Determination of Corrosion Rate of Rhenium and Its Alloys

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The polarization curves were measured on the specimens of rhenium and several its alloys with molybdenum, nickel and tungsten in the NaCl solutions free of additives and containing NaOH or HCl additives, and also in the sulfuric acid and nitric acid solutions. The corrosion current densities were determined by the method of Tafel extrapolation. The corrosion rates in the linear and weight units were calculated for several metals and alloys. The effect of the metal (Mo, Ni, W) nature on the corrosion behavior of rhenium alloys with these metals was shown.

1. Introduction

Corrosion is an important phenomenon, which restrict the service life of varies equipment (Gomes and Beck, 2013), for example, in petrochemical industry (Nicola et al., 2013).
Rhenium has a very high melting point, is resistant to many chemical reagents, and exhibits a high catalytic activity.
The alloys of rhenium with molybdenum, tungsten, and nickel exhibit high heat resistance and are used for the parts of air and space crafts.
The corrosion resistant properties are of importance in almost all cases of rhenium application.
However, only in few works, the corrosion rate of rhenium (Tomashov and Matveeva, 1970) and some its alloys in NaCl solution (Byalobzheskii and Vladimirov, 1970), in acids, alkali and NaCl solution (Petrov et al., 1983) was estimated.
In this work, the corrosion rates of rhenium, molybdenum, nickel, tungsten, and several alloys of rhenium with these metals are estimated by the electrochemical method of Tafel extrapolation.
The alloying metal affects the corrosion behavior of the alloys depending on its content in the alloy.

2. Experimental

The experiments were performed in 0.5 M NaCl solution free of additives and with HCl or NaOH additives, and also in the H_2SO_4 and HNO_3 solutions under the conditions of natural aeration. Prior to the experiments, the electrode surfaces (the end-faces of the rods 3-4 mm in diameter with insulated side surface) were polished with 25.8 µm emery paper and washed with ethyl alcohol and, then, with distilled water. Prior to the onset of electrochemical experiments, the test specimens were held in the solution for one hour up to reaching virtually constant open-circuit potential E_{oc}. The voltammograms were measured with a potential scan rate of 10^{-4} V/s. The curves were measured starting from E_{oc} in the direction of more negative potentials up to reaching the current densities of 5 to 12 µA/cm^2 in different experiments. Then, the potentiostat was switched off and the electrode was held at in the solution up to reaching the initial value of E_{oc}. Thereafter, the potential was scanned in the direction of more positive values up to reaching the current densities of 12 to 120 µA/cm^2 in different experiments. The experiments were performed in the thermostated three-electrode electrochemical cell at 20 ^{0}C. A saturated silver-chloride electrode served as the reference electrode. The potentials in the text and figures are given against this electrode.

The experiments showed that the polarization curves have pronounced Tafel portions. Therefore, the method of Tafel extrapolation was used to determine the corrosion potential E_{corr} and the corrosion current density i_{corr}. The value of E_{corr} and i_{corr} were determined by the coordinates of intersections of extrapolated anodic and cathodic Tafel portions of the voltammograms.

3. Rhenium-molybdenum alloys

In this part of the work, the alloys containing 21, 30, 40 and 50 wt % rhenium were studied. These alloys are the solid solution based on molybdenum (Lyakishev, 1999).

