DEVELOPMENT OF THE UNDERSTANDING OF CORROSION IN METALS OVER THE LAST FIFTY YEARS IN THE SOVIET UNION

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The development of our understanding of metal corrosion is closely related to the development of industry. The first work in this direction was carried out in Russia by M.V. Lomonosov, who studied the dissolution of metals in acids in 1738 and was the first to observe the passivation of iron in strong nitric acid. There was no stimulus in Tsarist Russia, with its backward industry, for these investigations, and they were not developed very far. The required stimulus only appeared after the Great October Socialist Revolution, when corrosion science was founded, together with its various engineering applications. Of the work carried out in the first years of Soviet power, we must mention the extensive investigations of V.A. Kistyakovskii and his school, which yielded data relating to the electrochemistry of magnesium, chromium, iron, and aluminum, and formulated original concepts regarding the processes underlying the corrosion and electrocrystallization of metals. As a result of these investigations, V.A. Kistyakovskii developed the film theory of the passivity of metals, based on the idea of the colloidal-electrochemical formation of a thin oxide film, impenetrable to oxygen, on the metal surface.

In the development of the electrochemical theory of corrosion a great deal of significance attaches to the work of N.A. Izgaryshev, whose extensive experimental data demonstrated the important effect exerted by the nature of the electrolyte and solvent on the rate of metal corrosion.

A sharp increase in the number of investigations, accompanied by an improvement in their experimental and theoretical level, took place at the end of the 20's and beginning of the 30's, when the Fourteenth Party Congress urged the nation toward the creation of heavy industry. Beginning from this period, the science of metal corrosion continued to develop under the constant demands of a growing industry. Accordingly, the last few years have seen the development of a large number of new corrosion-resistant alloys and also effective and economically-favorable methods of corrosion protection. This has not only ensured the reliability and long service life of various machines, equipment, installations, buildings, transport systems, and telecommunications, but has also cooperated in the progress of industry and technology. It is well known, for example, that the wide use of light metals in the construction of aircraft and rockets has only become possible as a result of the creation of various constructional alloys based on these metals and the development of simple and efficient methods of protecting them from corrosion. A large number of corrosion-resistant alloys and methods of protection have been developed for the chemical and metallurgical industry, where problems of combating corrosion are of special and urgent significance in connection with the use of aggressive media. In many cases this has not only promoted the extended service life of apparatus and constructions in existing undertakings but also created the possibility, in principle, of realizing new processes involving the participation of especially aggressive media.

For the development and successful operation of the machine-building industry, the many methods of depositing protective metallic coatings and also methods of briefly protecting objects by means of inhibitors developed in these years had particular significance. The wide use of pipelines for transporting natural gas, oil, and oil products became economically feasible and technologically justified only after the protection of these pipelines from corrosion by insulating coatings and electrochemical methods. The use of these methods not only made a considerable contribution to industrial economics and promoted technical progress in the power, chemical and petrochemical industries, but also promoted the well-being of the populace by providing gas lighting for towns and work places. For developing the canning industry and the long-term storing and transporting of food products, the hot galvanizing (tinning) of ferrous metals was of enormous significance, leading to the creation of special factories for the manufacture of white tin plate.

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The successes achieved were largely the result of fruitful endeavors of the Soviet school of corrosion workers formed in these years, the leading part in the creation of which was played by Corresponding Member of the Academy of Sciences of the USSR G.V. Akimov. The first Soviet specialized research laboratory on metal corrosion (in TsAGI), the first Faculty of Corrosion and corrosion course in the world, and also the whole network of corrosion stations in the Soviet Union were organized on Akimov's initiative.

