ELECTROCHEMICAL ASPECTS OF THE CORROSION OF METALS*

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Questions of the influence of excess phases, nonmetallic inclusions, and impurity elements in metals and alloys on their electrochemical characteristics and stability to various types of corrosion in electrolytic media are discussed. It is concluded that an important role in the corrosion of metallic materials is played by their surface heterogeneity, segregation of the components of the alloys and impurity elements along the grain boundaries, and the selectivity of the dissolution of the alloys. The interrelationship of the corrosion and electrochemical characteristics of heterogeneous metallic materials and the promise of the scientific line associated with the study of the electrochemistry of soluble heterogeneous metallic surfaces is emphasized.

Among the allied divisions of physicochemical science, which widely and fruitfully utilize electrochemical methods and approaches, an important place is occupied by the science of corrosion and anticorrosion protection of metals. Although the problem of corrosion is not new, its significance has increased continuously during recent decades, and recently in all the industrial countries it has been one of the most important problems for the national economy [1-7]. This is due to a substantial degree to the fact that now, i.e., under the conditions of the scientific and technical revolution, the provision for a rapidly developing industry and technology of construction materials with increased chemical stability has become one of the most important problems of technical progress.

The importance of the problem is due to no less a degree to the large extent of the losses from corrosion, which in all the industrial countries have become comparable with the expenditures for the development of large branches of industry. According to recently published data, for example, at the present time the total losses from corrosion are estimated at: in the United States 15 billion dollars [5], in the German Federal Republic 7 billion marks [6], and in England 1 billion 365 million pounds sterling, which is equivalent to 3.5% of the gross national product [7].

The importance of the problem of control of corrosion has not always been promptly recognized. However, as corrosion losses have increased, it has become increasingly evident that enormous expenditures for the development of industry may prove ineffective if at the same time effective measures are not taken to prolong the service period of the metal produced, which still remains the basic construction material in industry, transport, and even in building construction.

At the present time, in all the industrial countries, a broad network of corrosion laboratories, testing stations, and anticorrosion services at the enterprises is in operation. In certain countries national institutes and centers for corrosion work have been organized.

The joint efforts of corrosion specialists, metallurgists, and chemists in recent years have achieved great successes in the development and application of effective methods and means of protection from corrosion. In all the industrialized countries, an industry producing these facilities and equipment for protection has been created.

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These and many other practical achievements have been the consequence of the successes of corrosion science, in the formation and development of which an important role has been played by electrochemical science. The influence of the Soviet electrochemical school has been especially fruitful; it has rendered great service in the formation of the modern electrochemical theory of corrosion, with the appearance of which, as is well known, broad possibilities for the fruitful use of electrochemical methods and approaches both for the investigation of corrosion processes and for the improvement of methods of protection, have been opened up [8-11].

Under the influence of the demands of developing technology, the level of requirements for corrosion science changes continuously, which leads to a change in the science itself. Such changes have become especially perceptible in recent years, chiefly after it has been clearly revealed that many construction alloys exhibit an increased tendency for structural or local forms of corrosion, such as corrosion cracking, intercrystallite corrosion, pitting, knifeline, and crevice corrosion. The search for reliable methods and means of control of these types of corrosion, accompanied by a substantial increase in the experimental and theoretical level of all corrosion investigations, has revealed the need for concentrating the main attention on the detection of the role of structural factors. And since all structural factors of corrosion proved to be sensitive to electrochemical parameters of the system and, in particular, to the value of the electrode potential of the corroding metal, new problems also have arisen for electrochemistry.

From the standpoint of chemical kinetics, the processes of corrosion of metals should unquestionably be classed among the heterogeneous chemical processes. However, it is important that in this case the surface of a solid is not only a catalyst for redox conversions of the components of the liquid or gas phase, as is the case in heterogeneous catalysis or in many electrochemical conversions, but itself is a participant in the reaction, i.e., undergoes oxidation and decomposition. Insofar as we know, this type of reaction thus far has not been considered within the framework of the general theory of chemical kinetics, although it is of great interest primarily from the standpoint of the development of a general theory of chemical stability of metallic surfaces.

