cdot m^{-2}\cdot day^{-1}$)

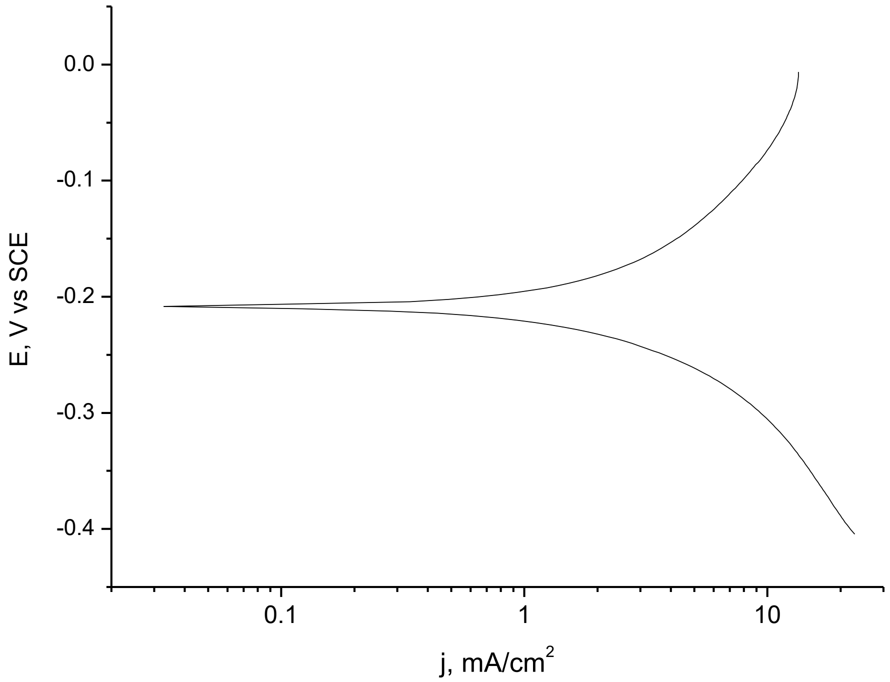

Figure 2 Polarization curve in the region of the Tafel's dependence at a scan rate of 1 mV·s^{-1} for EN 1.4713 steel in 0.5 mol dm^{-3} HNO$_3$.

Corrosion current density (and thus corrosion rate) was about 22% higher than the value obtained by the LPR method. However for the determination of the $j_{corr.}$, this difference can be treated as an excellent agreement in the results and the compatibility of the methods.

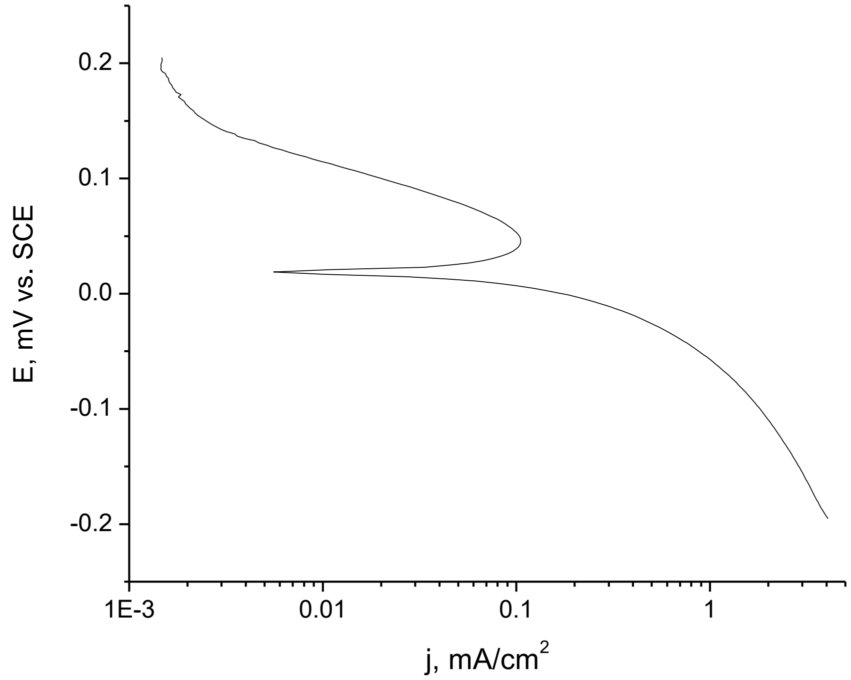

Figure 3 Polarization curve in the region of the Tafel's dependence at a scan rate of 1 mV·s^{-1} for heat-treated EN 1.4713 steel in 0.5 mol dm^{-3} HNO$_3$.

