STATE OF INVESTIGATIONS IN THE FIELD OF THE THEORY OF THE PASSIVATION OF METALS IN EAST GERMANY

K. Schwabe, Kh. D. Zushke, and M. Time

UDC 620.193.01

The work of East German investigators in the field of oxide and salt passivity and of the local breakdown of the passivity of metals, as with respect to the properties of surface layers on atmospherically stable steels, is discussed and correlated. Taking account of recent data, a brief exposition is given of the state of the kinetic theory of passivity developed by Schwabe, and the possibility of explaining it on the basis of the different behavior of metals under passivation conditions is demonstrated.

Introduction

With the development of technology, economic factors have an ever greater effect on the selection and use of materials. In view of this, the importance of passivity, regarded as the natural property of metals of resisting corrosion due to regeneration of the passivating layer without additional expenditures for protection, for example, for paint coatings, is rising. A timely problem is the development and effective industrial use of new metallic materials with improved ability to be passivated. Under these circumstances, it is necessary to make a transition from the empirical selection of the composition of alloys to deliberately directed work which will ensure a great probability of success, on the basis of a deep understanding of the passive state, and the reasons which cause it. Investigations in this field are very complex, and embrace a great number of thermodynamic and kinetic problems, connected with sorption processes and the formation of surface layers.

In recent years special attention has been paid to the study of the nature of oxide passivating layers, and to the investigation of the kinetics of their growth and dissolution. The possibilities of electrochemical investigations have been considerably broadened, thanks to the application of a whole series of modern methods. Investigations have been published carried out using the methods of electron diffraction [1, 2], radioactive indicators [3, 4], and of ellipsometric [3, 5-7] and spectroscopic [105, 107] measurements. It has been shown using the method of the diffraction of electrons [2] that the protective properties of an oxide coating are connected with its structure, obviously thanks to its effect on the conductivity. It has been established that passivating layers obtained electrochemically on Fe–Cr alloys, with an increase in their chromium content (and, with a corresponding increase in the corrosion resistance of the alloy), change their structure from crystalline to amorphous.

The fundamental problem is connected with the question of the initial cause of passivity. On the basis of a number of investigations too great to review, theories and models have been developed, and the conditions for the appearance of the passive state have been elucidated; there has been a long-term discussion as to whether a chemisorbed layer of oxygen or an oxide phase is required for passivation.

Along with already existing theoretical justifications [8, 77-79] and experimental data [9-16] supporting the chemisorption theory, we must note investigations using tagged atoms, carried out recently by Siejka et al. [4], which provide a very graphic additional proof that even a monomolecular coating of oxygen leads to passivation.

According to Schwabe [91], the oxide phase and chemisorption theories are compatible and, in principle, are not contradictory in their concepts, if it is taken into account that the decisive energy barrier

Scientific Research Institute, Meinzberg, East Germany. Translated from Zashchita Metallov, Vol. 10, No. 5, pp. 491-507, September-October, 1974. Original article submitted April 16, 1973.

to the departure of an ion of the metal from the metallic lattice is the metal–oxide interface. In the oxide phase itself, there is only diffusional displacement along defect points. The zone of "cross-linking" between the metal and the oxide phase may also be regarded as a chemisorbed layer which, with a defectless structure, ensures effective protection against corrosion.

General Information on the Subjects and Methods of Experimental Investigations

In view of the variety of passivation phenomena, it is expedient to divide the work under consideration in accordance with the subject of the investigation, as well as in accordance with the type and method of formation of the passivating coatings. We shall distinguish between metals with oxide and salt passivating layers and, in the first of these groups, between metals with electrochemical and mechanical passivity.

To metals with "electrochemical passivity" we assign those which are anodically passivated in aqueous solution and which, with a further increase in the polarization, reach a passivated state, connected with the evolution of oxygen or with a transition to a state with a higher degree of oxidation. This type of behavior is characteristic for transition metals: Fe, Co, Ni, Cr, and their alloys.

Metals with "mechanical passivity" (Al, Ti, Zr, Ta), are, in general, self-passivated in aqueous solutions. The oxide layers forming on them, in connection with the special characteristics of the conductivity, are not subject to repassivation in the above sense.

By salt passivation there must be understood the direct formation of a passivating salt layer, with a reaction between anions and the surface of the metal. It is preceded by the deposition of a porous salt layer from a supersaturated solution.