The kinetic analysis of such processes proves to be simple and leads to comparatively simple relationships only in the case when the material has one component and one phase, while the reacting solid surface is homogeneous. If the aggressive medium is a solution of an electrolyte and the corrosion process occurs according to an electrochemical mechanism, then the equations of electrochemical kinetics, the constants of which can be reliably estimated from polarization and analytical measurements [10, 11], are applicable not only for the description of the process as a whole, but also for the estimation of its rate at all stages of the process.

However, in practice, as a rule, we must deal with construction materials of technical purity, the surface of which already is distinguished by the great heterogeneity on account of the polycrystalline and multiphase nature of the material.

The influence of the degree of surface heterogeneity on the chemical stability of a surface can be judged according to the data of Fig. 1, which presents curves characterizing the dependence of the equilibrium rate of dissolution on the potential for quenched and tempered samples of steel of the same composition [12]. It is known that in the case of quenching from a sufficiently high temperature, a solid solution acquires the most homogeneous structure, whereas slow cooling or exposure at lower temperatures leads to the liberation of excess phases of various compositions. The lower stability of the tempered sample observed in this case is due to the formation of chromium-poor boundary zones as a result of the liberation of chromium carbides. This dehomogenization of the structure provides for the development of intercrystallite corrosion.

At first glance it might seem that the reactivity of a heterogeneous surface should be determined by the reactivity of the phase structural components of the material and that, consequently, in this case no special problems can arise, and the problem should be reduced only to a sufficiently reliable determination of the phase composition of the material and a separate estimation of the reactivity of each of the phases.

An analysis of the numerous data available shows, however, that actually the situation is substantially more complicated, and that in the evaluation of the reactivity of the surface of a material with a multiphase structure, the principle of additivity is far from always applicable. However, frequently a direct or indirect mutual influence of the phases is observed, and sometimes cases when, depending on

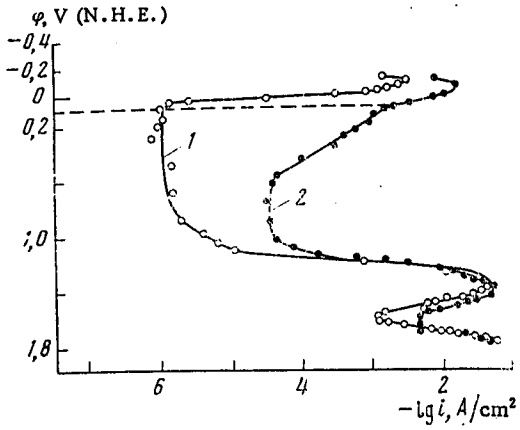

Fig. 1. Anodic potentiostatic curves for the steel Cr18Ni5Mn10 (0.13% C) in 1 N H_2SO_4, 70°: 1) quenching from 1100°, cooling in water; 2) quenching from 1100° but tempering at 650°, 2 h.

the conditions, the same structural component of the material may either increase or decrease the reactivity of the basic phase and thereby change the chemical stability of the entire surface.

The situation is very greatly complicated by the fact that the composition of the surface layer of the corroding metal does not remain constant with time. As a rule, especially when we must deal with construction alloys, the composition of the surface layer under conditions of an equilibrium corrosion process differs very greatly from the initial composition.

From all the aforementioned it follows that the electrochemistry of dissolving metallic surfaces, and especially of heterogeneous surfaces, which has begun to be formed into an independent division of electrochemistry during the last decade, merits especially fixed attention, since fruitful approaches to the creation of new corrosion-resistant metallic material and effective methods of modification of metallic surfaces can be found along this way.

