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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE PASSIVATING PROPERTIES OF SULFATE IONS

(Presented by Academician A. N. Frumkin, December 23, 1957)

The passive state of alloys of iron with chromium and nickel (stainless steels) in the presence of chloride ions is usually disrupted, and the alloys therefore undergo corrosion in chloride solutions. Until now it has been known that the activating action of chloride ions can be completely eliminated or suppressed by introducing passivators into the electrolyte (1).

We have discovered and studied a new phenomenon indicating that sulfate ions possess analogous properties with respect to chloride ions.

In Fig. 1 are presented the anodic polarization curves of steel 1Kh18N9T in a 0.1 N NaCl solution with various sulfate additions. In a 0.1 N NaCl solution, a characteristic bend is observed on the polarization curves, caused by disruption of the passive state of the electrode and its transition to the active state. The potentials corresponding to the minima of the curves may therefore characterize the stability of the passive state.

Fig. 1. Anodic polarization curves of steel 1Kh18N9T.
1 –in 0.1 N NaCl solution; 2 –0.1 N NaCl + 0.1 N Na_2SO_4; 3 –0.1 N NaCl + 0.5 N Na_2SO_4; 4 –0.1 N NaCl + 1.0 N Na_2SO_4; 4a –1.0 N Na_2SO_4.

From Fig. 1 it is clearly seen that, in the presence of sulfates, the stability of the passive state increases. As the sulfate concentration increases, the activation potential shifts strongly into the region of more positive potential values. Finally, activation is not observed at all if

$$C_{\mathrm{NaCl}} : C_{\mathrm{Na_2SO_4}} \leq 1 : 10.$$

In such electrolytes, the polarization curves for most stainless steels coincide with analogous curves obtained in pure sulfate.

Fig. 2. Anodic polarization curves.

Figure 2: Fig. 2. Anodic polarization curves.

With sufficient amounts of sulfate, stainless steel behaves as a passive electrode, and it can be polarized to relatively high potential values without passing into the active state.

There is a noticeable difference in the character of dissolution of the electrodes; on anodically polarized electrodes in NaCl + Na_2SO_4 solutions there was less-

a greater number of pits than on electrodes polarized in NaCl solutions. If the ratio $C_{\mathrm{NaCl}} : C_{\mathrm{Na_2SO_4}} \leqslant 1 : 10$ was maintained in the solution, no destruction of the electrodes was observed at all.

In order to clarify the electrochemical behavior of the components comprising stainless steels, anodic polarization curves were recorded for iron, nickel, molybdenum, chromium, and also, for comparison, for pure chromium steel Kh28 (Fig. 2).

On iron, which has a potential of about −0.3 V, the effect we observed does not appear. Moreover, the introduction of sulfate into the electrolyte leads to a shift of the stationary potential in the negative direction and facilitates the process of anodic dissolution of iron.

The activating action of chlorine ions with respect to chromium does not appear; the latter is passivated very easily under anodic polarization even in chloride solutions, and therefore the influence of SO_4'' cannot be detected. On a molybdenum electrode, sulfate ions in the presence of chlorides exert no influence. With respect to the iron-chromium solid solution (steel Kh28), the passivating properties of sulfate ions are manifested quite definitely (cf. curves 6 and 7 in Fig. 2). In pure chloride this steel can be polarized only up to a potential of +0.6 V, after which it passes into the active state. In the presence of sulfate, however, the steel can be polarized up to +1.2 V. The observed effect is analogous to that obtained on chromium-nickel steel 1Kh18N9T.

Fig. 2. Anodic polarization curves.
1 –Fe in 0.1 N NaCl + 1.0 N Na_2SO_4; 2 –Fe in 0.1 N Na_2SO_4; 3 –Fe in 0.1 N NaCl; 4 –Mo in 0.1 N NaCl; 4a –0.1 N NaCl + 1.0 N Na_2SO_4; 5 –Ni in 0.01 N NaCl; 6 –Kh28 in 0.1 N NaCl; 7 –Kh28 in 0.1 N NaCl + 1.0 N Na_2SO_4; 8 –Ni in 0.01 N NaCl + 1.0 N Na_2SO_4; 9 –Cr in 0.1 N NaCl.