The usual form of the experimental study of passivity consists in electrochemical investigations. In these investigations, the connections between three quantities are determined: the electrode potential U (or the overvoltage η), the current density i, and the time τ. With other methods of investigation, which in a majority of cases are combined with electrochemical methods, belong radiochemical, optical, electron-optical, and spectrometric methods.

I. Metals with Electrochemical Passivity

Experimental Justification of Chemisorption Theory. Electrochemically passivated metals lie at the center of the discussion between supporters of the oxide-film and chemisorption theories. The experimental justification of the latter is supported by experiments on the polishing of anodically polarized electrodes under a solution, carried out with nickel [13], iron [14], alloy steels [16], and chromium [15].

It was found that the ability of a metal to be passivated declines in the order Cr, Ni, Fe. Thus, under conditions of galvanostatic polarization (i_a = 300 mA/cm^2) polished iron is passivated only in alkali media: nickel in acid media not containing chlorides; chromium even in 10 N HCl. Although under these circumstances the currents in the passive region are greater by one order of magnitude than on unpolished electrodes, the form of the polarization curve, from the region of the drop in the current, characteristic for a passivated metal, is retained. This obviously would not take place if the initial cause of passivation was the formation of a porous salt layer, in accordance with Müller [17], or of an oxide phase.

Capacitance measurements, carried out on passive iron and platinum in alkaline solutions, also point to the formation of a chemisorbed layer, since the capacitance–potential curves for both metals were found to be similar [50, 83].

The Role of Water in Passivation and the Effect of pH and Anions. With the formation of a passivating oxide coating or of an oxide phase, in aqueous solutions or in an atmosphere containing water vapor, the decisive role is that of water itself. This has been demonstrated directly using tagged atoms [4] and has been confirmed by electrochemical methods [18, 19]. Potentiodynamic polarization curves for nickel in dimethyl formamides (DMF) and acetonitriles (AN) in 1 M solutions of H_2SO_4 showed that, for passivation in these solutions, definite minimal concentrations of water are required: 0.2% in DMF and 3% in AN. The importance of water is also emphasized by the fact that, with a rise in its concentration, the passivation potentials U_{pass} are shifted toward the side of more negative values; the density of the passivation currents i_{pass} at first decreases; however, with higher water contents, it again rises, in view of the development of the dissolution reaction.

With the potentiodynamic polarization of Armco iron in DMF in a 1 M solution of H_2SO_4, the minimal limiting concentration of H_2O which is sufficient for passivation was 0.1% H_2O. In anhydrous dimethylsulfoxide (DMSO) in a solution of H_2SO_4 of the same concentration, on the contrary, there was observed a retardation of the dissolution of the metal, which can be explained by the formation of sorption bonds with inhibition, and by electrochemical interaction between the metal and molecules of the solvent. However, this effect was overlapped by acid passivation, which set in with the attainment of definite potentials, with a water content of $\geq 0.1\%$. This latter again illustrates the decisive importance of water in passivation. A large number of investigations has been made of the effect of ions of the electrolyte on the polarization curves, particularly on the passivation characteristics. In the anode behavior of a metal, in connection with the indicated function of water, the pH of the solution plays an important role. It has been repeatedly established, particularly for nickel, that the dependence of the passivation potential on the pH has the form $\partial U_{pass}/\partial pH \approx -2.303\ RT/F$ [20, 21, 31]. In spite of some variations, the logarithms of the passivation current and of the current in the passive region, in general decrease linearly with the activity of the hydrogen ions or with its square (see also [102]).

The effect of ions of the dissolving metal was studied by Ritter [20], who showed that, in acid solutions, nickel ions have no effect either on the rate of dissolution or on the passivation of nickel.

Anions have a considerable effect on the anode behavior of metals, depending on the nature and activity of the anions.

In their effect on the ability of metals to be passivated, a definite gradation has been brought out which, as is shown by a comparison with the results of radiochemical investigations (see below), is in agreement with the ability of the anions to be adsorbed (the particularly strong action of halogen ions, leading to a change in the form of the corrosion and in the form of the potential–current density curve, will be discussed separately below). Dietz [13] observed an increase in the density of the passivation current for nickel, in the order of the anions $CH_3COO^- < ClO_4^- < SO_4^{2-}$. This same tendency has been noted for the density of the dissolution current of passive iron in solutions of the identical ionic strength, containing ClO_4^- and SO_4^{2-} ions [21, 22]. In addition, there has been observed an increase in the value of i_{pass} with a rise in the concentration of ions at a constant pH [34]. A broad investigation has been made of the action of the ions CN^-, $CN^- + Cl^-$, $SO_4^{2-} + F^-$, SO_3^{2-} in other mixtures of electrolytes on the ability of iron to be passivated [23].

