The Effect of Metal Ions on the Corrosion of Stainless Steel in Concentrated Solutions of HNO$_{3}$

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The Effect of Metal Ions on the Corrosion of Stainless Steel in Concentrated Solutions of HNO_3

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It is known that in solutions with a high oxidation-reduction potential, the passive state of stainless steel may be disrupted and the corrosion process will proceed at high rates by the mechanism of transpassivation. Such a phenomenon is observed at a high positive potential of the steel and is associated with a loss of the protective properties of the films, owing to the formation of metal ions of higher valence (^1-6). Media with a high oxidation-reduction potential include, in particular, concentrated solutions of nitric acid at the boiling temperature. For example, the potential of 12-14 *N* acid solutions, measured on platinum, is 1.4-1.48 V. As a result of corrosion of stainless steel in these solutions, ions of the metals alloying the steel will accumulate. Here the formation of compounds of metals of higher valence is possible (Cr^{6+}, Mn^{7+}, Mn^{4+}, Fe^{3+}).

The formation of metal ions of higher valence under these conditions is possible both as a result of oxidation of lower-valence metal ions in the bulk of the solution and during oxidation of protective (oxide) films and surface layers of the steel. Of course, in the corrosion process reduction of metal ions of higher valence and participation of the reduction products of the medium in the corrosion process are possible. Thus, boiling concentrated solutions of HNO_3 with ions of metals of variable valence represent complex oxidation-reduction systems.

The present communication is devoted to elucidating the influence of ions of metals of variable valence on the corrosion of stainless steel in boiling solutions.* Despite its definite interest, this question has received insufficient attention in the literature (^7-9). Meanwhile, it was to be expected that the products of steel corrosion would exert a substantial influence on the corrosion process.

It is known that the high corrosion resistance of stainless steel in HNO_3 is associated with the stability of the passive state over a wide range of potentials. The strongest corrosion of steel is observed in concentrated solutions of HNO_3 at the boiling temperature. In this case corrosion is accompanied by a shift of the steel potential into the region of high positive values (for example, in 14 *N* acid the stationary potential of the steel is close to 1.3 V), and by facilitation of the cathodic and anodic processes. The shift of the steel potential into the region of high positive values leads to disruption of the passive state, and the

Fig. 1

Figure 1: Fig. 1

corrosion process proceeds at high rates by the mechanism of transpassivation. In this case the corrosion products, as shown below, will act as accelerators of the corrosion process. It should be noted that at low temperatures the cathodic processes of reduc- reduction of nitric acid to nitrous acid proceed on the passivated surface, and in boiling concentrated solutions—on the metal surface in the transpassivation region.

The presence of Cr^{3+} ions in boiling concentrated nitric acid solutions leads to an increase in the corrosion of stainless steel. The corrosion rate increases with increasing acid concentration, with the addition of Cr^{3+} to the acid, and also with increasing time of contact of the steel with the solution (Fig. 1). This increase in the corrosion rate is accompanied by a shift of the steel potential into the region of high positive values (Fig. 2), sufficient for the corrosion process to proceed by the transpassivation mechanism. The observed intensification of corrosion of stainless steel by the Cr^{3+} ion over time should be explained by an increase in the depolarizing properties of the solution due to the formation of higher chromium oxides in the bulk of the solution, and also during oxidation on the steel surface. The Cr^{6+} thereby formed, being an effective cathodic depolarizer, leads to intensified corrosion of the steel. The process of formation of chromium compounds of higher valence in boiling concentrated HNO_3 solutions is quite possible(5,10), since these solutions have a high oxidation-reduction potential—higher than the equilibrium potential of the reaction $Cr^{3+} \rightleftarrows Cr^{6+}$.

Fig. 1. Effect of Cr^{3+} on the corrosion rate of stainless steel in boiling 12-14 *N* HNO_3 solutions over time: 1—5 h, 14 *N*; 2—10 h, 14 *N*; 3—10 h, 12 *N*.