The solution of practical problems became possible thanks to the great advances of Soviet scientists in the development of metal-corrosion science. Like many other fields of science closely connected with the development of technology, corrosion science developed with a due regard for real practical questions, primarily those associated with the large number of factors on which the nature and velocity of metal-corrosion processes depended. These factors include the nature and structure of the metal itself, the chemical composition of the corrosive medium, the temperature, the hydrodynamic conditions of service of the object in question, and many others. Under these conditions, metal-corrosion science was only able to develop successfully by taking advantage of the advances of a whole series of contiguous branches of knowledge. However, the central question in this science always remained the mechanism of the corrosion process, which in the overwhelming majority of cases is of an electrochemical nature. Thus the development of metal-corrosion science is strictly related to the development of electrochemistry. The fundamental scientific basis of corrosion processes could only be established after electrochemistry had developed into an independent science and its principal laws had been formulated. The famous experiments of Galvani, stimulating the development of our understanding of electromotive force, the work of Volta, Petrov, and Jacobi, leading to the creation of the first steady sources of electric current, and the work of Faraday, who formulated the first fundamental laws of electrolysis, not only laid the foundations for the independent existence of electrochemical science but also constituted the first fundamental concept of metal corrosion, then known under the title of the theory of local cells. Great merit in perfecting and developing this theory goes to the Soviet school of corrosion workers, and first of all to G.V. Akimov and his students, V.P. Batrakov, R.S. Ambartsumyan, N.D. Tomashov, I.L. Rozenfel'd, A.V. Ryabchenkov, S.G. Vedenkin, P.A. Akol'zin, and many others.

The initial position of the theory is the principle that corrosion is due to the operation of galvanic microcells arising on the surface of the corroding metal as a result of chemical or structural inhomogeneity in different regions. Basing his views on this concept, G.V. Akimov gave a classification of such inhomogeneities and proposed that the surface of the corroding metal should be regarded as a complex, in general multi-electrode system, the velocity and distribution of the corrosion processes in which are determined by the electrochemical characteristics and area of the electrodes and also the resistance between them. Akimov developed and successfully applied the concept of the equivalence of the polarization of the electrodes to an ohmic resistance. G.V. Akimov and N.D. Tomashov proposed analytical and graphical methods of calculating the processes for various special cases and for the general case of a multi-electrode system. For the experimental verification of the validity of the concepts and computing methods developed, Akimov (together with A.I. Golubev and others) developed micro-electrochemical methods of studying real corroding surfaces, and in this way measured the potentials of individual structural elements of real alloys. As a result of this work, the theory of local cells was brought to its most perfect form. Subsequently, the principle was widely and successfully used for explaining the corrosion behavior of construction metals and alloys under various conditions. The most fruitful and important use of the principle was in explaining nonuniform (local) corrosion. The theory was employed, in particular, as a basis for explaining the intercrystallite corrosion of aluminum alloys, which was studied extensively by G.V. Akimov, S.E. Pavlov, and A.I. Golubev. I.A. Levin and S.A. Gintsberg first experimentally confirmed the earlier-expressed view that the intercrystallite corrosion of stainless steels was the result of impoverishment of the grain boundaries with respect to chromium owing to the combination of the latter with carbon to form carbides. This provided a basis for explaining the preferential dissolution of the grain boundaries as being due to the operation of a three-electrode system: grain, chromium-depleted grain boundary, carbide. G.V. Akimov used these results to explain the action of carbide-forming elements (titanium and niobium) introduced into steel in order to reduce its tendency toward intercrystallite corrosion. It was shown in subsequent papers of A.I. Levin, G.L. Shvarts, N.D. Tomashov and A.V. Shreider, and N.P. Zhuk that the intercrystallite corrosion of stainless steels might also be produced by the selective dissolution of nonequilibrium carbides and intermetallic compounds precipitating along the grain boundaries, by the formation of certain metallic phases, and by increased stresses.

In A.V. Ryabchenkov's research, the theory of local cells was successfully used in order to explain corrosion fatigue. It was convincingly shown that, as a result of the nonuniform distribution of stresses,

effectively operating galvanic cells developed on the surface of corroding metal, the anodic section of the surface acting as stress raiser, thus intensifying and accelerating the corrosion of the metal. In contemporary papers by G.V. Akimov together with E.P. Paleolog and G.B. Klark, the theory of local cells was extended to the corrosion of metals with various protective films.

