EFFECT OF HYDROGEN PEROXIDE ON THE KINETICS OF IRON DISSOLUTION IN SULFURIC ACID SOLUTIONS DURING CATHODIC POLARIZATION

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A study was made of the trends which govern the effect of hydrogen peroxide on the active dissolution of iron in sulfuric acid solutions with a pH from 0 to 3. It has been established that, within the $0 < pH < 1$ range, an increase in the concentration of H_2O_2 ($C_{H_2O_2}$) above a certain critical level causes an increase in the rate of iron dissolution (i_d) at sufficiently negative potentials and, moreover, maintains the ratio $(\partial \log i_d/\partial \log C_{H_2O_2}) = 1$. Within the $3 > pH > 1.3$ range, on the other hand, i_d does not depend on $C_{H_2O_2}$. At a constant H_2O_2 concentration, furthermore, i_d increases with increasing acidity of the solution throughout the entire test range of pH. The results are explained in the light of concepts pertaining to the chemical mechanism of iron dissolution. It is suggested that at a $pH > 1.3$ this process occurs with the participation of hydroxonium ions, while at a $pH < 1.3$ it occurs with two simultaneous reactions: involving H_3O^+ ions and H_2O_2 molecules, respectively.

The rate of iron dissolution in solutions of nonoxidizing acids at sufficiently negative potentials does not depend on that potential and increases with increasing acidity of that solution, which may be attributed [1-5] to an indirect chemical interaction between the metal and the oxidizing component (H_3O^+ ions) in the solution as, e.g., according to the reaction

$$Fe+2H_3O^+=Fe^{+2}+H_2+2H_2O. \quad (1)$$

No data are available to indicate a possible analogous interaction between iron and other oxidizing particles. It is well known [3] that in sulfuric acid the rate at which polarized iron dissolves cathodically does not depend on the aeration of the solutions. Some acceleration of the process upon replacement of sulfuric acid with nitric acid has been noted in [5].

Here the authors studied the effect of adding hydrogen peroxide on the dissolution of iron at sufficiently negative potentials in sulfuric acid solutions at a higher temperature (90°C). *

The tests were performed with a wire electrode 0.5 mm in diameter and with a rotating-disk electrode 4.0 mm in diameter. In both cases we used iron produced by vacuum smelting, with the following inclusions: 0.005% C, 0.03% Si, 0.02% Mn, 0.004% S, 0.001% P, 0.05% O_2, 0.003% N_2, and 0.0003% H_2.

For comparison, we also tested wire specimens with a higher carbon content (0.58% C).

The electrode was held in a solution inside a three-electrode cell and in an inert-gas atmosphere for a definite length of time at a specified potential, whereupon the solution was analyzed for iron content by either the photocolorimetric or the radiochemical (with Fe^{59} [6]) method. The solutions were prepared with grade "extra pure" sulfuric acid and twice-distilled water. The H_2O_2 concentration was varied from 10^{-2} to 6.0 M, the pH of the solutions was varied from 0.3 to 3.0. The potentials were measured relative to a normal hydrogen electrode.

*In the absence of hydrogen peroxide under such conditions, iron is dissolved much faster by the chemical mechanism than by the electrochemical mechanism [1, 2].

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov, Vol. 12, No. 4, pp. 369-372, July-August, 1976. Original article submitted August 6, 1974.

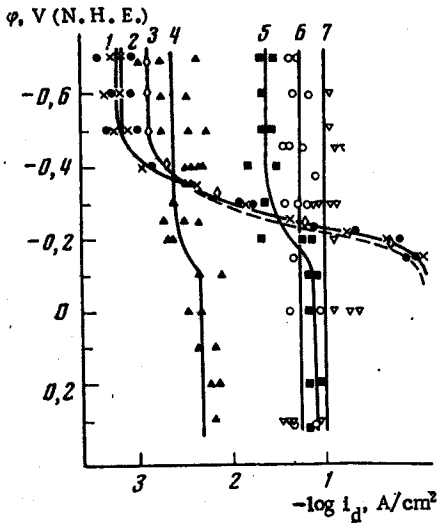

Fig. 1

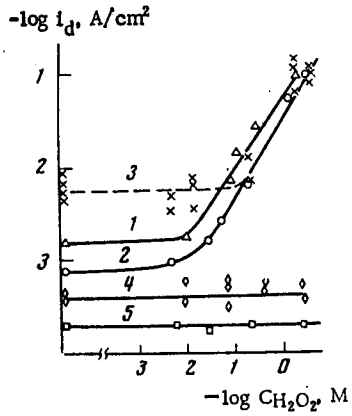

Fig. 2

Fig. 1. Rate of iron dissolution, determined analytically, as a function of the potential in H_2SO_4 with the pH = 1.2 and with hydrogen peroxide in concentrations: 1) 0; 2) 0.02 M; 3) 0.05 M; 4) 0.15 M; 5) 1.5 M; 6) 2.3 M; 7) 4.00 M. Dashed line represents the polarization curve for iron in 0.1 N H_2SO_4.

