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Stainless 08X18H10T and Low-Alloyed 15X1M1Φ Steels Protection from Corrosion with Emulsions of Thermostable Amines

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Chromium - nickel (08X18H10T) and chromium - molybdenum - vanadium (15X1M1Φ) steels together with emulsions of corrosion inhibitors - thermo stable amines have been investigated. Stainless steel was investigated in a aggressive medium of monoethanolamine (MEA) having absorbed CO_2. Effectiveness of steel corrosion inhibitors Kotamina P/2A, JM-T HTDOX, JM-T/CD and Kotamina Plus! was evaluated using electrochemical, optical and X-ray diffraction analysis methods. Anodic polarization curves of samples, passivated at 200 – 500 °C temperature were recorded and limits of passive state from –0.10 to +0.40 V for stainless steel and from –0.13 to +0.80 V for low-alloyed steel have been established. Kotamina JM-T/CD emulsion decreases corrosion rate of stainless steel in aggressive medium ~7 times according to reference sample. It was established that emulsion of Kotamina Plus! is the most effective corrosion inhibitor of the steel. Cathodic polarization method has been selected for modelling corrosion processes taking part in different medium. Current of corrosion of 15X1M1Φ steel was calculated using Tafel's experimental dependence. It was established, that decrease of corrosion current in medium with Kotamina Plus! depends on inhibitor screening effect.

Keywords: steel, passivation, corrosion inhibitor, thermostable amines, protecting film.

INTRODUCTION

One of the effective ways to protect steel against corrosion is its additional passivation by formation of protective film [1, 2]. Chromium-nickel steel 08X18H10T prominent for its good resistance to corrosion [3, 4] is often used in various heat exchange equipment and chemical industry. Because of imperfections of water preparation technologies and technical problems linked with monitoring water constituents during technological processes, water at high temperatures and pressures contains dissolved carbon dioxide, oxygen, other elements and compounds, which may be formed because of water and the metal surface interaction [5]. Investigations [6 – 9] were aimed protect of stainless steel from corrosion in aggressive medium of monoethanolamine (MEA) having absorbed CO_2.

Low-alloyed steel 15X1M1Φ is widely used in energy industry especially as boiler steel because its resistance to high temperatures and pressures [10]. During exploitation of boiler corrosion is taking part [11, 12]. Being oxidation and heat proof and having anticorrosive properties Kotamina can be used for passivation of boiler steel. Kotamina is emulsion of branched structure amines stable at temperatures up to 500 °C. Additives HTDOX, CD and others inhibit deposit and oxide formation and in doing so reduce steel corrosion. These amines enable regulation of boiler water properties and replace hydrazine, ammonium and phosphates which are used now [13 – 15]. Phosphatation leaves iron oxides on the boiler walls not removed; it makes formation of iron phosphate deposits possible. Application of multifunctional amines solves this problem partly by reducing deposits and slowing down corrosion and erosion [10]. However, amines used are not heat resistant enough and their disintegration begins already at 300 °C. For this reason their amounts used must be comparatively large. Polyamines are decomposed into amines having smaller molecular mass and ammonium compounds, thus, the pH of solution increases.

The aim of this work is investigation of protection against corrosion stainless and low-alloyed steels with emulsion of thermo stable amines, modelling of corrosion processes taking part in different medium.

EXPERIMENTAL

Stainless 08X18H10T and low-alloyed 15X1M1Φ steel of the main vapour collector boiler was used for the experiments. The steels samples sized 2 × 2 × 65 mm were prepared for investigation of corrosion process using potential and corrosion current relationship. For investigation of the surface changes steel plates sized 5 × 10 × 15 mm were used. They were spread over in the aluminium tube with epoxy resin, then were grinded and polished using special equipment. To prepare water phase of high temperature a special vessel, ensuring tightness at pressures up to 20 MPa was used. Steel of 08X18H10T was passivated with water emulsion of: 10 % Kotamina P/2A and JM-T HTDOX, 1 % and 10 % emulsions of Kotamina JM-T/CD at different temperatures and durations. Steel 15X1M1Φ was passivated with 1 and 5 % Kotamina Plus! at temperatures 200 – 500 °C in second grade demineralised water. The polarization curves of passivated steel were drawn for 0.5 % Kotamina Plus! emulsion in second grade demineralised water. Steel resistance to corrosion was investigated in 0.5 % oxalic acid solution having temperatures 18 ±2 and 90 ±2 °C.

