EFFECT OF THE NATURE OF THE ANIONS ON THE KINETICS AND MECHANISM OF THE DISSOLUTION (CORROSION) OF METALS IN ELECTROLYTE SOLUTIONS

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It is well known that the velocity of the spontaneous dissolution of metals in solutions of electrolytes depends greatly on the composition of the solution. Usually this dependence is associated with the cathodic process, the kinetics of which are affected by the pH of the medium and the presence of dissolved oxidizing agents, ions of electropositive metals (the deposition of which may lead to catalytic acceleration of the cathodic process), and so forth.

There are many cases, however, in which the components of the solution directly influence the kinetics of the anodic ionization of the metal atoms. Investigations in recent years have shown that this process is usually sensitive to the presence and concentration of a whole series of anions, the actions of which are, as a rule, quite specific. One and the same anion accelerates the anodic process in some cases and retards it in others. A study of the laws governing this effect is of no less importance than that of the laws governing the influence of the composition and structure of an actual alloy on its corrosion resistance. Clearly it is only on understanding such laws that the conditions for the safe use of any particular alloy or metal can be determined, or the selection of materials for particular service conditions be decided.

In this article we shall generalize and correlate a number of results obtained in recent years in the Laboratory of Corrosion and the Electrochemistry of Metals of the L. Ya. Karpov Institute, regarding the effect of the components of a solution on the kinetics of the anodic dissolution of metals, both in the active state and in the course of passivation.

ACTIVE DISSOLUTION OF METALS

It has been considered for a long time that the elementary acts of anodic dissolution involve the formation of simple metal ions and that the part played by the anions should be considered as the result

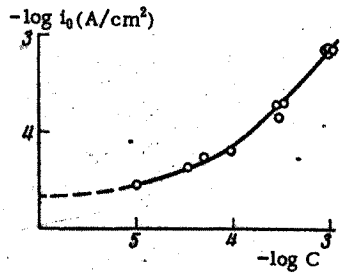

Fig. 1. Exchange current measured at a bismuth amalgam electrode (amalgam concentration $3 \cdot 10^{-3}$ M) in a solution of 2 M $HClO_4 + 10^{-3}$ M $Bi(ClO_4)_3$ + NaCl, as a function of NaCl concentration.

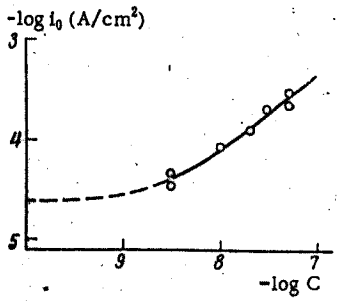

Fig. 2. Exchange current between bismuth amalgam ($3 \cdot 10^{-3}$ M) and a solution of 2 M $HClO_4$ + 10^{-3} M $Bi(ClO_4)_3$ + NaI as a function of NaI concentration.

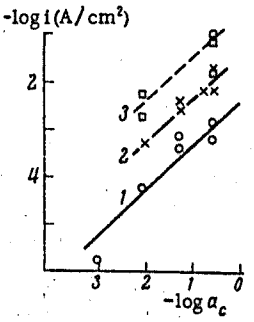

Fig. 3. Dissolution rate of iron in $H_2SO_4 + Na_2SO_4$ solution as a function of the activity of the sulfate. Potential 0.35 V; pH values: 1) 3 ± 0.1; 2) 4 ± 0.2; 3) 5.

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of their subsequent interaction with these simple ions. Investigations by many authors have shown, however, that this view is incorrect. Gerischer [1], for example, was above to show that, in a large number of cases, the dissolution of amalgams and solid metals took place by way of the direct formation of complexes between the metal, on the one hand, and the anions and other components of the solutuon, on the other, in the electrochemical stage. This gave rise to the idea that the dissolution of metals might take place by a complexing mechanism. It was further found that this mechanism applied to the dissolution of cadmium in iodide solutions (Kolotyrkin and Medvedeva [2]), platinum in acid chloride solutions (Érshler [3]), zinc and cadmium amalgams in cyanide and oxalate solutions (Gerischer [1], Stromberg [4]), and indium amalgam in halide and sulfate solutions (Losev and Molodov [5]).

The mechanism in question is not, however, the only one possible. The direct participation of anions in the anodic process may also take place in cases in which the final products are not complexes, but simple metal ions or products of their hydrolysis. In this case, the part played by the anions in the electrochemical stage of the process reduces to the formation of an intermediate complex, which subsequently decomposes. With this "catalytic" mechanism, the anions do not enter into the stoichiometric equation of the overall process, and the mechanism underlying their action can only be discovered by studying the velocity of the anodic process or exchange current as functions of the concentration of the anion.