However, as often happens in science, as the sphere of application of the theory of local cells developed and extended, its limitations became more obvious. In particular, it gradually became clear that the principle on which this theory was based (the initial nonequipotential nature of the metal surface and the complete and obligatory spatial separation of the cathodic and anodic reactions) could not be used in order to explain the dissolution of pure metals or amalgams without having recourse to further, less well-founded assumptions. In addition to this, the later development of electrochemistry, and in particular the results of studying the kinetics of electrode reactions, demonstrated convincingly that the dissolution (corrosion) of metals in electrolytes should be considered not as a result of a departure of the metal surface from its equipotential state but as a result of the contiguous and independent occurrence of cathodic and anodic reactions, the velocity of which, according to the laws of electrochemical kinetics, are determined by the total potential at the metal/solution interface, the composition of the solution, and the conditions governing the diffusion of the components or reaction products in solution. According to these principles, the presence of chemical or structural inhomogeneities on the surface of the corroding metal may lead to partial localization of the reactions taking place, although this need not necessarily be accompanied by a departure from equipotential properties on the surface, and does not prevent the application of the laws of electrode kinetics for each of the reactions and the corroding process as a whole. The equipotential properties of the surface may be disrupted in the corrosion of certain technological alloys in media with a low electrical conductivity. The local galvanic cells arising in this case have a considerable influence on both the velocity and the distribution of corrosion. It follows from this that the theory of local cells should be regarded as a particular case of the general electrochemical theory of metal corrosion.

In developing these points of view, chief credit goes to the Soviet school of electrochemists, and especially A.N. Frumkin and his students, whose labors have had the greatest influence on the formulation of modern theoretical electrochemistry. In 1932 A.N. Frumkin first showed the possibility of quantitatively applying the laws of electrochemical kinetics in order to explain the laws governing the dissolution of sodium amalgam in alkali solutions. Analogous views on the mechanism of metal corrosion in aqueous solutions of electrolytes were independently expressed and formulated by A.I. Shultin and Ya.V. Durdin.

An important stage in the development of these principles was reached in the work of Ya.M. Kolotyrkin and A.N. Frumkin on the laws governing the dissolution of lead and nickel in acids. It was found that the corrosion rate determined from the volume of hydrogen evolved agreed quantitatively with that calculated from electrochemical measurements. Thus it was shown for the first time that not only amalgams but also solid metals dissolved in full agreement with the laws of electrochemical kinetics.

Further advances in the development of corrosion theory are decidedly associated with the separate study (of the kinetics and mechanism) of the cathodic and anodic reactions.

In research carried out by N.D. Tomashov, A.I. Krasil'shchikov, V.S. Bagotskii, L.I. Antropov, and A.S. Afanas'ev, special attention was devoted to studying the reaction of oxygen reduction. Fundamental kinetic laws were established for this reaction on different metals, and it was shown that, depending on the conditions (electrode potential, nature of the metal, pH of the medium), the final product of the reaction might be either H_2O or H_2O_2. The main credit in using these laws in order to explain corrosion processes involving oxygen depolarization belongs to N.D. Tomashov. Starting from the theory of local cells, Tomashov made a detailed study of the influence of the size, shape, and arrangement of the electrodes of a corrosion pair (couple) on the efficiency of the operation of the cathode. It was further shown that, on allowing for the subsidiary modes of access available to the oxygen, a quantitative theory relating the rate of oxygen reduction to the size of the cathode and the thickness of the diffusion layer could be developed, and the fact that cathodic impurities in the metal had only a slight effect on the rate of a corrosion process involving oxygen depolarization could be explained.

As a further development of this work, the reduction of oxygen on the surface of a metal covered with a thin film of moisture was studied (i.e., under conditions arising during the atmospheric corrosion of metals). Tomashov showed that, owing to the increased transport of oxygen in very thin (adsorption) films, the velocity of the cathodic process in such conditions was very high compared with the ordinary conditions of corrosion in electrolyte solutions. This amounts to saying that the corrosion process as a

whole becomes limited by the velocity of the anodic reaction, which in its turn may be retarded by passivation. On the basis of these results, N.D. Tomashov explained the increased stability of copper steel in the atmosphere, the passivation of which is promoted by both the increased velocity of the cathodic reaction in thin films of moisture and the precipitation of metallic copper on the surface of the steel itself. For understanding the corrosion mechanism of these steels the work of V.V. Skorchelleti and T.S. Tukachinskii is of special importance; these workers indicated the prime importance of the adsorption properties of the corrosion products in the formation and maintenance of the film of moisture on the surface of the metal. The considerable influence of the products of atmospheric corrosion on the corrosion and electrochemical behavior of metals was also established by G.B. Klark and G.K. Berukshtis. Analyzing the results of Soviet corrosion stations, these workers found a quantitative relationship between the rate of atmospheric corrosion and the meteorological conditions determining the period spent by the metal under liquid-drop films of moisture.

