DEVELOPMENT OF ELECTROCHEMICAL METHODS OF STUDYING THE CORROSION OF METALS

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In view of the increasing amount of metal coming into service, the total losses of metal from corrosion failure are continually increasing; the more complex conditions under which modern constructions operate and the increasing numbers of metals and alloys employed in technology make the problem of protecting metals from corrosion failure all the more complicated.

It has by now become quite obvious that a reduction in the vast material losses and the attainment of the desired stability of metallic materials under complex operating conditions will only be achieved by discovering and studying the fundamental laws underlying corrosion processes [1, 2]. For this reason we have in the last few decades been witnesses of an intensive development of scientific research into corrosion processes; especially rapid has been the development of electrochemical research methods, since the electrolytic character of the majority of natural and technological aggressive media determines the electrolytic mechanism of corrosion failure (the chemical mechanism of corrosion only appears in electrolytical media under restricted conditions [2, 3]).

In this brief review we wish to demonstrate some of the most interesting (as we believe) examples of the use of electrochemical research methods of particular importance in the development of the science of corrosion and of the discovery of new, efficient methods of combating metal corrosion in the Soviet Union.

Determination of Stationary Potentials

In the course of electrochemical corrosion, the electrochemical processes of the anodic dissolution of the metal and the cathodic reduction of the oxidizing agent contained in the corrosive medium take place at finite velocities, and accordingly there is a displacement of the potential of the metal (on account of the anodic process) and of the reduction-oxidation (redox) potential (on account of the cathodic process) from their respective reversible values, the potentials moving toward each other. Some time after the onset of the corrosive effect of the medium on the metal, when the values of the partial (cathodic and anodic) currents have to a greater or lesser degree become stabilized (if, as is usually the case, the ohmic resistance of the corrosion system is very small), the value of the nonequilibrium stationary potential is established; in general, this is intermediate between the equilibrium potential of the metal and the potential of the cathodic reduction-oxidation reaction [1-4].

From the change in the stationary potential and its final value, we may draw indirect but in many cases quite definite conclusions regarding the corrosion resistance of metals under specific conditions and the character of the corrosive process. For this reason, the measurement of the stationary potentials of metal samples under corrosive conditions was one of the first electrochemical methods of studying corrosive systems, and even now it has not lost its value. By reference to changes in the stationary potential, the influence of various internal and external factors on the corrosion process has been studied [1, 2, 5-7]. In particular, the influence of the composition and concentration of the components of corrosive media [8-11] on the value of the irreversible potentials of metals has beed studied, and the results have been interpreted with due regard for the characteristics of the electrode reactions taking place and the secondary chemical processes of film forming. The change in the potential resulting from corrosion-inhibiting processes has been used to determine the nature of the inhibition; if this is accompanied by a negative displacement of the potential, it is the cathodic process which is being retarded, and if by a positive displacement it is the anodic process [1, 2, 5].

The influence of protective surface films on the potentials of metals in a number of corrosive solutions has been estimated from the potential displacements obtained after mechanically cleaning the films under the electrolyte [12]. From the results of such observations, and by studying the behavior of metal with protective films in aggressive media, the authors of [13] demonstrated the effect of the thickness and other characteristics of the films on the potential and proved the existence of corrosion pairs of the film-pore type on such surfaces. The method of determining the potentials of metals and taking polarization curves with constant renewing of the surface of the metal under the solution was greatly improved in [14, 15].

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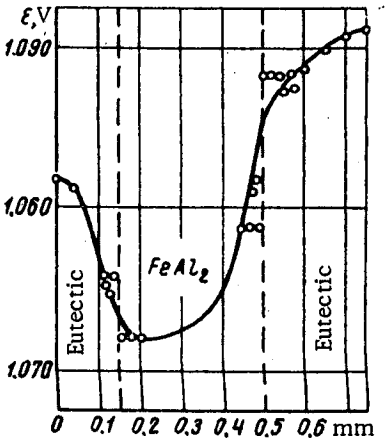

Fig. 1. Potential distribution on the surface of the structural components of an aluminum-iron alloy in a 0.1 N solution of NaOH [19].

