DEVELOPMENT OF ELECTROCHEMICAL THEORY OF CORROSION PROCESSES IN THE PROGRAM OF SCIENTIFIC – TECHNICAL COOPERATION BETWEEN MEMBER-NATIONS OF THE COUNCIL OF MUTUAL ECONOMIC AID (COMECON)

(AN ATTEMPT AT A DEDUCTIVE SURVEY)*

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On the basis of the pioneering work of the Soviet electrochemical school and the fundamental principles of related physicochemical disciplines, the author discusses the main aspects of a unified mechanism of interactions in metal – solution systems, including the principles of the crystal – electrochemistry of corrosion and passivation processes, the chemistry of hydrated cations, and other details, which by interacting promote spontaneous transition from one characteristic state of corrosion of a system to another, according to the electrode potential. The theoretical conclusions are confirmed and developed with the aid of extensive experimental material obtained as a result of cooperation between COMECON member-nations.

Like every applied science, the science of corrosion and protection of metals has a theoretical foundation, the truth of which ultimately determines the effectiveness, reliability, and further progress of all engineering methods of corrosion protection. Therefore, theoretical research was the first theme in the program of scientific – technical cooperation between COMECON member-nations on the problem of "Development of Measures for Protecting Metals from Corrosion" [1]. This research concerns the mechanism of the behavior of all possible corrosion systems in practically any states.

This review article is an attempt to deductively elucidate the principal elements and tendencies in the development of the present-day electrochemical theory of corrosion processes on the basis of fundamental science, including the investigations in the cooperative program.

In the formation of a general theoretical and methodological concept forming the basis for particular approaches and trends in the research program, the pioneering work was done by the Soviet electrochemical school. As early as the 1940s, at the L. Ya. Karpov Physicochemical Scientific-Research Institute the opinion had been formulated and justified [2-4] that the essence of electrochemical corrosion does not at all consist in division of a surface into parts with different electrode potentials. The rule is rather equipotentiality, i.e., the potential is practically uniform and has no sharp fluctuations along the surface. This means that in finding the overall rate of the process, we can represent the corroding surface as a single electrode on which, according to its potential φ and averaged kinetic characteristics, all the electrochemical reactions constituting the corrosion process occur simultaneously. The rate I_j of each of them has its own kinetic equation, e.g.,

$$I_j = S\bar{K}_j e^{\varphi/b_j}, \quad (1)$$

where S is the total area of the surface and $\bar{K}_j$ is the velocity constant of the reaction averaged over the surface.

At the usual rates of overall corrosion, all the cathodic and anodic currents are interrelated only by the algebraic balance equation $\Sigma I_j = 0$. Apart from this, all the reactions are statistically independent and are separated on the inhomogeneous surface only inasmuch as their kinetic constants (mainly K_j) have different spatial distributions.

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While this distribution, and thus also the averaged $\bar{K}_j$, were regarded as constant for each electrode, Eq. (1) was applied only to corrosion in the so-called active state. In the middle 1950s a fundamentally new consideration was raised [5,6]: In fact, each of the K_j is a nonmonotonic function of potential, and Eq. (1) for the reaction of anodic solution of a metal should be written in the form

$$I_a = S[K_a(\varphi)]e^{\varphi/{}_1b_a} = S[k_a e^{\varphi/{}_2b_a(\varphi)}]e^{\varphi/{}_1b_a}, \quad (2)$$

where the expression in brackets is the functional dependence of $\bar{K}_j$ on φ. In the region where $|{}_2b_a(\varphi)| \gg {}_1b_a$, expressions (1) and (2) are practically identical. In the region where $-{}_2b_a > {}_1b_a$, the derivative of the anode current with respect to potential becomes negative. Finally, in the region where $-{}_2b_a \approx {}_1b_a$, the current does not depend on the potential.

This was a revolutionary idea. It turned out that the solution of a passive metal does not have to reduce to some kind of "chemical solution" of passivating oxide. It can perfectly well be represented as a purely electrochemical process. Furthermore, a single general equation of electrochemical kinetics (2) represents the slopes of all parts of the potentiostatic polarization curve of a passivated metal.

The quantity $K_j(\varphi)$ is an inertial function of potential. The surface changes with which it is associated occur rather slowly as the potential changes. At first, before they have taken place, the derivative of the solution current with respect to potential should always be positive in both the active and the passive regions.

This was experimentally proved by the method of tagged atoms in the 1960s at the L. Ya. Karpov Physicochemical Scientific-Research Institute. It was demonstrated that when there is a sudden rise of potential, the rate of solution of passive iron [7] or titanium [8,9] always increases at first. Only when part of the anode current is expended on depositing additional passivating oxygen does the rate fall to its former stationary value. When there is a sudden fall in potential, the rate of solution falls and remains below the stationary value until an excess amount of passivating oxygen for the given potential has been removed from the surface [7,10,11].

These fundamental results were then confirmed many times for various systems by investigators in various countries.

The electrochemical concept of corrosion received its third and perhaps last necessary point of support, again at the L. Ya. Karpov Physicochemical Scientific-Research Institute when, in the early 1960s, the anode pitting potential and its almost Nernstian dependence on the activator ion concentration were discovered [12], together with the relation between the electrochemistry of pitting and of stress corrosion cracking of austenitic stainless steels [13]. It was clear that the electrochemical concept was unfailingly fruitful in the study of practically any states of corrosion systems.