I.L. Rozenfel'd and his colleagues developed fine methods of electrochemical measurements under a film of moisture of adjustable thickness. As a result of these investigations, it was shown that the transport of oxygen to the surface of the metal remained the main factor determining the rate of atmospheric corrosion, both in neutral and acid media. A convection mechanism was observed in the transport of oxygen through thin films; this arose as a result of the self-agitation of the electrolyte under the influence of differences of surface tension in different parts of the film. It was shown, however, that, if the thickness of the film were reduced too much, the convection-diffusion mechanism became purely diffusion. In experiments with large-scale models of corrosion cells covered with a film of moisture, large potential gradients, arising as a result of ohmic resistances and leading to a considerable localization of the corrosion process, were observed. When studying the influence of SO_2 impurities in the atmosphere, it was found that the acceleration of the corrosion process observed in this was associated not so much with the acidification of the moisture film as with the direct reduction of the SO_2 dissolution products.

The study of the laws of oxygen reduction in various conditions was also extremely useful in understanding the corrosion of metals in soils. N.D. Tomashov and Yu.M. Mikhailovskii showed that under these conditions the corrosion of metal was limited mainly by the transport of oxygen, the velocity of which depended very greatly on the composition, structure, and moisture content of the solid and might vary by one order of magnitude. The nonuniform access of oxygen to different parts of a metal construction, leading to the development of corrosion pairs of differential aeration, is frequently the cause of soil corrosion. The study of the kinetics and mechanism of oxygen reduction was also of great significance in understanding the laws of metal corrosion in sea water. Of the research work directly relating to this field, we must mention that of V.F. Negreev, who established, as a result of long tests, that the maximum corrosion rate occurred in the zone of periodic wetting at about 0.5 m above sea level. This conclusion was extremely important in developing methods of protecting the bases of metal structures in the marine oil installations of the Caspian sea. L.A. Suprun carried out some important investigations on determining the effect of the rate of flow on the corrosion of steel in sea water. In recent years I.L. Rozenfel'd has determined the coefficients for converting the results of laboratory experiments with a rotating disc electrode to the case of full-size ships (disc velocity to the velocity of the ship).

One of the main methods of combating the corrosion of metals in soils and sea water is cathodic protection in one of its many forms. In the development of this method, an important part was played by G.V. Akimov and I.N. Frantsevich, A.F. Lunev, K.K. Nikol'skii, V.L. Pritul, L.A. Suprun, V.V. Krasnoyarskii, Yu.Ya. Iossel', and others.

Another important depolarizing reaction, the evolution of hydrogen, was studied in detail by A.N. Frumkin and colleagues. A.V. Durdin, Ya.M. Kolotyrkin, L I. Antropov, and A.Ya. Shatalov showed that a knowledge of the kinetic laws of this reaction offered a quantitative explanation for the observed relationship between the corrosion rate and stationary potential of many metals and the pH of the solution.

Important advances have been achieved in studying the kinetics and mechanism of the anodic reaction, the ionization (or oxidation) of the metal atoms. Work of Ya.M. Kolotyrkin, B.N. Kabanov, Z.A. Iofa, G.S. Vozdvizhenskii, N.D. Tomashov, and others has established the manner in which the rate of this reaction depends on the potential for many metals and alloys under various conditions. These data constitute, in particular, the basis for a quantitative calculation of the cathodic protection required to prevent corrosion in metal constructions.

In connection with the solution of practical problems principally associated with the correct choice of construction materials for the specific working conditions encountered, a great deal of attention has been devoted to studying the rate of the anodic reaction as a function of the composition of the solution. The results and laws thus obtained have led to important conclusions regarding the role of the solution components, chiefly the anions of the electrolyte, in the process of ionizing the metal atoms.

It was considered for a long time that the elementary acts of anodic dissolution involved the formation of simple ions of the metal, and that the participation of the solution components, and especially the anions of the electrolyte, should be considered as the result of their subsequent interaction with these simple ions. Research proved, however, that this was an incorrect view and that the dissolution of metals took place, as a rule, with the formation of a complex between the metal and the anions or other components of the solution in the actual electrochemical stage. This gave rise to the concept of the dissolution of metals by a complexing mechanism. However, it was shown in subsequent research work that this mechanism was not the only one possible, and that the direct participation of anions in the anodic process could also occur when the final product was not a set of complexes but simple metal ions or the hydrolysis products of these. Such a participation of the anions in the electrochemical stage of the process may amount to the formation of an intermediate complex which then decomposes.