Figures 1 – 2a give the polarization curves for rhenium, molybdenum, and Re40-Mo60 alloy in 0.5 M NaCl solution; Figure 2b gives the polarization curve for rhenium in 1 M H_2SO_4 solution.
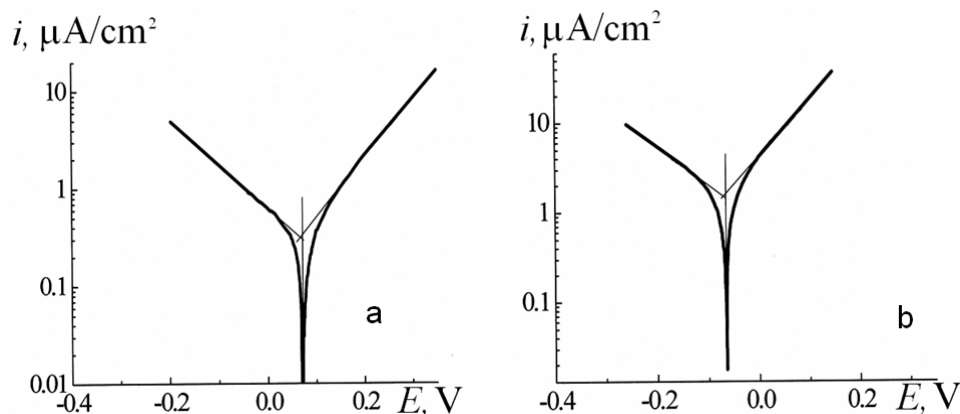

Figure 1: Voltammograms of (a) rhenium and (b) rhenium alloy containing 60 wt % molybdenum in 0.5 M NaCl solution
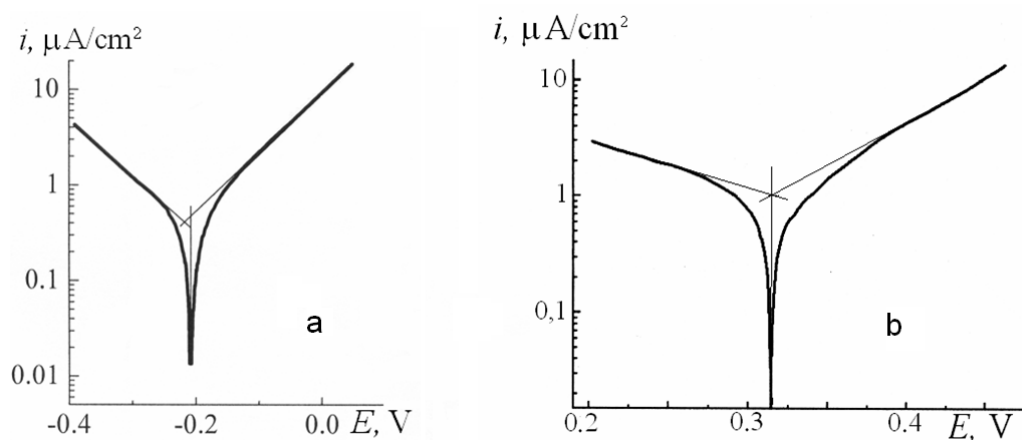

Figure 2: Voltammograms of (a) molybdenum in 0.5 M NaCl solution and (b) rhenium in 1 M H_2SO_4 solution

Figures 3 and 4 give the dependences of corrosion potential and corrosion current on the alloy composition, including unalloyed rhenium and molybdenum.

The corrosion potential shifts to more negative values in the series of alloys from pure rhenium to pure molybdenum. A similar dependence is observed for the solutions with the additions of alkali and acid; the higher is the acidity, the more positive are the values of E_{corr}. It should be noted that the values of E_{oc} for rhenium and molybdenum differ significantly. A similar difference is observed between the standard potentials of these metals (Sukhotin, 1981).

In the neutral and acidic NaCl solutions, the corrosion currents of molybdenum and rhenium are low: 0.5 $\mu A/cm^2$ for molybdenum and 0.4 $\mu A/cm^2$ for rhenium. The corrosion current of rhenium and molybdenum in the alkaline solutions is by 6 and 11 times higher than in the neutral NaCl solution.

In the neutral and acidic solutions, the corrosion currents of all studied alloys are higher than those of the components: molybdenum and rhenium. The alloy with 50% molybdenum exhibits the highest currents (Figure 4).

