Corrosion Resistance of Hastelloy-B in the Ozonized Medium

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Abstract—Corrosion–electrochemical behavior of Hastelloy-B and its components nickel and molybdenum is investigated at various concentrations of sulfuric acid in the presence of ozone. It is found that in ozonized solutions of sulfuric acid the alloy is corrosion-proof, and the effect of molybdenum reduces to ordinarily diminishing the anodic dissolution of nickel.

INTRODUCTION

Chemical industry masters more and more novel environmentally clean manufacturing processes. The use of ozone in oxidizing reactions, as a rule, enhances both the yield and quality of end products, and reduces the quantity of the wastes that are not utilized [1]. At present, it is known [2, 3] that ozone, being a depolarizer of cathodic processes, makes stainless steels passive in solutions of sulfuric acid with a concentration of up to 20% and enhances the corrosion resistance of titanium and its alloys in hydrochloric acid up to the same concentration.

Transition (*d*) metals dissolve in aqueous solutions of electrolytes with the formation of ions of variable valency, and can transfer into passive state due to the formation of either chemisorptive bonds between the metal atoms and water's oxygen, or oxides (hydroxides) that decelerate the dissolution process. The alloys of transition (*d*) metals inherit their basic properties. Hastelloy-B has been developed to manufacturing welded structures operating at a high temperature in several acids (hydrochloric, phosphoric, sulfuric) and in other media characterized by reducive properties. However, being resistant to the action of sulfuric acid of medium concentrations [4, 5], this alloy is not resistant to corrosion under oxidizing conditions.

It is the objective of this work to study the effect of ozone on the corrosion behavior of an alloy of the Hastelloy-B type, and of its constituents, that is, nickel and molybdenum in sulfuric-acid solutions.

EXPERIMENTAL TECHNIQUE

Potentiodynamic and potentiostatic investigations were carried out in a three-electrode glass cell. The reference electrode is silver chloride (the potentials having been referred to n.h.e.), the auxiliary electrode is platinum, and the working electrode is molybdenum, nickel, and Hastelloy-B. The chemical composition (at. %) of this stainless alloy is as follows: the base is nickel; Mo 27, V 1.5; (Mn, Si, C no more than 0.5, 0.2, 0.05, respectively); density is 9.25 g/cm^3, and effective resistivity 135 $\mu\Omega$/m. The surface of the working electrode was scraped bright till the roughness R_a = 2.5 μm, degreased and cathodically activated at a current density of 10 A/m^2 during 3 min. The tests were carried out in 2, 5, 10, 20, 30, 40, and 70% solutions of chemically pure sulfuric acid. The solutions were ozonized by passing the ozone-air mixture through the working volume of a cell at a rate of 0.06 m^3/h. The concentration of ozone in the mixture was 0.1 mol/m^3. Potentiodynamic investigations were carried out with a P-5848 potentiostat according to the standard technique at a polarization rate of 1.44 V/h. Potentiostatic measurements were carried out with the use of a computer provided with analog-to-digital and digital-to-analog converters and a device electronically scaling the output signal, which allowed recording high-rate electrochemical processes at the working electrode. Gravimetric investigations, according to standard technique, were carried out separately.

RESULTS AND DISCUSSION

Polarization measurements have shown that alloying nickel with molybdenum affects but slightly the hydrogen overvoltage but increases the overvoltage of anodic processes, thus favoring the anodic control of the alloy corrosion rate. The increase in the anodic polarizability can most likely be caused by either the hampering action of molybdenum on the hydration of
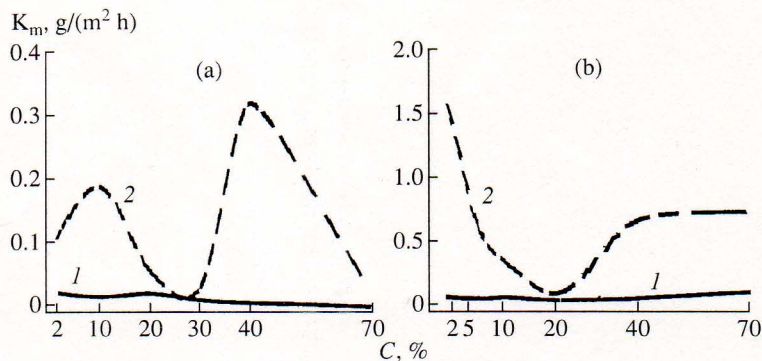
Fig. 1. Corrosion rates of (a) Hastelloy-B and (b) nickel in solutions of sulfuric acid: (*1*) aerated, and (*2*) ozonized.

the metal ions or the formation of a porous film of molybdenum oxide as a diffusion barrier.

