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Figure 1

Figure 1: Figure 1

Abstract

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ON THE MECHANISM OF THE ORIGIN AND DEVELOPMENT OF PITTING CORROSION ON STAINLESS STEELS

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The remarkable ability of chloride ions to activate locally the surface of alloys that are in the passive state and to cause point-like, deep damage (pits) has been the subject of repeated investigations (1–10). Nevertheless, many regularities in the development of the process have not been established, and there is no complete clarity regarding the mechanism of this interesting phenomenon.

A necessary condition for the appearance and development of pitting corrosion is the presence in the solution, along with the activator, of a passivator as well. The probability of the process (the number of pits) and the rate of its development (the average depth of the pits) are in a complex dependence on the ratio between the concentrations of the passivator and the activator. At a constant activator concentration, an increase in the passivator concentration greatly increases the probability of the appearance of pitting corrosion, and only at high passivator concentrations does the number of pits begin to decrease. If the chloride-ion content (activators) is increased, the probability of the appearance of pitting corrosion grows only up to a certain concentration, after which it begins to decrease (Fig. 1A and B, curves 1).

Fig. 1. Development of pitting corrosion on steel 1Kh18N9T. **A**—under the influence of the passivator $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in a solution of NH_4Cl (0.5%). **B**—under the influence of the activator NH_4Cl in a solution of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (0.5%). Duration 25 h. 1—number of pits; 2—average depth of pits; 3—maximum depth of pits.

Attention is drawn to the circumstance that the probability of the appearance of pitting corrosion in electrolytes containing high concentrations of passivators is much higher than in electrolytes containing high concentrations of activator.

Figure 2 and Figure 3: distribution curves of pits by depth

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The rate of corrosion penetration into the depth of the metal increases up to a certain limit both with an increase in the concentration of the activator and with an increase in the concentration of the passivator. A further increase in the concentration of one of the components of the mixture leads to a decrease in the mean depth of corrosion penetration (Fig. 1 A and B, curves 2). As can be seen, the activator and the passivator act in the same direction; at low concentrations they increase the probability of occurrence and the rate of pitting corrosion, while at high concentrations they reduce them. It should be noted that these results are somewhat unexpected if one proceeds from the film theory of the activating action of chloride ions; it is difficult to understand why, after some limiting value, an increase in the concentration of the activator decreases the probability of the occurrence of pitting corrosion and the rate of its development.

Fig. 2. Distribution curves of pits by depth for steel 1Kh18N9T.
1 –0.5% NH_4Cl + 0.5% $NH_4Fe(SO_4)_2 \cdot 12H_2O$;
2 –0.5% NH_4Cl + 2.0% $NH_4Fe(SO_4)_2 \cdot 12H_2O$;
3 –0.5% NH_4Cl + 8.0% $NH_4Fe(SO_4)_2 \cdot 12H_2O$

Fig. 3. Distribution curves of pits by depth for steel 1Kh18N9T at different times of exposure to an electrolyte containing 2% passivator and 3% activator. 1–1 h, 2–5 h, 3–15 h.

Likewise, if the role of the passivator is reduced to the restoration of regions of the passive film destroyed by chloride ions, it cannot be explained why an increase in the concentration of the oxidizer leads to an increase in the probability of the occurrence of pitting corrosion. It would seem that, in the presence in the electrolyte of some minimal amount of oxidizer necessary for the course of the adjacent cathodic process (dissolved oxygen could also perform this role), pitting corrosion should occur, and its probability should continuously decrease with increasing oxidizer concentration. As for the rate of corrosion penetration into the depth of the metal, it should continuously increase with increasing oxidizer concentration because of the acceleration of the cathodic process.

A quantitative analysis of data on the rate of development of the process at individual points, with the use of concepts of the adsorption nature of the activation and passivation process ([2],[3],[6]), makes it possible to explain the regularities established above and to remove the existing contradictions.

In studying pitting corrosion, the method of constructing distribution curves proved very useful. If all the pits that have arisen on the surface are distributed by size, a typical distribution curve is obtained, indicating that the process at individual points develops extremely nonuniformly (the rates differ by approxi-

Fig. 4

Figure 3: Fig. 4

mately a factor of 40).

A large number of medium pits and a small number of shallow and deep ones arise on the surface (Fig. 2).

With increasing oxidizer concentration, the distribution curves shift to the left, with the exception of the right-hand branches of the curves, which shift to the right. From this it may be concluded that, as the oxidizer concentration increases, the process is slowed at most points and only a small number of active centers (∼ 2–3%) remain on the surface, in which the process develops intensively. In these active centers a continuous increase in corrosion depth is already observed with increasing concentration of the activator and passivator (Fig. 1A and B, curves 3).

Fig. 4. Dependence of the electrode potential of steel 1Kh18N9T on the concentration of passivator or activator. 1–0.5 NH_4Cl + 0.25-8.0% $NH_4Fe(SO_4)_2 \cdot 12H_2O$, 2–0.5% $NH_4Fe(SO_4)_2 \cdot 12H_2O$ + 0.25-0.8% NH_4Cl

It is interesting to follow the character of the development of the process with time. The distribution curves show that not all pits develop uniformly over time either (Fig. 3). At most points the process slows with time, some of the shallow pits do not grow at all, and only in a small number of active centers does corrosion continuously penetrate deep into the metal.

The process of activation of stainless steels by chloride ions depends strongly on the electrode potential and, consequently, we are dealing with a surface phenomenon. According to our data ([8,9]), as well as the data of Uhlig ([2]), activation occurs only at potentials more positive than +0.15–0.20 V. If one proceeds from the film theory, destruction of oxide layers may occur at any potential.

The potential of stainless steel in ammonium chloride, as is evident from Fig. 4, is more negative than the critical potential, and therefore the probability of the appearance of pitting corrosion is zero. With the introduction of a passivator into the electrolyte and an increase in its concentration, the potential shifts more and more in the positive direction, which facilitates, on the one hand, adsorption of negatively charged chloride ions and, on the other hand, makes them more active. All this also increases the probability of pitting corrosion. Beginning with a certain oxidizer concentration, the potential of the steel ceases to shift in the positive direction, which should not increase adsorption of chloride ions. From this moment the probability of the appearance of pitting corrosion also ceases to grow. Moreover, an increase in the ratio of the concentration of passivator to activator, as our adsorption measurements with labeled atoms (Cl^{36}) have shown, hinders adsorption of chloride ions ([10]), which should also decrease the probability of the appearance of pitting corrosion.

As for the rate of the process, as the oxidizer concentration increases the rate of the cathodic reaction increases; in connection with this, the rate of the coupled anodic reaction, leading to penetration of corrosion into the depth of the metal, should also increase.

However, beginning with a certain oxidizer concentration, the current density in most pits reaches a value that is already sufficient for appreciable inhibition of the anodic reaction, and in some of them also for the onset of anodic passivity. In connection with the latter, the process is also slowed at most points. Only in a few active centers, where the current density proves insufficient for inhibiting the anodic reaction, does the process continue to develop. Since the process at most points is inhibited, then, at a relatively high rate of the cathodic

reaction, favorable conditions are created for the process to develop at a higher rate in the active centers.

As the concentration of the activator increases, the potential of the steel shifts increasingly in the negative direction (Fig. 4), which hampers the adsorption of chloride ions and reduces the probability of the appearance of pitting corrosion. The decrease in the rate of the process at high concentrations of chloride ions is due, as observations show, to the formation of special phase layers.

Pitting corrosion should, in our opinion, be regarded as a special type of crevice corrosion and interpreted on the basis of the concepts developed by one of the authors in works (11).

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