The corrosion rates were converted from the electrical units ($\mu A/cm^2$) into the linear units (mm/year) using the following equation:

$$V_l = (A\ i_{corr})/(nF\rho) \tag{1}$$

Here, A is the atomic weight, F is the Faraday number, ρ is the metal density (10.2 g/cm^3 for Mo and 21 g/cm^3 for Re (Dritz, 1985)), and n is the number of electrons involved in the dissolution reaction (n = 6 for Mo and n = 7 for Re). Molybdenum dissolves in the aqueous solutions of salts by the following reactions: Mo + 4 H_2O = MoO_4^{2-} + 8H^+ + 6e (Gmelin, 1988); rhenium dissolves in the aqueous sulfate solutions (Gomez et al., 1989) и chloride solutions (Giraudeau and Gross, 1974), by the following reactions: Re + 4 H_2O = ReO_4^- + 8H^+ + 7e.
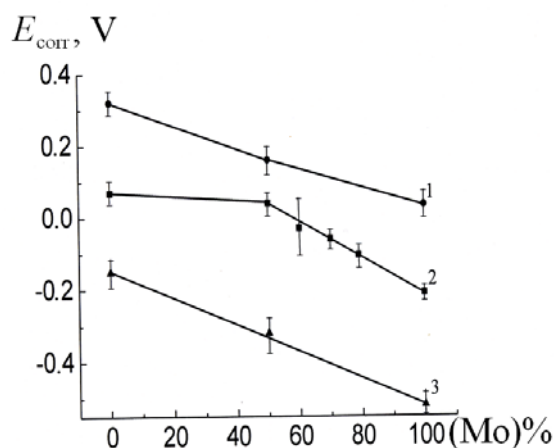

Figure 3: Dependences of corrosion potential on the composition of test specimen in the solutions (1) 0.5 M NaCl + 0.1 M HCl, (2) 0.5 M NaCl, and (3) 0.5 M NaCl +0.1 M NaOH

The results for molybdenum and rhenium are as follows: V_l = 0.0026 mm/year for Mo and V_l = 0.0017 mm/year for Re. Calculating A of the alloy by the equation $A = A_{Mo}x_{Mo} + A_{Re}x_R$, where x is a fraction of molybdenum in the alloy, and the alloy density ρ by a similar equation, for the Mo50-Re50 alloy, we obtain V_l = 0.028 mm/y.
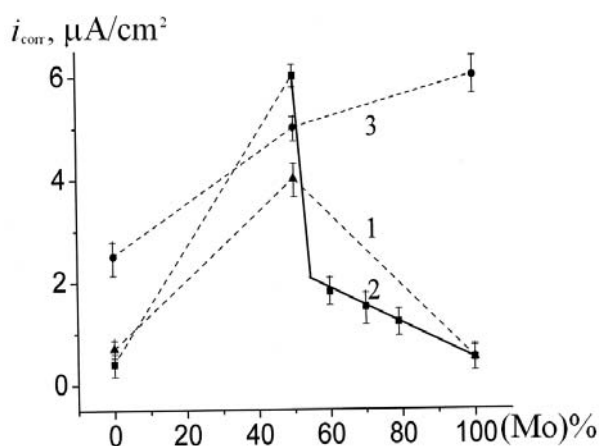

Figure 4: Dependences of corrosion current density on the composition of test specimen in the solutions: (1) 0.5 M NaCl + 0.1 M HCl, (2) 0.5 M NaCl, (3) 0.5 M NaCl +0.1 M NaOH. The curve portions, where the values of i_{corr} were not measured within a wide range of alloy composition, are shown dashed

The data on the corrosion rates of molybdenum and rhenium in the 0.5 M NaCl solution in the weight units can be calculated by the following equation:

$$V_w = (A\ i_{corr})/(nF) \tag{2}$$

The corrosion rate was 0.072 g/(m^2 d) for molybdenum and 0.095 g/(m^2 d) for rhenium.

For Mo50-Re50 alloy, using again equation $A = A_{Mo} \cdot 0.5 + A_{Re} \cdot 0.5 = 96 \cdot 0.5 + 186.3 \cdot 0.5 = 141.15$, we obtain $V_w = 1.1$ g/(m^2 d). The value of V_w for other alloys can be estimated by the same procedure.