Fig. 2. Rate of iron dissolution in sulfuric acid solutions at a potential of 0.6 V, as a function of the H_2O_2 concentration, with the pH: 1) 0.3; 2) 1.2; 3) 1.2 (Fe + 0.58% C); 4) 2.3; 5) 3.0.

RESULTS AND DISCUSSION

With the pH of the solution equal to 0.3 or 1.2, adding hydrogen peroxide up to 0.01 M alters neither the shape nor the position of the curve of dissolution rate vs potential (Fig. 1). As the H_2O_2 concentration is increased from 0.02 M to 0.05 M, the rate of iron dissolution within the range of cathodic polarization remains independent of the potential but becomes higher than in an acid without additives. At peak-current and Tafel potentials we find that the behavior of iron only begins to be affected by hydrogen peroxide in concentrations of 0.15 M or higher and, moreover, the rate of iron dissolution increases regularly with increasing peroxide concentration, until it becomes independent of the potential over a wide range of the latter (up to +0.4 V). At the same time, the static potential shifts appreciably in the positive direction and the Tafel range on the curve of dissolution rate vs potential vanishes, which indicates that the electrochemical reaction of iron dissolution has been inhibited by hydrogen peroxide.

The manner in which hydrogen peroxide affects the rate of iron dissolution (within the range where this rate does not depend on the potential) is different at different levels of acidity (Fig. 2). When the pH of the solution is 0.3 or 1.2, then the dissolution rate first does not change with increasing H_2O_2 concentration until the latter reaches some critical level $C^{cr}_{H_2O_2}$, beyond which it increases linearly with the oxidizer concentration (so that $\partial \log i_d / \partial \log C_{H_2O_2} \approx 1$). This effect has been observed in the case of iron containing 0.005% carbon or 0.58% carbon.

This regular increase in the rate of iron dissolution with higher concentrations of hydrogen peroxide is noticeable in sufficiently acidic solutions only. With a pH $\geq$ 2.3, the rate of iron dissolution remains independent of the H_2O_2 concentration over a wide range of the latter (Fig. 2, curves 4 and 5). Meanwhile, its dependence on the pH remains the same as in sulfuric acid without oxidizing additives.

One can explain the results obtained with a pH < 2 if one presupposes that in the presence of hydrogen peroxide reaction (1) is accompanied by a simultaneous direct chemical interaction between iron and H_2O_2 molecules. At low concentrations of hydrogen peroxide (Fig. 2, curves 1-3), however, the rate of iron dissolution by this interaction is still low as compared to the rate of reaction (1) and it depends on the pH as well as on the carbon content in the iron — just as in the case of sulfuric acid without additives [7]. Apparently, in the reaction between iron and hydrogen peroxide hydrogen ions participate such as, e.g.,

$$Fe + H_2O_2 + 2H_3O^+ \rightarrow Fe^{2+} + 4H_2O \quad . \qquad (2)$$

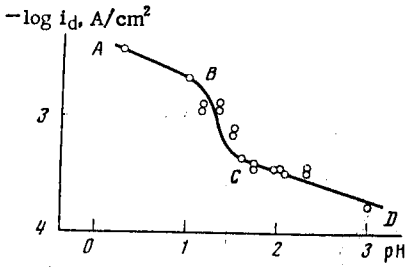

Fig. 3

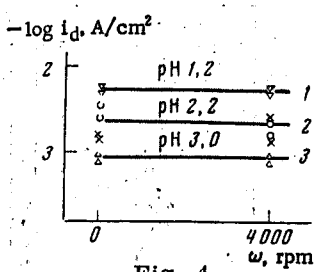

Fig. 4

Fig. 3. Effect of the acidity of the solution on the rate of iron dissolution in sulfuric acid solutions, at a constant potential (−0.6 V) and a constant concentration of hydrogen peroxide ($2.5 \cdot 10^{-2}$ M).

Fig. 4. Effect of the rotational speed of a disk electrode on the rate of iron dissolution in sulfuric acid solutions (at the potential of −0.6 V): 1) pH 1.2, $C_{H_2O_2}$ = 0.2 M; 2) pH 2.2, $C_{H_2O_2}$ = 0.2 M (○), 6.0 M (×); 3) pH 3.0, $C_{H_2O_2}$ = 6.0 M.