In the very earliest studies, it was already shown [13] that not only homogeneous, but also known heterogeneous metallic surfaces corrode in full agreement with the principles of electrochemical kinetics, and that electrochemical methods can also be successfully used to determine the general principles of the corrosion process in this case. However, using these methods it has proved to be impossible to solve such problems as the determination of the degree of localization of the corrosion process over the surface, the elucidation of the role of individual structural components of the material in the origin and development of local forms of corrosion, and the change in the composition and state of the surface layer with time, i.e., questions that should constitute the basis of the electrochemistry of dissolving heterogeneous metallic surfaces.

To solve these and many other problems, in recent years electrochemical methods have been used in conjunction with other physicochemical and physical methods, including various variations of the method of labeled atoms, auger and electron spectroscopy, x-ray and nuclear microanalysis, ellipsometry, and a number of other methods.

The investigations conducted have already permitted, in particular, the accumulation of extensive factual material, characterizing the electrochemical properties and behavior of a whole series of individual metal-like compounds of the type of carbides, nitrides, or intermetallic compounds, which usually are present in steels and certain other construction alloys in the form of the so-called excess phases [14]. In conjunction with the results of other investigations, these data have permitted an understanding and evaluation of the nature and mechanism of the influence of the indicated phases on the chemical stability of the corresponding materials. We shall limit ourselves to one example on account of lack of time.

It is known that one of the methods now used to control intercrystallite corrosion of stainless steel in weakly acidic media is their stabilization with small quantities of titanium or niobium. The use of steels stabilized with niobium has shown, however, that they are distinguished from the original steels not only by high resistance to intercrystallite corrosion in weakly acidic media, but also by an increased ability for spontaneous passivation in aggressive media, appreciably lower stability in strongly oxidizing media, and a distinct tendency for knifeline corrosion.

Investigations conducted in recent years in our laboratory have shown that the causes of such differences lie in the electrochemical properties of titanium carbide. This is easily ascertained if we compare the curves characterizing the dependence of the rate of dissolution on the potential for steel stabilized with titanium and titanium carbides (Fig. 2) [14, 15].

At potentials lying more negative than 0.5 V, i.e., in the region corresponding to the corrosion potentials of steel in reducing and weakly oxidizing media, titanium carbide possesses high stability and dissolved at a significantly lower rate than steel. Consequently, the corrosion of steel in the indicated media should be accompanied and, as was shown by special investigations, actually is accompanied by an accumulation of titanium carbide on its surface. This naturally leads to some hindrance to access of the aggressive

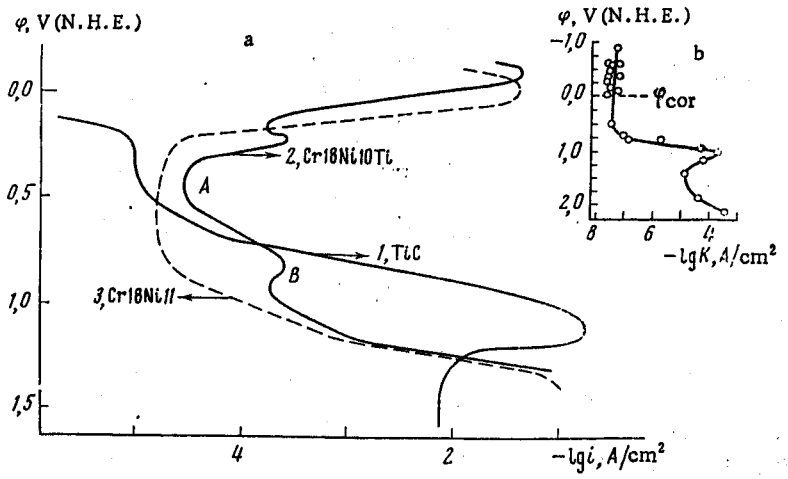

Fig. 2. Comparision of the corrosion-electrochemical behavior of stainless steels of the Cr18Ni10 type and titanium carbide: a) anodic potentiodynamic curves (1 V/h) for steel 03Cr18Ni11 (3), Cr18Ni10Ti (2), and titanium carbide (1) in boiling 3.4 N H_2SO_4; b) dependence of the equilibrium rate of corrosion of titanium carbide on the potential in 1 N H_2SO_4 at 22°.

solution to the surface of steel and a certain decrease in the rate of its dissolution. However, it proved more important that titanium carbide is characterized by a low overvoltage of the liberation of hydrogen. As a result, its accumulation on the surface of steel is accompanied by a substantial increase in the rate of depolarizing cathodic reactions, which in turn causes a shift of the corrosion potential in the positive direction. As a rule, very soon this shift proves to be sufficient for the reaching of the passivation potential, which is responsible for the spontaneous passage of the steel into the passive state, and, consequently, a significant increase in its stability.