An example of a reaction taking place by the catalytic mechanism is the dissolution of iron. It was shown by Kabanov, Leikis, Burshtein, and Frumkin [6] for alkali solutions and by Bonhoeffer and Heusler [7] for acid solutions that the retarded electrochemical stage of iron dissolution involves the participation of OH^- ions, which, however, are released in subsequent stages.

The example given reflects the simplest case of the direct participation of an anion (in the present case OH^-) in the retarded electrochemical stage of the anodic dissolution of a metal. In general form, the velocity i of such a process is expressed by the equation

$$i = ka_A^m \exp(\alpha\varphi nF/RT), \quad (1)$$

where k and m are constants, n is the number of electrons taking part in the retarded stage of the reaction, α is the true transport coefficient, and a_A is the activity of the anion.

The mechanism of the process may also be of a different type. Thus, according to Bockris et al. [8], when iron dissolves in acid, the electrochemical interaction of the iron atoms with the OH^- ions takes place rapidly and leads to the formation of $FeOH_{ads}$ complexes. The following electrochemical stage, however, is retarded; in this the anion does not take any direct part, but the complex formed by the divalent iron ion and the OH^- ion decomposes.

A further complication of the dissolution mechanism involving an anion may occur when two or more ions, rather than one, take part in the reaction. In this case, the different ions may, in principle, take part either in parallel reactions or in successive stages in the process.

The question as to which of the various mechanisms described takes place in any particular case depends on a number of factors, and particularly on the nature of the metal and the anion. This may be demonstrated by reference to data obtained in our own laboratory. Let us first, however, consider the dissolution velocity as a function of the nature of the metal and the anion.

Since the processes involved in the anodic dissolution of solid metals are quite complicated and the results obtained are not always susceptible to a clear explanation, some of our work was carried out with model amalgam systems. The ordinary method of plotting polarization curves was used in combination with the radiochemical method, which, by continuous or periodic measurement of the radioactivity of the solution (and amalgam), enabled us directly to determine the exchange currents between the amalgam of the metal and the solution of its salt (at the equilibrium potential) or the rate at which metal ions passed into solution (at nonequilibrium potentials).

Using these methods, Losev and Gorodetskii [9] obtained data relating to the influence of halogen ions on the kinetics of the discharge and ionization of bismuth at the boundary between its amalgam and acid perchlorate solutions. It was found that even slight additions of chloride, bromide, or iodide to this solution had a considerable accelerating effect both on the anodic dissolution and the cathodic deposition of bismuth; this appeared in the increased exchange current and the corresponding displacement of the anode and cathode polarization curves. At the same time the equilibrium potential of the system

in all these cases was simply determined by the concentrations of the amalgam and the bismuth salt in solution (10^{-3} M). This means that, in full agreement with published data, the introduction of halide salts does not lead to any complexing of bismuth ions, which in all cases remain in solution in the form of simple Bi^{+3} ions.

The nature of the observed effect of halide concentration on the velocity of the anodic process may be judged from the data presented in Figs.1 and 2, where the radiochemically-determined exchange-current density relates to the same unchanging equilibrium potential 0.233 V. We see that, starting from some critical value of concentration, there is a clear power relationship (straight lines in log coordinates) between the concentration and the velocity of the process. Since the slope of the anode polarization curve remains unaltered on introducing halides, the results entirely correspond to an Eq. (1) of the type

$$Me + mA^- \rightarrow MeA_m^{+(n-m)} + ne,$$

which indicates the direct participation of the halide ions in the limiting stage of the anodic process.

Investigations showed that the value of m in this equation depended greatly both on the nature of the matal and on that of the anion. This is illustrated by the table, in which data obtained earlier for indium amalgam are also presented for comparison.

Whereas, for indium amalgam, the anion series $I^- \rightarrow Br^- \rightarrow Cl^-$, corresponds to $m = 3 \rightarrow 2 \rightarrow 1$, for bismuth amalgam $m = 1$ for both the chloride and the iodide. We also see from the table that the critical concentrations of the halides (above which their accelerating influence on the process of anodic dissolution becomes substantial) is 10^3 to 10^6 times lower for bismuth amalgam than for indium. This difference is evidently due to the fact that, at the equilibrium potential, the surface of the bismuth amalgam carries a large positive charge, promoting good adsorption and a strong bond between the anions and the surface; the equilibrium potential of indium amalgam lies almost 0.5 V more negative and corresponds to a slight negative rather than positive charge on the surface.

It follows from this that, in considering the effect of the anions on the kinetics of the anodic process and the overall corrosion velocity, we must take account of not only the nature of the metal but also the position of the stationary (corrosion) potential relative to the zero-charge point of the metal.

It is not only the halide ions which may have an activating capacity. The anodic dissolution of bismuth amalgam in acid perchlorate solutions is also accelerated by sulfate ions. However, this accelerating effect occurs at much higher anion concentrations, close to 0.3 M, which is some 10^4 times greater than the critical concentration of the chloride.