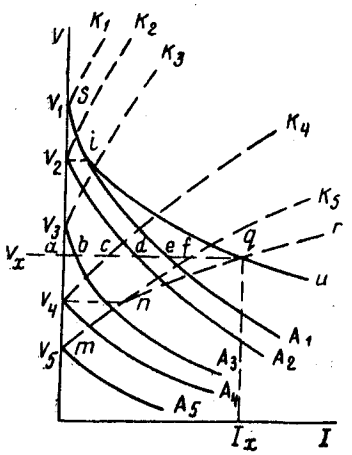

Fig. 3. Graphical solution of a multi-electrode system [2] based on real anodic (continuous lines) and cathodic (broken lines) polarization curves: siqu = total curve of the anodic process; mnqr = total curves of the cathodic polarization; V_X = common potential of the multi-electrode system; I_X = common macro-corrosion current.

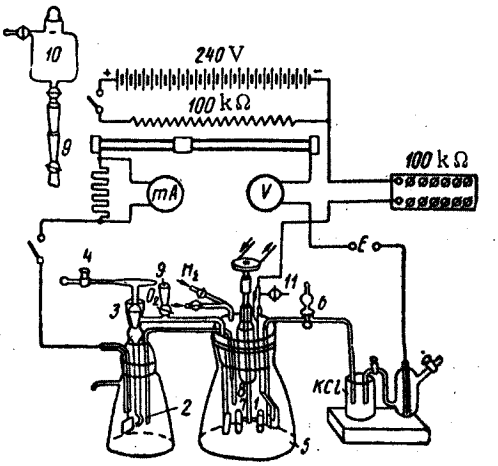

Fig. 2. Experimental apparatus for taking polarization curves [22]: 1) electrode under study; 2) vessel for auxiliary electrode; 3) tap of electrolytic key; 4) conduit for filling key; 5) main vessel; 6) connecting key for calomel electrode; 7) stirrer; 8) bell of hydraulic shutter; 9) ground joint for additional vessel; 10) additional vessel; 11) conduit for communicating with the air.

The negative displacement of the potential following the deformation of metal covered with a natural passive film is associated with the breaking of the protective films (which are less ductile than the underlying metal), since the experimentally-measured potential displacement is much greater than that calculated from the energy of deformation [2, 16].

In order to develop corrosion-resistant alloys, it is essential to know the laws governing the change of potential resulting from protective alloying. Generalization of the results of potential determinations [1, 2, 17, 18] made it possible to establish the principal laws governing the electrode potential and the corrosion resistance of binary solid solutions as functions of the composition of the alloys and other factors. A fine method was developed in [19] making it possible to measure the potentials (Fig. 1) of the structural micro-constituents of alloys by means of a micromanipulator and special capillaries. The relation between the potentials for individual structural components and the phase diagram of the corresponding alloys was established in [20].

On the basis of measured values of the stationary potentials and tabulated data relating to the standard potentials of the anodic and cathodic processes, the authors of [2, 21] established the nature of the controllable factors in the corrosion process, which is of particular importance for establishing the corrosion mechanism and the most efficient method of protecting metals.

Plotting of Polarization Curves

The furthest development in electrochemical methods of studying corrosion is the analysis of the kinetics of electrode processes (by plotting and analyzing polarization curves). Galvanostatic polarization curves represent the relation between the change in electrode potential and the applied polarization current; such curves constitute important characteristics, not only of the kinetics of cathodic and anodic reactions, but also of the corrosion process which these determine.

