PROGRESS AND PROBLEMS IN THE THEORY OF CORROSION*

Ya. M. Kolotyrkin

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The author sketches the progress in the most important aspects of the theory of electrochemical corrosion (especially local corrosion), made in the last few decades with the aid of the kinetics of electrode reactions and of combined electrochemical and physical research on surfaces. He analyzes various types of action of technological impurities in metal, either dissolved or segregated at grain boundaries, or forming independent phases. He discusses the laws of selective solution and interaction of the processes of solution, oxidation, and transfer of individual components of an alloy in various types of corrosion in the active and passive states and in relation to the crystal structure and substructure of the metal. He outlines the prospects for further research.

For many centuries the war against corrosion was pursued purely by empirical methods. Protection of metal articles and structures was regarded as a craft, or at best an art, but not a science. This view of the problem lasted a long time. However, as the applications of metals multiplied, it became increasingly obvious that empirical methods alone, even if highly developed, can solve only a limited range of problems. Further progress in this sphere must be based on fundamental research on corrosion processes.

Such research, begun in the 19th century and developed very widely after the Second World War, led to elucidation of the fundamental features of the mechanism and of a number of important laws of corrosion processes.

An important feature of the development of corrosion science in the last few decades has been an increasingly firm rejection of the concept of local cells as a natural basis for the electrochemical theory of corrosion. It was established that the true scientific basis of this theory is the study of electrode processes, including electrode equilibria and the laws of electrode reactions remote from equilibrium [1-7].

In recent years, theoretical and experimental bases have been found for applying the laws of electrochemical kinetics to corrosion processes, and it has been shown that any available way of influencing the kinetics of the cathodic and anodic reactions composing the corrosion process can be used to regulate the rate of corrosion. This stimulated wide research on the kinetics and mechanisms of these reactions and a search for realistic possibilities of controlling their rates, either by modifying the composition of the aggressive medium, or by regulating the composition and structure of the metal.

Attention centered on the mechanism and kinetics of the anodic reaction, which directly characterizes the chemical stability or reactivity of the material.

An important result of the research was the development of the idea that electrochemical reactions of ionization of metal atoms usually include a purely chemical stage [8]. On this basis it was possible to explain why the chemical stability of metallic materials often depends on the nature and concentration of components of the aggressive medium which are not subject to the oxidation–reduction reactions composing the corrosion process [9]. Today there is no doubt that in most cases the transfer of a metal atom to the solution in the form of an ion is preceded by adsorption of, and chemical interaction with, some components of the medium to form a surface complex, and that this chemical stage can influence the rate of the subsequent electrochemical stage and hence the rate of the corrosion process as a whole.

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In many cases adsorption stimulates the oxidation of a metal atom, which goes into solution in the form of a ready-made stable complex with the adsorbed component of the solution, which is often an anion of the electrolyte. In this case the rate of the process is known to be expressible in the form

$$i = k \cdot C_A^m \exp\left(\frac{\beta n F}{RT}\varphi\right),$$

where C_A is the concentration of the active component of the medium.

Since adsorbed components of the solution can not only promote but also inhibit the electrode reactions, the development of these ideas stimulated the use of electrochemical methods to find effective inhibitors and to develop engineering bases for protection of metals from corrosion by artificially modifying the aggressive medium, with paint coatings or greases, or by means of packing materials.

Recent researches have brought us closer to an inderstanding of the difference between promotive and inhibitive adsorption, and in particular have led us to understand why the same component of the medium can promote corrosion in some conditions and inhibit it in others.

Analysis of the results of kinetic and adsorption measurements made in identical conditions has revealed that this difference is entirely due to differences in the strength of the adsorption bond, which can in turn vary with the natures of the metal and adsorbate and with the electrode potential. Inhibition of the solution process is observed when the adsorbed particle is so tightly bound to the metal that it practically loses its link with the solution. On the other hand, for promotion it is necessary that the adsorbed particle shall be equally tightly bound to the metal and solution [10].

These investigations have enabled us to understand why the solution rate can be reduced by adsorption of an inhibitive component in amounts sufficient only for the formation of a few tenths or sometimes even hundredths of a monomolecular layer.

These effects are often attributed to some mechanism whereby the adsorbed particles exert an influence at a distance considerably greater than their own dimensions. However, it seems that they are rather due to the heterogeneity of the surface of a solid metal. On such a surface there are always a certain number of very active centers which in dissolving make the major contribution to the overall rate of the anodic reaction, and on which, therefore, the inhibiting particles are preferentially adsorbed.

Central to corrosion science is the doctrine of passivity of metals. This is because passivity is very important in practice. The hope of understanding the nature of the phenomenon itself and the mechanism and laws of passivation, and of learning how to control these processes and to use them in engineering practice, has stimulated unflagging interest in research on passivity.