Furthermore, investigations of both pitting and of model liquid-amalgam electrodes revealed that anions and other components of a solution which influence corrosion take a direct part in the events of solution and passivation of a metal [14,15]. Thus, the composition of the solution near the electrode, which varies during the reaction, proved to be one of the dependent variables via which the potential essentially influences the activity of the surface and the character, rate, and distribution of the processes occurring there.

Such were the basic elements of the theoretical foundation which helped to coordinate and develop further fundamental research on the mechanism of corrosion processes with equitable and fruitful participation of academic institutes for physical chemistry from Bulgaria, Poland, and the USSR, the Institute of Chemistry of the Academy of Sciences of the SRR, the Budapest and Veszprem universities, Hungary, the Dresden Technical University, the German Democratic Republic, the Institute of Protection of Materials of Czechoslovakia (the first such specialized institute in the world), and many other research establishments and educational institutions in the COMECON member-nations.

The fundamental question of the whole theory of corrosion is: Through what intermediate states of chemical combination does a metal atom pass on its way from the lattice to its final ionic state in solution? Without a complete answer to this, we cannot be sure of stopping a corrosion process. But the question is complicated, and investigators are still trying to elucidate some particular aspects — in particular, in the formation of a multiply charged cation, are all the electrons transferred to the metal at once, or one by one? Only the second alternative fits our present ideas concerning the charge distribution in a hydrated cation. The hydrate shell carries a large part — sometimes the greater part — of the positive charge [16,17]. It cannot emit this number of electrons before they are formed, but for its formation the metal atom itself must already be to some extent ionized. Thus, transfer of all the electrons at once is improbable. But then some of the side or intermediate products of the main anode process in the solution might be excess low-valence cations. Many electrochemists are trying to find these.

Soviet and Hungarian authors [18-22] have chosen as the objects of these investigations a number of metals (In, Cu, Al, etc.) for which univalent ions in equilibrium with them in aqueous or nonaqueous solutions are almost entirely oxidized to multivalent ions (In^{3+}, Cu^{2+}, Al^{3+}, ...). In various ways it has been shown that during anodic polarization of these metals their univalent ions appear in solution in greater excess, the more positive is the anode potential. The redox potential associated with the solution via the electrode becomes the more negative, the more positively polarized is the electrode itself. This "thermodynamic paradox" can be explained only by supposing that the anodic formation of univalent cations from the metal is easier than their oxidation to multivalent ones. We may disagree with the authors who state that the entire process of formation of multivalent cations occurs via low-valence cations detected in solution. The latter are more probably a product of desorption of truly intermediate anions arising at the metal — solution boundary. In any case, the result shows that the formation of multiply charged ions is a multistage process.

For a corroding metal this is fraught with a special danger if the easily formed low-valence cations can be chemically oxidized by oxidants in the solution. By avoiding the difficult stage of the anode process and part of the hindrances to the cathode process, this chemical reaction can sharply accelerate corrosion, especially if the multiply charged cations which are formed are in turn capable of being reduced at the metal, causing anodic formation of new portions of low-valence particles [21].

Another, more profound aspect of the problem of intermediate states of a dissolving metal involves the particular chemistry of the intermediate stages. Some idea of this is afforded by evidence that solvent molecules and anions take direct part in these processes. These have been investigated and described by research workers in Hungary, the German Democratic Republic, and the USSR [14,15,22,23]. Using their results, let us consider just a few alternative ways in which this diverse participation can occur.

At constant potential and pH in aqueous solution, the rate of anodic solution of iron is proportional, e.g., to the total content of sulfate in the solution, irrespective of whether it is in the form of H_2SO_4, HSO_4^-, or SO_4^{2-} ions [24]. If the sulfate concentration is constant, the well-known dependence of this rate on pH is preserved. In general, however, the rate of solution can be represented as a linear function of the product of the sulfate concentration and the formally defined activity of OH^- anions [24]. This interesting relation, which is far from being completely understood, throws doubt on the soundness of the well-known hypotheses of Heusler and Bokris [25-27] concerning the catalytic participation of hydroxyls in the solution of metals of the iron group.

The catalytic action of sulfate is in no doubt. If hydroxyls also acted as a catalyst in the anodic process, if they acted independently, the effects due to both ions should be added rather than multiplied [24]. Their competition is all the more ruled out, since then one of them would interfere with the other. True bimolecular participation of both anions in solution of the same doubly charged cation is also improbable. However, the dependence would be just as it actually is if an increase in pH were to influence the process, not via an increase in hydroxyl concentration, but via a decrease in surface coverage by chemisorbed hydrogen, the marked inhibitory action of which has been demonstrated for a dissolving nickel anode by changing an argon atmosphere for hydrogen [28].

Regardless of these and other details, the fact that sulfate and certain other anions have an activating effect is very important to practicing scientists. No less interesting to them is information on the opposite action of ions of another type — e.g., phosphate. The latter not only bring iron cations into the deposit, which settles on the surface of the metal and retards its solution. With sufficient access to the electrode, they can also enter into direct anodic interaction with it, leading to "phosphate passivation" of iron. This passivation is expressed in the same fall in solution current as ordinary "oxide passivation," but begins at a less positive potential. On the attainment of the potential of "oxide passivation," the phosphate is displaced from the surface [29].

