CORROSION-ELECTROCHEMICAL BEHAVIOUR OF LOW-ALLOY STEEL IN ALKALINE MEDIA

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Abstract. The authors demonstrated that low-alloy chrome-molybdenum-vanadium 12Cr1MoV steel has more positive open circuit potential and lower hydrogen evolution overvoltage in concentrated alkaline solution, compared to ordinary-quality St3 steel. After 1100 A·h·m^{-2} charge passing, 12Cr1MoV anodic dissolution rate becomes lower than St3 dissolution rate. It does not increase with current density increase.

Keywords: alkaline water electrolysis, 12Cr1MoV steel, hydrogen, oxygen.

1. Introduction

Hydrogen has high specific energy density, so it is a promising fuel [1]. Hydrogen is used in the refining and chemical industries. Though only 4 % of hydrogen in the world is produced by water electrolysis, it is promising for the future sustainable energy, when used in combination with renewable source of energy [2]. Only electrolyzers for alkaline water electrolysis currently have high productivity [3]. Practical considerations of industrial electrochemical engineering have led to the conclusion that the alkaline water electrolysis is still the best way to produce hydrogen [4].

Nickel, Raney nickel and cobalt are the most applied materials for alkaline electrolytes [5] due to the acceptable price, corrosion resistance and chemical stability. However, nickel cathodes are sensitive to atomic hydrogen [6, 7]. It is suggested to add compounds of iron and molybdenum [8, 9], chrome [10] and vanadium [11] into alkaline electrolyte to reactivate nickel cathodes. Cathodes of electrolysers may be made of ordinary carbon steel. This steel has accessible price and it is well processed. Furthermore, such steel has rather low overvoltage of hydrogen evolution [12, 13]. Steel grids are usually used as electrode material. In certain cases, they are coated with a layer of porous Raney nickel [14]. In the case of using steel anodes with nickel coating, both base material and nickel coating quality are important, because, for example, layer of matte nickel of 80–100 µm thickness has about 15 pores dm^{-2} [13].

Anodes should be stable not only at potentials of oxygen evolution. They also need to be corrosion-resistant at an open circuit potential. Anodes should not generate the products of dissolution worsening cathode operation, they should guarantee constant potential after initial break-in period [15], and they should be chemically resistant at lower values of a current density, including conditions stray currents formation in assembly of the electrolyzer [12]. Nickel anodes corrode in a number of tests, including the steady-operating conditions and some types of shutdowns [16].

The aim of the study is to determine electrochemical lows of the low-alloy chrome-molybdenum-vanadium 12Cr1MoV steel behaviour in an alkaline medium depending on a condition of their surface, in comparison with nickel and ordinary-quality steel of St3 grade.

2. Experimental

Polarization curves were obtained using PI-50-1.1 potentiostat. The results were recorded in digital form by means of two-channel voltmeter and TeleMax software at the rate of 20 signals per second. The ohmic resistance was not compensated. The samples of nickel and steels of St3 and 12Cr1MoV grade were used as working and counter electrodes. The St.3 and 12Cr1MnF steels have similar ranges of content (%): C (0.14–0.22 and 0.1–0.15, respectively), Si (0.15–0.3 and 0.17–0.37, respectively), Mn (0.4–0.65 and 0.4–0.7, respectively), Ni (< 0.3), S (< 0.05 and < 0.025, respectively), P (< 0.04 and < 0.03, respectively), and Cu (< 0.3 and < 0.2, respectively). Unlike St3, 12Cr1MoV steel is composed of up to 0.35 % of molybdenum and up to 0.3 % vanadium. Moreover, the 12Cr1MoV steel has 3-4 times more chromium and no arsenic in its composition, compared to St3 steel. The surface area of the working electrodes was 1–20 cm^2. Some samples had an activated surface, and some of the

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samples had oxidized surface. To activate the surface, samples were cleaned successively by carbide-silicone paper of No. 500, 100, 2000, and 3000 grit, degreased in acetone, and then washed with distilled water. To reduce the oxide film, the electrodes were treated at current density of 0.1–10 mA·cm^{-2} until constant potential has been reached. The oxide film on electrode surface of anode was obtained in galvanostatic mode at current density of 100 mA·cm^{-2}. We used mercury oxide electrode and the mentioned potentials were recounted with respect to the standard hydrogen reference electrode (SHE).

Solution volume in a three-electrode electrochemical cell was 100 cm^3. Quasi-stationary voltamperogramms were obtained at the potential sweep rate of 1 mV·s^{-1}. The electrolysis was performed in 5 M NaOH solution at room temperature without stirring. The solution concentration after preparation was corrected based on titration with 0.1 M HCl solution. The solutions were not deaerated.