The last 25 years have been particularly fruitful in the solutions to these problems. In this period it has been proved that electrochemical methods and approaches can be used to investigate and treat passivation processes [11]. The use of these methods and approaches, especially the potentiostatic method of determining how the anodic solution rate depends on the potential over a wide range of the latter, has enabled us to elucidate the fundamental laws of the behavior of metals in passivation and in the passive state. It was found that the electrode potential has a crucial role in passivation and depassivation of metals; quantitative parameters characterizing the liability of metals and alloys to passivation have been found; and many data have been obtained characterizing the dependence of this liability on the nature of the metal, the composition of the alloy, or the composition and nature of the aggressive medium [12].

It was perhaps these researches which first opened up real possibilities of using passivity phenomena in engineering practice in combatting corrosion of metals, and they may serve as a very clear example of the fruitful influence of fundamental research on practice in the war against corrosion. For example, it has become obvious that the potential dependence of the rate of anodic solution, found by the potentiostatic method, is a very important characteristic of a corrosion system, and determines the useful range of applications of the material. A realistic possibility has appeared for controlling corrosion rates by means of the electrode potential. A new method of electrochemical protection has arisen, and has been given the name of "anodic protection" [13]. A method has been proposed for protecting water-moderated–water-cooled nuclear reactors from corrosion, based on keeping their internal surfaces in the passive state by saturating the coolant with oxygen [14], i.e., by raising the oxidation potential of the medium. It has been shown that the tendency of some metals and alloys to spontaneous passivation in acid media can be increased by alloying them with small extra amounts of metals with low hydrogen-ion discharge overvoltages [15].

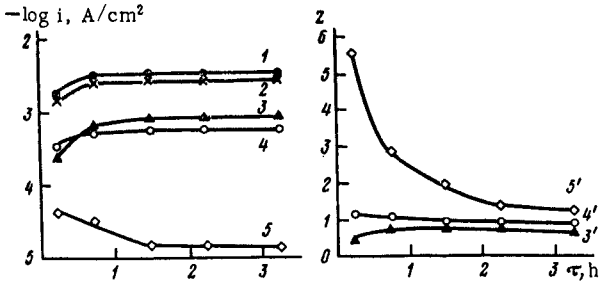

Fig. 1

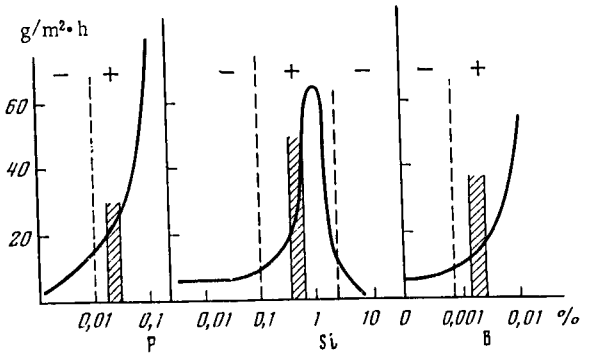

Fig. 2

Fig. 1. Total (1) and partial (2-5) rates of solution of components of hardened steel Cr20Ni20 (0.097% P, 0.003% C), and coefficients of selective solution Z (3'-5') vs anodic etching time in 1 N H_2SO_4 (t = 40°C), at potential of 1.30 V (N.H.E.): 2) Fe; 3, 3') Cr; 4, 4') Ni; 5, 5') P.

Fig. 2. Influence of actual contents of P, Si, and B on tendency of hardened austenitic steel 12Kh18N10T to intercrystallite corrosion in $HNO_3 + Cr^{6+}$ solution. Plus sign means that tendency is present; minus sign means that it is absent.

The results of research on passivity, and especially on the laws governing the resistance of the passive state to the action of the aggressive components of the medium and other external factors, have proved very useful in order to understand the mechanism of local types of corrosion and to find means of combatting them; these types have become particularly injurious in the last decades, mainly owing to the increasing severity of the conditions in which metals are used.

It has been found that most local forms of corrosion are by nature electrochemical, and consequently electrochemical methods can be used to elucidate their general laws.

However, these methods alone have not been able to solve such problems as determination of the character and degree of localization of the process on the surface, elucidation of the roles of individual structural components of a material in the origination and development of local types of corrosion, and alteration of the state of the surface layer of a corroding metal with time – i.e., problems without which it would be meaningless to study the corrosion of metals.

To solve these and many other problems, recently electrochemical methods have been increasingly combined with other physicochemical and physical methods. Thus, to determine the roles of the individual components of an alloy in the origination and development of local forms of corrosion, successful use has been made of gamma spectroscopy, which can determine the rate of solution not only of an alloy as a whole but also of its individual components, including those present as technological impurities [16].