Considering this phenomenon, on the one hand, we must bear in mind the high chemical stability of iron phosphates including ferric phosphate (the standard potential of the direct anode reaction $Fe + HPO_4^{2-} = FePO_4 + H^+ + 3e$ is, e.g., close to −0.2 V); on the other hand, we must remember the large size of the phosphate ion, which cannot squeeze itself between the iron atoms like oxygen, nor occupy the areas belonging to one, two, or even three iron atoms. In other words, phosphate, being anodically chemisorbed on the surface, screens more metal atoms than can be bound in a chemical compound. This enables it to act as a good inhibitor, but above the potential of oxide passivation passivating oxygen can displace it from the surface, e.g., by the reaction

$$FePO_4 + n\overline{Fe} + 3(1+n)H_2O = (1+n)FeO_{1.5} + HPO_4^{2-} + (5+6n)H^+ + 3e,$$

where $\overline{nFe}$ is a set of screened but not oxidized metal atoms.

A similar appearance is presented by the anodic inhibition of nickel by I^- ions, which at a sufficiently positive potential also displace oxygen which is present on the surface in a large number of equivalents.

In referring to passivating oxygen, which oxidizes surface metal atoms and thus introduces additional states of chemical combination (i.e., additional traps) on the path of the metal going into solution, it is very important to know what is the source of this oxygen. Most information on this point is given by research, widely developed in Hungary, the German Democratic Republic, and the USSR, on the corrosion-electrochemical behavior of metals in nonaqueous electrolytes [20, 30-33]. In many such solutions, chromium [31], titanium [32], stainless steels [33], and other easily passivated metals can be passivated only in the presence of a certain threshold concentration of water, which can range from a fraction of a percent to a few percent. This clearly shows that it is water which is the main source of the passivating oxygen.

It logically follows that passivation of a metal in a solution is not a property of the metal as such, but of the metal — solvent system or even of the actual process of solution in the given system. Let us demonstrate and elucidate the meaning of this assertion for the case of aqueous solution.

An oxygen atom from each of the solvating water molecules takes part in donor — acceptor interaction with an ionized metal atom [34]. There is then an increase in the effective charge on the hydrogen atoms and their capacity to split off from the molecule in the form of positive ions. These acidic properties are the more marked, the greater the total charge on the cation and the less the hydration number (the larger the charge per hydrogen atom).

When a hydrate shell is created near a dissolving atom of the metallic lattice, the tendency of its first molecules to emit protons to the solution is increased by two factors: The first is the chemical affinity of the metal for an oxygen atom; the second is the field of the ionic double layer acting on the molecule. Emission of protons, occurring for sufficiently strong total action, is none other than anodic decomposition of a water molecule, as a result of which the bond of its oxygen with the metal is changed from donor — acceptor to a strong ionic — covalent one, while a corresponding number of conductivity electrons are displaced to the lattice:

$$\begin{matrix} \leftarrow 2e & :\mathrm{H} \\ \mathrm{M} + \mathrm{O} & = 2e + \mathrm{M}: :\mathrm{O} + 2\mathrm{H}^+. \\ :\mathrm{H} & \end{matrix} \qquad (3)$$

Thus, we can assert that a rise in potential leads to an acceleration of solvation only until the limit of electrochemical strength of the solvent in contact with the given metal is reached at the electrode boundary. The solvent then dissociates and becomes a passivator. It is curious that in the 1740s M. V. Lomonosov wrote in his dissertation that in concentrated spirits of saltpeter, i.e., nitric acid, "... the solution of iron ceases, since the solvent stops working" [35].

Water is not the only possible source of passivating oxygen and oxygen is not the only passivating agent.

In the USSR it has been shown, e.g., that in the presence of a sufficient amount of hydrogen peroxide there is a regular decrease not only in the critical current but also in the passivation potential [36], and this is possible only if peroxide is a better donor of passivating oxygen that water is. Concentrated phosphoric, sulfuric, and other acids act similarly toward metals [37]. At low anode potentials their molecules solvate a metal, and at sufficiently high potentials they dissociate in the electrode layer, emitting protons to the solution and forming on the surface a compound of the acid radical with the metal. Passivating dissociation in contact with a metal can also occur in aprotonic solvents such as dimethyl sulfoxide in which sulfur and oxygen are thermodynamically enormously more active than in H_2S and H_2O. Obviously in this connection solution of nickel in dimethyl sulfoxide is sharply retarded, and at low potentials addition of water activates it [38].

It is known that at the start of passivation the solution of the metal does not stop immediately or entirely. In the kinetic theory of passivity, developed by scientists of the German Democratic Republic [30], this is seen as the result of competition between several processes occurring at finite speed. If we ignore the fact that the authors did not succeed in dispensing with the old postulate of "chemical solution of passivating oxides," the idea of kinetic competition between different reactions on the passivated surface is itself rational. However, here it is not continuous processes, to which the concept of velocity applies, which compete, but rather discrete events, i.e., probabilistic occurrences. Therefore, the resultant process rate can correctly be calculated only in terms of comparison between the probabilities of separate events.

It must be emphasized that passivation counteracts not only solution of the metal but also further disintegration of the solvent. Combining with surface metal atoms, the anionic component of the solvent reduces their affinity to its next portions. Furthermore, by its negative charge it shifts to the surface layers of the solid

phase part of the electric field (surface potential difference), thus reducing the voltage in the ionic double layer. All this reduces the probability of acts of dissociation of the solvent and increases the probability of its reverse cathodic association. When these become roughly equal, a stationary state sets in.

