

EFFECT OF NITRATE AND CHROMATE ON THE LOCALIZED CORROSION OF IRON AND NICKEL

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The combined effect of some inorganic inhibitors — chromate and nitrate — on the rate of localized corrosion of iron and nickel was investigated. The efficiency of these inhibitors and the mechanism of their effect were found to depend on the potential. If the breakdown potential is lower than the second passivation potential, the corrosion rate decreases owing to the competitive adsorption of inhibitor and of aggressive ions and owing to a change in the activation energy of the metal dissolution. Substances that are strongly adsorbed on the electrode act in this region as strong inhibitors. In the range of the second passivation potential there operates another mechanism consisting in a favourable effect of the water molecules in the inhibitor hydration sphere on the rate of the passivation reaction. In this range, even such substances that are only weakly adsorbed on the electrode can act as strong inhibitors.

The kinetics of localized corrosion are well known to be appreciably affected by inhibitors. The effect of such substances has received much attention both in theory and in practice, and a great deal of the results indicate that the inhibiting effect of inorganic salt is associated with adsorption of anions on the sample surface and consequent partial displacement of chloride ions¹⁻⁵. A majority of the works give information about how the localized corrosion is affected by individual inhibitors, but considerably less attention has been paid to the effect that could be expected if a combination of inhibitors were used.

The objective of the present work was study of the combined effect of chromate and nitrate on the localized corrosion of iron and nickel.

EXPERIMENTAL

The resistance of iron and nickel to the localized attack was examined based on the values of the breakdown potentials and corrosion rate after surpassing that potential. The potentiostatic and potentiodynamic methods were employed. The potentiodynamic polarization curves were scanned using the potential sweep rate $dE/dt = 10$ mV/s. In the potentiostatic conditions the rate of corrosion was measured so that the electrode was first polarized for five minutes in the passive region, then the potential was raised so as to exceed the depassivating value and the corrosion current density was measured in dependence on time. The iron and nickel metals used were 99.999% purity, the chemicals were reagent grade. The potentials are given against saturated calomel electrode at $21 \pm 1^\circ\text{C}$.

RESULTS

Iron

The effect of nitrate on the pitting corrosion of iron in 0.03M-KCl solution is demonstrated by the polarization curves in Fig. 1. The breakdown potentials increase only slightly with the nitrate concentration, which indicates that the inhibiting effect of nitrate ions is weak (curves 1–3). The effect, however, increases considerably after the electrode potential surpasses a certain limiting value; with a suitable concentration of the inhibitor, passivation of the electrode can even take place (curve 3). The potential at which this passivation appears will be referred to as the second passivation potential E_{F2} .

Chromate ions exhibit a considerably stronger inhibition of localized corrosion as compared with nitrate ions (curve 4), but, in contrast, do not bring about passivation at higher potentials.

From these results one could deduce that a simultaneous application of nitrate and chromate should provide iron protection over a wide potential region: chromate should protect the material particularly at low potentials, whereas at higher potentials this protective role should be taken over by the nitrate ions. This assumption, however, disagrees with the experiment, which showed that in solutions containing both chromate and nitrate, iron is much more liable to the pitting corrosion than in solutions containing chromate solely. While in a solution of 0.03M-KCl + 0.08M- K_2CrO_4 no corrosion occurs at $E < E_{F2}$ (curve 4), an addition of KNO_3 in 0.1M concentration results in an intense localized attack in this region (curve 6). Apparently, in combined solution of chloride and chromate, nitrate not only no more retains its inhibiting properties, but it even accelerates the pitting. The stimulating effect of KNO_3 can be better seen in Fig. 2.

Only at potentials exceeding the second passivation potential value, nitrate acts as inhibitor even in the presence of chromate, promoting thus the effect of the latter (curves 4 and 5).

Nickel

The effect of nitrate ions on the localized corrosion of nickel is apparent from Fig. 3. Analogously to iron, both the breakdown potential and the second passivation potential appear on the polarization curve for a suitable nitrate-to-chloride ratio (curve 4). The inhibiting effect of nitrate again is lower than that of chromate (curves 3 and 5). As to the combined effect of nitrate and chromate ions on the pitting corrosion rate, the results are similar as in the case of iron. At potentials below E_{F2} the breakdown potential in KCl + K_2CrO_4 solutions is lowered in the presence of nitrate (curves 1 and 2). The stimulating effect of nitrate is weak, but clearly apparent under potentiostatic conditions (Fig. 4). At potentials exceeding the second passivation