The alloy dissolution rate in H_2SO_4 solutions throughout the entire investigated concentration range (Fig. 1a) remains low. However when introducing ozone it increases by an order of magnitude, and the maxima appear at concentrations of 10 and 40% H_2SO_4 up to 0.35 g/(m^2 h), but virtually no dissolution is noticed in a concentration range of 20–30%.

Polarization curves of Hastelloy-B in media causing the maxima of dissolution rates, show (Fig. 2) that in a 40% H_2SO_4 E_{cor} decreases by 0.2 V, and anodic current density i_a is lower than in a 10% solution. With an access for ozone to the solution, E_{cor} reaches approximately 0.3 V in both the concentrations, whereas i_a, in the vicinity of E_{cor} is, on the average, by an order of magnitude higher than without ozonizing, which points to an increase in the corrosion rate. It is known [5] that air oxygen, as well as other oxidizing agents, accelerates the corrosion of the Ni–Mo type alloys. Sulfuric acid of moderate concentrations is sometimes related to reducing media, but an admixture of ozone makes it acquire oxidizing properties. Nickel-molybdenum alloys are not passivated in such media, and a slight increase in E_{cor} leads to an increase in both the anodic current density and the corrosion rate.

The E_{cor} values were determined as a function of the H_2SO_4 concentration (Fig. 3) upon immersing a specimen in the solution and freely exposing it there no less than 30 min until the potential change for the last 10 min became no more than 0.03 V. E_{cor} was also calculated from the voltammograms by a commonly accepted method. In the aerated solutions, E_{cor} values do not substantially change with an increase in the acid concentration and stabilize within a range of 0.15–0.20 V. The calculated and experimental values agree well, differing beyond the experimental error only in the 2 and 40% solutions. In the presence of ozone the

E_{cor} increases by 0.1 V in all the solutions except for 70% H_2SO_4. On the whole, the electrochemical behavior of the alloy in the ozonized solutions is determined by the reactions taking place on molybdenum.

Voltammograms of Hastelloy-B, Ni, Mo in ozonized 10% H_2SO_4 solution show that its electrochemical behavior even in the presence of ozone is intermediate compared with the pure metals (Fig. 4). Under the effect of ozone, the corrosion rate of nickel increases by nearly an order of magnitude, and is maximum in a 2% H_2SO_4 solution (Fig. 1b). With an increase in the con-
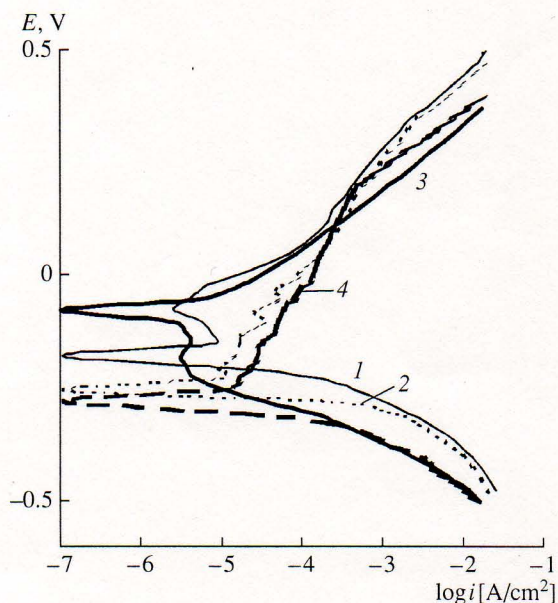