Many measurements made in various countries with various electrodes reveal, of course, that the stationary amount of passivating compound on the surface increases linearly and continuously with potential. Considering the discreteness of its developing elementary layers, this can only be interpreted as successive chemisorptive filling of each layer [10, 17]. After the filling of the first one, the stationary potential of the Helmholtz layer almost ceases to be a function of the electrode potential owing to a compensatory change in the surface potential in the solid phase [10, 39]. Correspondingly, the solvent in contact with the passive surface, having reached a stationary state, is always at the limit of its stability and retains an unchanged capacity for electrochemical solvation of the oxidized metal.

Obeying Eq. (2), the passive electrode becomes a current stabilizer with delayed negative feedback. Any rise in electrode potential, increasing the rate of solution, simultaneously implies a transition through the "red line", above which, for the given protective film thickness, instability of the solvent in contact with it progressively increases. As a result of its decomposition, the quantity of passivating compound on the surface increases, until the previous stationary conditions are restored at its boundary with the solution. The potential being reduced, acts of association of the solvent begin to predominate, and, owing to slow removal of some quantity of passivating compound from the surface, the system is restored to a stationary solution current.

Investigations of these transition processes on titanium and iron anodes [7, 11] revealed that in a complete theory of passivity it is necessary to take account of at least three facts.

In the first place, acts that are electrochemical by definition include those involving change of charge not only at the film–solution boundary but also at the metal–film boundary (in the latter the film plays the part of electrolyte). Consequently, with the formation of the passivating film the ordinary metal–solution boundary splits (spatially and kinetically) into two intermediate boundaries separated by a region which transmits both electrons and ions.

In the second place, the conductivity of the passivating compound, which was previously regarded as one of the most important constants of the system, is in fact always adjusted to the frequency of electrochemical acts which generate or consume conducting point defects on both boundaries of the film.

In the third place, as well as liquid solution products, the substance of the passivating film is continually expended on the formation of solid disperse recrystallization products, which, despite their low solubility, do not form a continuous protective layer.

Passivation and the associated changes in the characteristics of the solid surface counteract electrochemical changes in the composition and properties of the layers of the solution near the electrode; these changes are especially marked at the sites of intense anodic solution.

Here it is known that cations of the dissolving metal accumulate, and are then removed further into the solution by the electric field. By the condition of electrical neutrality, the mean statistical total charge of the cations and anions at each point in the solution must be close to zero. This means that if the cations give with the existing anions products which are easily soluble or tend to supersaturation, then their stationary concentration in the electrode layer as a whole is determined by how many anions from the bulk of the solution can gather there and hold the same electric field which expels the cations. If there were no dynamic hindrances, then, according to Boltzmann's distribution, on the way from the bulk of the solution to the surface the active concentration of univalent anions would increase tenfold every time the potential on this path increased by 58 mV; for divalent anions the corresponding figure is 29 mV. This increase is in some measure impeded by the countercurrent of cations from the solution site (which acts like the current of mercury or oil vapor in a diffusion pump). The cations equally energetically remove solvating water from the site.

Therefore, at a plane surface, even with a local solution current density of 10^{-1}–10^{1} A/cm^2 (and at a small hollow with an even smaller one) a deficit of water is created and a large number of incompletely solvated cations is formed. These, as we have seen, possess the properties of a strong acid; at the metal surface they create high acidity, from which an ordinary buffer solution in the bulk cannot afford protection. The fall in activity of the water hinders its passivating anodic decomposition at the metal surface, and the rise in acidity facilitates the reverse removal of passivating oxygen. In this electrochemically regenerated solution, passivation of the metal is greatly impeded. With deficit of water, solvation of the cations involves anions,

and it can be continued provided that the anions themselves do not become involved in passivating interaction with the metal.

These phenomena can greatly hinder and even alter the character of passivation for those metals for which it begins at high critical current. Investigators from the German Democratic Republic and the USSR have obtained many confirmatory results. For example, they have shown that in the presence of large concentrations of sulfate the potential of passivation of iron in buffer solutions can in certain limits lose its usual dependence on the pH, and at the same time can become a function of the activity of the SO_4^{2-} ions [40, 41].

As a rule, the critical passivation current for this regeneration of the solution is insufficient on easily passivated metals. However, it can occur locally on an already passivated electrode. For a number of reasons (spontaneous recrystallization of the passivating compound, exposure of structural and substructural defects in the metal, etc.), on any passive metal from time to time there must appear points with reduced passivity. At a moderate positive potential a surge in solution current at such a point is rapidly suppressed by passivating decomposition of the solvent; the stronger the surge, the more intense is the suppression. However, there is a fundamental danger of overloading, in which this repassivating process is "suffocated" owing to lack of water and excess of protons. This will occur if a strong surge causes the above regeneration of the solution in the Helmholtz layer. Then passivating decomposition of the solvent is overshadowed by cathodic acts of its regeneration from protons and surface passivating oxygen, and the passivation mechanism is reversed at this point. Its stabilizing negative feedback becomes positive, and activation continues to the end, so that it augments solution and merely deepens the regeneration of the solution, which is its cause. Further localization of the process at a gradually deepening and spreading focus of solution is due to the fact that just here there is automatic and easy reproduction of the necessary and sufficient conditions for its continuation. Some Polish scientists found out how to remove regenerated electrolyte from real pitting and show that its pH is close to zero; for this purpose they used a rapid freezing method [42].