Figure 3 shows a typical phenomenon of passivation, due to which the anodic Tafel slope cannot be determined. Therefore, there are no calculated parameters of Tafel extrapolation. From the appearance of the cathode part of the curve, it can only be estimated that the corrosion current density could be between 0.2 and 0.3 mA·cm^{-2}. This is almost ten times less than in the case of the untreated sample.

The corrosion potential value can also not be obtained directly, but a value can be taken where the current from the cathode to the anode (theoretically, it should correspond to $E_{corr.}$). According to the graph in Figure 3, it can be assumed that $E_{corr.}$ = +18.3 mV.

The occurrence of passivation begins relatively close to the OCP, at about +50 mV vs. SCE. In this case, j is between 1 and 2 μA·cm^{-2} at a potential of about +200 mV. At the end of the measuring potential, the current density drops to values considered in the passivity range. These values are slightly higher than typical for passivated SSs; however, it must be taken into account that this is a highly corrosive environment (very low pH value) and that the values are approx. 1000x less than current for untreated steel, so that passivity is a very justifiable expression. In addition, the shape of the curve is typical for the transition to the passivation area. The results suggest the possibility of passivation of the heat-treated steel in the nitrate medium and higher potentials. As nitric acid has oxidizing properties, higher potentials somewhat simulate higher acid concentrations, so the curve in Figure 3 suggests that higher concentrations of HNO_3 could also lead to passivation of heat-treated steel and that it could be more stable in them than in moderate concentrations (0.1-1 mol·dm^{-3}).

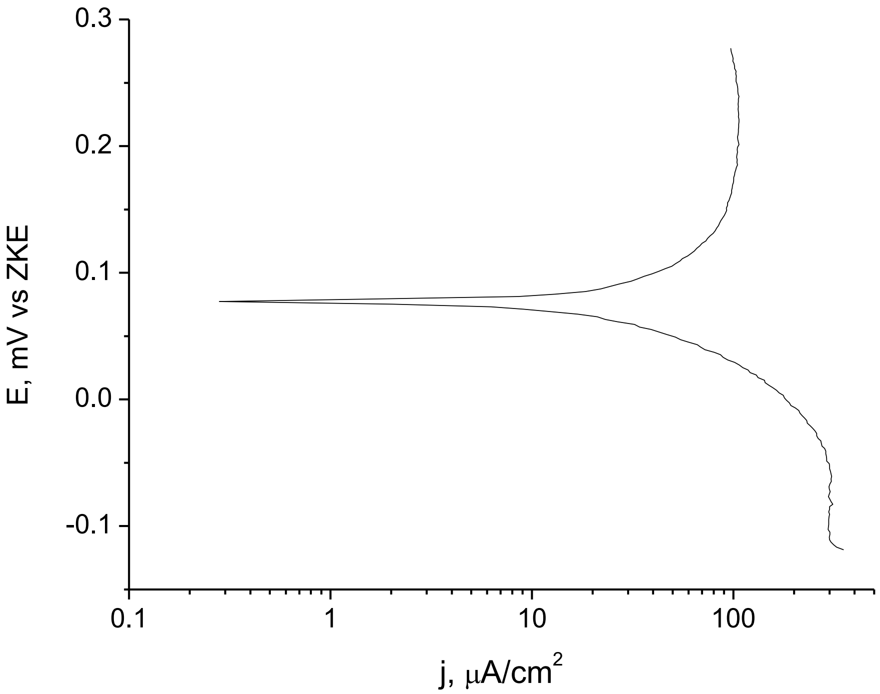

Figure 3 Polarization curve in the region of the Tafel's dependence at a scan rate of 1 mV·s^{-1} for EN 1.4713 steel with alumina/titania coating in 0.5 mol dm^{-3} HNO_3.