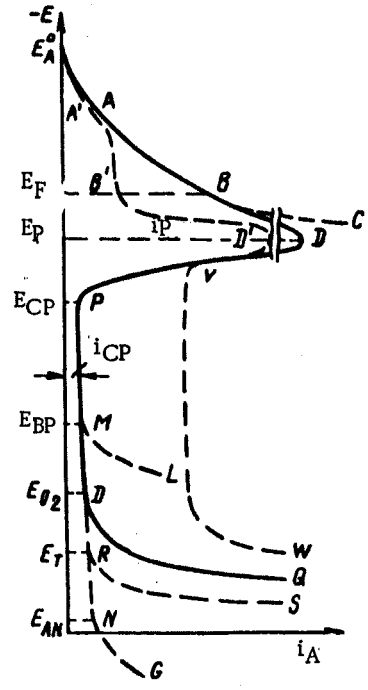

Fig. 4

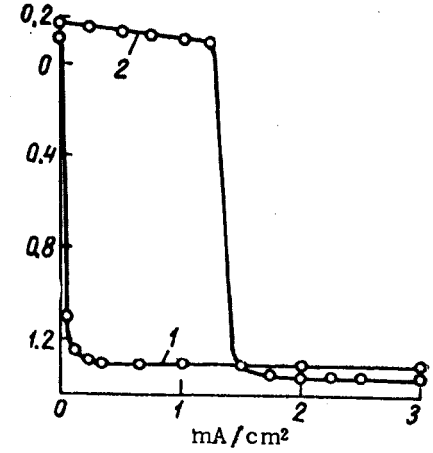

Fig. 5

Fig. 4. Generalized scheme of an anode polarization curve [26]. The meanings of the main characteristic points and sections of the anodic curves are as follows: E_A^0 = equilibrium potential of the metal; E_F = potential of the thermodynamically-possible development of an adsorbed or phase oxide film (the beginning of the deviation of the anodic curve from the semilogarithmic relationship); E_P = potential of the limiting passivation current (potential of the onset of spontaneous passivation); E_{CP} = potential of complete passivation; E_{BP} = potential of pitting (breakdown potential); E_{O_2} = potential of the onset of the anodic evolution of oxygen; E_T = potential of overpassivation (transpassivity); E_{AN} = potential of anodizing (growth of thick oxide films); ip = limiting passivation current; i_{CP} = current of complete passivation.

Fig. 5. Anodic polarization of chromium (1) and 1Kh18N9T steel (2) in a solution of 30% H_2SO_4. Temperature 20°C [30].

The method of plotting the curves of anodic and cathodic polarization varies with the subject of study and with the corrosion media and conditions to be imitated. Important results have been obtained with the apparatus shown in Fig. 2, which is adapted for studying a variety of conditions: feeding-in gases, stirring, taking samples of the solution and so on [22]. Modern systems are furnished with potentiometers and cathode voltmeters, and for cases in which the potentials have to be recorded rapidly, with cathode-ray oscillographs, incorporating automatic recording, as well.

The problem of the multi-electrode element (cell) in corrosion was solved by the method of polarization curves [23]. For multi-electrode, completely-polarized systems, the polarity of the electrodes is determined by graphical construction (Fig. 3) on the actual polarization curves in potential/current coordinates. The solution is based on the fact that, on short-circuiting the electrodes, a common potential of the system V_X is established, and in the stationary state the sum of the cathode currents equals the sum of the anode currents. Since the line $V_X q$ is intersected by the cathode polarization curves of the electrodes 4 and 5 and the anode curves of electrodes 1, 2, and 3, electrodes 4 and 5 will correspondingly act as cathodes (currents proportional to ac and af) and electrodes 1, 2, and 3 as anodes (currents proportional to ae, ad, and ab). Further refinement and development of this solution may be achieved if we replace the real polarization curves (in practice obtained by polarization with an external current) by ideal (theoretical) ones incorporating data regarding the self-dissolution of the electrodes [2].

The formation of clear ideas regarding the mechanism underlying the corrosion of real technological materials in electrolytic media is inconceivable without a detailed study of the cathodic behavior of the metal materials under conditions approximating reality. Research of this kind was carried out by plotting cathodic polarization curves

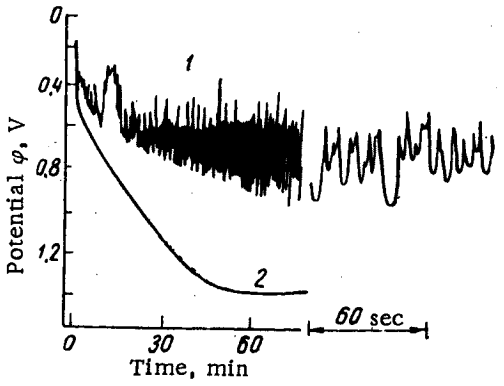

Fig. 6. Charging curve of Kh18N10T steel (i = 2 μA/cm²): 1) In 0.1 N NaCl; 2) in 0.1 N NaCl + 0.04 N $NaNO_2$ [42].

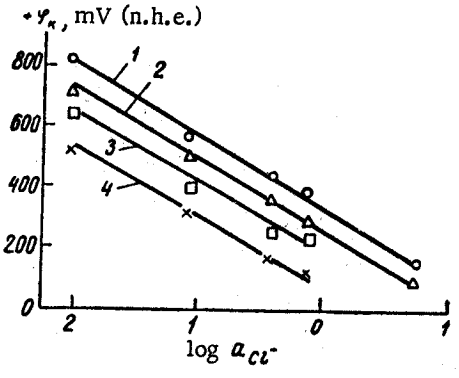

Fig. 8. Pitting potential as a function of the activity of the chlorine ions in aerated solutions of NaCl under heat-transfer conditions [61]. Temperature of the medium 25°. Temperature of the wall 25, 45, 65, and 85°C for curves 1, 2, 3, and 4.