The acidity necessary for the maintenance of pitting in the active state is created by the cations of the dissolving metal itself, and in this sense pitting can be regarded as autocatalytic local self-activation of anodic solution of the metal. However, the rapidity of development of pitting and even its possibility depend to a great extent on the presence of anions with a certain combination of properties. Having outlined the main process in pitting, we can easily enumerate those properties of the anions which should promote it: a) High mobility (without which the anions would find it hard to overcome the ejecting action of the countercurrent of cations en route to the solution focus); b) high solubility or tendency to supersaturation of compounds of the anions with cations of the dissolving metal (otherwise in pitting we should not get a high concentration of cations and a low activity of water); c) low affinity for protons, i.e., strong acidity (otherwise, acting as a buffer base, the anion would prevent the creation of strong acidity during pitting); d) capacity of comparatively easy and reversible replacement of water in the solvate shell of the cation (otherwise the anion either would not be effectively able to participate in solvation of the cation, or would be irreversibly removed from pitting with the solution products); e) absence of a marked capacity to split off oxygen in strongly acid solutions (otherwise the anion would repassivate the metal directly or via intermediate products).

All these properties are possessed to a great degree by the chloride, bromide, and iodide ions, which, of course, are the strongest and most universal pitting formers. But in general, as shown by many authors [40, 43-46], other anions of strong acids can maintain pitting to some extent. However, with strong anodic polarization the nitrate ion (say) is capable of repassivating chloride pitting [47-51], since in acid water-deficient solution at an active focus it forms an energetic passivator – nitric acid.

Of course, replacement of a more or less significant part of the water by some nonaqueous solvent which is not liable to passivating decomposition should promote the formation of pitting; and this has been confirmed by a number of investigators [31-33].

The theory also enables us to name those main characteristics of an alloy on which we must operate in order to increase its resistance to chloride pitting. Ordinary alloying of steel with chromium, which increases its passivability, is in two respects also favorable from the viewpoint of pitting resistance: On a passive surface it reduces the probability of appearance of points with dangerously low passivation, and at a new solution focus in the presence of water it promotes its passivating decomposition. However, chromium as an alloying element also possesses properties which promote pitting. By Soviet investigators it has been shown that in the active state chromium in acid solutions is not only able to dissolve two orders of magnitude faster than iron, but also to impart this high solution rate to the whole of the steel in which it is contained, at any rate to the extent of 10-20% [52]. Furthermore, it is known that it usually gives trivalent cations, which are enormously more acid than Fe^{2+}, and are very liable to include chloride ions instead of 1-2 water molecules

in their solvate shells. Thus chromium, more than any other component of steel, promotes electrochemical regeneration of the solution at an active focus, and this is dangerous to it. It is quite obvious that to avoid this danger, the alloy must contain components which will arrest or at least slow down its solution precisely at an active focus. Such properties are found, e.g., in molybdenum [53]; when the solution is acidulated, molybdenum dissolves more slowly, and not at all with participation of chloride ions, because its affinity to chlorine is too low (there is also a hypothesis that, accumulating in the oxide film, it also improves its protective properties [54]). Further development of the special theory of pitting – and it is undoubtedly still in an embryonic state – is impossible without a profound investigation of the chemistry and electrochemistry of the accompanying formation of unstable solutions and their interaction with the metal. The possibility of evolving such investigations has sharply risen in recent years thanks to the successful development in Hungary and the German Democratic Republic of potentiostats with automatic compensation of the ohmic potential difference [55, 56].

In the prevention of pitting, together with the basic composition of the alloy, much attention must be paid to impurities, which cause local disturbances to the structure of the alloy, especially various nonmetallic inclusions [57, 58]. As shown in the USSR [58, 59], close to them the solution current density is always somewhat enhanced, and here local reversal of the passivity mechanism occurs more easily.

The atomic crystal structure of a metal and the crystallochemical mechanism of its interaction with the solution generally play an important part in the processes of anodic solution and corrosion. Tabulated values of the free energy of a solid metal, which are used, in particular, in calculating the equilibrium electrode potentials, do not include the surface energy. Therefore, they directly characterize the work functions only of those atoms which do not influence the surface energy of the system when they are removed. This requirement is satisfied only by atoms which occupy end positions in the extreme incomplete row of an incomplete atomic layer. Only from such a "step" can an atom be removed leaving the next atom in exactly the same configuration as that previously occupied. This is also the position of normal reactivity of an atom. Any of the middle atoms of the same edge are less reactive, because there is an extra bond which when broken increases the surface energy of the crystal.

With very weak anodic polarization the metal atoms dissolve almost entirely in sequential chains – only as long as removal of one leaves the next in line in a position with normal reactivity. "Point" acts of solution, following in succession, sum up to a row of atoms; rows in sequence at one atomic spacing apart constitute a layer. Thus during gentle "equilibrium" etching the solution process, like the electron beam on the screen of a television set, scans all the incomplete layers on the surface of a well-formed crystal. Scarcely any atoms with normal reactivity are left on the surface, and the electrode becomes very inert (its equilibrium exchange current is much reduced). On the other hand, with strong anodic polarization the excess electrical energy makes solution of atoms from the middle of an edge fairly probable also. Each such act brings two new atoms into a position with normal reactivity and starts off two new chains or "rows" for solution. If this happens sufficiently often, the apparent reactivity of the metal may be increased by several orders of magnitude. Here there is a certain analogy with the crushing of large fragments of a reagent into many small ones. The difference is that in our case the total number of atoms with normal reactivity is increased, not by increasing the total surface area, but by increasing their surface concentration. Returning to our analogy with scanning of a surface by an electron beam, we can say that here we have hundreds or thousands of such beams, each of which draws on only a small part of the surface. It is clear that if the rate of action of each beam is the same, the time required for collective scanning of the whole surface decreases in inverse proportion to the number of beams.