Parameters from the Tafel extrapolation for the coated sample were:

Anodic Tafel slope (β_A): 202.9 mV/dec
Cathodic Tafel slope (β_C): 130.0 mV/dec
Corrosion potential: +77.10 mV vs. SCE
$j_{corr.}$ = 40.56 mA·cm^{-2}
CR = 0.469 mm·year^{-1}

The value of Ecorr is slightly more positive than that obtained by the OCP method. The difference is small, and it can be confirmed that the methods agree on this parameter, i.e., that the deviations in OCP measurement are low. The corrosion current density is the lowest of all tested samples in HNO3 with a concentration of 0.5 mol·dm^{-3}. It is two orders of magnitude lower than that obtained for the polished sample without coating, measured by the same method (approximately 50 times). This is more than a significant improvement. The cause of annealed (oxidized) steel cannot be directly compared because the Tafel method did not apply to that sample due to the earlier transition to the passivation region (at lower potentials), and it is not possible to directly compare results of the Tafel method for annealed and coated samples. As with other samples, it can be concluded that LPR and Tafel extrapolation are comparable methods.

Finally, the weight-loss corrosion method was applied to all three samples. Values of the corrosion rates are given in Table 2.

Table 2 Corrosion rates for untreated, heat-treated, and alumina/titania coated EN 1.4713 steel, performed by weight-loss method, during the exposition period of 10 days.

Time [h]	Corrosion rate [mm·year^{-1}]		
	Untreated sample	Heat-treated sample	Sample with coating
1	18.69	2.80	0.433
24	9.52	5.79	0.287
48	11.94	12.87	0.113
72	9.34	11.43	0.078
96	10.58	9.58	0.067
120	9.52	9.04	0.05
144	10.93	8.14	0.035
168	8.27	7.55	0.027
192	9.22	7.35	0.017
216	9.58	7.19	0.014
240	9.46	7.17	0.008

After the first day (24 h), corrosion rates were about half compared to the started values, and then they decreased. The basic conclusion is that HNO_3 with a concentration of 0.5 mol·dm^{-3} represents a highly corrosive environment for the untreated tested material (EN 1.4713 steel). For the untreated sample, the corrosion rate is relatively constant, in the time after 24 h of exposure to the corrosive environment, until the end of the experiment, i.e., that the difference between the minimum and maximum value is less than 50%. Contrary to other samples, for the heat-treated sample, corrosion rate was significantly increased in the first 48 h of the measurement and then slowly decreased but only slightly below the value for untreated steel. The decomposition of the oxide layer at the surface can explain this phenomenon. Figure 3 illustrates this well since the current peak is very near the OCP. Coated sample was very well protected in the corrosion environment. Data for Table 2 showed that corrosion rate sharply decreased with time, and after ten days, it reached more than 50 times lower value than at the start of the experiment. It is also about 60 times lower compared to EH methods. It can be explained by clogging the pores in the coating and consequently lowering the porosity of the alumina/titania coating.

4 Conclusion

Based on the study the following conclusions can be drawn:

- Ferritic 1.4713 steel is not corrosion resistant in 0.5M HNO_3.
- The results showed significant improvement in corrosion resistance with the heat-treatment. Heat-treatment lowers the rate of corrosion to a great extent only in the first 24 h. However, due to the structure change, corrosion rates were only a bit lower than for the untreated sample in the whole measured time interval. The results indicate that anodic protection of heat-treated steel would lead to good results in the examined corrosion environment.
- Alumina/titania coating has shown even better results, with the current density decrease of two orders of magnitude. The weight-loss method has shown similar results with a somewhat larger difference when compared to the untreated material. This type of coating could improve the corrosion resistance of the base material in the acid solutions and probably lower the effect of the land flare gasses, which should be confirmed in future research.

- Finally, the fair agreement between the different methods of determining the corrosion rate for all samples was found in this study. This is especially significant for similar results between weight-loss and electrochemical methods.

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