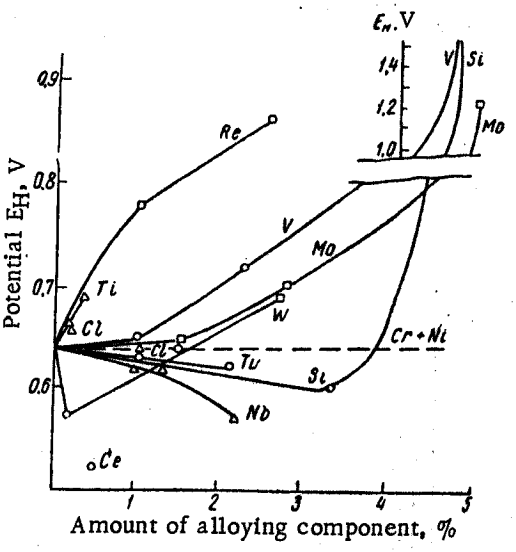

Fig. 7. Effect of alloying elements on the breakdown potential of 18-14 steel in 0.1 N NaCl. Temperature 25°C [56].

galvanostatically for the most important technological metals and alloys, allowing for the influence of the concentration of the oxidizing agent in the corrosive medium, the roughness of the cathode surface, and other factors. This work demonstrated the most important influence of oxygen depolarization in the corrosion of real metal constructions and enabled the basic laws governing this action to be established [22].

Passivity of Metals and Potentiostatic Method of Studying This

The effect of passivity opens the possibility of the practical use of commercial metals, despite the fact that the overwhelming majority of these are characterized by thermodynamic instability in practical conditions of service. Passivation raises the corrosion resistance as a result of the retardation of the anodic process. A spontaneous positive shift of the potential at the onset of passivation makes it difficult to study passivity by the galvanostatic method. The corrosion/potential relationship in the region corresponding to transformation of the metal from the active to the passive state and conversely may only be plotted by means of the potentiostatic method, in which a constant value is automatically given to the potential of the electrode under study and maintained by means of special electronic devices (potentiostats) [24, 25].

The operation of passivating corrosion systems is analyzed by evaluating the characteristic values of current and potential in the most important sections and at the most important points of the anodic potentiostatic curve (Fig. 4) [26, 27]. Research of this kind reveals, for example, the effect of various alloying elements in iron and steel on the stability of the passive state of the metal.

Research carried out in the Soviet Union on the passive state of chromium and iron-chromium alloys led to the discovery of the effect of overpassivation [28-31], an intensification of corrosion resulting from the fairly high anodic polarization of passive metal. The potential reaches a value at which soluble oxides of a higher degree of oxidation may be formed and the metal may pass into solution in the form of ions of higher valence (Cr^{+6}). The potentials corresponding to the transformation of the metal on anodic polarization are of the same order for chromium and chromium-nickel steel (Fig. 5), namely, 1.25 to 1.3 V. Overpassivation under the influence of strong oxidizing agents or anodic polarization occurs not only for chromium and chromium-containing steels but also for molybdenum [32] and a number of other metals.

Recently the passivation characteristics of iron, iron-chromium alloys, and nickel in acid solutions have been studied; a relation has been obtained between the anodic behavior and the characteristics of the passive state, and

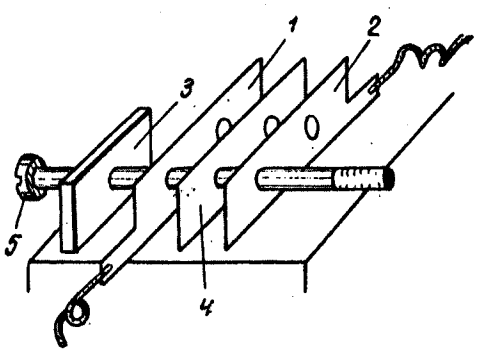

Fig. 9. Model of a pack-type microcorrosion battery (at the moment of assembly) [77]: 1) iron plate; 2) copper plate; 3) support; 4) insulator; 5) fixing bolt.

also the effects of the adsorption of oxygen and the congruent adsorption of electrolyte anions [33]. The existence of a critical temperature for the self-passivation of iron-chromium alloys has been established [34]. In studying the anodic behavior of copper-nickel alloys in ammonia solutions by the potentiostatic method it has been shown that the passivation potential changes spasmodically in alloys in which the atomic proportion of nickel is a multiple of $^1/_8$ [35].