Passivation effectiveness was evaluated according to corrosion current in the stationary state and according to

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the calculated corrosion rate *K*. Corrosion current was determined from the polarization curves drawn by the potentiostate PI-50-11 and the programmer PR-8. Potential was either increased or reduced from its stationary value at the rate of 0.5 mV/s and measured to the saturated sodium chloride electrode (EVL-1M3.1). The samples surfaces area was 1.9 – 2.6 cm^2. Steel surface alterations after passivation were explored using the microscope Olympus and the video-camera Sony DXC-151 AP with the computer code NIH Image 1.61 and scanning electron microscope JEOL JSM-5600. X-ray structure analysis of the steel 15X1M1Ф was carried out using DRON-2 device. The emulsions Kotamina was received from Polish Institute of Heavy Organic Synthesis "Blachownia".

EXPERIMENTAL RESULTS AND DISCUSSIONS

Corrosion of steel 08X18H10T in 20 % water solution of MEA which contains up to 100 g/l CO_2 at temperatures up to 115 ^oC is zero [6]. Steel corrodes at considerable rate in real conditions of heat exchanger work and it is necessity of efficient passivators for piping made of stainless steel and filled during operation with heat medium saturated with CO_2.

Structure of amines used for steel passivation was different including monoethanolamine $H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$, Kotamina P/2A R-$NH_2$ and Kotamina JM-T HTDOX, JM-T/CD – primary aliphatic amine with highly branched alkyl chains (Primene JM-T) in which the amino nitrogen atom is linked to a tertiary carbon [16, 17]. Stainless steel was passivated in 5 % water solution of MEA (duration – 3 days, temperature – 20 °C); in 10 % water emulsions of Kotamina P/2A and Kotamina JM-T HTDOX (duration – 2 hours, temperature – 120 °C). Anodic polarization curves of passivated steel 08X18H10T are shown in Fig. 1.

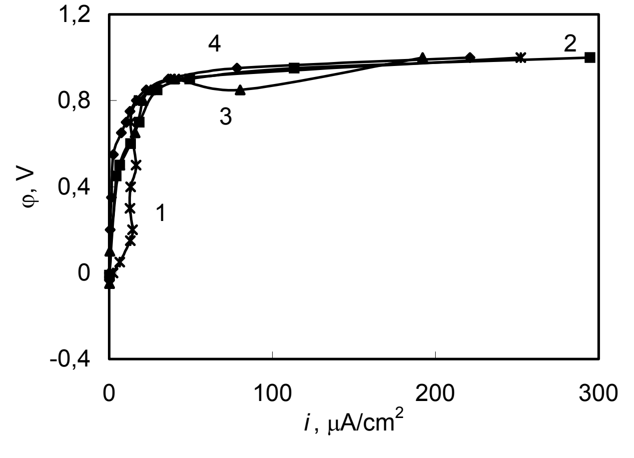

Fig. 1. Steel 08X18H10T anodic polarization curves in 20 % MEA with 60 g/l CO_2 solution at temperature of 20 °C: 1 – sample passivated with 5 % solution of MEA, 2 – 10 % emulsion of Kotamina JM-T HTDOX, 3 – 10 % emulsion of Kotamina P/2A and 4 – reference

Samples remain passive up to potential +0.4 V (curves 1 – 3) but corrosion current of reference sample grows from the polarization beginning (curve 4) and its corrosion rate is 0.045 g/ m^2·24 h. With the experimental solution temperature increase up to 90 °C corrosion rate of steel without passivation increases nearly 40 times. Emulsions of Kotamina as passivators are more effective than monoethanolamine and reduce corrosion rate 5 to 7 times. During passivation with amines of steel on its surface the monomolecular or several molecules thick layer is apparently formed. Film stability and passivation efficiency depend on the amine molecular structure [18]. Due to special structure Kotamina emulsions (on the base of Primene) are suitable for steel protection from corrosion at high temperature and pressure.