3. Results and Discussion

Corrosion and electrochemical behaviour of low-alloy chrome-molybdenum-vanadium steel of 12Cr1MoV grade, nickel and St3 steel were studied depending on their surface condition. The samples were cathodically treated to determine the cathode behaviour in conditions of current flow and at open-circuit conditions. The samples with oxide film (not activated samples) were used to estimate the behaviour of the electrolyzer anodes.

Fig. 1a presents corrosion diagrams for pre-activated samples obtained using quasistationary polarization dependences. The diagrams demonstrate the high enough activity of cathodically activated nickel sample (*curve* 1) and St3 steel (*curve* 2) in alkaline solution. Their corrosion potential is lower than –0.8 V. In contrast to St3 steel, the chrome-molybdenum-vanadium steel (*curve* 3) has more positive open circuit potential. This indicates the higher corrosion resistance of the surface of this steel in an alkaline medium. Corrosion diagrams for oxidized samples are shown in Fig. 1b.

Fig. 1b shows corrosion diagrams for the same samples after oxide film formation on their surface. In this case, the oxide film was formed after passing of charge of 20 mA·h·cm^{-2}. The diagrams for these samples are shifted to the positive potentials region. This shift reflects improvement of protective properties of the surface with oxide film. The most significant shift was observed for the case of chrome-molybdenum-vanadium steel (cf. *curves* 3, Fig. 1a and Fig. 1b).

With the growth of the oxide film thickness due to the anodic treatment of electrode, their open circuit potential increases. At the same time nickel (*curve* 1, Fig. 2) becomes more positive than St3 steel (*curve* 2),

and then more positive in comparison with chrome-molybdenum-vanadium steel (*curve* 3).

The complex nature of dependencies of the mass change of electrodes on the charge passed through the cell (Fig. 3) is the result of a competition of process of the oxide films formation on their surface and oxidation of the electrode material in the form of soluble compounds. Thus, oxide film was formed on the surface of St3 steel samples at the beginning of electrolysis (Fig. 3a). The overweight of electrode is inhibited for some charge. The greater the charge, the higher the anodic current density (*curves* 1-3). The oxide film does not form on the surface of chrome-molybdenum-vanadium steel at all densities (Fig. 3b). The dissolution rate of the electrode made of chrome-molybdenum-vanadium steel, after passing of the charge of 1100 A·h·m^{-2} becomes lower than the St3 steel dissolution rate, and it practically does not depend on the anodic current density (*curves* 1-3, Fig. 3b). The changing of nickel electrode mass is less than mass loss of steel electrodes (cf. Figs. 3a, 3b and 3c). When the quantity of the passed electricity increase, resistance to dissolution of nickel and chrome-molybdenum-vanadium steel electrodes is higher than in the case of St3 steel.

Whereas during the initial stage of anode loading, for example, after passing of the charge of 120 A·h·m^{-2} (Fig. 4a), the mass of electrodes, generally, increases in the wide range of current density values, and the oxide layer forms on their surface, after passing of the charge of 2000 Ah·m^{-2} (Fig. 4b), the soluble compounds generation prevails over the formation of solid compounds, and the mass change of all electrodes significantly decreases. Partial oxidation rate of chrome-molybdenum-vanadium steel (*curve* 3) does not increase with current density increase, unlike steel of St3 grade (*curve* 2).

Quasi-stationary potentiodynamic dependences of oxygen evolution on the activated surface of St3 steel (*curve* 1', Fig. 5a) and chrome-molybdenum-vanadium steel (*curve* 2', Fig. 5a) are practically the same. The presence of the oxide film on their surface (*curves* 4' and 5') influences oxygen evolution process much less than oxide film on nickel electrode (*curves* 3' and 6'). The oxygen evolution on nickel electrodes occurs with a lower overvoltage than on steel electrodes. This is true for both activated electrodes (cf. *curve* 3' with *curves* 1' and 2') and for already passivated electrodes (cf. *curve* 6' with *curves* 4' and 5').