It is interesting to compare the accelerating effect of a given anion, for example, the chloride, on the anodic dissolution of the amalgam and the corresponding solid metal. As shown by Pchel'nikov and Losev, addition of 0.2 mole/liter NaCl to an acid solution of perchlorate (at constant potential and with otherwise equal conditions) accelerates the anodic dissolution of solid indium by almost 500 times and that of indium amalgam by about 250 times. Thus the accelerating effect of chlorine ions is almost the same in the two case, although passing from the amalgam to the solid indium is accompanied by a displacement of the zero-charge potential from -0.25 V (Frumkin and Polyanovskaya [10]) to -0.65 V (Butler [12]); in the case of the solid indium the anodic process takes place on a positively- and not a negatively-charged surface. Clearly, on the amalgam the specific adsorption of the halide ions is much stronger than on solid indium, and this compensates the difference in surface charge.

Analogous relationships are obtained on comparing the effect of chlorine ions on the anodic dissolution of a dilute bismuth amalgam and solid bismuth in 2 M $HClO_4$. Thus the anodic dissolution of the solid bismuth is appreciably accelerated by the addition of $1 \cdot 10^{-4}$ mole/liter NaCl and that of bismuth amalgam by $3.5 \cdot 10^{-5}$ mole/liter NaCl. Thus although the surface charge of solid bismuth during anodic dissolution is rather more positive* than that of the amalgam, the specific adsorption of the chlorine ions on the amalgam is, even in this case, stronger than on solid bismuth. The idea that the specific adsorption of the chlorine ions on dilute amalgams is stronger would appear quite logical, since for mercury the strength of the chloride complexes is greater than for indium and bismuth.

An example of a more complicated reaction involving the simultaneous participation of two forms of anions is clearly the dissolution of iron in acid solutions.

According to the earlier-mentioned views of a number of investigators, the kinetics of iron dissolution may be described by postulating the interaction of iron atoms with OH^- anions; this agrees with

* The zero-charge potential of bismuth is between -0.2 and -0.4 V [13].

the mechanisms accepted for other metals of the iron group: cobalt (Heusler [14]) and nickel (Sato and Okamoto [15]). On the other hand it has been found in a number of experiments [9, 16] that the dissolution rate of iron depends not only on the pH of the solution but also on the nature of the electrolyte anions. It has often been assumed, in order to explain this phenomenon, that the anions of the solution may displace the OH^- ions from the iron surface and that the degree of this displacement differs for different anions. Recently Heusler and Cartledge [17], studying the behavior of iron in sulfuric acid containing iodine ions, developed an idea according to which these ions, just like the OH^- ions, played a catalytic part in the dissolution process.

We have ourselves advanced the view that other electrolyte anions as well as OH^- ions take part in the electrochemical acts of the dissolution of iron in acid solutions. By way of checking this, Florianovich and Sokolova made some polarization measurements on iron in solutions containing sulfuric acid and sodium sulfate in the pH range 0 to 5 and with total sulfate concentration 10^{-3} to 1 N. The slope of the anodic straight lines was 35 mV, and, for constant potential and constant activity of the anions, the logarithm, of the current density depended linearly on the pH of the solution, with a slope equal to unity, which agrees with the results of a large number of experiments [8, 18]. It is an important fact, however, that the logarithm of the current rose in the same way with the logarithm of sulfate activity (for constant pH and potential). This is illustrated by the data of Fig. 3.

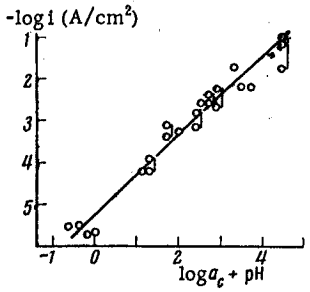

Fig. 4. Rate of dissolution of iron in solutions of H_2SO_4 + Na_2SO_4 at potential −0.35 V as a function of the sum pH + log a_C (a_C is the activity of the sulfate). Ranges: pH 0 to 5, a_C 0 to 3. Connected points represent the results of parallel experiments.

The existence of the two functional relationships over a wide range of concentrations of the sulfate and hydroxyl ions eliminates the idea that these ions might take part in two parallel reactions of dissolution taking place at commensurable velocities. The idea of the displacement of OH^- by sulfate ions is also at variance with the results obtained, since in this case an increase in sulfate concentration at constant pH would have been accompanied by a fall in over-all velocity rather than a rise.