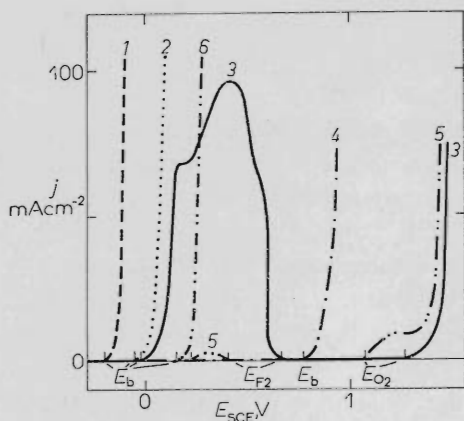


FIG. 1

Effect of nitrate and chromate ions on the potentiodynamic polarization curves of iron. 1 0.03M-KCl, 2 0.03M-KCl + 0.3M-KNO₃, 3 0.03M-KCl + 0.5M-KNO₃, 4 0.03M-KCl + + 0.08M-K₂CrO₄, 5 0.03M-KCl + 0.08M-K₂CrO₄ + 0.5M-KNO₃, 6 0.03M-KCl + + 0.08M-K₂CrO₄ + 0.1M-KNO₃

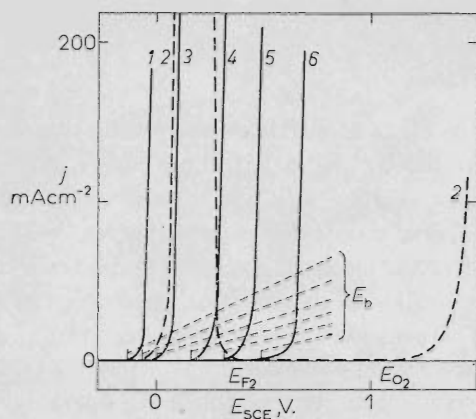


FIG. 2

Effect of nitrate ions on the breakdown potentials of iron. 1 0.1M-KCl + 0.5M-KNO₃, 2 0.1M-KCl + 0.2M-K₂CrO₄ + 3M-KNO₃, 3 0.1M-KCl + 0.2M-K₂CrO₄ + 0.5M-KNO₃, 4 0.1M-KCl + 0.2M-K₂CrO₄ + 0.2M-KNO₃, 5 0.1M-KCl + 0.2M-K₂CrO₄ + 0.1M-KNO₃, 6 0.1M-KCl + 0.2M-K₂CrO₄

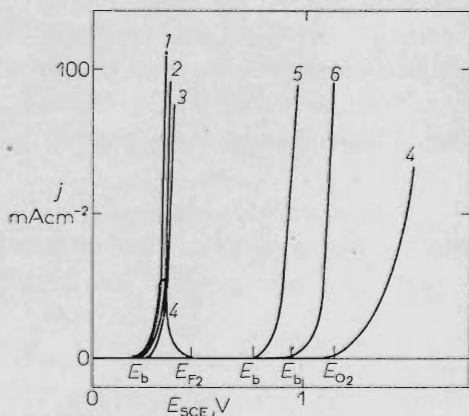


FIG. 3

Effect of nitrate and chromate ions on the potentiodynamic polarization curves of nickel 1 0.4M-KCl + 0.005M-K₂CrO₄ + 1.5M-KNO₃, 2 0.4M-KCl + 0.005M-K₂CrO₄, 3 0.1M-KCl + 0.5M-KNO₃, 4 0.05M-KCl + + 0.5M-KNO₃, 5 0.1M-KCl + 0.2M-K₂CrO₄, 6 0.1M-KCl + 0.2M-K₂CrO₄ + 0.5M-KNO₃

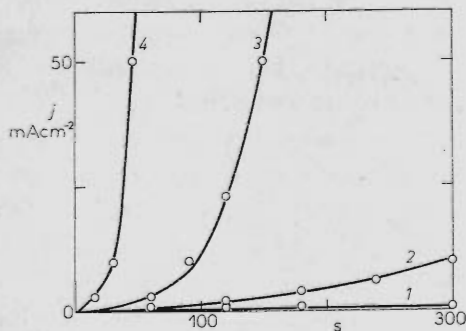


FIG. 4

Effect of nitrate ions on the localized corrosion of nickel at a potential below the second passivation potential value. Potential 305 mV, system of 0.4M-KCl + 0.005M-K₂CrO₄ + x M-KNO₃, x: 1 0, 2 0.4, 3 0.8, 4 1.5

potential value, the rate of the pitting corrosion is suppressed by nitrate (Fig. 3, curves 5 and 6).