These fundamental crystallochemical causes, which follow from repeatedly verified principles of the growth theory and solution of crystals, create many peculiarities and nuances in the anodic behavior of metals and alloys.

For example, anodic formation of new sites with normal reactivity, enhanced with rise of potential and leading to complication and scale reduction in the surface relief, must kinetically lead to spontaneous increase in the anode current, and hence to a reduction in the stationary slope of the anodic polarization curve. This slope is naturally structure-dependent, because the relative kinetic values of the anode changes are the less, the finer the crystals and the greater the imperfection in the original structure of the metal.

These phenomena are clearly illustrated by polarization and electron-microscope investigations of the anodic behavior of nickel, made in the USSR and Bulgaria [28, 59-62].

Via a crystallochemical mechanism the process of solution can be strongly influenced by components of

the solution which are not known to take part in interaction with each of the dissolving atoms. For example, if even a small number of heavy aggressive ions, capable of tearing a metal atom from an edge, are present in the solution, then, as we have seen, this leads to a proportionate rise in the surface concentration of reactive atoms. In turn, there will be a proportionate rise in the overall rate of solution involving quite different, less powerful, but more numerous and mobile agents. An example of such influence might be the above-described accelerating influence of sulfates on the anodic solution of iron. On the other hand, for inhibiting or passivating particles to retard the process of solution, it is also sufficient that they sometimes block, not the whole surface, but merely atoms with normal reactivity appearing on it.

Special possibilities are offered by a crystallochemical mechanism for the mutual influence of different metals on their solution from an alloy which is a solid solution. For example, a case is possible in which the main component of the alloy dissolves at a given potential almost entirely via a position with normal reactivity, while atoms of a less noble alloying element are relatively easily removed from edges also. Then the solution of each alloying atom acquires for the alloy the same value which in the preceding example pertained to the act of opening up the edge by an aggressive anion. Every time, two atoms of the main component on either side of the dissolved one come into a position with normal reactivity and two new solution rows open up. The number of these rows on the surface will grow, until the alloy acquires the solution rate set by the alloying element. A qualitatively similar kinetic effect has been observed, as remarked above, in the solution of chrome steels [52]. In research on model alloys (indium–zinc, zinc–copper, etc.) it was shown [63, 64] that in the initial period of solution a diffusion layer depleted of the less noble component forms on the surface of the alloy.

The processes are complicated if the nonnoble element constitutes the basis of the alloy and imparts to it that potential at which the noble component does not dissolve in individual form. On the other hand, during solution of nonnoble atoms surrounding a noble one on the surface, part of the energy of solvation is each time expended on breaking the bond between the noble atom and the dissolving atom. Therefore, after solution of all or most of the neighbors of a noble atom, the latter can remain on the surface in such a weakly bound (and anomalously reactive) state that, despite the negative potential, it can be anodically converted to an anion which easily moves about the surface or even to a normal hydrate cation in solution. These processes of solution of copper from brass have been investigated in detail in the USSR, in particular with the aid of a rotating disk electrode with a ring [65]. On the other hand, however, hydrated cations of the noble metal accumulating in the solution, or its adions, can in certain circumstances be cathodically discharged, forming surface nuclei of the intrinsic phase. Then the process becomes selective: The nonnoble component will dissolve, but the noble component will be electrochemically recrystallized on the surface into an independent phase. If there is a high concentration of copper in the lattice this process can occur by direct movement of residual noble atoms into vacant positions freed by solution. According to Soviet investigators [66, 67], the processes of selective extraction of zinc, leading to cracking of brass, can be retarded by alloying the brass with small amounts of aluminum, nickel, tin, or silicon. In the authors' opinion, atoms of these elements (or their oxides) play the part of stoppers on the surface, mainly hindering the recrystallization of copper.

Strictly speaking, solution of the alloy is always selective, because the components do not go into solution in proportion to their contents in the surface layer. The stationary ratio of the apparent rates of solution of the components, equal to the ratio of their atomic fractions in the bulk of the alloy, is established, not because actual electrochemical solution has ceased to be selective, but because the ratio of the active concentrations of the components in the surface layer has varied in inverse proportion to its selectivity.

With the start of passivation the ratio of the specific probabilities of solution of the noble and nonnoble components can be completely reversed. Let us say, in contact with a chromium atom passivating decomposition of water, preventing its solution, occurs more readily than in contact with an iron atom. Therefore, on passage through the passivation potential, not chromium but iron begins to be selectively extracted from the surface of chrome steel. At even more positive potentials, at which a film of passivating compounds appears and the electrode boundary (as stated above) splits up, special importance attaches to the different selectivity of electrochemical processes on the internal and external boundaries of the film. The components forming the strongest bonds with oxygen have a clear thermodynamic advantage over the others in emerging from the metal lattice to the oxide film (as also in high-temperature oxidation). On the other hand, in the film itself, precisely because of this high bond strength they will be the least mobile. They are also, as a rule, less prone to go into solution at the external boundary than the others (here, of course, an important part is played by the ratio of the solvation energies). As a result of this double selection, the film must be continually enriched with oxides of those metals which have the greatest tendency to passivation and the least rate of solution in the passive state.

This useful spontaneous process, however, has a danger. As the film is increasingly enriched with a certain chemical compound, there is an increase in the tendency to recrystallization of its alien defect structure into its own stable crystalline phase. But, as we have seen, a recrystallized substance retains only its chemical stability, while the properties of the continuous protective barrier are lost, as it is essentially converted to a residual solid product of the activity of the film. Therefore, each act of such spontaneous local recrystallization unavoidably causes a surge of the solution current and returns the process of passivation at the site of the event almost to its original phase.