More positive than 0.7 V, i.e., precisely in the region of potentials in which steel stabilized by titanium is characterized by reduced stability, titanium carbide begins to dissolve at an appreciable rate, increasing with the potential in accord with the usual Tafel straight line.

The interrelationship of these two phenomena is unquestioned. It is indicated, in particular, by the relative increase in the content of titanium in the products of the dissolution of steel during passage into this region of potentials. A more detailed analysis shows, however, that the rate of dissolution of carbide observed in this case constitutes only a small fraction of the observed increase in the rate of dissolution of steel. From this it follows that the oxidation of carbide is accompanied in this case by an appreciable acceleration of the dissolution of the basic phase. The mechanism of such an acceleration has not yet been established. However, it is suggested that the oxidation of the carbide proceeds with an absorption of oxygen, necessary for the passivation of the adjoining regions of the solid solution.

As for the tendency of titanium-stabilized steel for knifeline corrosion, as has recently been established [14, 16, 36], it is also associated with the dissolution of titanium carbide and is observed under conditions when the carbide precipitates on the grain boundaries, forming unique chain structures there.

From the example cited it follows that the influence of the excess phase on the chemical stability of the material may be very great and that, consequently, by regulating the phase composition, a serious increase in its chemical stability can be achieved.

It is usually assumed that from the standpoint of the chemical stability of a material, the presence of impurities in it, and especially of excess phases, is undesirable in all cases. In the first place, this is not always correct. Under certain conditions alloys containing an increased amount of impurity elements prove to be chemically more stable than the pure alloys [14, 37, 38]. In the second place, high chemical stability is not the only characteristic that is considered in the selection of a construction material for concrete purposes. In certain cases a decrease in the content of impurities is undesirable from the standpoint of the technological and operating properties of the material.

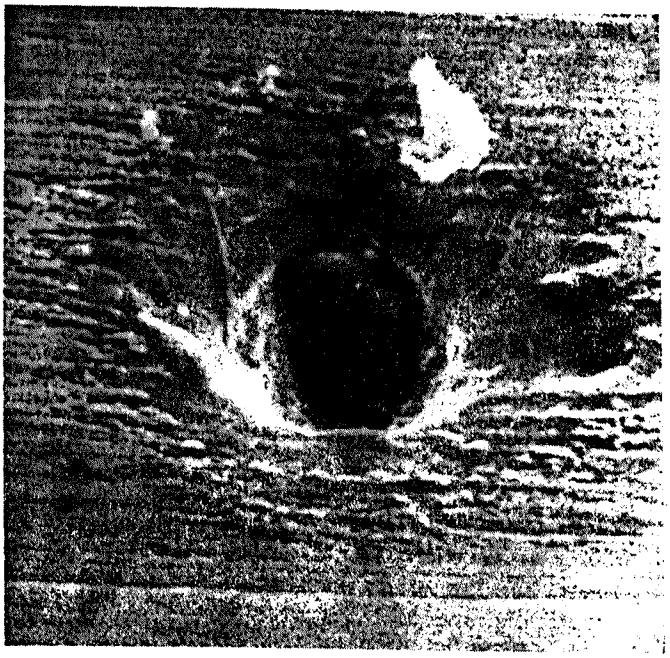

Fig. 3. Pitting formed near a nonmetallic inclusion on the surface of 03Cr17Ni14Si2 steel in galvanostatic anodic polarization ($6 \cdot 10^{-5}$ A/cm^2) in 5 N NaCl at 30°.