The overvoltage of hydrogen evolution on a nickel electrode is lower (*curve* 3, Fig. 5a) than on steel electrodes (*curves* 1 and 2). It is lower on the surfaces of chrome-molybdenum-vanadium steel (*curve* 2, Fig. 5) than on the surface of St3 steel (*curve* 1). Cathodic polarization curves obtained on the oxidized surface of the electrodes (*curves* 4-6), show smaller hydrogen evolution overvoltage. It is especially essential in the case of chrome-molybdenum-vanadium steel (*curve* 5).
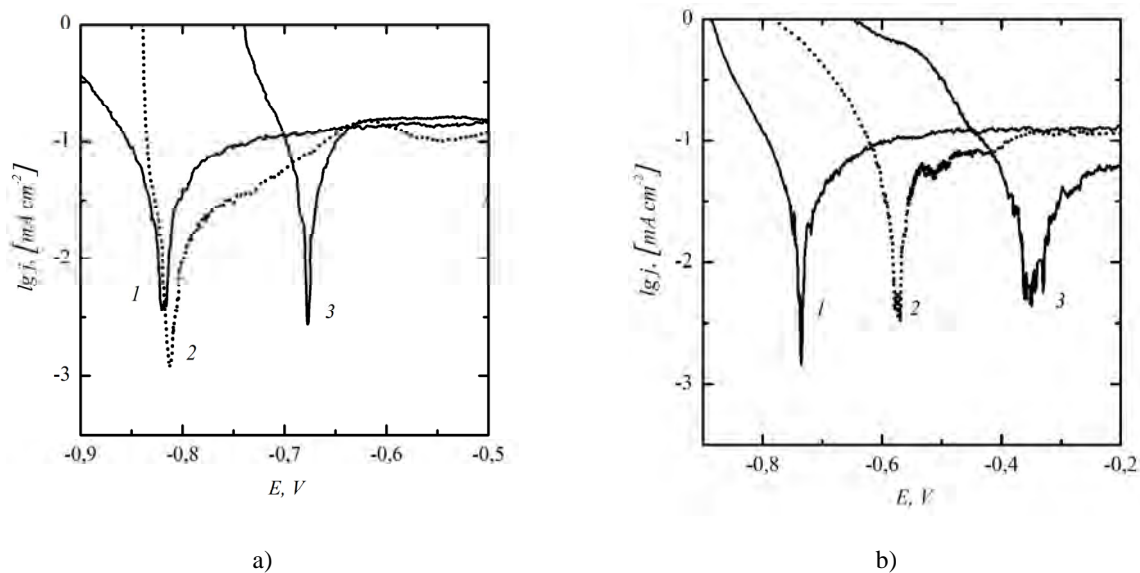
a)

b)

Fig. 1. Quasistationary polarization diagrams in 5 M NaOH solution for activated (a) and non-activated (b) electrodes made of nickel (1), St3 steel (2) and 12Cr1MoV steel (3)
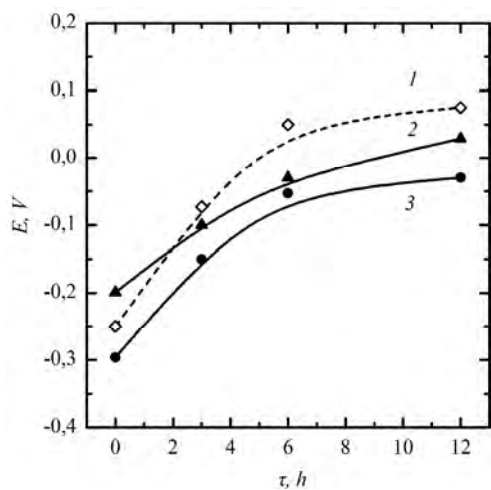

Fig. 2. Change of open circuit potential E_{oc} of the samples made of nickel (1), 12Cr1MoV steel (2) and St3 steel (3) after anodic treatment for time τ
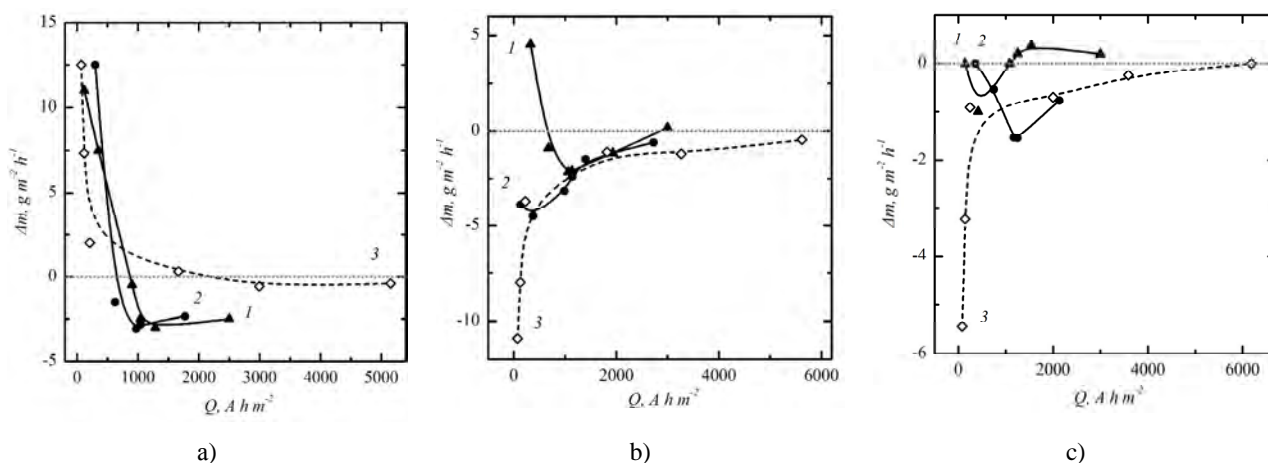