Principal credit in the development and establishment of these ideas belongs to Soviet scientists. Studying the dissolution of iron in alkalis, B.N. Kabanov and D. Leikis were the first to conclude that $OH^{'}$ ions played a direct part in the first stage of the anodic reaction. B.V. Érshler observed an accelerating effect of chlorine ions ($Cl^{'}$) on the anodic dissolution of platinum in acid solutions. Systematic data relating to the influence of anions were obtained by Ya.M. Kolotyrkin and colleagues when studying the kinetics of the dissolution of cadmium, iron, nickel, indium, bismuth, and the amalgams of the latter two metals in acid solutions of electrolytes. The specific nature of this effect was particularly noted, i.e., the magnitude and even the sign of the effect observed (the change in the velocity of the reaction) depended both on the nature of the actual anion and the nature of the metal. It was shown on the basis of kinetic and adsorption measurements that the influence of the anions on the anodic process was associated with their specific adsorption on the metal surface, which preceded the actual electrochemical stage.

It has often been suggested in the literature that the dissolution of metals giving multivalent cations may be effected through the formation of intermediate particles of lower valence. However, this mechanism was first unequivocally established by V.V. Losev when studying the kinetics of the dissolution of indium in acid electrolyte solution. It was shown by electrochemical and radiochemical methods that the first stage in the dissolution of this metal was the formation of univalent ions, the subsequent oxidation of which to the stable state was effected both electrochemically (on the surface of the metal) and chemically, i.e., by direct interaction with hydrogen ions of the solution. The existence of this latter reaction explains the frequently-observed phenomenon of the increased evolution of hydrogen during the anodic polarization of the metal, which is commonly called the "negative difference" effect.

Thanks to the successful development of electrochemical theory in science, the conviction has gradually developed that, in all practically important cases of corrosion in electrolyte solutions, the electrochemical mechanism of the dissolution of metals is not only the most likely but the only one possible. In recent years, however, it has been established that this view is erroneous; Ya.M. Kolotyrkin and G.M. Florianovich showed that iron, chromium, and chromium steel as well as manganese dissolved mainly by a chemical mechanism under certain conditions in acid electrolyte solutions (i.e., by ionization of the metal atom and reduction of the oxidizing component of the solution in one stage), and established the conditions promoting chemical corrosion. Analogous results were obtained by A.N. Frumkin for amalgams of alkali metals and V.I. Veselovskiĭ for silicon in alkali solutions.

Under certain conditions, metals may pass into a passive state, which is characterized by a relatively low velocity of the anodic reaction. This phenomenon is of enormous importance in practice, since it is solely responsible for the fact that many construction metals and alloys have a relatively satisfactory corrosion resistance. For this reason the study of passivity has always remained a center of attention for research workers, who regard this phenomenon as a most important part of the general theory of corrosion resistance.

Ideas on the nature of the passive stage might until recently have been divided into two sharply delimited points of view.

The first was set forward a long time ago and has developed since the 20's mainly on the basis of various physical methods of studying surfaces; it associates the retardation of the anodic reaction with the formation of a poorly-soluble oxide film on the metal surface; the film insulates the metal from direct contact with the aggressive medium in a purely mechanical way. The development of this theory in the Soviet Union is associated primarily with the names of V.A. Kistyakovskii, A.V. Krotov, P.D. Dankov, N.A. Izgaryshev, G.V. Akimov, L.K. Lepin', and others. In recent years a great contribution to the establishment of this principle has been made by A.M. Sukhotin, who observed a definite similarity in the behavior of a number of passive metals and their oxides. Almost obligatory from this point of view is the idea of the oxide film as an independent, homogeneous phase, which is capable of cathodic reduction, but at the potentials of the passive state may only send its ions into solution as a result of purely chemical dissolution. It is this dissolution which creates the conditions for the subsequent electrochemical formation of the oxide on minute exposed parts of the metal, or these may be formed by the oppositely-directed diffusion and electric-transport flow of metal and oxygen ions through a thin film already existing on the surface.

The second point of view (differing in principle from the first) was set forward and established mainly by Soviet research workers (B.V. Érshler, B.N. Kabanov, Ya.M. Kolotyrkin, and A.I. Krasil'shchikov); it arose as a result of refined research into the electrochemical behavior of corroding metals. This theory associates passivation with the specific adsorption (chemisorption) of oxygen, which impedes anodic ionization and the dissolution of surface metal atoms, either as a result of the saturation of their free valences, or as a result of the creation of a surface potential jump, making the difference of potentials in the ionic double layer less positive. It is usually considered that the amount of passivating adsorbed oxygen may fluctuate within the limits of one monolayer.