The ratio of the rates of chemical dissolution i_1 and i_2, by reaction (1) and by reaction (2), respectively, depends on the concentration of H_2O_2 and on the pH of the solution, and is determined for the pH = 0.3, e.g., according to the empirical expression

$$i_1/i_2 = \frac{2.3 \cdot 10^{-2}}{C_{H_2O_2}} \qquad (3)$$

with $C_{H_2O_2}$ in mole/liter. It follows from this expression that, with the pH = 0.3, i_1 and i_2 become comparable in magnitude when $C_{H_2O_2}$ is close to 0.02 M.

The rates of iron dissolution measured at a constant potential in solutions with a constant oxidizer concentration (higher than $C^{cr}_{H_2O_2}$) but a variable pH (Fig. 3) reveal that, in complete agreement with the data in Fig. 2, there is a certain critical pH value at which the trend of the log i vs pH curve ceases to be monotonic. This critical value of the pH is 1.3.

The fact that the rate of iron dissolution does not depend on the concentration of hydrogen peroxide at a pH > 1.3 could, theoretically, be associated with the fact that reaction (2) proceeds in a mode where the diffusion of H_3O^+ ions is slowed down. If reaction (2) is regarded as proceeding to one stage with a slowed down diffusion of reagents, then, according to the laws of diffusion kinetics, its rate should depend on the concentration of both reagents (H_2O_2 and H_3O^+) only when their concentrations are in a certain ratio which satisfies the requirements of so-called diffusion stoichiometry ($D_1C_1/\nu_1 = D_2C_2/\nu_2$), where D_1 and D_2 are the diffusivities of the two reagents, C_1 and C_2 are the concentrations of the two reagents in the solution, and ν_1 and ν_2 are the stoichiometric factors. Otherwise, the rate of this reaction should be determined by the concentration of one reagent only, namely the one whose amount in the solution is stoichiometrically deficient (in our case, possibly, H_3O^+) — as has been demonstrated in the case of zinc, cadmium, and aluminum dissolution in solutions of mineral acids with oxidizing additives [9].

If the proposed hypothesis were correct, however, then stirring would increase the process rate in solutions with a pH > 1.3 and containing hydrogen peroxide. This is not the case (Fig. 4) and, therefore, the process is not limited by the supply of H_3O^+ to the electrode surface.

It is also possible that reaction (2) cannot take place at all in insufficiently acidic solutions. This may be attributable, e.g., to a lower adsorption of H_3O^+ ions needed for the reaction, or to the catalytic decomposition of hydrogen peroxide near the electrode surface in the presence of Fe^{3+} ions (this decomposition being accelerated [10] by a decrease in the acidity of the solution). In the light of this hypothesis, the AB segment of the curve in Fig. 3 represents a process involving two simultaneous reactions (1) and (2), while the CD segment of this curve represents a process involving only one reaction (1).

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THERMODYNAMIC ANALYSIS OF THE EFFECT OF CHROMIUM AND CARBON ON INTERGRANULAR CORROSION OF STEELS CONTAINING 20% NICKEL

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The proneness to intergranular corrosion of austenitic chromium—nickel steels with a 20% nickel content and a variable content of chromium (14-24%) and carbon (0.01-0.045%) has been determined experimentally. The tests were performed by boiling according to the AM method for 24 h, on specimens quenched from 1200°C and subsequently tempered at 450-900°C for 10 min to 1000 h. It has been established that chromium and carbon have opposite effects on the size and the coordinates of the range where a steel is prone to intergranular corrosion. The effect of chromium and carbon on the parameter of intergranular corrosion, namely the T_{max} of its occurrence, has been evaluated.

In earlier studies concerning the effect of alloying element on intergranular corrosion [1-4] there was no attempt made to determine exactly the carbon content [3, 4] or the temperature range within which intergranular corrosion occurs [1, 2]. The strong effect of carbon on intergranular corrosion [5] and the imprecise plot of Rollason's diagrams make it difficult to interpret the data in [1-4]. These methodological shortcomings were, apparently, overcome for the first time in [6].

METHOD OF THE EXPERIMENT

The steels were produced by smelting refined carbonyl iron, metallic chromium, and electrolytic nickel in a 60-kg open induction furnace. Each ladle with a uniform chromium and nickel content (Table 1) was then broken up into 10-kg ingots to which 0.01-0.045% carbon was added in the form of graphite. The ingots were forged into billets, the latter hot-rolled into sheets 3 mm thick and then cold-rolled down to 1 mm thickness. The specimens were tested for intergranular corrosion according to the AM GOST 6032-58 method with boiling

*N. M. Mel'nikova also participated in this study.

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