To investigate the composition and state of the surface layers of metals, successful use has been made of Auger spectroscopy [17] and electron spectroscopy, x-ray microanalysis and nuclear microanalysis [18], ellipsometry, and various other methods.

In many cases the combination of these methods has established fundamental relations between the composition and structure of structural alloys, on the one hand, and their corrosion resistance on the other. The examples offered by a number of systems have made it possible to gain the first proper understanding of the role played in the corrosion behavior of an alloy by its components and by technological impurities and various phase structure components. Without exaggeration we can say that these investigations have made a great contribution to that trend in present-day materials science which may be called chemical resistance of materials.

From the results of these investigations it has become obvious that one of the effective ways of increasing the chemical stability of structural metallic materials is to increase their tendency to passivation and to increase the stability of the passive state. This is largely the effect produced by corrosion-resistant additives. For example, it is well known that alloying of iron with chromium causes a reduction in the critical passivation current by more than two orders of magnitude, a reduction in the critical passivation potential by more than 0.7 V, and a reduction in the corrosion rate in the passive state by three or four orders of magnitude [19].

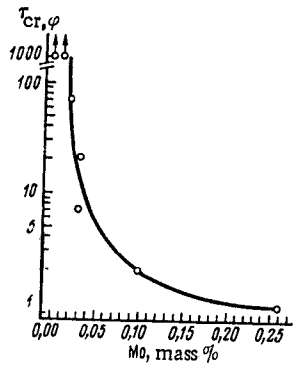

Fig. 3

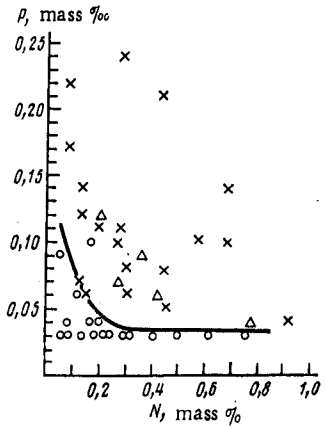

Fig. 4

Fig. 3. Time to failure of stressed specimens of austenitic chrome–nickel steel of type 18-10 in a boiling 42% solution of $MgCl_2$ vs molybdenum content of steel (Kowaka and Fujikawa).

Fig. 4. Regions of instability (×), partial stability (Δ), and complete stability (○) of steel 18-10 to transcrystalline stress corrosion cracking in boiling 42% solution of $MgCl_2$ vs nitrogen and phosphorus contents of metal (Kowaka and Fujikawa).

In many cases alloying makes it possible to change the critical parameters of passivation in such a way that the alloy acquires the capability of spontaneously going into the passive state on contact with an aggressive medium.

Much success has been recently attained in these directions. An extensive assortment of alloys with high chemical resistance to aggressive media has been developed and is being made commercially.

Additional alloying is an important way of increasing the chemical stability of structural alloys, but is not the only one. Research in recent years has revealed that many possibilities also lie hidden in regulation of the composition of alloys by means of technological additives.

In principle, additive elements can be divided into two groups. The first group includes those which, as a rule, remain in solid solution; the second includes elements forming independent phases (sulfides, carbides, nitrides, or oxides).

Impurities of the first type can have a marked influence on the characteristics of steels, including their chemical stability, owing to segregation on the surface and at the grain boundaries of the solid solutions. These impurities include, for example, phosphorus, silicon, and boron, which have been investigated in our laboratory. The character of their influence can be judged from the results obtained in research on the role of phosphorus as impurity in austenitic steels.

It is known that in strongly oxidizing media (boiling nitric acid mixed with chromates) austenitic steels of commercial purity can undergo ICC [intercrystallite corrosion] in the hardened state, i.e., when there are no separations of excess phases at the grain boundaries. It has been suggested but not proved that this damage is due to segregation of impurities at the grain boundaries. Such a proof has been obtained in joint work by the Karpov Scientific-Research Physicochemical Institute [NIFKhI] and the Central Scientific-Research Institute of Ferrous Metallurgy [TsNIIchermet].

In this investigation, by means of radiochemical methods the partial rates of transition of the main components of the steel and impurity into the solution were precisely determined, and with the aid of the optical microscope and the scanning electron microscope the character of the damage to the steel was elucidated. The results are plotted in Fig. 1, where we show the time dependences of the partial rates of solution (left) and of the selectivity coefficients Z for iron, nickel, chromium, and phosphorus (right). The fact that the value of Z for phosphorus is greater than unity at first means that during this period it goes into solution in amounts exceeding its mean content in the alloy [20]. Since the corrosion here is intercrystallite, this result means that the grain boundaries are actually enriched with phosphorus, and this is why their chemical stability is reduced.