The sulfate ion also prevents activation of nickel by chlorine ions. However, at the ratio $C_{\mathrm{NaCl}} : C_{\mathrm{Na_2SO_4}} = 1 : 10$, nickel is still at the boundary of the active-passive state; the potential of nickel under anodic polarization in this solution is very unstable and fluctuates over broad limits bounded by curves 5 and 8 (Fig. 2). Only at $C_{\mathrm{NaCl}} : C_{\mathrm{Na_2SO_4}} \leqslant 1 : 100$ does the passive state of nickel become stable, and the latter is polarized without potential oscillations to relatively high potential values.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Thus, it should be concluded that the passivating action of SO_4'' ions on stainless steels is due to a considerable extent to the presence of chromium in their composition and, to a lesser extent, nickel. The passivating properties of sulfate ions can be studied and clearly demonstrated by the method of recording potential-time curves during anodic polarization of steel at a constant current density.

The diagrams we obtained (Figs. 3, 4) were recorded on an automatic electronic potentiometer with a direct-current amplifier. In a solution of chloride alone, the steel surface is in an active-passive state and its potential, as is evident from the diagrams (Fig. 3A), undergoes considerable changes. By the frequency of potential oscillation and the limits of its variation,

determined directly on the diagram recorded with a high feed rate (see the right-hand part of the diagram), it is possible to characterize quantitatively the degree of stability of the passive state. From the diagram it is clearly seen that, with the introduction of sulfate into the electrolyte, the frequency of the potential oscillations

Fig. 3. Potential-time diagrams at a current density of 2 μA/cm^2 for steel 1Kh18N9T.
A—in 0.1 N NaCl solution. *B*—in 0.1 N NaCl + 0.1 N Na_2SO_4 solution. At the beginning of the measurement the tape feed rate was 120 mm/hour, at the end 4800 mm/hour

decreases sharply. After 1.5 hours at an anodic current of 2 μA/cm^2, the potential of the steel undergoes, on average, in 0.1 N NaCl solution, 12 oscillations per minute within the limits from +0.55 to +0.95 V; in the same 0.1 N NaCl + 0.1 N Na_2SO_4 solution, 2-3 oscillations per minute within the limits from +0.65 to +1.25 V; and when the sulfate content is ten times that of chloride, the frequency of oscillations becomes equal to zero: the steel is subjected to anodic polarization without oscillations of potential (Fig. 4).

Fig. 4. Potential-time diagram at a current density of 2 μA/cm^2 for steel 1Kh18N9T in 0.1 N NaCl + 1.0 N Na_2SO_4 solution. Tape feed rate 120 mm/hour

According to the film theory of passivity, the activating action of chloride ions is explained by the fact that the latter, owing to the small radius of the ion and their ability to penetrate readily through protective films, destroy them. The functions of passivators, in turn, are reduced to healing the defective regions in the film that arise as a result of the action of chloride ions. Such an action on the part of sulfate ions cannot be expected, since they do not possess oxidizing properties and do not form insoluble compounds with the components present in stainless steels.

The effect observed can be given a satisfactory explanation on the assumption that the processes occurring on the electrode surface in the presence of chlorine and sulfate ions are of an adsorption character. According to this mechanism, the stability of the passive state must be determined by adsorption of anions from the solution.

There are sufficient grounds to assert that the passivating properties of sulfate ions are due to their preferential adsorption by the metal surface and to the displacement of chlorine ions from it.

As a result of exchange adsorption, chlorine ions are either completely displaced from the surface or their concentration becomes so insignificant that they are incapable of activating the metal.

The process of adsorption of ions from electrolytes was studied in detail by A. N. Frumkin and his pupils (^{2}). In these works the dependence was studied—

dependence of adsorption on the surface charge has been established, and it has been shown that, at certain potentials, strong adsorption of anions is observed, including on an oxidized surface. As applied to the ion SO_4'', this has recently been demonstrated by the tracer-atom method by N. A. Balashova (^{3}).

The adsorption of ions in the presence of SO_4'' and Cl' in the electrolyte was studied by Ackerman and Powers on chromium (^{4}). It was shown that Cl' and SO_4'' ions participate in exchange adsorption with CrO_4'' ions, displacing the latter from the chromium surface. It is very important to emphasize that the SO_4'' ions proved in this case to be considerably more active than the Cl' ions: SO_4'' ions produce the same effect of displacing CrO_4'' at a concentration approximately 500 times lower than the concentration of Cl'. From this it may be concluded that SO_4'' ions are more readily adsorbed by the metal surface than Cl' ions and, consequently, can displace the latter.

The results obtained by us support the adsorption mechanism of the action of chloride ions developed by B. N. Kabanov and co-workers (^{5}), according to which the activation of metals by these anions is explained by adsorption and by the displacement from the surface of oxygen responsible for passivity.

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Note: Figure translations are in progress. See original paper for figures.