On the basis of the results obtained we may suppose that the dissolution of iron takes place in accordance with a scheme similar to the following:

$$Fe + H_2O \rightleftarrows Fe(OH^-)_{ads} + H^+ \quad (A)$$

$$Fe(OH^-)_{ads} \rightleftarrows (FeOH)_{ads} + e \quad (B)$$

$$Fe(OH)_{ads} + HSO_4^- \rightarrow FeSO_4 + H_2O + e \quad (C)$$

$$Fe(OH)_{ads} + SO_4^{--} \rightarrow FeSO_4 + OH^- + e \quad FeSO_4 \rightarrow Fe^{++} + SO_4^{--}. \quad (D)$$

If we also suppose that stages (C) and (D) take place slowly and with similar or equal velocities, then it may be shown that the rate of the process may be expressed by the equation

$$i = K a_{H^+}^{-1} \cdot a_c \exp(1 + \beta)\varphi nF/RT$$

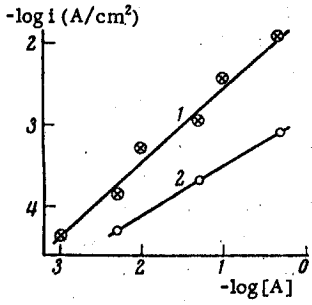

Fig. 5. Effect of anions (sulfate and chloride) on the rate of dissolution of 1Kh14 steel at pH 3 and potential −0.25 V in solutions of: 1) H_2SO_4 + $NaSO_4$; 2) HCl + KCl.

Halide ion	Value of coefficient, m		Value of critical concentration, g-equiv/liter	
	for indium amalgam	for bismuth amalgam	for indium amalgam	for bismuth amalgam
Cl^-	3	1	0,02	$3{,}5 \cdot 10^{-5}$
Br^-	2	—	$5 \cdot 10^{-3}$	$5 \cdot 10^{-7}$
I^-	1	1	$2 \cdot 10^{-3}$	$3 \cdot 10^{-9}$

or

$$\log i = K' + pH + \log a_c + (1 + \beta)\varphi nF/RT, \quad (2)$$

where a_c is the sum of the activities of the SO_4^- and HSO_4^- ions and $(1+\beta)$ is the apparent transport coefficient determined from the slope of the anode polarization curves.

According to Eq.(2), for $\varphi = \text{const}$ there should be a linear relationship between log i and the sum $pH + \log a_c$, with a slope equal to unity. The data presented in Fig.4 show that this agrees closely with experiment.

The anodic dissolution of iron and its alloys is accelerated not only by sulfate but also by several other anions. Florianovich and Golovina [19] of our own laboratory showed that, for example, chlorine ions had an analogous effect. This is made plain by Fig.5. Comparison of the curves shows that, under ordinary conditions, the dissolution of iron in sulfates takes place at a considerably higher velocity than in chloride solutions. It was natural to expect, on the basis of these data, that the addition of chloride to sulfate would suppress the activating effects of the latter, and that this suppressive action would only occur up to a certain limit, after which further increases in the chloride concentration would increase the dissolution rate. We see from Fig.6 that the experimental curves representing the relation between the dissolution rate of 1Kh13 steel in sulfuric acid solution and the concentration of chloride and bromide additives pass through a minimum, in complete accordance with the fore-going conclusions.

These results enable us to explain the present controversy regarding the nature of the influence exerted by chlorine ions on the dissolution rate of iron and iron alloys. (It is well known that in some investigations the introduction of chloride has led to a considerable slowing of this process, while in others an accelerating effect has been observed).

The anodic dissolution of nickel is also accelerated by sulfate ions. Here parallel experiments, in which the adsorption of iodine ions introduced with the sulfate was measured, showed that the acceleration of nickel dissolution induced by sulfate ions was accompained by the desorption of the iodine ions (Fig.7). It follows from these data that the influence of anions on the anodic dissolution of metals is associated with their adsorption and mutual adsorption-displacement from the metal surface.

PASSIVATION AND BEHAVIOR OF METALS IN THE PASSIVE STATE

The anions of the electrolyte may considerably affect the kinetics of the dissolution of metals in the passive state and in the process of passivation as well as in the active state. Until recently, however, little attention had been paid to this question, it being assumed that the anions of the electrolyte took part neither in the process of passivation nor in the dissolution of the metal in the passive state. Exceptions were the halide ions, regarding which it was already known that in some cases these were able

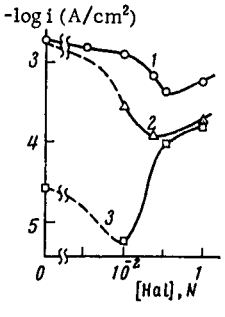

Fig. 6

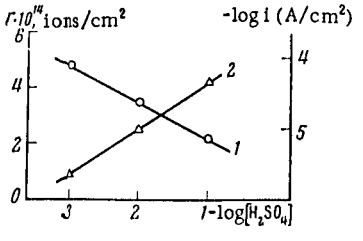

Fig. 7

Fig. 6. Effect of adding halide ions on the dissolution rate of 1Kh13 steel at a potential of -0.25 V in solutions of 1) 10^{-1} N H_2SO_4 + KCl; 2) 10^{-1} N H_2SO_4 + KBr, and 3) 10^{-3} N H_2SO_4 + KCl.