Table 1 lists the corrosion rates of rhenium, molybdenum, and Mo50-Re50 alloy in the acidic solutions.

Figure 2b gives the polarization curves, which were measured on rhenium in 0.5 M sulfuric acid solution.

Table 1. The corrosion current densities (µA/cm^2) of metals and several alloys in the solutions of various compositions

Metal (alloy)	1 M H$_2$SO$_4$ solution	1 M HNO$_3$ solution	0.5 M NaCl solution	0.5 M NaCl+ 0.1 M HCl solution	0.5 M NaCl+ 0.1 M NaOH solution
Re	0.9	0.5	0.5	0.65	2.5
Mo	0.5	0.33	-	-	-
Ni	-	-	pitting	9.0	*
W	-	-	0.85	*	9
20Re-80Ni	-	-	0.08	6.0	*
27Re-73W	-	-	0.5	1.0	40
50Re-50Mo	4.0	4.5	-	-	-

*No Tafel regions are observed, passivity

From these data it is seen that, in the acid solutions, as well as it was shown above for the NaCl solution, the corrosion rate of the alloy is significantly higher than those of molybdenum and rhenium. Byalobzheskii et al. (1970) determined the corrosion rates by the gravimetric method (the procedure was not described in detail). It was also found that the corrosion rate of molybdenum-rhenium alloy (53 wt % Mo) was considerably higher than the corrosion rates of the alloy components. Similar results were obtained by Petrov Yu.N., et al. (1983). Byalobzheskii et al. (1970) supposed that this could be associated with the properties of oxide films on the metals and alloys. In connection with this, it should be noted that both standard and corrosion potentials of rhenium and molybdenum differ essentially. Assuming that molybdenum and rhenium atoms virtually independently pass from the alloy to the solution, we obtain that, for example, the dissolution of molybdenum from Mo50-Re50 alloy at the alloy's corrosion potential occurs at a potential by 250 mV more positive than E_{corr} of unalloyed molybdenum. This effect can lead to a higher corrosion rate of the alloy.

4. Rhenium-nickel and rhenium-tungsten alloys

The polarization curves for nickel, tungsten, the nickel-rhenium alloys containing 10, 20, and 30 wt % rhenium, and tungsten-rhenium alloy containing 27 wt % rhenium were measured in the 0.5 M NaCl, 0.5 M NaCl + 0.1 M HCl, and 0.5 M NaCl +0.1 M NaOH solutions.

Nickel, as a component of nickel-rhenium alloys, differs essentially from molybdenum in its electrochemical properties. In the anodic polarization curve of nickel in 0.5 M NaCl, a region of passivity is observed; it passes into a region of metastable pitting, which ends with an abrupt increase in the anodic current at a potential of 0.08 V (stable pitting, Figure 5).