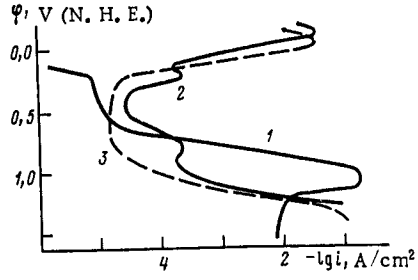

Fig. 5

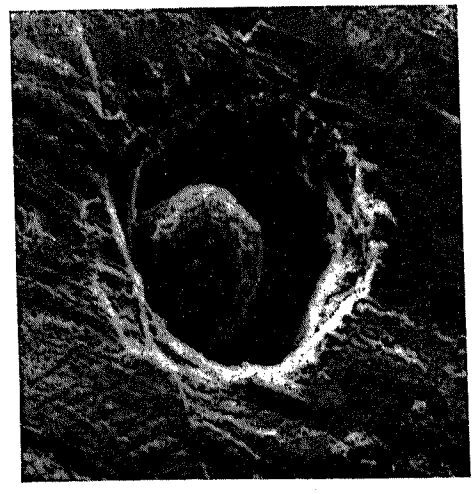

Fig. 6

Fig. 5. Anodic potentiodynamic curves (1 V/h) obtained in boiling 3.4 N H_2SO_4. 1) TiC; 2) 1Kh18N10T; 3) 03Kh18N11.

Fig. 6. Pitting at nonmetallic inclusion on surface of stainless steel of type Kh17-N14S2 in 2 N H_2SO_4 at 50°C ($\varphi = -0.15$ V; $\tau = 30$ min).

The final results of the investigations for all three impurities are plotted in Fig. 2.

Phosphorus always increases the corrosion rate of the steel. When its content is above 0.01%, the corrosion becomes intercrystallite. Silicon has a nonmonotonic effect: when its concentration is raised from 0.1 to 1%, the corrosion rate increases, reaching a maximum at 1%, but then sharply falls at higher concentrations. Between 0.1 and 3% the damage is intercrystallite in nature.

Boron present in concentrations of order 0.001-0.003% in stainless steels has a marked adverse effect on the corrosion resistance even at a content of about 0.001%.

Some impurities of the first group, including nitrogen, molybdenum, arsenic, phosphorus, and bismuth, even in amounts of order 0.01% or sometimes even lower, can cause one of the most serious types of local damage – transcrystallite stress corrosion cracking. The effect may be illustrated by means of some results from Japan (Fig. 3). We see that even with 0.02-0.03% of Mo in the metal, the time to failure is shortened by two orders of magnitude [21].

From Fig. 4 we see that to obtain resistance to transcrystallite stress corrosion cracking when the nitrogen content of the metal is 0.01%, the phosphorus content must not exceed 0.008%.

On the basis of similar results, Ryabchenkov and Gerasimov [22] came to the conclusion that in high-nickel austenitic open-melted steel Kh20N35B, the total N and P content should not exceed 0.035%; and in vacuum-melted steel the figure is 0.05%.

Some success has already been achieved in industry in regulating the contents of this group of impurities.

In particular, it is known that in this way a very important method of production of corrosion-resistant steels has been created and developed – the production of so-called superferritic steels.

The high corrosion resistance of the chrome steels Kh18, Kh25, and Kh28 has long been known. These steels have low tendency to stress corrosion cracking in chlorides and high pitting resistance. However, the realization of these properties appears to have met two insurmountable obstacles – the high tendency of these steels to intercrystallite corrosion and, what is worse, their irremovable cold brittleness in welded joints.

It has now been established that both these defects are due to certain technological impurities in the steels, mainly carbon and nitrogen. By reducing the total content of these impurities to 0.01% it has been found possible to remove both the tendency to intercrystallite corrosion and that to cold brittleness.

Thus, we have seen a rebirth of the very first generation of stainless steels, which now combine high resistance to uniform attack, pitting, and stress corrosion cracking with good manufacturing qualities and plentiful supply.

Of the impurities which can take part in the formation of independent phases, let us first consider carbon. It is well known that in stainless steels carbon can form chromium-containing carbides which separate preferentially at the grain boundaries. This leads to depletion of chromium from the boundaries and makes such steels liable to ICC in acid media, especially in the zones of welded seams, while in neutral media containing chlorides it also leads to intercrystallite stress corrosion cracking and intercrystallite pitting.

Known methods of increasing the resistance of such steels to ICC include: a) stabilization by adding strong carbide formers such as titanium and niobium; b) reduction of the carbon content to 0.3-0.04%.

Use of titanium-stabilized steels has revealed, however, that as well as possessing high resistance to ICC in weakly oxidizing media, they are distinguished from ordinary steels by an increased capability of self-passivation in acid media, reduced stability in strongly oxidizing media, and marked tendencies to knife-line attack.

It has been found that the causes of these differences lie in the electrochemical properties of titanium carbide (Fig. 5).