Fig. 7. Adsorption of iodine ions on nickel (1) and anode current (2) as functions of the concentration of sulfuric acid in a solution of 1 M $HClO_4$ + 10^{-6} M KI. Potential 0.00 V (normal hydrogen equivalent).

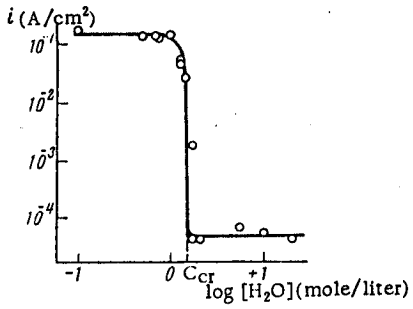

Fig.8. Steady dissolution rate of chromium in a 1·M solution of HCl in methyl alcohol as a function of water concentration. Potential -0.05 V with respect to the saturated calomel electrode (water).

to produce local depassivation of metals and initiate the development of pitting corrosion.

In considering passivity not associated with the formation of salt films, it has usually been considered that the passivity was due to the interaction of surface atoms of the metal with molecules of H_2O or OH^- ions and that the phase or adsorption-type oxide film thus formed completely determined the corrosion and electrochemical behavior of the metal. In accordance with this, in many investigations principal attention has been devoted to establishing the dependence of the potential and critical current of passivation, and also the dissolution rate of the metal in the passive state, on the acidity of the solution.

In the majority of case this explanation of passivity has failed to receive adequate confirmation; this has been largely due to the well-known difficulties involved in studying the part played by water in passivation in aqueous media. In addition to this, there has always remained some doubt as to whether it were permissible to ignore the influence of the anions of the electrolyte on the behavior of metal during passivation and in the passive state.

A considerable amount of data indicating that, in many cases, the neglect of this factor is impermissible has now been gathered together. Although, owing to the complexity of passivation processes, these data can as yet only be given a qualitative and conjectural interpretation, even at this moment we can sketch out the main ways in which the anions and molecules of the solution affect the behavior of metals under passivation conditions and in the passive state.

On the basis of the above data it is natural to suppose that passivation should be accompanied by the displacement from the metal surface of those anions which take part in the elementary acts of metal dissolution in the active state. Hence the kinetics and the very possibility of forming a passivating layer should in general depend on all the factors influencing the adsorption of passivating and activating particles. Such factors include, in particular, the energy binding these particles to the surface and the ratio of their concentrations in solution.

The necessity of such an approach is borne out by data recently obtained in our laboratory by Kossyi when studying the anodic behavior of chromium in methyl alcohol solutions of acids. It was found that in such HCl solutions the Cl^- ions took part in the process of active chromium dissolution and that in the absence of water the chromium was not passivated in this medium. We see from Fig.8 that at constant potential a sharp fall in dissolution rate, indicating the transition of the metal into the passive state, occurs at a certain critical concentration of water. For constant acidity of the solution, this critical concentration of water increases with increasing content of Cl^- ions, and for constant concentration of Cl^- ions it increases with increasing acidity (Fig.9).

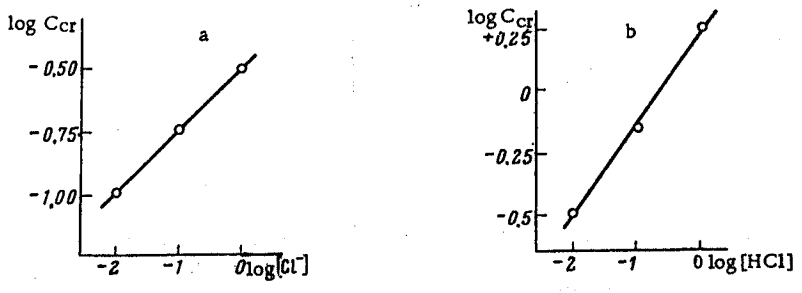

Fig.9. Critical concentration of water (C_{cr}) in a methyl alcohol solution of HCl + LiCl, a) as a function of the concentration of Cl^- ions ([HCl] = 0.01 M); b) as a function of acidity ([Cl^-]=1 M).