The impossibility of satisfactorily explaining all the known cases of passivity by using just one of these theories has for a long time compelled research workers to separate the cases of "phase" and "adsorption" passivity, or sometimes to propose an additive combination of the two mechanisms simultaneously (N.D. Tomashov). In recent years the work of Soviet (V.M. Novakovskii) and other scientists has drawn attention to the fact that the final transfer of the surface cation into solution does not cease being an electrochemical act simply because the outer layers of the metal lattice are replaced by oxides. This opens the possibility of organically uniting many well-known elements of electric-field theory and the transport of ions and electrons in growing oxide films with elements of the theory of electrochemical kinetics, and, generalizing the principal kinetic concepts of the adsorption theory of passivity, to use these in order to explain the action of thicker surface oxide films also (these also reduce the electrochemical potential of the surface cations as a result of the strengthening of the chemical bonds and a fall of electric potential in the oxide layer).

Although these investigations have not yet led to a complete understanding of the nature of the passive state, the facts and laws established enable us to use this phenomenon intelligently in combating corrosion in technology.

One of the oldest methods of increasing the resistance of a metal to corrosion is the chemical treatment of its surface in order to create specially strong oxide and other films having a passivating action (tinting, phosphating, etc., methods of chemical oxidation). The most significant contributions in this field were the theoretical and practical research investigations of P.I. Pryanishnikov, A.G. Samartsev, I.V. Krotov, G.M. Badal'yan, and others.

Electrochemical methods of oxidizing metals are widely used at the present time; in the development of these, great credit goes to G.V. Akimov, N.D. Tomashov, M.A. Timonova, A.V. Shreider, A.I. Golubev, and others.

A method of introducing special oxidizing pigments and additives into paints in order to create favorable conditions for the passivation of metals under paint coatings has been studied and developed by V.V. Chebotarevskii, L.V. Nitsberg, I.L. Rozenfel'd, and others.

The increased capacity of a metal to become passivated on alloying has always been considered as being one way of creating corrosion-resistant construction metals. Mainly guided by this principle, G.V. Akimov turned his attention on the way in which the properties and structure of passivating films depended on the composition and structure of the alloy itself. This idea was formulated most clearly by A.I. Shultin and V.V. Skorchelletti, who were the first to show that "ennobling" the potential of a metal (making it more

positive) by alloying with more electropositive components and creating a structure promoting self-passivation were necessary conditions for the creation of chemically-stable alloys. V.V. Skorchelletti also showed that the heterogeneity of an alloy was not an absolute sign of its low corrosion resistance. In this connection we should mention the work of V.N. Lapin, N.G. Gudtsov, S.G. Vedenkin, and V.V. Ipat'ev, who showed that small quantities of Cr, Ni, Cu, and P increased the corrosion resistance of steel by a factor of two or three. A further development of these ideas is the method of alloying passivating metals by the so-called cathodic additives of platinum and palladium, proposed by N.D. Tomashov. In the creation of new corrosion-resistant alloys, great credit also belongs to V.P. Batrakov, A.A. Babakov, A.A. Bochvar, F.F. Khimushin, N.F. Tavadze, I.I. Kornilov, and many others.

Another way of using the phenomenon of passivity in order to raise the resistance of a metal consists of the artifical maintenance of its potential at a level ensuring passivation in the surrounding medium. This is the basis for the anodic protection of metal apparatus in nonoxidizing or weakly-oxidizing media, first tested in practice by V.M. Novakovskii at the beginning of the 50's and developed in work of N.D. Tomashov and colleagues, Ya.M. Kolotyrkin and colleagues, and others. In order to avoid too high positive potentials, leading to overpassivation of the metals (discovered by G.V. Akimov, M. Kurtepov, and V.P. Batrakov for stainless steel in very concentrated nitric acid), the basis of the protector and cathodic protection of alloys liable to overpassivation in especially oxidizing media was proposed by V.P. Batrakov.

The possibility of using and perfecting all such methods of protection has become particularly important in recent years, when the potentiostatic method has enabled the relationship between the rate of an anodic reaction and the potential to be followed both in the region of active dissolution and in the regions of passivation and overpassivation.