At a potential corresponding to the corrosion of steels in reducing or weakly oxidizing media (i.e., more negative than 0.5 V), titanium carbide has higher resistance than the steel. In these conditions, corrosion of the steel is accompanied by accumulation of titanium carbide on its surface. Since the carbide has a very low hydrogen overvoltage, this must shift the corrosion potential toward the positive; some time after the start of corrosion, the passivation potential may be exceeded, and the steel spontaneously changes to the passive state.

To the positive of 0.7 V, i.e., in just the region where titanium-stabilized steel is less stable, titanium carbide itself begins to dissolve at an appreciable rate. There is shown by the relative increase in the titanium content in the solution products of the steel when we go into this potential region.

Later it was found that electrochemical instability at high potentials is characteristic not only of titanium carbide but also of a number of other carbides – those of molybdenum, chromium, chromium–molybdenum, iron–chromium, etc. [23]. For steels in which chain structures of carbides form along the grain boundaries, this effect is one of the most important causes of ICC in strongly oxidizing media. It is absent in steels with low carbon contents.

It follows that for use in strongly oxidizing media it is desirable to choose not titanium-stabilized, but refined (low-carbon) steels. On the other hand, in many but not all weakly oxidizing media, in which carbides are chemically stable, stabilized steels are preferable.

It has long been known that the corrosion stability of carbon steels can be reduced by sulfur present as an impurity. In the late sixties and early seventies, new Swedish results appeared on the influence of sulfides on the corrosion of carbon steels [24]. In some Soviet work done mainly at the Physicomechanical Institute, Lvov [25], it was shown that nonmetallic inclusions play a part in the corrosion fatigue and hydrogen embrittlement of carbon and low-alloy steels. In Poland, Szklarska-Smialowska et al. [26] have shown that in chloride solutions pitting begins on certain stainless steels mainly at oxide–sulfide and less often at oxide inclusions. At the Karpov NIFKhI this effect was confirmed for stainless steels of all classes, and was studied from the viewpoint of its possible influence on the corrosion resistance of stainless steels, primarily austenitic chrome–nickel steels [27].

It has been found that sulfides, like oxides, are preferred centers of pitting (Fig. 6). The most important characteristic of pitting resistance, the so-called pitting potential, can shift 100-200 mV to the negative. For this reason, in some cases steels contaminated by active inclusions can undergo marked pitting corrosion in chloride solutions, whereas uncontaminated steels remain passive and are scarcely corroded at all.

In joint work by our laboratory with TsNIIchermet, it has also recently been shown that reduction of the sulfur and/or manganese contents to a level ensuring the absence of MnS inclusions not only reduces the tendency of steel to pitting corrosion but also improves its passivity (Fig. 7). The greater [Mn], the earlier does i_{cr} begin to increase with rise of [S]. The dependences of i_{cr} on [Mn] for various [S] levels and the dependences of the corrosion rate K on [S] and [Mn] are similar. If we plot i_{cr} and K vs the logarithm of the product of the sulfur and manganese concentrations $\Pi_{S,Mn}$, almost all the points for each of these parameters lie on the same curve (Fig. 8). At low values of $\Pi_{S,Mn}$, i_{cr} and K remain practically constant; however, on attainment of a certain critical value of this product, i_{cr} and K suddenly increase and then continue to rise smoothly. The fact that i_{cr} and K are independent of $\Pi_{S,Mn}$ at low $\Pi_{S,Mn}$ shows that sulfur and Mn dissolved in the austenite have no effect on the solution and passivation of the steel.

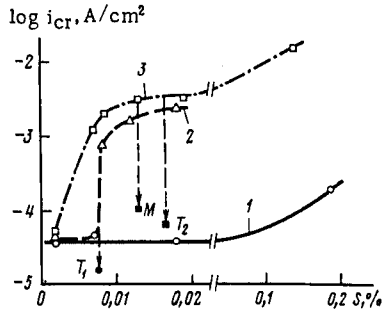

Fig. 7

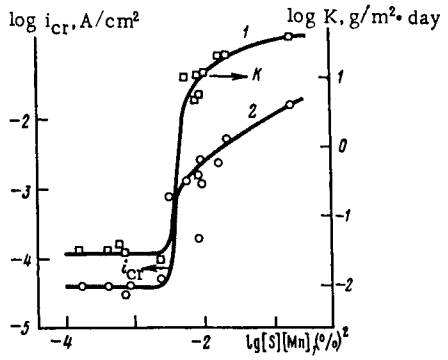

Fig. 8

Fig. 7. Critical passivation current of steel 18-11 in 0.1 N HCl at 20°C vs sulfur content of metal with the following manganese contents in percent: 1) 0.04-0.08; 2) 0.4; 3) 1.2-1.4. Here T_1 denotes steel Kh18N10T of high purity with respect to S and Mn; T_2 denotes the same steel of ordinary purity; M denotes steel Kh17N14M3 of ordinary purity with respect to S and Mn.