After series of experiments in search for optimum passivation materials for low-alloyed steel 15X1M1Ф it was found, that the most suitable for steel passivation and corrosion slowdown is Kotamina JM-T/CD emulsion. In the beginning of last year scientists of the "Blachownia" slightly changed the composition of emulsion and renamed it as Kotamina Plus! although active substance of it remained the same – Primene JM-T. New emulsion was used in the latest experiments. Samples were kept for 6 hours in a sealed vessel filled with 1 % emulsion of Kotamina Plus! at temperatures of 200 – 500 °C. Anodic polarization curves were registered and investigation results after qualitative evaluation and generalization are presented in Table 1.

Table 1. Influence of 1 % Kotamina Plus! emulsion temperature on passive state and corrosion rate of steel 15X1M1Ф

Passivation temperature, °C	Passive state limit, V	Rate of corrosion *K*, g/m^2·24 h
Reference		0.450
200	–0.200 ÷ +0.400	0.390
250	–0.190 ÷ +0.400	0.140
300	–0.150 ÷ +0.600	0.015
400	–0.130 ÷ +0.700	0.009
450	–0.190 ÷ +0.300	0.008
500	–0.130 ÷ +0.800	0.007

After exposure of steel samples at 200 °C temperature their passive state limits are –0.200 ÷ +0.400 V and when temperature reaches 500 °C it increases from –0.130 to +0.800 V. In the case of presence in solution 1 % inhibitor, corrosion rate of steel at 300 °C temperature decreases 30 times in comparison with the reference sample, and at 500 °C temperature – even 58 times.

The changes of steel 15X1M1Ф surface after ground and polished samples were kept in the pressure vessel in water vapour and in vapour with 1 % Kotamina Plus! were investigated using optical methods and presented in Fig. 2. Comparison of the surfaces of steel kept for 6 hours at 400 °C in vapour of demineralised second grade water (a) and in vapour with 1 % Kotamina Plus! (b) indicates significant differences between them. It is common knowledge that when water temperature is >250 °C the magnetite (Fe_3O_4) is formed on the surface. This can be seen in photo (a). More fine Fe oxide grains, which are a structure more corrosion-resistant, forms if in experimental medium 1 % inhibitor Kotamina Plus! is present (b, c). Formation of magnetite on the surface of steel was confirmed by X-ray diffraction analysis (Fig. 3).

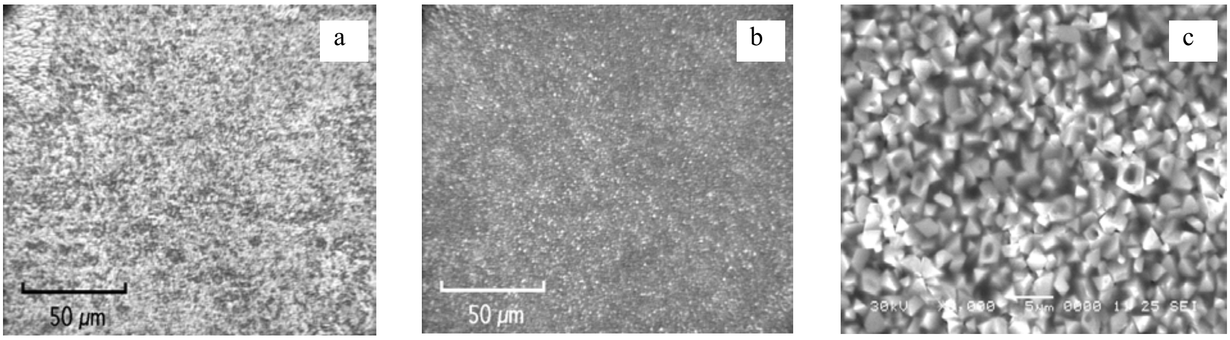

Fig. 2. Surface of steel samples after exposure at 400 °C temperature. Photo: a – demineralised second grade water, b – emulsion of 1 % Kotamina Plus!, c – the same (electron scaning microscope was used)