It was proposed in the Soviet Union for the first time [26, 36-39], on the basis of an electrochemical study of the anodic passivation of a number of metals, that the stability of the passive state should be increased by increasing the efficiency of the cathodic process. Experiments showed real possibilities of achieving this effect by introducing alloying additives of more electropositive metals with reduced hydrogen overvoltage. It was shown [40, 41] that as the result of a build-up of the electropositive alloying component in the initial stages of the corrosion of the alloy there was an increase in the cathodic surface, the current polarizing the anodic parts became stronger, and the alloy was thus passivated and transformed into a corrosion-resistant state.

At the present time titanium containing 0.2% palladium is being produced on a commercial scale and the possibility of the practical production of stainless steels containing palladium or platinum additives is being studied. Prospective materials for cathodic alloying include alloys based on nickel, zirconium, tantalum, cobalt, niobium, and so on. The conditions for the effectiveness of alloying with cathodic additives include the capacity of the metal to become passivated ("passivatability"), a moderate value of the critical passivating current (below the current of the cathodic process at the passivating potential), the absence of overpassivation or breadkown of the passive films at the potentials which may be established as a result of alloying, fairly negative values of the passivation and complete passivation potentials, and, finally, fairly low dissolution currents in the passive state. Hence the question of the suitability of a specific metal for cathodic alloying may be quickly and conveniently solved by analyzing the corresponding potentiostatic polarization curves [26, 37, 39].

Taking Charging Curves and Other Electrochemical Methods

New possibilities for studying the mechanism of corrosion processes are opened by using methods of plotting charging curves based on oscillographic recording. By taking anodic charging curves we may in particular establish the influence of electrolyte composition on the stability of the passive state of Kh18N10T steel; on adding $NaNO_2$ to 0.1 N NaCl the periodic fluctuations of potential (characterizing unstable passivity) cease, and the steel passes into a stable passive state (Fig. 6) [42]. Anodic charging curves make it possible to study the composition of an alloy surface in the course of self-dissolution or anodic dissolution [41].

A study of oscillograph records of cathodic charging curves, together with a comparison of the experimentally-established potentials for the formation of oxides, calculated from thermodynamic data, made it possible to establish the chemical composition of the oxides formed under various conditions by the action of alkalis on certain nonferrous metals and alloys [43].

The use of the reduced or so-called φ scale of potentials [44] (i.e., a scale in which the potentials are reckoned from the zero point of the corresponding metal) for corrosion problems, in addition to providing fresh information on the mechanism and laws of inhibitor protection, is useful in explaining a number of other corrosion effects, for example, the corrosion cracking of nonferrous metals. For example, a particular copper-zinc alloy is inclined to stress corrosion in an ammoniacal medium, whereas copper, zinc, nickel, German silver, and cadmium are not; correspondingly the φ potential of the alloy in question differs greatly (even in sign) from that of the other metals [45].

Recently, methods have been developed on the basis of electrical circuits constituting models for electrochemical processes. These methods have been used to study the stability of protective films on metals under conditions of strain [46], polarization phenomena in media with large ohmic resistances (with the application of a discontinuous current) [47], and the influence of hydrogen sulfide and other sulfides on the behavior of iron and cobalt [48]. The determination of the components of impedance (polarization capacity and resistive impedance) in a circuit designed to model a titanium electrode proved that the passive film formed on titanium at the more negative potentials (−0.02 to −0.07 V) had an adsorption character, while that formed at the more positive potentials (+0.20 to +0.75 V) constituted an oxide phase [49].

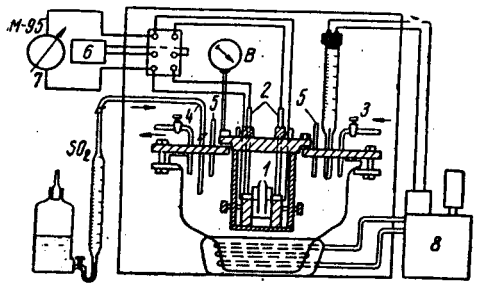

Fig. 10

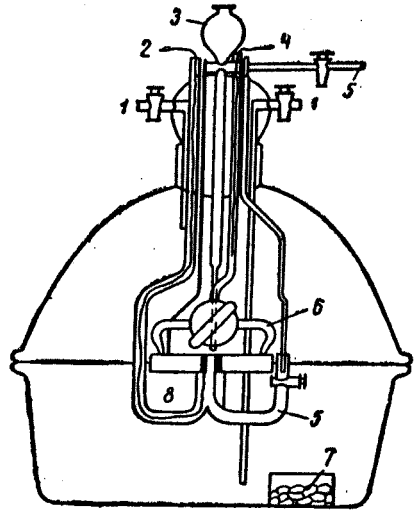

Fig. 11

Fig. 10. Arrangement of the apparatus [78]. 1) Electrodes; 2) half cells; 3) moist-air inlet; 4) SO_2 inlet; 5) wet and dry thermometers; 6) cathode voltmeter; 7) microammeter; 8) thermostat.