Fig. 2. Voltammograms of Hastelloy-B in solutions of sulfuric acid: (*1*, *3*) aerated; (*2*, *4*) ozonized; (*1*, *2*) 10% H_2SO_4; and (*3*, *4*) 40% H_2SO_4.
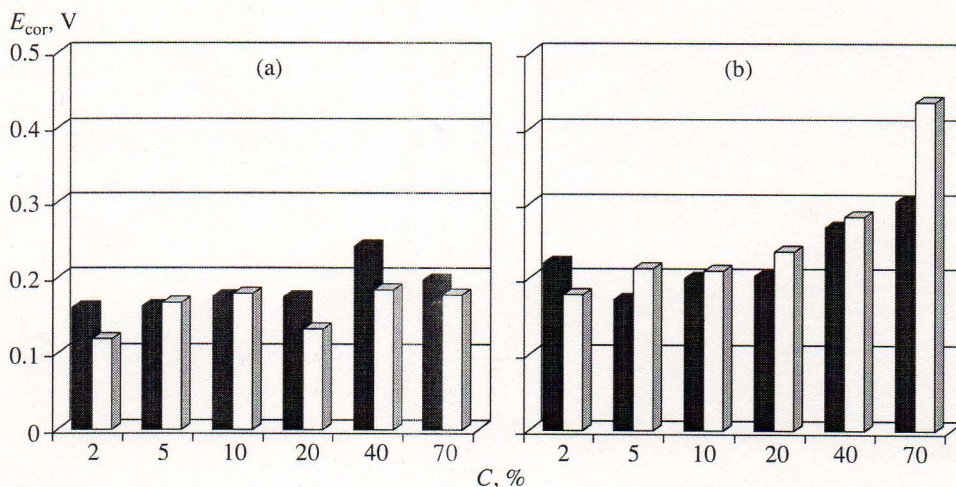
Fig. 3. Corrosion potentials of Hastelloy-B in solutions of sulfuric acid: a = aerated ones; b = ozonized ones; ■, E_{cor} (measurement), and □, E_{cor} (calculation).

centration, corrosion rate decreases and reaches its minimum in a 20% H_2SO_4 solution.

Molybdenum behaves analogously, except for by an order of magnitude lower corrosion rate. Added to nickel, molybdenum increases the corrosion resistance of the former, especially to acids. Already small additions of molybdenum (5–7%) reduce the solubility of nickel in acids. However, only additions of 15 to 30% Mo result in obtaining industrially used corrosion-resistant alloys.

In sulfuric acid solutions, corrosion potential of such alloys has been reported to increase by 0.1–0.4 V on the addition of ozone [6]. In the present work, E_{cor} remains virtually constant (nearly ≈0.2 V) as the concentration of H_2SO_4 in the ozonized solutions changes. The corrosion rate increases by a half an order of magnitude compared to nonozonized silutions, but molybdenum remains a corrosion-resistant metal. In a general case, adding molybdenum ennobles the nickel potential, but does not enhance its passivability. The effect of molybdenum is reduced to decelerating the anodic dissolution of nickel, irrespective of whether ozone is present or not. Of interest is a low corrosioin rate of the alloy in a range of 20 to 30% concentration of H_2SO_4 (Fig. 1a).

A favorable configuration of d-electrons favors both the chemisorption and passivity of alloys. It is thought that a more passive component of an alloy is an acceptor of electrons, whereas a less passive one is a donor. Molybdenum alloys keep corrosion-resistance until d-orbital becomes occupied. It is known [7] the corrosion of nickel may decelerate with time due to the adsorption of atomic hydrogen on the atoms found in semicrystal positions. Hydrogen dissolved in metal partly dissociate into protons and electrons, while the latter are able to fill up the vacancies of the d-orbitals of

nickel atom. Hence, the metal containing a sufficient quantity of hydrogen seems to be already unable to chemisorb oxygen and be passivated, because its d-orbital is filled up. According to [8], nickel contains 0.6 electron vacancy per atom; therefore, it tends to be hydrogenated in acidic media, and does not dissolve at all the concentrations of sulfuric acid under investigation (Fig. 1b).