The current flowing through a passive electrode may be connected with processes of the reactivation of the metal, including the chemical dissolution of the layer under the action of hydrogen ions, and the competing adsorption of anions. For nickel in $HClO_4$ and H_2SO_4, it has been established by a rather sensitive analytical method [22] that, in the regions of potentials from 300 to 1040 mV, with respect to a saturated calomel electrode, with a 100% power yield, divalent nickel ions are formed. Subsequently, the dependence of the rate of dissolution in the passive zone on the potential was demonstrated.

To investigate the adsorption of anions it has been found useful to use radioactive isotopes, for example, C^{14}, S^{35}, Cl^{36}, and I^{131}. On the one hand, this method makes it possible to make a qualitative (with an auto-radiograph) local identification of a determined component of the reaction. One the other hand, thanks to their high sensitivity, radiometric measurements permit a quantitative determination of a tagged substance [24]. The materials investigated (Pt, Ni, Fe) were used both in the form of sheet metal and in the form of spray-deposited layers. In the first case, intermittent measurements were made with stripped electrodes, while the second variant offered the possibility of the continuous investigation of the adsorption kinetics under conditions of deaeration [25-29].

An investigation of the adsorption of various anions and of their ability of displace one another permitted obtaining the order of rising adsorption capacities [29]:

$$ClO_4^- < SO_4^{2-} < Cl^- < I^- < HS^- < CN^-.$$

In the absence of oxygen, sorption of the ions takes place very rapidly, while on samples coated with oxygen it is retarded. This makes it possible to justify the use of concepts with respect to the adsorption of anions in the kinetic theory of passivation [80].

In the latest investigations of the adsorption of $^{35}SO_4^{2-}$ ions on steels, it was noted that steels of type KTS (KTS-6, KKS-9) have a considerably greater capacity for adsorption and for the formation of layers than structural steel St-38.

Quantitative Justification of the Kinetic Concept. With the investigation of the quantitative laws governing passivation (see below, section 3), new information has been obtained on it. Krause [31, 37], who made measurements for nickel in acid sulfate electrolytes, showed that the density of the nonstationary currents in the passive region depends on the method of the measurements. In accordance with the theory of [88, 37], with identical potentials and with an identical duration of the holding, the currents at the electrodes from a surface which is renewed before each experiment ("potentiostatic holding times" according to [32]), are greater than with a stepwise change in the potential at exactly the same electrode ("experiments with an unchanged potential" [32]). In the second case, this may be due to the presence on the metal of a coating formed during the preceding region of potentials.

Calculations made by Ebersbach [88] made it possible to clarify some of the criteria of the passivation mechanism. Experiments with the connection of a potentiostatic polarization somewhat higher than the passivation potential on nickel [33, 34, 37] and Armco iron [35-37] in acid solutions showed that, in accordance with the theory, on the curves of $\log i \sim \tau$, there are linear sections whose slopes (m) are connected exponentially with the electrode potential. This result is in agreement with the assumption adopted in the classical concept, to the effect that the rate of the passivation reaction is determined by the stage of the charge transfer. In addition, for the systems $Ni/HClO_4$ (I), Ni/H_2SO_4 (II), and $Fe/HClO_4$, $NaClO_4$ (III), the possibility of diffusional retardation of the passivation is excluded by the established lack of dependence of the kinetic parameters on the rate of rotation of the disk. However, this conclusion does not extend to the system Fe/H_2SO_4, Na_2SO_4 (IV) [35, 36].

For the corresponding passivation mechanisms, the values of $(\Delta \log m/\Delta u)_{pH,I}$ can be used to calculate the transfer coefficients of the inhibited stages of the passivation reaction.

In an analogous manner, from the values of $(\Delta \log m/\Delta pH)_{u,I}$ there are calculated the orders of the reaction with respect to hydrogen ions. For systems I, III, and IV, they are close to -1, and, for system II, to -2. Investigation of the effect of anions on the passivation kinetics has shown that this process depends only slightly (II) or not at all (I) on the anions SO_4^{2-} and ClO_4^-. On iron, it is accelerated by the ions SO_4^{2-} and ClO_4^-; however, it is still impossible to make concrete assumptions with respect to the mechanism of this effect.