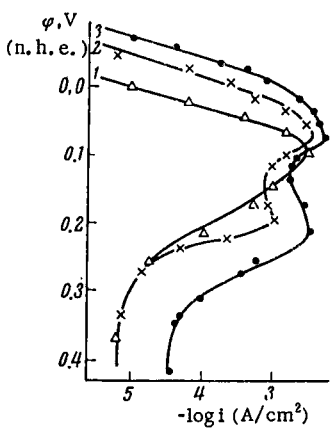

Fig.10

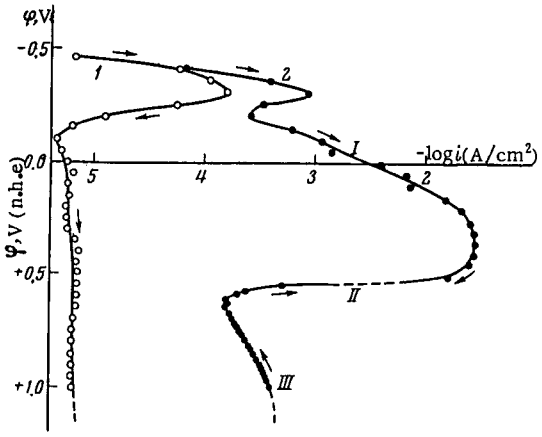

Fig.11

Fig.10. Anode polarization curves of nickel in solutions of: 1) 1 M $HClO_4$; 2) 1 M $HClO_4$ + 0.01 N H_2SO_4; 3) 1 M $HClO_4$ + 1 N H_2SO_4.

Fig.11. Anode polarization curves of iron in a borate buffer solution (pH 7.4). 1) Without additives; 2) with the addition of 0.1 g-equiv/liter of Na_2SO_4. The arrows indicate the direction of potential displacement in obtaining the curves.

Constituting as they do an experimental confirmation of the passivating effects of water, these results indicate the decisive part played by the competing adsorption of water molecules and anions of the solution in the process of passivation.

Data now available show that the nature of the anion and its concentration must also be taken into account when considering the properties of passivating layers. One of the first indications of this was obtained in our laboratory by Buné, who showed that the potentiostatically-obtained anode-polarization curve of nickel in chloric acid had one maximum corresponding to the onset of passivation, while the corresponding curve for sulfuric acid had two. This effect was explained as being due to the rupture of the first passivating layer by sulfuric acid anions. It was later shown by Lopovok and Medvedeva that a similar effect appeared quite sharply on the potentiostatic curve of nickel in chloric acid containing various quantities of sulfuric acid (Fig.10). In the second part of the curve, where the current rose with potential, there was also a rise in the current with time, while the metal surface developed pitting corrosion similar to that obtained on activation of metals by halide ions. Indirect adsorption measurements carried out with radioactive iodine as indicator strongly suggested that in this case also the activating effect of the sulfuric acid was associated with the adsorption of its anions on the surface of the nickel.

In the case under consideration, both the first and second passivation should be associated with the formation of passivating oxide layers. This is borne out by the data of Buné, who observed a regular pH-dependent displacement of the two recorded passivation potentials relating to sulfuric acid, the potentials becoming more negative as pH increased (for constant concentration of $SO_4^{--} + HSO_4^-$. Yet if the passivating layer formed on first passivation is ruptured by the anions of sulfuric acid, then the second passivation can of course only be explained by the development of a different kind of passivating layer. We see from Fig.10 that the potential corresponding to the formation of this layer (i.e., the potential of second passivation) moves in the positive direction as the concentration of sulfuric acid in the chloric acid increases, the acidity remaining practically unaltered. This kind of displacement may be associated with the effect of competing adsorption between the anions of sulfuric acid and water, the oxygen from which is responsible for the formation of the passivating layer.

Judging from the well-known fall in the passivating properties of metals in the order Cr-Ni-Fe, we might expect that the passivating layers on iron would be still less stable with respect to activation by SO_4^{--} ions than on nickel. However, as shown by Freiman [30], these ions interact with iron so

strongly that, in addition to the activation mentioned, a qualitatively new effect begins to appear; the new effect may be associated with the participation of the anions in the passivation process.

Figure 11 shows anode polarization curves of iron in a borate buffer solution with and without the addition of 0.1 g-equiv./liter of H_2SO_4. In accordance with published data [20, 21], the potentiostatic curve in the base-electrolyte solution has a single current maximum. The passivation potential corresponding to this maximum (φ_1) does not change on addition of sulfate, but moves in the direction of more negative values on raising the pH. This shows that the first passivation of the iron is due to the development of a passivating oxide layer in virtue of the direct interaction of the metal with water molecules or OH^- ions.

For the more positive potentials (part I of curve 2), as in the case of nickel, the SO_4^{--} ions activate the iron electrode, and pitting corrosion sets in upon the latter. The potential corresponding to the onset of activation falls and the number of pits increases with increasing concentration of SO_4^{--} ions in solution. For still more positive potentials (part II of curve 2), there is a secondary passivating process, and, starting from some specific potential (φ_2), the polarization curve records a region corresponding to a second passive state (part III of curve 2). However, from the point of view of the mechanism underlying the second passivation, this similarity with the behavior of nickel is purely external.