Fig. 8. Critical passivation current i_{cr} and corrosion rate K of steel Kh18N11 in 0.1 N HCl at 20°C vs product of S and Mn contents of metal.

The influence of alloying with titanium on the behavior of the steel also depends on $\Pi_{S,Mn}$. From our results it follows that one of the main reasons for the favorable influence of titanium on the corrosion resistance of steel in these conditions is "displacement" of manganese from the sulfides, which sharply reduces their corrosion activity. Thus, the protective action of titanium in steel is more complex than has been supposed, because it is combined into insoluble phases with two harmful impurities – carbon, which increases the ICC tendency, and sulfur, which reduces the resistance to uniform attack and the passivity of steel.

These results convincingly indicate that regulation of the technological impurity composition of steels is actually one of the most important way of further improving their chemical stability. However, it must not be forgotten that in determining this stability a fundamental and decisive role is played by the main phase, i.e., by the solid solution of alloying elements in the base.

In this connection, it has recently become evident that the study of the laws of solution of solid solutions is a very important problem in corrosion and electrochemical science [29].

The solution of solid solutions belongs to the class of complex electrode processes including several parallel anode reactions, and to establish quantitative laws of such a process we need to know the partial rate of each of these. The kinetics of parallel electrochemical reactions can usually be quantitatively based on the principle that they occur independently. However, this principle does not apply to the solution of alloys, because the kinetics and even the mechanisms of the partial reactions – the solution of the various components of the alloy – are interrelated. Moreover, in this case the problem itself is so complex that it cannot be solved purely by electrochemical methods, although the process of solution of an alloy is by nature purely electrochemical. Electrochemical methods make it possible to determine the overall rate of solution of the alloy, which coincides with the partial rate of solution of one of the components only in rare cases. Independent methods are required to determine the partial rates and to study the changes in composition and structure of the surface layers of the alloy.

In recent years, as a result of the appearance of γ-spectroscopy and other physical methods, these difficulties have been overcome, permitting the establishment of a number of important laws of solution of solid solutions.

The simplest case is that in which an alloy consisting of components with different positions in the electrochemical series dissolves while preserving the active state of its surface. In this case, uniform solution of the alloy is preceded by a period in which the electronegative components go preferentially into the solution and the surface is enriched with the electropositive components. We observe nonsteady diffusion of the electronegative component from the bulk to the surface of the alloy, and continuous generation of vacancies in the alloy lattice, due to selective solution, creates favorable conditions for this diffusion, giving high rates of solution even at ordinary temperatures.

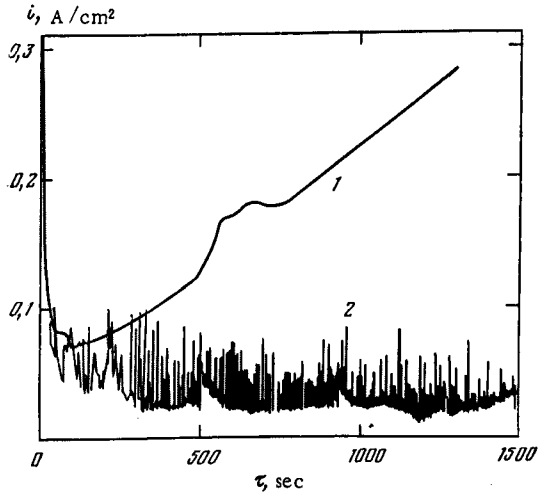

Fig. 9

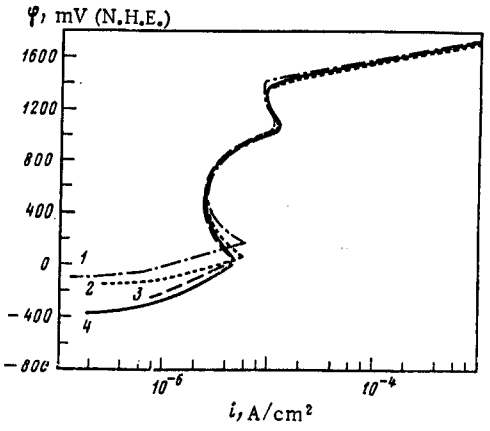

Fig. 10

Fig. 9. Curves of anode current vs time at 0.2 V potential relative to sat. calomel electrode for whisker crystals of iron in borate solution (pH = 9.39) containing 0.01 M NaCl (Haruyama et al.). State of metal: 1) after twisting (360°/cm); 2) not twisted.