This is also confirmed by other experiments of ours; for example, if Cr^{3+} is introduced into boiling concentrated HNO_3 solutions in the form of Cr_2O_3 (which is known to be an oxide sparingly soluble in acids), the corrosion rate of the steel increases considerably. At the same time, it should be assumed that during the corrosion process Cr^{6+} will be reduced to Cr^{3+}, and then again oxidized in the bulk of the solution to the higher oxide.

In our laboratory it has been shown repeatedly that the introduction of Cr^{6+} into nitric acid solutions leads to an increase in the corrosion rate of stainless steels. In boiling concentrated HNO_3 solutions with Cr^{6+}, corrosion proceeds

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[*] Steel 1Kh18N9T in the quenched state was used for the investigation. Metal ions were introduced into 12-16 *N* solutions of HNO_3 in the form of nitrate salts and $K_2Cr_2O_7$.

Fig. 2

Figure 2: Fig. 2

at high rates at high positive potentials (1.3-1.4 V). The dependence of corrosion rate on time passes through a maximum. Moreover, with time a constant corrosion rate is established, depending on the content of chromium ions in the solution. The existence of such a dependence is evidently connected with oxidation-reduction processes occurring in the solution and on the steel surface, i.e., with the establishment over time of the equilibrium $Cr^{6+} \rightleftarrows Cr^{3+}$.

Fig. 2. Potential-time curves for stainless steel in boiling 14 N HNO_3 solutions with Cr^{3+}. 1—without addition; 2—1 g/L Cr^{3+}; 3—5 g/L Cr^{3+}.

During corrosion of stainless steel, a large amount of iron passes into solution; in a strongly oxidizing medium it will be present in the form of Fe^{3+}. Experimental data show that the presence of the Fe^{3+} ion in boiling concentrated nitric acid solutions leads to severe corrosion of the steel. The corrosion rate increases with increasing Fe^{3+} content in the solution (Fig. 3). Let us note that in the same solutions, at more

At low temperatures (up to 100°), no increase in steel corrosion by the ion Fe^{3+} is observed, since the steel is in a passive state. Appreciable corrosion of steel also occurs in boiling dilute solutions of HNO_3 when they contain a considerable amount of Fe^{3+}. In all cases, the intensification of corrosion is accompanied by a shift of the steel potential into the region of high positive values, sufficient for the corrosion process to proceed by the repassivation mechanism, and by facilitation of cathodic processes (Fig. 4).

In our studies it was shown that additions of MnO_4^- to nitric acid, even at low temperatures, lead to a marked increase in the rate

[Figure 3 and Figure 4 graphs]

Fig. 3. Effect of Fe^{3+} on the corrosion rate of stainless steel in boiling HNO_3 solutions (test time 10 h). 1—12 N, 2—14 N

Fig. 4. Effect of metal ions (25 g/l) on the cathodic polarization of stainless steel in boiling solutions of 12 N HNO_3: 1—without addition, 2—Fe^{3+}, 3—Mn^{2+}, 4—Cr^{3+}, 5—1 g/l Cr^{6+}

of corrosion of stainless steel. When Mn^{2+} is introduced into these solutions, an analogous effect is not observed. However, the presence of Mn^{2+} in boiling concentrated solutions of nitric acid, where under these conditions it is readily oxidized to ions or compounds of higher valence, leads to an increase in the corrosion rate. Simultaneously with the increase in the corrosion rate, the potential of the steel shifts into the region of high positive values, and the cathodic process is greatly facilitated.

Under conditions in which the corrosion process in nitric acid proceeds by the repassivation mechanism, Ni^{2+} ions reduce the corrosion rate of stainless steel by hindering the cathodic process.

Thus, the observed increase in the corrosion rate of stainless steel in boiling concentrated solutions of nitric acid with time is due to the accumulation in the solution of corrosion products in the form of ions of variable-valence metals (Cr, Mn, Fe).

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