Usage of inhibitors may be only efficient when the mechanism of their action is known. For evaluation of the mechanism of action the most suitable is analysis of the cathodic polarization process in which only hydrogen is released while anodic polarization curves are difficult to interpret as the process is multistage one.

The Tafel's equation is valid for the cathodic polarization curves:

$$\eta_H = a_k + b_k \lg i_k , \tag{1}$$

$$\eta_H = -\Delta\varphi_k = \varphi_k - \varphi_p , \tag{2}$$

$$b_k = \frac{\partial \eta_H}{\partial \lg i_k} = \frac{\partial \varphi_k}{\partial \varphi_{ik}} , \tag{3}$$

here a_k and b_k are the constants, φ_k, φ_p is the electrode potential at current i_k and the equilibrium hydrogen electrode potential in the solution investigated, η is the overvoltage.

Using Tafel's dependence for cathode current it is possible to rewrite it in the following manner:

$$i_k = K_k^{'}(1-\theta)\left[H^+\right]^{n^{'}} \exp\left\{-2.3\left[\frac{\varphi_k^{'}}{b_k^{'}} + \frac{b_k^{'} - b_o}{b_o b_k^{'}}\psi_1^{'}\right]\right\} , \tag{4}$$

$$b_o = \frac{2.3RT}{F} = 0.059\, V \text{ , } (T = 300\text{ K})$$

here $K^{'}_k$ is the reaction rate constant, n is the reaction order, ψ_1 is the adsorption potential, R is the universal gas constant, T is the temperature, θ is the the electrode surface part which had adsorbed inhibitor. The values which may change with inhibitor added to solution bear primes.

It may be seen from the (4) that corrosion current i_k may be reduced with such inhibitors only, which increase the positive adsorption potential ψ_1 or increase θ.