Fig. 10. Anodic polarization curves (1 mV/sec) of amorphous alloy $Ni_{35}Fe_{30}Cr_{15}P_{14}B_6$ in chloride solutions (Devin). Cl^- concentrations in moles per liter: 1) 0.02; 2) 0.2; 3) 0.6; 4) 2.0; pH = 6.6.

During anodic solution or corrosion of an alloy, on the process of selective solution of the electronegative component there is superimposed continuous removal of the surface layers of the alloy, and as a result the selective solution ultimately becomes uniform. In general the mechanism of solution of the electronegative component depends on the overall rate of solution of the alloy. At low rates, it is most probable that there will be nonstationary diffusion of this component from the bulk of the alloy to its surface. However, with high rates, the limiting stage becomes removal of the surface layers of the alloy, which governs the rate of emergence of the atoms of the negative component at the surface.

Solution of alloys in the passive state is a fundamentally different process [30]. Our investigations of the electrochemical behavior of the alloy Fe–28Cr, e.g., has revealed that, in contrast with the region of active solution, in the passive region the surface layer is enriched not with the electropositive component, which is iron in our case, but with the component with the higher affinity for oxygen and the greater tendency to passivation, i.e., chromium, leading to a marked increase in chemical stability.

In conclusion, we must emphasize that further successes in development of a theory of corrosion will certainly involve the heterogeneity of the surface of the structural material, which not only largely governs its behavior in the transition to the passive state, but also creates special liability to various types of local corrosion damage, primarily pitting, intercrystallite corrosion, and corrosion under stress, which become the chief corrosion problems in various fields of application of metals.

In most cases these processes have the same origin – different bond energies and kinetics of interaction with the passivating oxygen of water, and correspondingly different capabilities for preservation or renewal of the passivity of phases emerging at the surface, interphase boundaries, grain boundaries of the same phase, slip lines, and dislocations. As a result, in certain conditions, the passive state does not arise or is not renewed on certain microregions of the surface. This leads to development of localized corrosion damage; the type of damage depends in a complicated way on the local processes of solution and passivation.

We must also remember that the different local rates of solution create nonuniformity of the composition of the solution along the surface, primarily on account of an increase in the concentration of a salt of the dissolving metal (with corresponding changes in pH) and especially of aggressive anions at the most active sites. The importance of these secondary changes differs for different processes of local corrosion. In most cases of intercrystallite solution, and possibly of intercrystallite cracking, they may be unimportant, but in the development of pitting corrosion and transcrystallite cracking they may become the most important factors.

Changes in the properties of the metal itself at the site of a local process (due to localized hydrogen absorption, phase changes in microvolumes of metal, etc.) can also be important.

At the same time we must remember that structural-chemical heterogeneity of the metal can sometimes even be favorable from the viewpoint of corrosion stability. This is supported by such well-known factors as the facts that in some media the passivation characteristics of one-phase austenitic and two-phase austenitic–ferritic steels are similar, that these two-phase steels are resistant to stress corrosion cracking, that the tendency to ICC is reduced in weakly oxidizing media when titanium carbides are formed in the structure instead of chromium carbides, etc.

A number of very important results have been obtained in recent years with the aid of electrochemical, radioisotopic, and new physical methods of investigation of the surface. They have not merely refined and supplemented previous ideas, but also allow us to speak of a new branch of electrochemistry – the electrochemistry of a dissolving heterogeneous metallic surface. This trend may play an important part in the further development of scientifically based methods of preventing local corrosion damage.

There are various possible approaches to this problem. Thus, owing to the electrochemical nature of local corrosion processes, they usually occur only in certain ranges of potential. Thus they can be prevented by means of electrochemical methods.

By alloying we can also so increase the affinity toward passivating oxygen that the differences in the strength of its bonds on different parts of the heterogeneous surface wholly or largely lose their value.

I shall now discuss some other fundamental approaches to the problem in hand.

The least degrees of heterogeneity are found in so-called dislocation-free single crystals and amorphous alloys. Dislocation-free crystals with a relatively ideal lattice can be prepared by crystallization from the gas phase or by means of special methods of electrodeposition, and can have high resistance to local corrosion. This may be illustrated by means of the results of Haruyama et al. [31] (Fig. 9). For ordinary polycrystalline iron their chosen potential corresponds to the region of rapid pitting solution at measured rates of up to 10^{-2} A/cm^2 or more. In this case (curve 1) we see only comparatively slight fluctuations of the anode current (about $3 \cdot 10^{-5}$ A/cm^2). These pulsations are evidently due to formation of short-lived active "points" on the passive surface, incapable of transformation to pitting. However, one need only break the homogeneity of such a crystal by twisting it to create dislocations, and the ordinary time dependence of the current arises (curve 2), associated with the origination and growth of pitting.