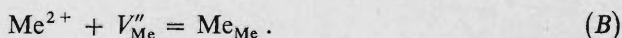
DISCUSSION

The rather complex course of the pitting corrosion in solution containing chromate and nitrate undoubtedly is associated with the mechanism of metal dissolution in the pits. It has been shown⁶ that the potential of the pit bottom is high enough for oxide to form, so that the metal dissolution in the pits proceeds through the oxide layer; the latter is assumed to possess a high density of defects and a good ionic conductivity, and thus to represent no serious barrier to the electrode dissolution.

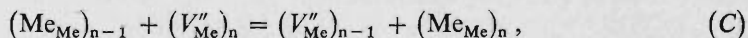
Using the Kröger and Vink symbols⁷ for the defects in the oxide crystal lattice, the reaction in pits can be described as follows: In the first step, the oxidation takes place



and the cation formed fills the V''_{Me} vacancy in the crystal lattice, being located in the cation nodal position Me_{Me} :

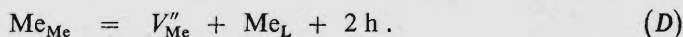


The metal ion migrates from the metal/oxide interface towards the oxide/electrolyte interface:



where n and $n - 1$ denote the nearer and the more remote positions, respectively, of the vacancy or cation with respect to the outer oxide interface.

The rather complex course of the localized corrosion in dependence on the potential is probably accounted for by reactions on the oxide/electrolyte interface; as a matter of fact, it is not very likely that the potential should so affect the rate of the electrochemical reaction on the metal/oxide interface or the transport of ions through the oxide film that the resulting dependence would be represented by a polarization curve with a maximum (Figs 1 and 3, curves 3 and 4). The dependence of the current density on the potential indicates that not only the oxide is dissolved but an electrochemical reaction proceeds here as well. The latter can be electrochemical oxidation of iron or nickel whose presence on the interface can be understood assuming that a metal cation passes from the oxide bulk to the surface as the atom Me_L , leaving a vacancy V''_{Me} and a positive hole h in the crystal lattice:



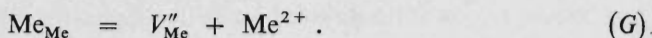
In the next step, the metal is oxidized,



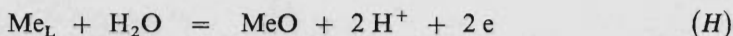
the electrons created reacting with the positive holes,



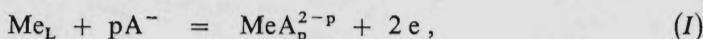
The overall reaction on the oxide/electrolyte interface thus is a sum of Eqs (D)–(F)



In view of the comparatively high potential in the pits and the concentration conditions in them, the general reaction (E) can be assumed to comprise the electrochemical formation of the oxide,



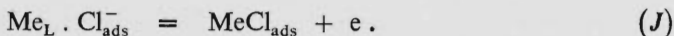
and the competitive complex or salt formation,



where A^- is the anion.

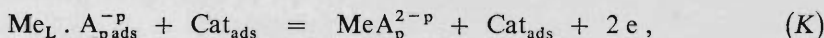
The rates of these two reactions depend on the concentrations of water, chloride ions, and the inhibitor. Owing to the low concentration of water and high concentration of salts in the pit electrolyte, the reaction (H) is suppressed and the reaction (I) favoured. The elucidation of the mechanism of the latter reaction is facilitated by the observation that some anions – nitrate in this case – operate both as inhibitors and as stimulators of localized corrosion, being, however, on their own unable to induce the pitting attack. Chloride must be present for the localized corrosion to take place.

Some authors⁸⁻¹⁰ suggest that in concentrated chloride solutions, a complex of iron with halide is formed, acting as a catalyst in the electrochemical oxidation of the metal. In the pits, we regard as the catalyst the unstable component created according to the equation



The existence of an univalent unstable substance on the electrode surface is corroborated, *e.g.*, by hydrogen evolving in the pits; the hydrogen evolution is probably a result of the reaction of the above component with water molecules¹¹.