Fig. 11. Apparatus for studying electrochemical processes taking place on metals under thin films of electrolyte in an atmosphere of given composition [79]: 1) taps for connecting to systems creating an atmosphere of given humidity; 2) conduit from the electrode under examination; 3) dropping funnel; 4) platinum wire (auxiliary electrode for polarization); 5) measuring key (connected through an intermediate vessel to a calomel half cell); 6) polarization key; 7) vessel containing inhibitor; 8) electrode.

We must also mention the use of double-layer capacity measurements [50, 51], potential-drop curves [52], and the method of polarization resistance [53] for determining corrosion rates. By determining the electron work function before and after the action of an aggressive medium on the surface of a metal it has been shown that in the course of corrosion the surface of an alloy becomes richer in the more stable component [54].

Study of Pitting and Fissure Corrosion

The first research carried out on the electrochemical study of pitting or point corrosion was based on anodic polarization, with a fixed potential of the sample, at a point corresponding to the sharp rise in the recorded current [1, 55, 7]. This method yielded useful information on the effect of the additional alloying of austenitic steel of the 18-14 type with Mo, Si, V, Re, W, Ti, Ce, Nb, Zr and Ta, and also on the effect of heat treatment on the tendency toward pitting in a chloride solution (Fig. 7) [56].

Considerably fuller information regarding the laws of point corrosion is obtained by using potentiostatic measurements. A criterion for the possibility of pitting is the onset of a rise in the potential of the metal (whether as a result of anodic polarization or the oxidizing effect of the medium) above a certain critical "pitting" potential (E_{BP}, cf., pitting or "breakdown" potential in Fig. 4). The effect of activators (halides, pH) on the critical pitting potential is discussed mainly in [57, 58].

The laws governing point corrosion have also been studied by means of a pitting model with a microscopic anode 0.0003 cm^2 in area. A reduction in the chloride content and the introduction of V, Si, Mo, and Re additives not only makes the E_{BP} of stainless steel more positive but also reduces the passivation current. The initial stage in the growth of pitting is a purely electrochemical process and takes place at a velocity determined by the overvoltage of the anodic process, obeying a tabular relationship. Addition of V. Si, Mo, and Re retards the anodic dissolution of the alloyed steels inside the developing pit [59].

Interesting studies of point corrosion have been made for a range of stainless steels by means of anodic charging curves. The variation in the tendency toward pitting was estimated from the frequency and amplitude of the periodic oscillations of potential, which were established by oscillographic recording. Pitting was retarded by introducing oxidizing agents into chloride media; as regards their capacity to prevent pitting, the anions of these oxidiz-

ing agents lay in the following order

$$NO_3^- > ClO_3^- > ClO_4^- > CrO_4^{-2} > SO_4^{2-},$$

which differed from the order of their oxidizing ability [42].

In studying the pitting corrosion of aluminum alloys it was shown [60] that different methods of determination yielded very similar values of critical pitting potential; such methods included the plotting of the anodic potentiostatic curve, the measurement of the changes in potential with time for given (stationary or varying at a known rate) current densities, and the plotting of charging curves. The effect of heat transfer on the development of point corrosion in Kh18N10T steel was determined by the potentiostatic method (Fig. 8) [61].

A wide study of metal corrosion in gaps and fissures was made in [62] by determining the potentials and polarization characteristics of models of fissures formed between metal samples and metallic or nonmetallic facing plates, the gaps between these being varied. The currents of galvanic pairs formed between the metal in the gap and metal in the volume of the electrolyte were also studied. It was found that in acid media the accelerated corrosion of iron and low-alloy steel developed in gaps and fissures as a result of the formation of a galvanic cell. The metal in the fissure served as anode for this cell (the pH of the electrolyte rose in the fissure so that the potential became more negative). Stainless steels were characterized by depassivation in fissures and by the formation of macroscopic pairs of the "active metal in the fissure/passive metal in the main volume" type; the operation of these caused accelerated corrosion of the metal in the fissures.

We must also mention electrochemical investigations on the influence of pH, bacterial flora, and overgrowth on the fissure corrosion of stainless steels [63].