The anodic behavior of nickel-rhenium alloys with 10 and 15 wt % rhenium is determined to a large extent by the properties of nickel: the regions of metastable pits, which are followed by the regions of stable pitting, are observed in the polarization curves. Such behavior of nickel and its alloys with 10 and 15 wt % rhenium (the absence of the Tafel regions) gives no way of determining the corrosion current. The polarization curve for nickel-rhenium alloys with 20 wt % rhenium has a Tafel region with several short-term current spikes, which correspond to the formation and passivation of metastable pits. No region of stable pitting is observed in the polarization curve. Such behavior of the alloy does not preclude the estimation the corrosion current density by the method of Tafel extrapolation. The results are presented in Table 1 and on Figure 6.
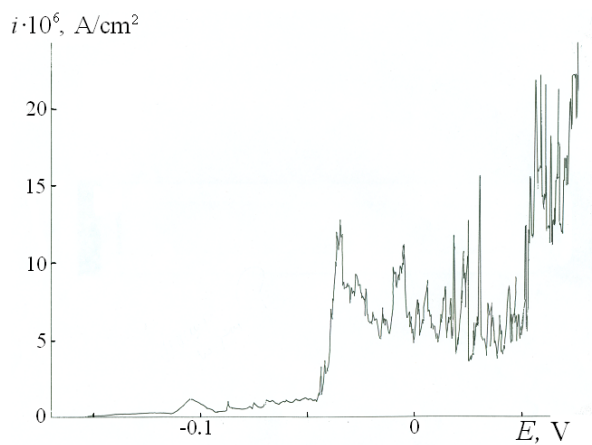
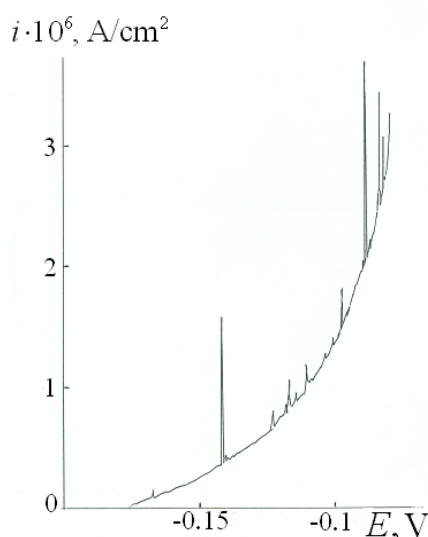*Figure 5: Anodic polarization curve measured on Ni in 0.5 M NaCl*

Figure 6: Anodic polarization curve measured on Re20-Ni alloy in 0.5 M NaCl

In the acidified NaCl solution, well-pronounced Tafel portions are observed in the anodic polarization curves; therefore, i_{corr} of these materials can be determined. A difference between the corrosion behavior of nickel in the neutral and acidified NaCl solutions can be explained as follows: pitting corrosion is the local breakdown of passivity, whereas the acid hampers the metal passivity.

The corrosion current density of 20Re-Ni alloy is by several times lower than i_{corr} of 20 Re-Mo alloy (compare the data presented in Table 1 and Figure 4). Here, the effect of nickel, which is more prone to passivity than rhenium in the neutral solutions, is observed. Rhenium, which is not prone to pitting corrosion, prevented the formation of stable pits on the alloy, which are typical for nickel in the NaCl solution.

It is seen that nickel, which readily dissolves in the NaCl+HCl solution, promotes the alloy corrosion in this solution. In the NaCl+NaOH solution, the effect of nickel, which is prone to the passivation in the alkaline solutions, on the alloy corrosion is observed. In this solution, no Tafel region is observed in the anodic polarization curve, the current smoothly increases with increasing potential and, then, reaches a virtually constant value of 1.3 µA/cm^2.

The corrosion current of Re-W alloy in the alkaline solution is very high, because both alloy components are easily dissolved in such solutions. In this case, the corrosion current of the alloy is also much higher than that of both alloy components in the NaCl+NaOH solution.

5. Conclusions

The voltammograms were measured on the electrodes of molybdenum, rhenium, nickel, tungsten, and several alloys of these metals with various ratios between the components in the 0.5 M NaCl solution free of additives and containing NaOH and HCl additives. It was shown that, in most cases, the voltammograms contained well pronounced Tafel regions.

The corrosion current densities in the above metal (alloy)/electrolyte systems were determined by the method of Tafel extrapolation.

The dependences of E_{corr} and i_{corr} on the composition of Re-Mo alloys are presented. The corrosion potential monotonically shifts to more negative values when passing from rhenium to molybdenum. In the dependence of corrosion current on the electrode composition, a peak is observed at 50 wt % molybdenum. Using the measured values of i_{corr}, the corrosion rates in the linear and weight units were calculated for several materials.

The values of i_{corr} for 20Re-Ni and 27Re-W alloys are presented. The effect of the alloy components on the anodic behavior and corrosion current of the alloys is considered.

Acknowledgements

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