Effect of State of Surface of Metal. It is well known that the chemical and physical heterogeneity of the surface of a solid metal has an effect on its ability to be passivated and on the stability of the passivating layer. It is very difficult to take exact account of the effect of this factor [90]. It has been found [38] that nonmetallic impurities prevent the formation of a homogeneous passivating layer.

Investigating samples of nickel of various kinds after an identical heat treatment, Kunze showed [16] that, with increased purity of the materials, the densities of the currents of passivation and of active dissolution increase, while the passivation potential is shifted toward the negative side [39]. This is obviously explained by the effect of impurities on the current density of the dissolution exchange reaction.

Foreign atoms can act not only as undesirable impurities. To improve corrosion properties, use is made of alloying with which chemical nonhomogeneity is knowingly created. A graphic example of this is constituted by low-alloy copper steels (of the Korten type, KTS), on which, under definite climatic conditions, there are formed strongly adhering protective layers [40].

Due to diffusion (particularly with heat treatment) and to Cottrell interaction, the foreign atoms are mostly concentrated at the boundaries of grains which, even without this, exhibit physical inhomogeneity. The effect of these two factors can be rigorously distinguished only when, at the same time, there are undeveloped grain boundaries. The concentration of the adsorbate along the grain boundaries was brought out by Nowak [41, 24] using a microautoradiograph. With a decrease in the mean size of a crystal, there is a rise in the adsorption rate. Simultaneously, U_{pass} shifts toward the side of negative values and there is an increase in the corresponding current density. With the investigation of single crystals [42], the effect of the grain boundaries is eliminated, and the results of adsorption and passivation investigations can be logically connected with definite tendencies in the properties of the faces.

Adsorption experiments with tagged SO_4^{2-} ions on nickel showed a growth of the adsorption in the order of faces (111) < (110) < (100), while, in the case of CN^- and HS^- ions, there was observed the order (111) < (100) < (110) [41, 29]. The octahedral plane (111) with the least surface energy was characterized by a minimal adsorption. Electrochemical investigations of single crystals of nickel also bear witness to the presence of an orientation effect. Garz [39] found the most positive passivation potentials for the plane

(111). However, the currents for passivation and dissolution in the passive state rose with statistical confidence in the order (100)–(111)–(110), which is not connected directly with the density and surface of the atoms or with the surface energy [43, 90].

Nowak [41] established the increased adsorption capacity of a metal subjected to cold working, which correlates with the increase in the density of the dislocations, and which may be explained by an increase in the surface energy. On the other hand, cold working promotes passivation and brings about a shift of U_{pass} toward more negative values. Simultaneously, the formation of a perfect coating is rendered difficult, so that the density of the passivation current rises with an increase in the degree of deformation [42].

The connection between the formation of pittings, the degree of purity, and the structure of a metal is discussed in the following section.

Local Breakdown of Passivity. Pitting Corrosion. Pitting corrosion must be regarded as the result of a local breakdown of the passivity. This problem is of great industrial importance and the reasons for pitting corrosion are being studied intensively in many laboratories.

First of all, the effect of the electrolyte, in particular of the nature and concentration of the anions, must be examined in detail. It is particularly essential to study chloride-containing media. Comparative studies have also been made with bromium, iodine, fluorine, and perchlorate ions as activating particles.

The first measurements in alkaline media, on iron, cobalt, and nickel were made by Tschö [44, 47], Gaunitz [45], Sonntag [45], and Garz [46]. With galvanostatic polarization in solutions without a halogen, the potential increases jumpwise, attaining a relatively constant value in the region of overpassivation. In the presence of Hal^- ions, the initial rise in the potential either underwent a rapid drop or was not observed at all. The time up to activation (the incubation period) increased in the sequence $Cl^- < Br^- < I^- < F^-$; its dependence on the concentration corresponded qualitatively to that anticipated. With identical times of action, iron and cobalt were activated by considerably smaller additions of a halogen than nickel.

The problem of the activation of nickel by halogen ions in alkaline solutions was discussed quantitatively in a later article [48]. A relationship was found between the concentration of halogen ions, the time, and the change in the potential during the activation process:

$$U(\tau)=U_0-A\frac{[Hal^-]}{[OH^-]}[1-e^{-k\tau}],$$

which in form is close to an equation derived on the basis of the assumption of the competing adsorption of OH^- and Hal^- ions.