These investigations made it possible for the first time to make a full estimate of the part played by the electrode potential in establishing and maintaining the passive state, to discover the principal laws governing these processes, and determine the critical potentials corresponding to the onset and breakdown of passivity in various metals and alloys and also in their structural components under various conditions. The role of oxidizing agents was established for particular cases, and it was shown that there was no difference in principle between the anodic and chemical passivation of metals in solutions of electrolytes (Ya. M. Kolotyrkin). Largely due to the efforts of Soviet scientists, a convincing demonstration was given of the electrochemical nature of pitting corrosion, which arises at a very specific critical potential as a result of competition between passivating and activating anions; some important laws governing the influence of external electrochemical factors and various alloying elements on the development of this process were discovered (Ya.M. Kolotyrkin, I.L. Rozenfel'd, N.D. Tomashov, V.P. Batrakov, V.M. Novakovskii, and others). The theory of structural corrosion (V.P. Batrakov, I.K. Marshakov, A.I. Golubev, and others) and the theory of the corrosion cracking of chemically-stable and high-strength steels under stress (A.V. Ryabchenkov, V.V. Romanov, V.V. Gerasimov, F.F. Azhogin, S.G. Vedenkin, N.P. Zhuk, and others) are also being developed. Very recently, a new branch of corrosion science has arisen; this is devoted to the behavior of corrosion systems under conditions of radioactive irradiation. Soviet science owes the vast store of data obtained and the first theoretical conclusions and generalizations made in this field to the work of A.V. Byalobzheskii, V.V. Gerasimov, I.L. Rozenfel'd, and Ya.M. Kolotyrkin, together with their colleagues.

In addition to the creation of a theoretical basis for electrical protection and the considerable expansion of the prospects of using this for maintaining full passivity of a metal by means of an adjustable potential, these investigations also indicate new possibilities of raising the intrinsic corrosion-resistance of alloys by more efficient alloying.

In the practice of protecting metals from corrosion, wide use has been made of inhibitors or special additives to the corroding medium; even a very small amount of these greatly retards the corrosion process. Soviet scientists have devoted special attention to studying the mechanism underlying the action of such additives; theoretical work has been carried out on a background of wide experimental investigation, which has led to the creation of a whole series of efficient inhibitors for acid and atmospheric corrosion, many of which are being successfully employed in industry and technology. The main achievements in this direction are associated with the work of L.I. Antropov, S.A. Balezin, V.P. Barannik, Z.A. Iofa, V.F. Negreev, I.N. Putilova, and I.L. Rozenfel'd.

Correlation of the experimental results has in a number of cases enabled important conclusions to be drawn regarding the relationship between the inhibiting effect and the composition of the corrosive medium

or the conditions under which the corrosion process is taking place. In this connection we must mention, for example, the observation of S.A. Balezin regarding the dependence of the inhibiting effect on temperature, and also the observation of V.P. Barannik on the mutual influence of different inhibitors when used at the same time.

The work of Soviet and other scientists has convincingly shown that, in the overwhelming majority of cases the action of inhibitors is due to their adsorption on the metal surface, which results in either the screening of the surface or the suppression of one of the reactions (cathodic or anodic). Basing their considerations on these principles and the achievements of contemporary electrochemistry, L.I. Antropov and Z.A. Iofa were the first to propose taking account of the sign and magnitude of the charge on the surface of the corroding metal when seeking and studying inhibitors. L.I. Antropov subsequently showed that this approach and the use of his own scale of potentials made it possible to foresee which type of particles would most probably be adsorbed on the metal surface and thus influence the corrosion process. Antropov also proposed a reasonable classification of inhibitors, taking account of their adsorption properties, and also noting the possibility of converting an inhibitor into an activator on passing from one metal to another, in view of the different probabilities of the surface protonization of the inhibitor particles on different metals. These investigations constituted a prerequisite for the rational choice and synthesis of corrosion inhibitors for applying to specific corrosion conditions.

The wide research of I.L. Rozenfel'd and his colleagues on the choice and synthesis of atmospheric-corrosion inhibitors led to some important conclusions regarding the relationship between the inhibiting effect and the structure of the inhibitor molecules.

A special place among methods of protecting metals from corrosion is reserved for the coating of an easily-corroded metal with a thin continuous layer of another metal or alloy, which by its nature is not susceptible to corrosion under the operating conditions envisaged.