Intercrystallite Corrosion. Corrosion Cracking and Fatigue

A method of obtaining polarization curves of microscopic alloy constituents (grain boundaries) has been developed in order to study intercrystallite corrosion. The first electrochemical study of the influence of heat treatment on the development of a tendency toward intercrystallite corrosion in 27% Cr steel was carried out by this method [64]. It was found that the tendency toward intercrystallite corrosion was only realized in a certain range of potentials, corresponding to the active state of the boundaries and the simultaneous passivity of the actual grains [65].

The development of the potentiostatic method of studying structural corrosion is exemplified by recent research into the optimum potentials and compositions of solutions for revealing the tendency toward this kind of corrosion, the effect of the chemical and phase composition of alloys (resulting from heat treatment) on their resistance to structurally-selective damage, and the use of potentiostatic etching for determining the relative corrosion resistance of various phase constituents in alloys [66-67], [98].

Research into the nature and mechanism of corrosion cracking and corrosion fatigue (both very important forms of corrosion damage in practice) is carried out in apparatus designed to combine mechanical (static, smoothly varying, or pulsating) loads with the effects of aggressive media. In many examples of such apparatus the potential may be recorded during the exposure of the stressed metal and the polarization characteristics may be obtained [68-72]. A special apparatus, the INK-2, has been built for the micro-electrochemical study of stress corrosion; with this apparatus the exposed metal may be examined under the microscope and at the same time its potential and that of its structural components may be estimated. Using a micro-manipulator, the coordinates of the point of potential measurement may be varied to an accuracy of 10 μ, or within the grain boundaries to 1 μ. The INK-2 makes it possible to estimate the effect of the stressed state of the metal on the polarization of its structural components, on the potential difference between microscopic regions subjected to stresses of different magnitudes, and so on [68].

As a result of numerous investigations [68-74 etc.] a deep-rooted connection has been established between electrochemical effects and the phenomena of corrosion fatigue and corrosion cracking. The complexity of these phenomena is due to the simultaneous appearance of an adsorption-induced loss of strength [45, 75, 76].

Study of the Mechanism of Atmospheric Corrosion

A direct experimental proof of the electrochemical nature of atmospheric corrosion taking place under an invisible film of moisture (for an air humidity of < 100%) was obtained by means of a model (microcorrosion battery) in which the scale of the corrosion micro-pairs on the surface of the metal was reproduced (Fig. 9). The anode plates of such batteries were made of the metal to be investigated and the cathode plates simulated the composition of the alloying additives and impurities in this metal. The battery was either placed in a thermal humidity cabinet or

tested under natural conditions. This method proved the predominance of anodic control for corrosion in a moist atmosphere and made it possible to study the effect of changes in air humidity, and in the temperature and state of aggregation of the electrolyte, on the contact corrosion current [77].

Later, a method of measuring the true electrochemical potentials in thin films was developed and the polarization following the application of an external current was studied [78]. The apparatus illustrated in Fig. 10 made it possible to study the effect of humidity, temperature, and contamination of the air on electrochemical corrosion processes. The work showed that, with diminishing humidity of the atmosphere, the anodic polarizability increased more rapidly than the cathodic, and the part played by the ohmic factor became more important. The addition of sulfur dioxide "unleashed" the anodic process and the damp-atmospheric corrosion increased accordingly [78].

The mechanism of practically-important corrosion processes under conditions of moisture condensation (wet-atmosphere corrosion) was studied by a rather different method. The principle was the determination of electrochemical effects on plane samples, the surface of which was covered with films of moisture varying in thickness. The experiments were carried out in an atmosphere of predetermined composition (Fig. 11). Effects established included the acceleration of corrosion as a result of the self-agitation of the moisture by evaporating from the surface of the metal, the cathodic control of corrosion in a wet atmosphere, and the inverse proportionality of the rate of cathodic reduction of oxygen to the thickness of the moisture film. The cathodic process is intensified in the presence of sulfur dioxide, since under these conditions it becomes an oxidizing agent, the depolarizing action of which continues even after the formation of the corrosion products on the surface of the metal [79].

Establishing the Mechanism of Soil (Underground) Corrosion

The electrochemical processes of soil corrosion have been studied with special cells and models of pipelines. It has been established that the anodic process for iron is only subject to considerable retardation in very dry soils, where the lack of moisture and the easy access of oxygen facilitates passivation, or else when the surface of the metal is screened by poorly-soluble corrosion products. The transport of oxygen in soils takes place mainly as a result of diffusion. The severe variations in oxygen permeability with the humidity and structural characteristics of soils raises the possibility of the formation of macroscopic corrosion cells of nonuniform aeration. A characteristic of electrochemical soil corrosion is the super-position of the operation of macroscopic pairs on the effect of self-dissolution. As the length of underground structures increases, there is a relative increase in the contribution of macroscopic corrosion effects, accompanied by local fractures in places of "oxygen deficiency" [2, 80].