In analogous galvanostatic investigations on iron [49] with $[Cl^-] \leq 0.12$ M, there was observed an incubation period which depended exponentially on the concentration of Cl^- ions. The competition between activating chlorine ions and passivating hydroxyl ions manifested itself, in particular, in the fact that, with a rise in the concentration of OH^- ions there was a rise in the minimal concentration of Cl^- ions required for activation.

Note must also be taken of potentiostatic measurements of the potential of pitting formation U_{pit} carried out by Paul [50] (an electrode with a new surface for each experiment). With this method, it was found possible to avoid the evolution of oxygen in the transpassive region, changing the ratio of the concentrations OH^-/Cl^-, which is of decisive importance for activation. Measurements on iron and nickel in alkaline halogen-containing solutions, as was to be expected, showed an increase in the activation potential with an increase in the ratio OH^-/Cl^-. Starting from definite premises with respect to the dependence of the adsorption on the concentration and the potential, it was found possible to derive a relationship between U_{pit} and the activities of OH^- and Cl^-. The conclusions flowing out of this for acid and alkaline electrolytes, as well as the other consequences, are in good agreement with the results obtained and with literature data (for example, [99]). Thus, for alkaline solutions, the approximate equation was obtained

$$U_{pit}\approx K_1 \lg\frac{a_{OH^-}+a_{Hal^-}}{a_{Hal^-}},$$

where the coefficient K_1, due to the dependence of the specific adsorption on the ionic radius, rises from Cl^- to I^-. The experiment actually attests to a drop in the activating action of the anions in the above order. Under these circumstances, for iron, which has a greater tendency toward pitting corrosion than nickel (U_{pit} is negative by several tens of volts), there is considerably less effect of the nature of the anions.

The inhibition of pitting corrosion by additives to an aggressive medium is important from both a practical and a scientific point of view. Göllner [51] showed that, for a number of materials (Fe, 50Fe –50Ni, Ni, high-alloy steels), the addition of a nitrate to a solution of NaCl leads to a drop in the current with potentials $U > U_{pit}$, or, more exactly, with a definite "upper" potential for pitting formation which limits the region of pitting corrosion from the side of positive potentials. This can be explained by the fact that, with high potentials, due to their large polarizability, NO_3^- ions are adsorbed more strongly than Cl^- ions. With a rise in the ratio $[NO_3^-]/[Cl^-]$, the upper potential of pitting formation is shifted toward the side of more negative values. Under these circumstances, for the metals investigated, except for nickel, the corresponding dependence is found to be logarithmic, which confirms the validity of the conclusions of Paul [50]. Effective inhibition is noted only on steels with a high chromium content. On nickel, only a temporary inhibition is developed, connected with the effect of nitrate ions. In the case of alloys based on iron, the relationship between the actions of NO_2^- and NO_3^- ions remains unclear.

A detailed study [52] was made of the effect of perchlorate on the pitting corrosion of Armco iron, nickel, electrolytic chromium, and chrome–nickel steels in solutions of NaCl and NaCl + Na_2SO_4 at a pH from 0.35 to 12.

ClO_4^- ions clearly inhibit the pitting corrosion of chrome–nickel steels, and decrease the weak activating action of chloride on chromium. Thus, in a molar ratio to chlorine ions of 1 : 7, they suppress the pitting corrosion of steel X6CrNi 17.12. Sulfate ions give the same result only with a ratio $[SO_4^{2-}]/[Cl^-]$ of 7 : 1.

On the contrary, the tendency of iron and nickel toward pitting corrosion rises with the introduction of perchlorate into a chloride solution, although pure perchlorate does not exhibit this action.

This unexpectedly strong inhibition of pitting corrosion by perchlorate, on the one hand, and its stimulating effect, on the other hand, is still not clear, although it can be asserted that the inhibiting action is connected with the presence of chromium in the metal.

The kinetics of the potentiostatic activation of passive nickel by chlorine ions in solutions of sulfuric acid was studied in earlier work by Gressmann [53], showing that, after the incubation period, the dependence of the current on the time has the form: $i \sim \tau^{3.3}$. This equation is close to a theoretical equation, derived under the assumption of an isotropic growth of the pittings and the simultaneous formation of new pittings. A power exponent close to 3 was also found by Anh [52]. The time required for the attainment of an arbitrarily selected current density decreases with an increase in the concentration of chloride, in the potential, or in the temperature. Additions of sulfate, on the contrary, inhibit the activation.