The investigations of recent years have shown that many peculiarities of the electrochemical and corrosion behavior of soluble metallic surfaces are due to nonmetallic inclusions (NI), which should be considered as an extremely important structural component of steels and many other metallic construction materials [17-19]. Although the content of most nonmetallic impurities in such materials usually does not exceed hundredths and rarely tenths of a percent, the number of particles of NI determinable may be very large. In the case of low-alloyed and stainless steels, for example, the number of NI calculated per cm^2 of surface usually reaches the order of 10^3.

Although metallurgists and metal scientists, occupied with the search for ways of improving the quality of steels and special alloys, have long been widely investigating the influence of NI on metallic and other physical properties of metals, until recently clearly insufficient attention has been paid to the elucidation of the role of such inclusions in corrosion processes.

Quite recently, important advances have also occurred in the development of this line. The basic conclusion following from the results of the investigations is that the least stable particles of metallic surfaces, as a rule, are the areas in direct contact with NI. As was convincingly shown in the studies of researchers of Poland [20], the German Democratic Republic [21], the USSR [22, 23], Sweden [24], and certain other countries, as a rule, local attack on passive surfaces, leading to the development of pitting corrosion, occurs precisely on these areas. The picture observed in this case is well illustrated by Fig. 3.

Pitting can arise close to NI of different types, although inclusions may differ substantially in their activity in this aspect. In the case of steels, for example, the most dangerous inclusions are complex oxidosulfides [20-23].

As is well known, local depassivation of a metallic surface, leading to the development of pitting corrosion, is manifested electrochemically in the form of a sharp increase in the current of dissolution at some definite potential, depending on the nature of the material and on the nature and concentration of the activating anion. The investigations of recent years have shown, however, that under definite conditions the value of this potential exhibits sensitivity to the nature of the NI as well. As can be seen from Fig. 4, in the presence of NI of various types in the material, not one, but two or more activation regions are detected on the potentiodynamic polarization curve, each of which corresponds to depassivation of the metal for an NI of a definite nature [22]. However, it is important that under these conditions stable depassivation and the development of pitting are observed only for NI of one definite type. Making the testing conditions more rigorous, including an increase in the concentration of the activating anions above a definite

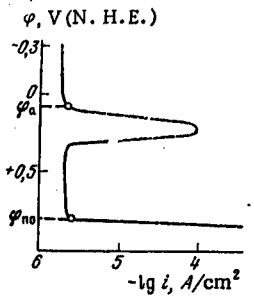

Fig. 4

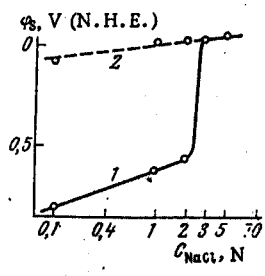

Fig. 5

Fig. 4. Anodic potentiodynamic curves (1.2 V/h) for 03Cr17Ni14Si4 steel in 0.1 N NaCl at 20°. The potentials φ_0 and φ_s correspond to the beginning of unstable and stable local activation of the surface, respectively.

Fig. 5. Dependence of the potentials of stable (1) and unstable (2) local activation of 03Cr17Ni14Si4 steel on the NaCl concentration at 20°.

limit, however, also frequently leads to a change in the centers of pitting formation, which, as can be seen from Fig. 5, is manifested in a sharp displacement of the corresponding potential in the direction of negative values. This figure shows the dependence of the potential of pitting formation for chromium – nickel – silicon steel on the concentration of chloride in solution. It was established by independent methods that the lower branch of this curve corresponds to the development of pitting in monotypic complex inclusions, and the upper portion to that on SiO_2 particles.

These and a whole series of other data indicate the presence of a close relationship between the electrochemical behavior of a metal under conditions of pitting formation and NI. It is suggested that in the future it will be possible to obtain results of great practical significance in this way, and in particular, to find a method of eliminating the decrease in the stability of chromium – nickel – molybdenum steels to pitting corrosion with increasing temperature observed in practice.