The catalyst reduces the activation energy of dissolution of the neighbouring metal atoms and makes possible their transfer into the solution. Owing to the high concentration of the pit electrolyte, the pit surface is largely coated by the adsorbed chloride, nitrate, or chromate ions; the fraction of the surface coated by water molecules can be thus looked upon as insignificant. In view of this, and also taking into account the fact that the metal passing into the solution is not only that from the chloride-coated surface, but also from, *e.g.*, the nitrate-coated surface (as the stimulating effect of nitrate indicates), the dissolution in the pits can be written as



where $\text{A}^- = \text{NO}_3^-, \text{Cl}^-, \text{or } \text{CrO}_4^{2-}$ and $\text{Cat} = \text{MeCl}$.

Reaction (K) reminds us of Heusler's mechanism of dissolution of iron except for the fact that the reaction mechanism in question does not involve water. The assumption that the metal dissolution in pits occurs without participation of water is supported by the observation that the current density in the pits is high even in nearly water-free solutions and is not affected by the pH of the solution^{6,12}.

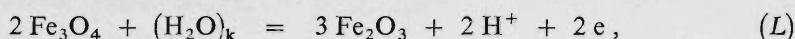
The corrosion rate is affected mainly by two factors: concentration of the catalyst and adsorption of anions on the electrode surface. The concentration of the catalyst increases with that of chloride ions and is favourably affected by their adsorption on the surface. With increasing concentration of the inhibitor, chloride ions are in part displaced from the electrode surface due to the competitive adsorption, and consequently the catalyst concentration decreases. As a result, the localized corrosion rate decreases and the breakdown potential rises. The lowering of corrosion is the more pronounced, the more strongly the inhibitor is adsorbed on the electrode. As indicated by adsorption¹³ and molar polarization¹⁴ measurements, the adsorption increases in the series nitrate < chromate < chloride. In accordance with this, nitrate is also a weaker inhibitor than chromate.

The effect of anion adsorption on dissolution of metals has been studied by Heusler¹⁵, who has found that the activation energy for the reaction of the catalyst with the metal atoms increases with rising adsorption of the anions. Thus, the more strongly the inhibitor will be adsorbed on the electrode, the more slowly will the reaction (K) proceed, and *vice versa*. Addition of nitrate to solution containing chromate and chloride results first of all in a displacement of chromate; the more strongly adsorbed chloride is displaced to a lesser extent. Replacement of chromate by nitrate brings about a decrease in the activation energy of the metal dissolution, with the resulting enhanced corrosion. This is the probable reason why in a solution of chloride with chromate, nitrate, appears to be a stimulator of the localized attack.

On the whole, adsorption of nitrate can be supposed to operate in two ways: on the one hand, it lowers the catalyst concentration, and on the other hand, it lowers the activation energy of the metal transfer to the solution. If the former effect

predominates, nitrate acts as inhibitor to the localized corrosion (iron (nickel)-chloride-nitrate system), whereas if the latter effect prevails, nitrate acts as stimulator of the pitting attack (iron (nickel)-chloride-chromate-nitrate system).

The above considerations concerning the effect of nitrate ions upon the kinetics of pitting only refer to potentials below E_{F_2} . At higher potentials, nitrate exhibits inhibiting properties only. The increase in its efficiency may be induced by another mechanism of the inhibiting influence of nitrate, *viz.* acceleration of the oxidation of the non-passive film in the pits to a passive one. In the case of iron, this probably is oxidation of Fe_3O_4 to Fe_2O_3 . At the second passivation potential this reaction proceeds in a way different from the analogous reaction at the E_{F_1} potential: at the first passivation potential the oxidation is conditioned by free water molecules^{16,17}, whereas at the second passivation potential the oxidation occurs with a participation of water bonded in the hydration sphere of the nitrate ion¹⁸,



where $(H_2O)_k$ represents water in the nitrate hydration sphere.

The stabilization of the passive state induced by hydrated anions is of general validity. Therefore, the second passivation potential has been found also in the case of nickel. So far it cannot be decided whether the passivity of nickel results only from changes in the physical properties of the film or whether its composition is altered too.

The rate of the reaction (L) is dependent on the adsorption of hydrated anions. The rate of the passivating reaction rises with increasing adsorption, and the resistance to localized corrosion grows. However, this is only true up to a certain limit; too high an adsorption induces an adverse effect, as it prevents water molecules in the coordination sphere of anions from contacting with the electrode surface, whereby their passivating effect is reduced. As a consequence, the second passivation potential is apparent notably in solutions containing weakly adsorbing ions — such as nitrate — and is not observed in solutions in which only strongly adsorbing anions (chromate, chloride) are present.

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