The state of the surface of the metal, as has already been pointed out, has a strong effect on the adsorption and passivation properties. The purity, structure, substructure, and crystallographic orientation of the metal affect pitting corrosion. This was demonstrated by Garz et al. on single crystals of nickel under potentiostatic conditions, mainly in an 0.5 M solution of $NiCl_2$ (pH 3.5). In principle, from phenomenological and topochemical points of view, there exists a close connection between the formation of pitting in the ordinary sense of the word and etching pits in the form of anisotropic figures [39]. Therefore, it is not reasonable to consider them separately.

It has been established that contaminants, in particular carbon and sulfur, increase the tendency toward pitting corrosion, shifting the potentials of pitting formation toward more negative values [39, 56]. It is obvious that foreign atoms promote the formation of an imperfect passivating layer, which facilitates local corrosion. Actually, an electron microprobe shows accumulations of sulfur, and to a lesser degree carbon, at the points of pitting formation [57]. The effect of contaminants on pitting formation cannot be considered separately from the structure, since the foreign atoms accumulate at the points of distortion of the lattice. This is also the basis of metallographic methods of etching to bring out dislocations (in accordance with Guard on carbon and Beland on sulfur [100]). Using the Barrett x-ray method and metallographic etching, it has been found possible to show that the etching pits appearing on single crystals of nickel under the above conditions correspond to emergences of dislocations. Under these circumstances, local breakdowns of the lattice, brought out by carbon and sulfur in the form of evolutions of Ni_3S_2, have a decisive effect.

It has been established that, at the faces of a single crystal of nickel, the potential of pitting formation varies in the order (100) < (110) < (111), i.e., that the planes with the greatest density of atoms have the least tendency toward pitting corrosion [39, 54]. Under these circumstances, in acid chloride solutions

the anisotropic course of pitting corrosion leads to the formation of polyhedral etching figures, while the current density, in distinction from the cases of polycrystalline iron and nickel [52, 53], rises proportionally to the time to a power from 0.3 to 1.5, depending on the orientation of the crystal. Here, the formation of new pittings is not taken into consideration.

Investigations of the Surface Layer. An oxide covering layer does not necessarily passivate a metal; this is borne out by the corrosion of iron under rust, and by the corrosion behavior of many metals. Although such layers always create a barrier to the supply of aggressive ions and to the removal of the corrosion products, true passivation with a clearly expressed negative U–i characteristic appears only when the oxide is strongly bound to all the parts of the surface of the metal. In the opinion of Schwabe [91], the main energy barrier for anodic dissolution of the metal is located at the boundary between the metal and the oxide, which he considers it possible to regard as a monomolecular oxide coating of the surface of the metal. This removes the principal contradiction between the chemisorption and oxide theories of passivity, and the problem of protective layers is bound up with investigations of processes at the boundary between the metal and the growing oxide phase. From these points of view, a study was made of a number of steels, including the economically promising steel KTS, and the role of the layers forming on stainless and corrosion-resistant steels in the overall mechanism of protection was evaluated.

A study was made above all of the effect of an atmosphere of sulfur dioxide.

To make a qualitative and quantitative investigation of small amounts of oxygen and of its distribution on the surface and beneath it, use was made of α-radiation arising with the proton bombardment of the isotope O^{18} in accordance with the nuclear reaction $O^{18}(p, \alpha)N^{15}$ [93, 94]. By enriching the oxygen in the isotope O^{18}, this method makes it possible to disclose even fractions of a monolayer of oxygen.

Measurements [93] on a high-alloy steel (X8CrNiTi 18.10) have shown that the content of SO_2 and the moisture content of the air have no effect on the thickness of the oxide layers; a thickness of 300-400 Å was found, considerably less than that after natural tests in an industrial atmosphere. The corrosion behavior of KTS, St-38, and nickel, on the contrary, in the presence of SO_2 depends on the length of the holding time and on the moisture content.