Processes of recrystallization in passivating compounds must undoubtedly be taken into account in quantitative interpretation of some very interesting Soviet work [68, 69], in which for the first time it was shown that the selectivity of solution of the components of stainless steels does not disappear with completion of the nonstationary period of passivation, but only reaches some stationary level and remains at it for days without showing any tendency for further decrease. However, the chief cause of the close attention which should be paid to these processes is, of course, the reduction in the practical stability of the alloys, which they must surely cause. Evidently the strongest exposure to recrystallization should be that of films on the surface of strong and relatively slightly alloyed two-component alloys. It is in these that the oxide of the alloying element accumulates, ultimately in the purest form, inheriting the most imperfect and uncharacteristic structure. So one of the most important problems of additional alloying must be to ensure accumulation of components which effectively suppress or prevent harmful spontaneous recrystallization of the main passivating compound in the film.

We have now considered a number of phenomena (passivity, pitting, combined solution of metals from alloys, etc.) for the understanding of which classical electrochemistry, which ignores the dependence of the main thermodynamic and kinetic properties of the solvent and metal surface on the electrode potential, has proved inadequate. Taking account of this dependence, one finds it possible to proceed from classical electrochemistry of an idealized electrode to the real electrochemistry of corroding metals and alloys, which is now beginning to be formulated as an important branch of fundamental science [70]. However, there is no doubt that potential does not itself influence the state of the electrode surface, but exerts its effect via certain electrochemical processes and reactions. Consequently, allowance for the influence of potential on the electrode characteristics ultimately involves the mutual influence of the electrode acts on one another.

This formal logical conclusion is prepared by all the preceding exposition, which elucidates its physical meaning. It is perfectly obvious that if the electrode process generates, consumes, or alters the activity of some substances or specific reaction centers, which are involved in another electrode process, the repetition frequency of the first process cannot fail to influence the resultant frequency of the second. In the examples considered by us the fundamental possibility or even necessity of similar mutual influence is easily seen if we approach the metal or alloy as a real crystallochemical object and the solvent and ions in solution as authentically multiatomic chemical compounds with a real set of properties. Although our examples referred primarily to anodic acts, the same approach is obligatory for cathodic ones. Then, in particular, it becomes obvious that the classical idea of the mechanism of discharge of hydrogen ions on an inert cathode is also insufficient to explain the possible alternatives of the interaction of real hydroxonium ions with a nonnoble metal.

The old joke about sewing the trousers to the buttons certainly applies to the custom of regarding the OH_3^+ ion simply as a hydrated proton. In respect of its structure and of the ratio of the masses and volumes, it would be much more reasonable to regard it as protonized water in which the oxygen has a reduced negative charge and has become a somewhat better acceptor and a weaker donor of electrons, but has not been able to lose its potential capacity to form chemical bonds with metals. In the complete thermodynamic balance of energy of interphase transition the final strength of the newly formed metal–oxygen bond is an independent term. It depends only on the particular parameters of the bond itself, and, of course, is independent of the origin of the oxygen atom or the binding electron pair and of the subsequent fate of the atoms with which the oxygen was previously bound. As an illustration let us consider three related and easily intertransformed versions of the decomposition of water accompanied by the formation of an M–OH bond.

With anodic polarization (and positive surface charge) the oxygen of the water, being the joint proprietor of its valence pairs, can act as a donor and share the pair with a metal. Then, as remarked above (Eq. (3)), a conductivity electron will be transferred to the external circuit, and one of the protons to the next water molecule in the solution:

$$M + 2OH_2 = \overleftarrow{e} + M - OH + OH_3^+. \qquad (4)$$

In the absence of polarization and in the presence of a sufficient number of valence electrons in the metallic

orbitals, the metal itself can denote an electron to the binding pair. Then the hydrogen of the water with an electron liberated from the pair will be detached in the form of a neutral atom and via a stage of chemisorption can be changed to the molecular state:

$$M+OH_2=M-OH+{}^1/_2H_2\Delta G_5. \quad (5)$$

Finally, with consumption of the cathode current by a participant of an analogous conversion the water may become protonized:

$$M+e+OH_3^+=M-OH+H_2\ E_6. \quad (6)$$

Both from the viewpoint of stoichiometry and from that of thermodynamics, reaction (6) is the sum of the classical reaction of discharge of hydrogen

$$e+OH_3^+=H_2O+{}^1/_2H_2 \quad (7)$$

and chemical reaction (5). However, kinetically this is an individual process with a special route on which the liberated H atoms do not need to overcome the usual charge barriers separately or to form intermediate chemisorption bonds with the metal, or to break them during molecularization. Participation of the valence electron of the metal in the formation of its chemical bond with the oxygen of the hydroxonium reduces the effective positive charge of the three hydrogen atoms of the ion. There is a corresponding increase in the probability that two of them, being displaced toward one another in the upshot by about 0.8-0.9 Å, will, with cathodic discharge of the ion, be able to obtain an electron pair in their own bonding orbital, will lose the bond with oxygen and be separated into the electrode layer immediately in the form of an H_2 molecule (of which anodic oxidation on a nonnoble metal is difficult).