a)

b)

c)

Fig. 3. Dependences of mass change of St3 steel (a), 12Cr1MoV steel (b) and nickel (c) samples on the charge passed at a current density of 2200 (1); 1700 (2) and 900 (3) A·m^{-2}

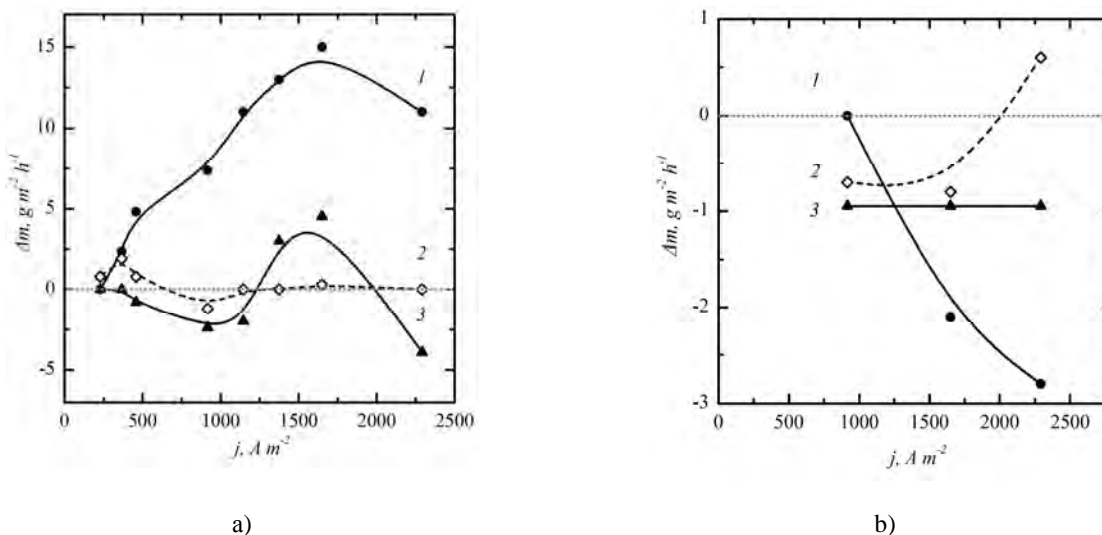a)   b)

Fig. 4. Dependences of mass change of St3 steel (1), nickel (2) and 12Cr1MoV steel (3) samples
on current density after passing of the charge of 120 (a) and 2000 (b) $A \cdot h \cdot m^2$

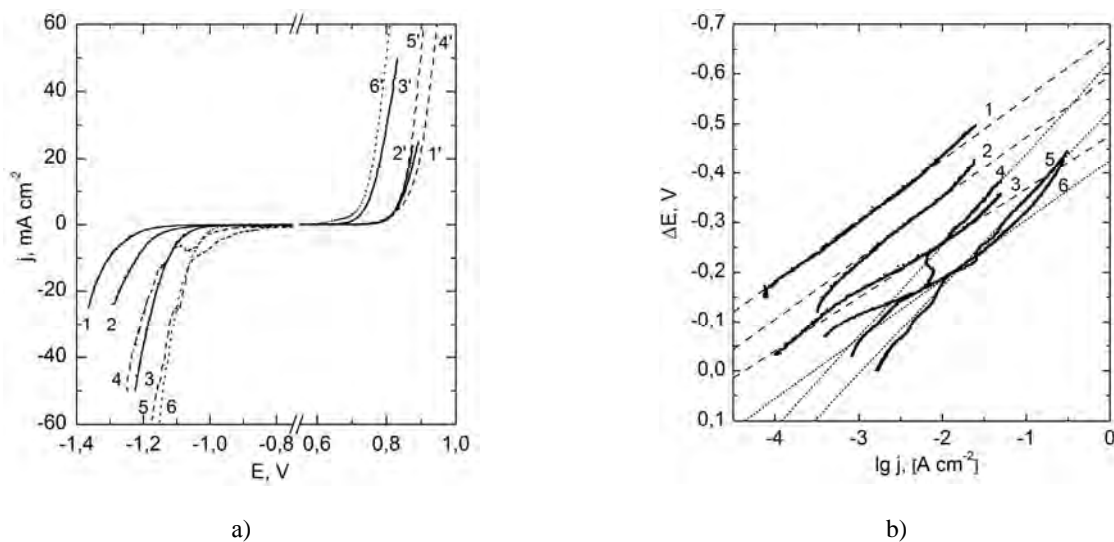a)   b)