The second passivation potential of iron in solutions of Na_2SO_4 is independent of acidity in the range pH 2 to to 12 (Fig.12), but on increasing the activity of the salt (Na_2SO_4 and $CdSO_4$), as indicated by Fig.13, the potential falls on a logarithmic law:

$$\varphi_2 = 0.51 - 0.03 \log a_C. \tag{3}$$

Moreover, considering the data of Fig.12:

$$\frac{\partial \varphi_2}{\partial \mathrm{pH}} = 0. \tag{4}$$

It should be noted for comparison that, in nitrate solutions, the passivation potential is displaced linearly in the negative direction with increasing pH (Fig.12, curve 2), while on raising the concentration of the anion it becomes more positive.

Analysis of the results obtained strongly suggests that the second passivation of iron in solutions of sulfates is not associated with the direct retardation of the dissolution of the iron by adsorbed SO_4^{--} ions, as might be thought on the basis of Eqs.(3) and (4). We should rather consider that a breakdown in the passivity of iron, attributable to SO_4^{--} ions, is possible at all potentials lying on the positive side of the potential corresponding to the onset of activation in the first passive region. At sufficiently positive potentials, however, it may well be that the process of activation begins to meet competition from the anodic formation of a new kind of passivating oxide layer.

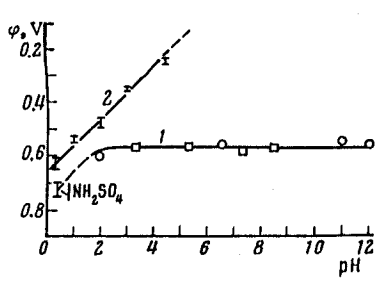

Fig. 12

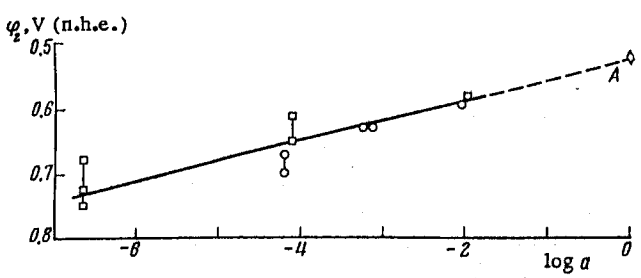

Fig. 13

Fig.12. The pH-dependence of: 1) the second passivation potential of iron in solutions of Na_2SO_4 ($[SO_4^{--}] = 1$ g-equiv./liter), ○) nonbuffer solutions ($Na_2SO_4 + H_2SO_4$ or Na_2SO_4 + NaOH); □) buffer solutions (borax + succinic acid or borax + boric acid); 2) the passivation potential of iron in solutions of $NHO_3 + NaNO_3$ ($[NO_3^-] = 1$ g-ion/liter).

Fig.13. Second passivation potential of iron as a function of the activity of sulfates: □) Na_2SO_4; ○) $CdSO_4$.

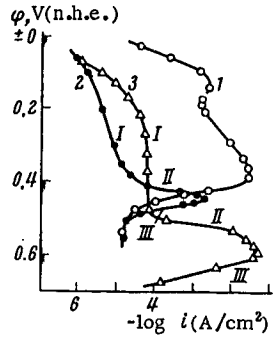

Fig. 14. Anode polarization curves of nickel in solutions: 1) 1 N H_2SO_4; 2) 1 N H_2SO_4 + CO; 3) 1 N H_2HO_4 + 0.01 M KI.

It should be noted that Eqs.(3) and (4) differ in principle from the well-known equations of the Fladet potential of iron (of the type E_F = 0.58-KpH), obtained by Frank [22] and Sukhotin and Kartashova [23]. This difference is presumably associated with the fact that the authors in question used solutions with different anion compositions (which also varied with varying pH) in studying the relationship between E_F and pH.

This shows that the results of measuring the passivation potential without having a constant anion composition of the solutions can hardly be regarded as reliable without additional proof.

In the cases considered above, the action of the anions reduced to the breaking down of passivity, together with the acceleration or retardation of the transition of the metal into the passive state. There are quite a few cases known, however, in which the addition of halide and other ions to the solution increases the dissolution rate, even without the breaking of passivity or the formation of pitting corrosion. For example, not long ago Mirolyubov and Razygraev [24] observed an acceleration of the dissolution of passive stainless steel on addition of SO_4^{--} ions to nitric acid.

Such effects are often associated with the fact that the anions, penetrating into the passivating layer at individual points, lower its protective properties. However, in addition to this, we must consider another possibility: the direct participation of the anions and molecules of the solution in the process of dissolving the passive metal. One of the variants of such a process may be the participation of the anion in the dissolution of the passivating oxide. This is indirectly indicated, for example, by the data of Azuma and Kametani [25], who found that the dissolution rate of iron oxide in acids was inversely proportional to the constant of instability of the complex formed by the ions of the metal and the anion of the acid.