The formation of an M−OH bond is such an inherent element of reaction (6) that by analogy with reaction (4) it can be called cathodic oxidation of the metal. The purely superficial paradoxicality of this expression is merely the result of the vagueness of present-day electrochemical terminology. In these two cases "cathodic" or "anodic" merely represents the path of liberation of the oxygen from its bonds with the hydrogen atoms, and the essence of its substitutive bond with the metal does not alter. As the strength of this bond increases, the standard potential of anodic reaction (4) is known to become less positive. Correspondingly, the potential of cathodic reaction (6) cannot fail to become less negative ($E_6 = -\Delta G_5/F$). In the normal hydrogen scale, for any metal which is thermodynamically capable of displacing hydrogen from water, the standard value of E_6 is positive. For example, on chromium, if we roughly regard the energy of formation of Cr−OH as equal to half the energy of $Cr(OH)_2$, the theoretical value of E_6 is close to 0.6 V.

At positive potential the nonnoble metal itself is intensively dissolved in the active state, so that its hydroxylized atoms must be anodically removed from the surface together with the hydroxyls without preventing the occurrence of reaction (6). Furthermore, as remarked above, increase in potential is accompanied by an increase in the anodic generation of new reactive atoms. By opening new sites for the occurrence of reaction (6), this can compensate for the retarding effect of anodic polarization on each individual act and create an apparent independence or weak dependence on potential.

Even more varied are the kinetic relations of reaction (6) in the conditions of cathodic polarization. Hydroxylation of a reactive atom is one of the possible initial stages of its ionization, say, stage *a*. Let us enumerate some of the competing acts which can follow it:

b) A second stage of cathodic hydroxylation of the same atom to $M::(OH)_2$, repeating scheme (6);

c) reverse cathodic reduction of a hydroxylated atom involving OH_3^+ ions with formation of free water, e.g.,

$$M::(OH)_2+2OH_3^++2e=M+4H_2O;$$

d) conversion of a hydroxylated atom to a partly hydrated adion, effected by cathodic incorporation of hydroxonium ions in the hydrate shell which is formed (with more or less partial charge transfer), e.g.,

$$M::(OH)_2+2OH_3^++(2-x)e=M_{ad}(OH_2)_4^{x+},$$

where $0 < x < 2$;

e) reverse cathodic reduction of an adion to metal with decomposition of its hydrate shell:

$$M_{ad}(OH_2)_4^{x+}+xe=M+4H_2O;$$

f) anodic oxidation and completion of the shell of the adion to a normal hydrated cation, e.g.,

$$M_{ad}(OH_2)_x^{x+}+2H_2O=M(OH_2)_6^{2+}+(2-x)e\ldots$$

The sum of stages *a*, b, d, and f is expressed by the equation

$$M+4OH_3^++2H_2O+2e=M(OH_2)_6^{2+}+2H_2,$$

which if detached from the preceding discussion might appear to be without any real meaning. In actual fact it indicates that, if instead of neutral water molecules, hydroxonium ions are used to build the hydrate shell, the overall reaction of synthesis of hydrate cations can be converted from anodic to cathodic. Its mechanism includes stages in which cathodic polarization has a retarding action at the same time as an accelerating action. Thus while accelerating the cathodic stages *a*, b, and d, it simultaneously retards anodic stage f, not only directly, but also indirectly via the acceleration of cathodic stages c and e, which expend its initial components.

Will these opposed effects on the potential completely cancel one another out?

Without making a rigorous kinetic analysis of the whole branched system of competing acts, we can make just one assertion. In a system of reactions in which the consumption of cathodic current involves not only acts which counteract the formation of hydrate cations but also acts which lead to it, such compensation is in any case more likely than in a system in which solution occurs only via chemical stages which are insensitive to potential changes (so that cathodic retardation remains).

In the last decade, in the USSR, Hungary, and the German Democratic Republic, many cases have been discovered and studied in which in the conditions of strong cathodic polarization the rate of solution of chromium, iron, and other metals and alloys increases with the concentration of OH_3^+ ions, but ceases to depend on potential [71-73]. Although this dependence induces us to regard these processes as chemical, the above considerations show that it rather implies a complex interaction of anodic and cathodic reactions.

In concluding this report, we must emphasize that one of its main aims was to show how great are the yet unutilized possibilities of electrochemistry for the elucidation of the mechanism of many anomalous corrosion phenomena, and how impressive is the number of problems which follow thence.

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ATMOSPHERIC CORROSION OF METALLIC SYSTEMS. I. CORROSION STATIONS OF MEMBER-NATIONS OF THE COUNCIL OF MUTUAL ECONOMIC AID (COMECON) AND IMPLEMENTATION OF THE LONG-TERM JOINT PROGRAM OF CORROSION TESTS IN NATURAL CONDITIONS

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UDC 620.193.2

The authors discuss the performance of natural tests in corrosion stations. They give the corrosion and meteorological characteristics of the atmospheric stations of the USSR, Czechoslovakia, Bulgaria, and Hungary. They discuss a program of 20-yr corrosion tests on pure metals, metallic protective coatings, aluminum-based alloys, low-alloy and stainless steels produced in the socialist countries, to be realized at the atmospheric stations of the member-nations of the Council of Mutual Economic Aid (Comecon).

1. Introduction

Reliable scientifically based recommendations on the protection of metals from corrosion and predictions of their service lives in natural conditions can be obtained only by means of field tests in special corrosion stations. The stations are intended for investigations of the action of atmospheric, soil, seawater, and biological factors on constructional materials, anticorrosion media, and finished articles or industrial components. A rough estimate suggests that there are several hundred corrosion stations in the world, most of them lying at latitudes between 20 and 60°N. With further growth in industrial potential, the network of corrosion stations will clearly be extended.

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