Fig. 5. Cathodic (1–6) and anodic (1'–6') quasi-stationary potentiodynamic dependencies on activated (1–3, 1'–3')
and not activated (4–6, 4'–6') surfaces of electrodes made of St3 steel (1, 1', 4, 4'), steel 12Cr1MoV (2, 2', 5, 5')
and nickel (3, 3', 6, 6')

Table 2

Indices of electrochemical behaviour of electrodes

Index	Ni		12Cr1MoV		St3	
	activated	passivated	activated	passivated	activated	passivated
Corrosions potential E_{cor}, V	–0.82	–0.67	–0.68	–0.33	–0.81	–0.57
Mass changes of samples m after passing of the charge of 2000 $A \cdot h \cdot m^{-2}$ at $J_a = 2250$ $A \cdot m^{-2}$, $g \cdot m^{-2} \cdot h^{-1}$	–	0.6	–	–0.95	–	–2.8
Coefficient of Tafel equation a, V	0.43	0.48	0.53	0.60	0.62	0.68
Coefficient of Tafel equation b, V	0.11	0.12	0.12	0.18	0.12	0.18

In the semi-logarithmic coordinates, the change of position of the Tafel regions of cathodic polarization dependencies is observed (Fig. 5b). Therefore, the hydrogen evolution overvoltage decreases in the row St3 steel – chrome-molybdenum-vanadium steel – nickel and on the surface of the electrodes coated with oxide layer. The values of the Tafel equation coefficients for these dependencies are shown in Table 2.

4. Conclusions

Corrosion potential of low-alloy chrome-molybdenum-vanadium steel in alkaline solution of 5 M NaOH is more positive as compared to both steel of ordinary quality (St3 grade) and nickel. Increase of oxide film thickness leads to the corrosion potential of the nickel sample becoming more positive than steel electrodes potential.

With the increase of charge passed the mass change of the electrode decreases. The dissolution rate of the chrome-molybdenum-vanadium steel electrode after passing of the charge of $1100\ A\cdot h\cdot m^{-2}$ becomes lower than St3 steel dissolution rate. As the current density increases, the rate of chrome-molybdenum-vanadium steel oxidation does not increase, unlike St3 steel oxidation rate.

Oxygen evolution on St3 and 12Cr1MoV steel electrodes (both activated and already passivated) occurs with the higher overvoltage than on nickel surface. Hydrogen overvoltage on the surface of chrome-molybdenum-vanadium steel is lower than on the surface of St3 steel. Cathodic polarization curves obtained on the oxidized surface of the electrodes show lower hydrogen evolution overvoltage. It is especially essential in the case of chrome-molybdenum-vanadium steel.

The investigations of corrosion-electrochemical behaviour of low-carbon chrome-molybdenum-vanadium steel in comparison with nickel and steel of ordinary quality (St3 grade) show the expediency of St3 steel replacement by chrome-molybdenum-vanadium steel in the process of hydrogen production by alkaline-water electrolysis both as a separate electrode material and as a substrate for the nickel and other catalytic coating, *e.g.* like antimony-doped tin dioxide and Cu/Ni-Cu multilayer coatings [17, 18].

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КОРОЗІЙНО-ЕЛЕКТРОХІМІЧНА ПОВЕДІНКА НИЗЬКОЛЕГОВАНОЇ СТАЛІ У ЛУЖНОМУ СЕРЕДОВИЩІ

Анотація. *Показано, що низьколегована хроммолібден-ванадієва сталь 12Х1МФ, у порівнянні зі сталлю звичайної якості Ст.3, у концентрованому лужному розчині має більш позитивний стаціонарний потенціал та більш низьку перенапругу виділення водню. Після пропускання 1100 А·год/м² кількості електрики, швидкість її анодного розчення стає нижчою у порівнянні зі сталлю Ст.3, і не збільшується з підвищенням густини струму.*

Ключові слова: *водно-лужний електроліз, 12Х1МФ сталь, водень, кисень.*