Most favored at the present time in this respect is the galvanic method of depositing metal coatings, the development of which has been especially promoted in the Soviet Union by N.T. Kudryavtsev, V.I. Lainer, Yu.Yu. Matulis, and A.T. Vagramyan with their colleagues.

The highly-advantageous method of chemical nickel-plating has been deeply studied and improved by K.M. Gorbunova and A.V. Ryabchenkov.

N.S. Gorbunov has devoted a great deal of research to the development and perfection of the thermodiffusion method of applying coatings, especially those of the heat-resistant type.

Soviet scientists have made a considerable contribution to the theory of the oxidation of metals and alloys by dry gases (gas corrosion). One of the leading achievements in this respect was the crystallochemical theory (developed by P.D. Dankov) of the first stages of oxidation, the characteristics of which were explained for the first time on the basis of an orientational and spatial correspondence between the crystal lattices of the metal and the oxide. Starting from the fact that the number of defects in the film through which metal ions diffuse to the oxide/gas interface diminishes with time, Dankov also explained the formation of oxide films of limiting thickness. The work of R.Kh. Burshtein and colleagues is very important for understanding the mechanism underlying the first stages of oxidation; Burshtein established a relationship between the depth of oxidation and variations in the electron work function. Wide acclaim has been given to the investigations of V.I. Arkharov, devoted to the establishment of a detailed relationship between the mechanism underlying the oxidation of iron and the structure of the surface scale. According to Arkharov's theory of heat resistance, which has been well supported by many experimental results, alloying should prevent the formation of the wüstite phase and lead to the formation of an oxide of the spinel type with as low a lattice constant as possible. This principle was successfully applied in the theory of the oxidation of Ni–Cr alloys developed by P.D. Dankov and later by D.V. Ignatov, and in the theory of the oxidation of Fe–Cr–Al alloys developed by I.I. Kornilov, who also showed the necessity of taking due account of chemical reactions between components of the alloy and the oxide film. An important part in the development of ideas regarding the processes underlying the oxidation of metals and alloys was played by the work of N.A. Shishakov, A.A. Smirnov, N.P. Zhuk, I.N. Frantsevich, and a number of other Soviet scientists.

As indicated earlier, the development of these fundamental ideas stimulated the creation of practical methods and approaches in combating corrosion in various fields of industry and technology. In this connection we must mention the fruitful labors of A.M. Sukhotin, I.Ya. Klinov, T.N. Sharonova, F A. Orlova,

A.V. Turkovskaya, G.L. Shvarts, I.I. Bulygin, A.L. Labutin, M.L. Rutkovskii, A.V. Shreider (chemical and petrochemical industry), S.G. Vedenkin (rail transport), A.V. Ryabchenkov (heavy machine construction), P.A. Akol'zin (electrical stations), I.Ya. Bogorad, B.V. Strokan, I.A. Stepanov (marine transport), I.V. Strizhevskii (communal economy), A.M. Zinevich, V.I. Glaskov, V.G. Kotik (gas and oil lines), A.F. Luneva, and K.K. Nikol'skii (telecommunications).

In enumerating the advances made by Soviet corrosion experts up to the fiftieth anniversary of the Great October Socialist Revolution, we must not forget the problems still remaining.

The growth of scientific and practical knowledge, the appearance of new corrosion-resistant materials and methods of protection, and especially the general industrial adoption of these, by no means always keep up with the tempo of developing industry and technology. In the course of such development there is a continuous increase in the strictness and variety of the demands made on these; in order to meet these demands we require further perfection of theory, opening the way to the controlled development of new corrosion-resistant materials, and the rational selection of these materials for specific conditions of use, and finally the creation of new more effective and economically-viable methods of protection. An important condition for future progress, in our view, is the further improvement of experimental techniques and the more complete and effective employment of developments in neighboring sciences. No less important are the problems of improving and standardizing methods of corrosion testing, the universal establishment and perfection of anti-corrosion protection in industrial undertakings, and the extension of the industry manufacturing the means of anti-corrosion protection, auxiliary materials, and equipment.

The Soviet Union, the first socialist state in the whole world, is entering the second fifty years of its existence. The next task in the coming half century, as formulated in the resolutions of the twenty-third congress of the Communist Party of the Soviet Union, is the creation of a material-technical basis for communism. There is no doubt that in fulfilling this task Soviet corrosion scientists will play a worthy part.