In view of the difficulty of preparing such crystals and the practical impossibility of processing them technologically without disturbing the homogeneity of the structure, from the corrosion viewpoint such materials are evidently of purely theoretical interest. Amorphous alloys may prove more promising; in particular, they are produced by superrapid cooling of liquid metal [splat quenching] or by condensation from the vapor.

To a first approximation, amorphous alloys have no grains, and thus cannot suffer intercrystallite corrosion cracking. In view of the absence of a crystal lattice and its inherent structural defects, amorphous alloys can evidently be regarded as even more homogeneous than dislocation-free single crystals. This is clearly manifested by the corrosion–electrochemical properties of amorphous alloys, e.g., the alloy of the "metglass" type produced by the firm "Allied Chemical Corporation" and investigated by Devin [32] (Fig. 10). In his experimental conditions, molybdenum-free stainless steels are easily subjected to local anodic activation. However, this process does not occur on the amorphous alloy: At potentials above 0.5 V, the rise of anode current is here entirely due to the development of the usual uniform solution on account of overpassivation, as if the solution were not of chloride but sulfate. It is interesting to observe that cold deformation does not cause the alloy to become liable to pitting (the curve for the deformed alloy is practically the same as that given) provided that no cracks are formed in the alloy during deformation. It is noteworthy that, despite the unusually large phosphorus, boron, and carbon contents of the amorphous alloys, their passivating layers consist mainly of chromium oxides, just as on ordinary stainless steels.

Considering that the already-known amorphous alloys have good resistance to local corrosion with comparatively low contents of nickel and chromium and no molybdenum, we can assume that in the near future attempts will be made to use amorphous alloys as corrosion-resistant structural or coating materials.

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AMBIGUOUS INFLUENCE OF CATHODIC POLARIZATION ON STRESS CORROSION CRACKING IN TITANIUM ALLOYS

V. A. Marichev and V. V. Lunin

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The authors investigate the influence of cathodic polarization on crack growth in stress corrosion cracking of titanium alloys in various electrolytes. They show that the ambiguous influence of cathodic polarization on crack growth is a general law of stress corrosion cracking of titanium alloys. They investigate the role of local anodic solution and hydrogen embrittlement in stress corrosion cracking, and determine the dependences of the critical coefficient of stress intensity K_{IHE} (above which stress corrosion cracking is due to hydrogen embrittlement) on the potential, the solution composition, the pH, etc. They discuss a method of plotting the kinetic curves of crack growth by the mechanism of hydrogen embrittlement in stress corrosion cracking. They consider the possibility of creating a general method of determining the mechanism of stress corrosion cracking for various structural materials.

Marichev [1-4] has suggested a method of determining the roles of local anodic solution and hydrogen embrittlement in the mechanism of stress corrosion cracking (SCC) of high-strength steels; it is based on investigation of the influence of cathodic polarization on crack growth in SCC in relation to the initial growth rate at the corrosion potential and on determination of the critical crack growth rate (CGR). This method does not have limitations due to the nature of the alloy, and potentially it might be a basis of a universal method of determining the mechanism of crack growth in SCC, not so much in steels as in other structural materials, in particular titanium alloys.

At present the mechanism of SCC in titanium alloys has not been established [5]: local solution and hydrogen embrittlement are equally often cited as the principal factor. To investigate the mechanism of SCC of titanium alloys by means of the method of Marichev [1-4], it is necessary to be sure that cathodic polarization has the same ambiguous influence on crack growth.

We have studied the SCC of commercial titanium alloys (VT5-1 (a), VT20 (pseudo-α), VT23 ($\alpha + \beta$), and TS6 (β)) in solutions containing various acids and mixtures of acids, halides, and oxidants (Fe^{3+}, Pt^{4+}, Cr^{6+}, H_2O_2, free halogens, etc.). Specimens measuring 210 × 25 × 8-10 mm with lateral fatigue cracks were cut from hot-rolled sheets of the appropriate thickness perpendicular to the rolling direction. The experiments were performed at room temperature in an apparatus in which, by measuring the electrical resistance of the central part of the specimen, we could continuously follow the growth of the crack and determine the changes in CGR when the electrochemical polarization is switched on [1]. The influence of polarization was studied in relation to the original CGR (V_i) at the corrosion potential, ranging from 0.001 to 100 mm/h, and we made quantitative estimates of the ratio $N = V_p/V_i$, where V_p is the CGR after the polarization is switched on.

We found that in SCC of titanium alloys in halide solutions, regardless of the dependence on V_i (at the corrosion potential), switching on the cathodic polarization slows down crack growth, and neither acidulation of the electrolyte with HCl, nor addition of hydrogen absorption promotors, nor replacement of the aqueous salt solution by a nonaqueous one accelerates crack growth during cathodic polarization. An exception is afforded by the system VT4–NaF, for which anomalously high values of the stress intensity coefficient K_I were

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