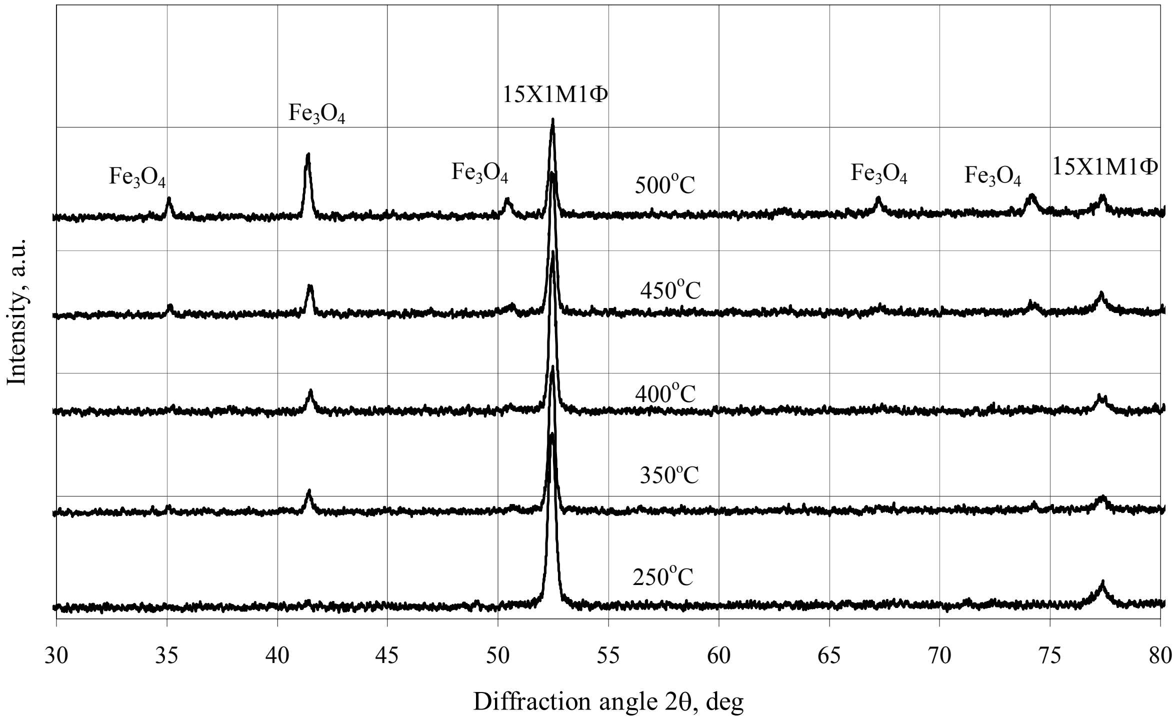

Fig. 3. The XRD patterns of steel 15X1M1Φ samples after exposure at 250 – 500 °C temperature in vapour of demineralised second grade water with 1 % Kotamina Plus!

The change $\Delta\psi$ may be calculated from the experimental cathodic and anodic polarization curves:

$$\varphi_s^{inh} - \varphi_s = \Delta\varphi_k = \left[1 - \frac{b_a \cdot b_k}{b_o\left(b_a + b_k\right)}\right]\Delta\psi_1 . \tag{5}$$

This dependence was derived under assumption that values b_a and b_k depend only slightly on inhibitor concentration in solution.

Determination of the occupied part of the electrode surface θ is more complicated because adsorption centres can be distributed on the electrode surface in a variety of ways and with various values of energy, dependence $\theta = (t)$ being related to it.

Let us choose several more characteristic $\theta = f(t)$ dependencies (isotherms)

$$\theta = 1 - \exp\left(K_2 t\right). \tag{6}$$

$$\theta = a_1 + b \ln t . \tag{7}$$

$$\theta = b_1 t^n . \tag{8}$$

The dependence (6) was obtained for the case of uniform distribution of the adsorption centres on the surface, while the dependence (7) also but with assumption that adsorption energy reduces linearly with increasing θ.

It appeared that variation of $\theta = f(t)$ can be simply determined if it be assumed that reduction of cathode is governed by inhibitor screening of the steel, so by θ. Then:

$$i_k = i_o(1 - \theta), \tag{9}$$

here i_o is the cathode current without inhibitor ($t = 0$), i_k is the cathode current after inhibitor was added to solution.

If reduction (or increase) of cathode current is determined by change of adsorption potential $\Delta\psi_1$, then:

$$i = i_o \exp\left(-K_1\theta\right). \tag{10}$$

This equation was obtained on condition that $\Delta\psi_1$ is directly proportional to θ. For the case when corrosion current is determined by inhibitor screening from equations (9) and (6 – 8) it was established:

$$\ln\frac{i_o}{i_k} = K_2 t . \tag{11}$$

$$i_o - i_k = a_1 i_o + b i_o \ln t . \tag{12}$$

$$\ln\left(i_o - i_k\right) = b_1 \ln i_o + n \ln t . \tag{13}$$

For the case when corrosion process is determined by change of the adsorption potential from equations (10) and (6 – 8) it was established:

$$\ln\ln\frac{i_k}{i_\infty} = \ln K_1 - K_2 t . \tag{14}$$

$$\ln\frac{i_o}{i_k} = a_1 + a_2 \ln t . \tag{15}$$

$$\ln\ln\left(\frac{i_o}{i_k}\right) = \ln b_3 + n \ln t . \tag{16}$$

Experimental $i_k = f(t)$ dependence was established in the following way. The cell of the device was filled with 0.5 % oxalic acid solution and sample of steel 15X1M1Ф was immersed. Then its stationary potential φ_s was determined. More negative potential than φ_s denoted by φ_k^o was given to sample using potentiostate and corrosion current i_o was established. To solution being stirred by a magnetic stirrer 0.001 % inhibitor solution was added (inhibitor was mixed with 0.5 % oxalic acid solution) and than at regular time intervals corrosion current values were recorded (gradually decreasing ones).