An increased rate of dissolution of metal close to an NI is also observed under conditions excluding the possibility of the formation of pitting. As was shown by recent investigations, even in this case such areas can dissolve at a rate two orders of magnitude greater than the rate of dissolution of the remaining surface, which is responsible for the appearance of numerous foci of local dissolution, up to depressions differing little in appearance from the usual pits, but substantially smaller in size [25].

The increased activity of the metal directly adjoining the NI in various cases may be due to various factors, including an increased imperfection of the crystal lattice of the metal close to the inclusion, a depletion of this layer in corrosion-resistant alloying components of the alloy, an activating influence of the dissolution products of the NI itself, and finally, the presence of a gap between the inclusion and the metal.

In concluding this section, we should emphasize that on the whole the situation is considerably more complex than it might seem from all the aforementioned. The presence of an NI in the material, while important, is not the deciding condition for the appearance and development of pitting even in the presence of activating anions. It is known, for example, that technical chromium, which also contains NI, undergoes practically no pitting corrosion in aqueous solutions under the same conditions in which stainless steels undergo pitting corrosion. On the other hand, in a number of investigations it has been shown that pitting also is sometimes detected on high purity metals, which contain practically no NI, and in this case the centers of their appearance are either dislocations, decorated with impurities, or intermetallic phases.

Not only excess phases, but also simple segregation of the components in a solid solution may have a significant influence on the chemical stability of material. The investigations of recent years have shown, for example, that the great sensitivity of the chemical stability and mechanical properties of construction alloys to the presence of negligible amounts of impurity elements in them, observed in practice, is associated precisely with the segregation of such impurities on the grain boundaries, as a result of which the difference between the volume and boundary concentration of impurities may reach enormous values [26-34]. It has been shown, for example, that for a sulfur impurity in iron such a difference reaches four orders of magnitude, i.e., the concentration of impurity sulfur in the boundary layer is 10^4 times greater than its average concentration in the material [28].

Depending on the conditions, many impurities may be segregated on the grain boundary; however, the depth of the layer to which segregation extends differs for different impurities. Judging by the available data, the segregation of antimony and tin extends to no more than 10 atomic layers, whereas the segregation of nickel and chromium extends to thicker layers [27, 29].

Depending on the composition of the aggressive medium, the segregation of the alloying element or impurity on the grain boundaries may lead both to an increase and to a decrease in the chemical stability of the material.

By combining electrochemical methods with Auger spectroscopy, permitting the reliable establishment of the change in the chemical composition of very thin surface layers of metal, it has recently been shown, for example, that the segregation of impurity sulfur along the grain boundaries leads to an appreciable decrease in the chemical stability of austenite stainless steels in strongly oxidizing media [27]. An analogous effect is also exerted by the segregation of nitrogen and phosphorus impurities, whereas the segregation of chromium leads to an appreciable increase in the stability of steels of the same class in weakly oxidizing media. There is some basis for believing that segregation along the grain boundaries and in the surface layers generally lies at the basis of the positive effect from the alloying of stainless steels with molybdenum and silicon, the introduction of which in comparatively small quantities (~3%), as is well known, leads to a substantial stabilization of the passive state and a decrease in the tendency of steels for pitting corrosion in solutions of chlorides.

Judging by the available data, the segregation of impurities along the grain boundaries may have a substantial influence on the mechanical characteristics of the materials as well. It has recently been shown [27], for example, that the so-called tempering brittleness of low-alloyed steels, detected after their heat treatment under definite conditions, is due to segregation of nickel and chromium, the concentration of which in this case is more than doubled in the transition from volume to grain boundaries.

In many cases the segregation of a given component or impurity can be increased or decreased by the presence of other components [27, 33]. It has been established, for example, that the segregation of sulfur is promoted by the presence of carbon in the material, while the segregation of nickel and chromium is promoted by the presence of manganese, silicon, and antimony [29]. There is no doubt that all this opens up real possibilities for a purposeful increase in the chemical stability of construction alloys on account of the regulation of their impurity composition [27].