A special method has been developed in order to make a comparative estimate of the corrosion activity of soils with respect to metals and to determine the character of the corrosion process; this method provides for the use of special probes, copper sulfate comparision electrodes, and circuits for measuring the electrode potentials of metals in soil and the electrical resistance of the soils themselves, as well as for plotting simplified polarization curves [7, 81]. Electrochemical methods are used for certain features of polarization and the corrosion of steel in soil [82], the corrosion of aluminum structures in salt marshes [83], and so on.

Corrosion Under the Influence of Variable Currents and Ionizing Radiations

Electrochemical methods have recently been applied to the solution of important problems in the corrosion of metallurgical constructions under the influence of stray currents. Special electronic apparatus has been developed for studying electrochemical corrosion after polarization by either sinusoidal or rectangular symmetric and antisymmetric currents of various amplitudes and frequencies. The characteristics of the processes underlying the polarization of metals by varying currents necessitated the construction of special cells for studying the electrochemical and corrosion behavior of metals. These cells are characterized by large surfaces of the auxiliary (polarizing) electrodes and the absence of any ground joints [84]. With the help of this method,a theory has been developed for the electrochemical processes underlying the corrosion of metals resulting from variable currents [85, 86]. In other papers, a detailed study has been made of corrosion damage when currents of industrial frequency act on metal structures, and the effects of the superposition of a steady current on a varying one during corrosion in soil [99] and sea water [87] have been considered.

The wide introduction of nuclear processes in technology has made it essential to study the effect of electron irradiation on corrosion. Some quantitative characteristics have been established for the effect of an electron flux on electrochemical polarization [88]. More complex electrochemical cells have been supplemented by special systems for estimating the absorption of electrons and other parameters necessary for describing electrochemical effects under such conditions [89]. The mechanism underlying the variations in the velocity of electrode reactions under the action

of electron irradiation due to radiation-electrochemical and photo-electrochemical effects has been worked out [90]. The influence of ionizing radiations on electrochemical effects has been specially studied for oxidized electrodes [91].

Some Special Electrochemical Research on Corrosion

The vast variety of technological media and the working conditions of metal equipment prevents us from giving a full list of all the work which has been carried out in studying corrosion processes by means of electrochemical methods. The electrochemical method has been used to discover the nature of corrosion damage to the metal in reinforced concrete [92], to establish the mechanism of metal corrosion in molten chlorides, using comparison electrodes, and to elucidate possible depolarization reactions by studying the activation energy of the cathodic process as a function of potential [93]. The corrosion of pipelines under the action of two-phase systems (aqueous solutions-hydrocarbons saturated with H_2S) has been studied [94]. Corrosion processes resulting in damage to ships have been considered by studying electrochemical effects of contact corrosion [95], modeling the multielectrode electrochemical systems by means of electrical circuits [96].

An express method has been proposed for estimating the resistance of welds by determining the potential variations of different parts of the welded joint with the help of a micro-manipulator. The experiments showed that the potential distributions so measured were closely correlated with the corrosion behavior of the weld metal and the surrounding zone, as estimated from metallographical examination and from the readings of a profilometer recording the depth of the corrosion damage [97]. The limited scope of our review and the vast store of material which has been built up on electrochemical methods of studying various kinds of corrosion process prevent us from touching on a number of other interesting and important methods. In particular we have been unable to include papers relating to protection from corrosion (by inhibitors, cathodic and anodic polarization, metallic and nonmetallic coatings, etc.) or research methods based on radioactive isotopes and so on.

In conclusion, we must emphasize that electrochemical methods will find a wide use in the near future for studying corrosion at high temperatures and pressures, and under the simultaneous action of cavitation, erosion, and the application of mechanical stresses.

Electrochemical methods offer the possibility of continuously measuring the processes being studied and automatically recording these by means of ossillographs and other electronic apparatus, thus being able to study the initial stages of corrosion and very rapid processes of corrosion damage. Various kinds of electrochemical determinations (of electrode potentials, pair currents, polarization curves, resistances, breakdown potentials, impedance, and so forth) will be used far more widely as accelerated methods of corrosion testing for various service conditions of metal construction materials.

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