Kolotyrkin and Gil'man [26] showed that the dissolution of passive zirconium in hydrofluoric acid should take place by way of the formation of a complex of molecules of the passivating oxide and HF:

$$Zr + 2H_2O = ZrO_2 + 4H^+ + 4e \quad (1)$$

$$ZrO_2 + n\,HF \rightarrow ZrF_n(OH)_{4-n} + (n-2)H_2O \quad (2)$$

Earlier still, Knyazheva [27] found that the rate of dissolution of passive chromium in sulfuric acid solutions increased on a power law with the concentration of added HCl. Clearly the limiting stage in the process of the dissolution of a passive metal cannot in general be reduced to a simple reaction of the type $MeO + 2H^+ = Me^{++} + H_2O$, which is often accepted in the phase theory of passivity.

For the transition metals considered, a retardation in the rate of anodic dissolution, similar in its results to passivation, may also be observed on interaction between the metals and certain substances belonging to the class of adsorption corrosion inhibitors.

This is indicated, for example, by the data of Fig.14, which contains potentiostatic curves of nickel in 1 N sulfuric acid, obtained in our laboratory by Sklyarov. The first of these curves relates to the pure acid saturated with nitrogen, the second to a solution saturated with CO (at atmospheric pressure), and the third to a solution saturated with nitrogen but containing 0.01 g-equiv./liter of KI. We see that the introduction of CO molecules or I^- ions into the solution is accompanied not only by a considerable slowing of the anodic process but also by a change in the relationship between the velocity of the process and potential. Over quite a wide range of potentials the current is almost constant (parts I of polarization curves 2 and 3), which is characteristic of the passive state.

The development of these regions is hard to explain by the same process of oxygen deposition as occurs at the first passivation potential in the pure solution of acid. For example, in the KI solution, region I is situated in the range of potentials at which the corresponding passivating layer is ruptured by sulfuric acid anions, while in the solution containing CO this region lies partly in the range of active dissolution. The analogous region on the polarization curve of iron in H_2SO_4+CO solution corresponds entirely to the range of active dissolution of the metal in the pure acid [28].

We may therefore consider that the phenomenon in question is due to the adsorption of I^- ions or CO molecules rather than to the formation of a passivating oxide layer.

It should be noted that, in addition to the development of steep sections on the polarization curve, there are also some other important features of similarity between this kind of passivity and the ordinary variety. Thus, as the potential moves to a more positive value, the current sharply increases and then slowly returns to the stationary value. After a rapid displacement of potential, in which the state of the surface is unable to alter, the current density rises exponentially with potential, as in the case of chromium passivated in sulfuric acid [29].

In addition to this, the passivating layer of I^- ions (or CO molecules) may be ruptured by other anions of the solution, in the same way as oxide layers. Comparison of the data for different acids (H_2SO_4, $HClO_4$, HCl), shows that the development of those regions on the polarization curves for which the current rises with potential (sections II on curves 2 and 3 of Fig.14) should be associated with just this kind of process. In the case of sulfuric acid, the activation of nickel must be due to the adsorption of sulfate ions, i.e., in principle, the same process as in the case of the breakdown of the first passive state in pure acid at potentials from +0.2 to +0.35 V. Although the role of the iodine ions in this process is still not quite clear, they certainly prevent activation, as indicated by the displacement of section II to more positive potentials on raising the concentration of KI in the solution.

On the basis of the data presented, we may consider that the fall in the dissolution rate in sections III of curves 2 and 3 is in principle due to the same process as the second passivation in the pure acid solution, i.e., to the formation of a passivating oxide layer. This is supported by the experiments of Lopovok and Medvedeva, who showed that I^- ions were desorbed from the surface in section III. It follows that the adsorbed I^- ions or CO molecules raise the potential of the second passivation of nickel. According to Sklyarov's data, this rise attains 200 mV on adding 0.1 N KI, which once more indicates the importance of allowing for the anion composition of the solution when measuring passivation potentials.

CONCLUSION

The existing view that the processes of metal passivation and dissolution in aqueous solutions of electrolytes are due to reactions in the $Me-H_2O-H^+-OH^-$ system is insufficient to explain all the main features of the electrochemical and corrosive behavior of metals in such solutions.

Anions and molecules of the corrosive media may become adsorbed on the surface of the metal and form complexes with the surface atoms, metal ions, or oxides. The binding strength and reactivity of such complexes determines the nature of the dissolution process and also its velocity. Hence existing ideas on the mechanism of passivation and dissolution may be further extended by studying the interaction of the metal with all the electrochemically- and chemically-active components of the aggresive media.

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