It seems that, although this trend in the science of chemical stability of construction materials is only in the development stage, its great promise is unquestioned, and precisely here there are great possibilities for the fruitful application of electrochemical approaches and methods of investigation.

It was noted earlier that many peculiarities of the electrochemical behavior of a dissolving metallic surface may be due to a change in its stage during the process of dissolution itself. It is important that the surface of the alloys may undergo a change not only as a result of the predominant dissolution of some phases and accumulation of others on it, but also as a result of the selective dissolution of definite components of the solid solution. Considering that metallic construction materials are primarily alloys, the elucidation of the principles of the selective dissolution of the components of solid solutions is of vital importance for the science of the corrosion of metals.

Unfortunately, on account of methodological difficulties, the possibilities for conducting such investigations have been extremely limited up to recent years. However, modern radiometric methods provide possibilities for the simultaneous determination of the rates of passage of several components of the alloy into solution under conditions when these rates are very low [34, 35]. On the other hand, using the method of x-ray microanalysis and Auger spectroscopy that have appeared in recent years, it is possible to reliably follow the change in the chemical composition of very thin surface layers.

By a combination of these and electrochemical methods, it recently has been convincingly shown [35] that a layer significantly more stable than the layer of the initial composition can be formed on the surface of the alloy in the process of corrosion. This is achieved on account of the fact that in the process of dissolution the surface of the alloy becomes enriched with a component that is the most corrosion-resistant under the given conditions.

The aforementioned is convincingly confirmed by the data obtained in an investigation of the principles of the selective dissolution of a binary iron – chromium alloy with 28% chromium. Figure 6 presents potentiostatic curves characterizing the dependence of the equilibrium rate of dissolution on the potential: for the investigated alloys (curve 1), pure chromium (curve 2), and pure iron (curve 4). The curve 3 cited on the same figure characterizes the change in the coefficient of selectivity for chromium (Z_{Cr}) with the potential. Let us note that this coefficient shows how many times the ratio of the chromium and iron concentrations in the dissolution products differs from the same ratio in the alloy. Consequently, when the coefficient of selectivity exceeds one, selective dissolution of the corresponding component should be observed; otherwise the component should be accumulated on the surface.

From the figure it is evident that in a broad region of polarizations, corresponding to a passive state of the alloy, transition from the active to the passive state and partially to the region of superpassivation,

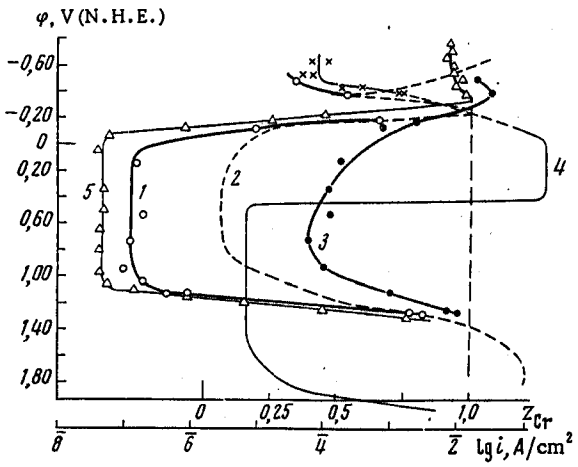

Fig. 6. Comparison of the corrosion-electrical properties of the alloy Fe – Cr28 (1-3), iron (4), and chromium (5) in 1 N H_2SO_4 [35]: 1, 4, 5) dependence of the rate of dissolution on the potential; 2) cathodic and anodic polarization curves (1 V/h); 3) dependence of Z_{Cr} on the potential; 1-3) at the temperature 40°; 4 and 5) at room temperature.

i.e., at all potentials where chromium is more stable than iron, the dissolution of the alloy occurs with predominant passage of iron into solution, and only at potentials corresponding to the active state of the alloy is there a selective dissolution of chromium.