An experimental curve of dependence $i_k / i_o = f(t)$, when an inhibitor chosen is Kotamina Plus! is presented in Fig. 4.

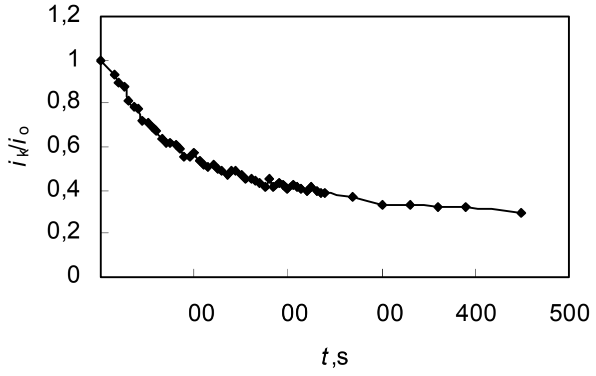

Fig.4. Cathode current variation when to 0.5 % oxalic acid solution 0.001 % inhibitor Kotamina Plus! was added ($\varphi_s = -0.487$ V, $i_o = 80$ μA/cm^2, $i_\infty = 25$ μA/cm^2, $\varphi_k^o = -0.60$ V)

As current i_k variation is very slow and i_∞ reaches > 300 s one is forced to acknowledge that we deal with chemosorption or a sort of special interaction in which π- electrons of inhibitor take part. If adsorption is governed by electrostatic or dispersive forces, i_∞ would be reached in a significantly shorter span of time.

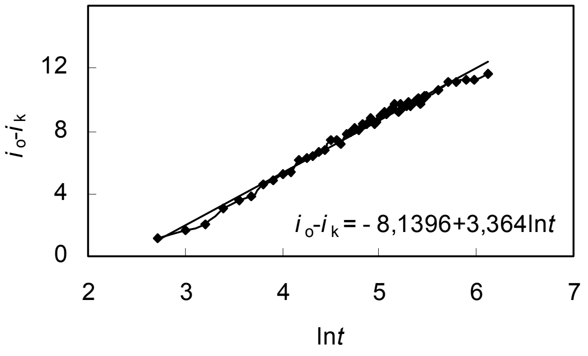

Fig.5. Adsorption of Kotamina Plus! on steel 15X1M1Ф surface in 0.5 % solution of oxalic acid with 0.001 % inhibitor

Using (11 – 16) equations according to the curve presented in Fig. 4 and dependencies obtained, only one is linear which is shown in Fig. 5. This straight line is obtained in the coordinates of equation (12). It means that corrosion current decreases because of Kotamina Plus! adsorption centres are uniformly distributed on the surface of steel (adsorption of inhibitor decreases with area covered increasing) and inhibitor screens the surface from hydrogen (H_3O^+) ions thus reducing electrode surface area.

CONCLUSIONS

Branched structure amine Kotamina JM-T/CD emulsion can be used for passivation of the austenitic chrome-nickel steel in 20 % monoethanolamine with 60 g/l CO_2 solution. Using various adsorption isothermal analytical dependencies with possible deceleration mechanisms of corrosion process (θ and $\Delta\psi_1$ – effects), it was established that adsorption of Kotamina Plus! process on the low-alloyed 15X1M1Ф steel is very slow. Corrosion current reduction is caused by the screening effect of inhibitor. At high temperature (200 – 500 °C) inhibitor is absorbed from its vapour phase and as results the steel surface becomes passive. This is clearly shown by anodic polarization curves recorded in 0.5 % inhibitor solution: passive state limits are from –0.13 to +0.80 V.

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