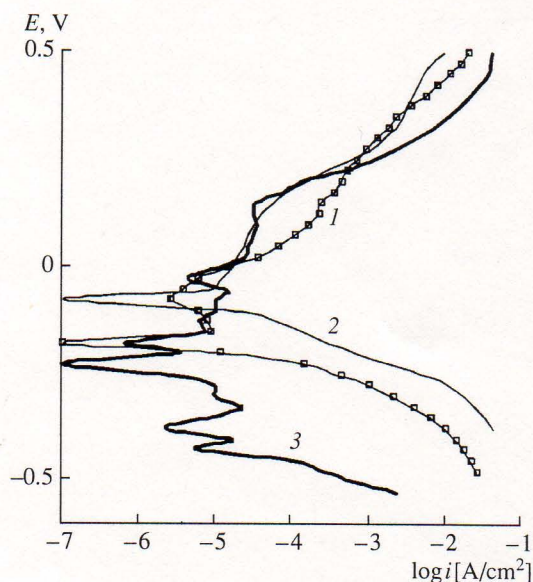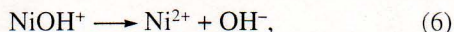Ozone corrodes metal at both low and high concentrations of H_2SO_4; while at a 20% concentration, the
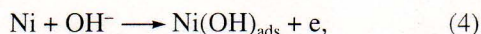

Fig. 4. Voltammograms of Hastelloy-B, Ni, and Mo in 10% solutions of sulfuric acid: (*1*) Hastelloy-B; (*2*) Ni; and (*3*) Mo.

minimum corrosion rate of Hastelloy-B is observed. By evacuation method we have already determined the hydrogenation of nickel specimens upon 24-h exposures to 5% H_2SO_4 with or without ozone. The hydrogen content in the samples amounted to 100 and to 20–30 cm^3 per kg metal in the solutions free of ozone and ozonized, respectively [9]. Markos'yan et al. [10] have found that during the corrosion of hydrogenated nickel with oxygen depolarization, at the initial moment, oxygen interacts predominantly with hydrogen diffusing from the depth of the electrode, while the nickel dissolution remains impeded. Consequently, ozone can accelerate corrosion of Ni by quickly reacting with the sorbed hydrogen.

In view of the proposed mechanism [11], we consider the formation of OH^- ions is possible in the acidic medium:

$$O_3 \longrightarrow O_2 + O, \quad (1)$$

$$O + 2e + H^+ \longrightarrow OH^-, \quad (2)$$

$$O_2 + 4e + 2H^+ \longrightarrow 2OH^-. \quad (3)$$
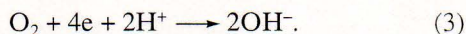
At the same time, the anodic dissolution of nickel in acidic solutions is accelerated by OH^- ions, and proceeds according to the following reaction sequence [12]:

$$Ni + OH^- \longrightarrow Ni(OH)_{ads} + e, \quad (4)$$

$$Ni(OH)_{ads} \longrightarrow NiOH^+ + e, \quad (5)$$

$$NiOH^+ \longrightarrow Ni^{2+} + OH^-, \quad (6)$$

the total reaction rate being determined by the concentration of OH^- ions. These reactions clarify the dissolution of nickel and, hence, the alloys of Ni–Mo type in the ozonized solutions of sulfuric acid.

It is also necessary to take into account that as the concentration of sulfuric acid increases up to 40%, the ozone solubility decreases to almost zero [13]. Consequently, we may assume that adding ozone to solutions of sulfuric acid contributes to neutralization of hydrogen ions on the metal surface [11], whereas its rate is a function of H^+ concentration in the double electric layer. Ultimately, ozone accelerates the discharge of hydrogen ions by reducing their concentration in the near-electrode layer. However, in 20–30% H_2SO_4 solutions, the concentrations of hydrogen ions and ozone are such that the absorption rate of hydrogen ions in the reaction of ozone reduction equals the diffusion rate of ozone to the electrode surface, which determines a low dissolution rate of both nickel and its alloy.

CONCLUSIONS

It is shown that basically, ozonizing makes sulfuric acid solutions, more corrosive as regards Hastelloy-B. Nevertheless the latter keeps its corrosion resistance in the solutions with a concentration of up to 30% and is fairly corrosion-resistant at concentrations in a range from 30 to 70%. Its corrosion–electrochemical behavior is intermediate between Ni and Mo. The presence of ozone in sulfuric acid solutions three to four times reduces the hydrogenation of nickel. Molybdenum imparts a more noble potential to nickel and, hence, diminishes the anodic dissolution rate, whether ozone is present or not.

In ozonized sulfuric acid media, it is reasonable to use alloys of the Hastealloy-N, C type with alloying elements Cr, Si, Ti that enhance the passivability of nickel, and the corrosion resistance of the alloy in oxidizing media.

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