The change in the chemical composition of the surface layer of the alloy during its dissolution can be detected by the method of x-ray microanalysis. This is evidenced by the data of Fig. 7, which shows the distribution of chromium and iron on the surface of the alloy and after its etching at a potential corresponding to the initial portion of the region of superpassivation. The characteristic x-ray spectra of these elements were obtained by scanning an electron beam along the selected direction. The percent content of each element was determined with the aid of a standard sample.

It is evident that the exposure of the alloy in the indicated region of potentials actually leads to an enrichment of the surface with chromium and a depletion of iron. However, such a change in the composition in this case is not detected on the entire surface, but only on individual portions of it, which, as was shown by a special investigation, are in direct contact with nonmetallic inclusions. In full agreement with the aforementioned, this result is evidence that the regions under consideration dissolve at an increased rate, as a result of which a thicker layer of metal is enriched with chromium on them than on the remaining

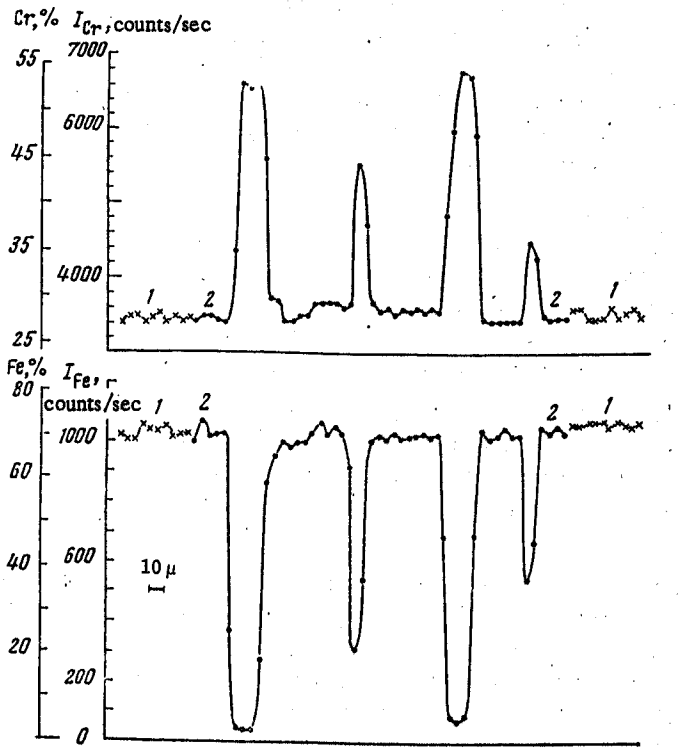

Fig. 7. Distribution of chromium and iron on an unetched surface of the alloy Fe – Cr28 (1) and on individual portions of the surface of this alloy after etching at a potential of 1.15 V for 28.5 h in 1 N H_2SO_4 at 40° (2), measured with an MS-46 microanalyzer.

surface, which dissolves more slowly. However, in the case of a longer exposure, enrichment is also detected on the remainder of the surface.

From this example it follows that an investigation of the principles of the selective dissolution of solid solutions holds great possibilities for corrosion science.

In my report I have attempted to show that the electrochemistry of dissolving heterogeneous metallic surfaces is a difficult but extremely promising and interesting line. I do not know whether I have achieved my goal, but I am convinced that a consideration of the real heterogeneity of solid metallic surfaces is essential not only for corrosion, but also for many purely electrochemical investigations, and that without such a consideration, in particular, the interpretation of the results of many kinetic investigations will remain ambiguous.

Unfortunately, on account of a lack of time, I was unable to take up some other electrochemical aspects of corrosion, such, in particular, as the role of specific adsorption in electrochemical processes of dissolution of metals, processes of passivation and disruption of the passive state, and the inhibition of corrosion by special additives. All these aspects are also of great significance for the further development of the science of corrosion of metals. However, considering the fact that they are considerably more often the subject of discussion, including that at special symposia and conferences, I consider it advisable to emphasize attention on the questions outlined in the report.

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