Using the method of electron diffraction, after exposure under different conditions, on the surface of steels St-38, KTS, and Korten, in part of the cases there were recorded crystalline iron oxides (α-FeOOH with a relative moisture content of the air $\varphi = 76\%$ in the presence of Cl^-, and γ-FeOOH with $\varphi = 90\%$), and in the other part, amorphous products ($\varphi = 76\%$, SO_2) [95]. In the initial stage of rusting, the steels investigated did not differ. Electron-microscopic stereophotos made it possible to investigate the mechanism of the formation of scale on iron and several of its alloys at temperatures of 250-570°C [106]. It has been shown that, due to the presence of defect sections on the surface of the metal, layers of magnetite are formed in the form of small islands and that, with the transition from the initial stage to the period of long-term oxidation, the "whiskers" of Fe_3O_4 grow. There was observed no increasing inhibition of the growth of the layer of Fe_3O_4 due to the covering of the surface by a homogeneous layer of Fe_2O_3. In many cases, the formation of "whiskers" of Fe_2O_3 is connected with the concentration of defects in the Fe_3O_4 and with diffusion along the points of breakdown of the lattice (along the grain boundaries and the helical dislocations). Cubic Fe_3O_4 is converted into cubic γ-Fe_2O_3 when 1/9 of all the cation lattice points remains vacant. A further increase in the concentration of defects makes the cubic lattice unstable and promotes the formation of the rhombohedral lattice of α-Fe_2O_3 [106].

Using Mössbauer spectrometry, after tests with 100% relative humidity (25°C) the surface layer on Armco iron was identified as γ-Fe_2O_3 with a small impurity of γ-FeOOH [96]; the presence of the latter under analogous conditions has also been demonstrated using electron diffraction. It must be noted that the relative Mössbauer constants have been tabulated for a large number of compounds of iron [97].

An analysis using an electron microprobe, in corrosion investigations carried out at the present time, has been used for a quantitative determination of sulfur in corrosion layers [93]. In accordance with the first measurements, the maximal fraction of sulfate in sulfate pockets attains values around a few percent.

II. Metals with Mechanical Passivity

In view of its broad use in technology, a relatively large number of publications has been devoted to aluminum [58-62]. Oxide layers formed by anodic oxidation in ammonium tetraborate and in fuming sulfuric acid have been investigated for porosity using radioactive substances (T_2O, $H_2{}^{35}SO_4$) [59]. It has been

found that, with the repeated polarization of already oxidized electrodes, there is electroosmotic dehydration of the layers, and release of the sulfuric acid which has penetrated into them. On the contrary, in the case of layers formed in 20% sulfuric acid, there was no additional dehydration, which points to another structure of the oxide layer.

In alkaline electrolytes, aluminum behaves like an active electrode. Curves of anode passivation in 0.1 M NaOH and a saturated solution of $Ca(OH)_2$ attest to the formation of a passivating layer [60, 61]. In the first case, the limiting current density, obtained in galvanostatic measurements, and partially using the method of interruption, was determined by diffusion. In the second case, as has been shown by Nowak on single crystals of aluminum in a saturated solution of $Ca(OH)_2$, it is affected by the crystallographic orientation. The observed order of the limiting current densities, (100) > (111), does not coincide with that found by Garz [43] for nickel, which also has a face-centered cubic lattice. In accordance with Nowak and others, the anode behavior of aluminum in alkaline electrolytes is affected by factors which have already been discussed: the degree of purity, heat treatment, and cold working.

In weakly acid buffer solutions of NaCl, the corrosion potential of aluminum is due to a combination of the reactions of the cathode evolution of hydrogen and anode dissolution ($Al + 4HO^- \rightarrow [Al(OH)_4]^- + 3\,e$) [62]. The increase in thickness of the oxide formed by oxidation in air or with anode polarization decreases the density of the corrosion current. Nevertheless, the initial section of the anode polarization curve is evidence of the active behavior of aluminum, which is connected with pitting formation. In the cathode region, the dissolution is reinforced by the leaching-out of the layer near the electrode. Under these circumstances, by analogy with [59], there is assumed a rise in the degree of hydration of the oxide layer due to electroosmotic effects.

Polarization measurements on titanium in acid media [63] were used to establish that, in solutions of HCl and H_2SO_4, typical curves with active and passive regions are observed only with a concentration greater than 3 M. The activating action of $HClO_4$ is somewhat stronger. Fluoric acid has a far stronger activating action, depending on the concentration of the electrolyte. In sulfuric acid, in distinction from H_2F_2, a dependence of the passivation potentials on the concentration is not observed. In this case, using the example of the reduction of hydroquinone, it has been established that there is electron conductivity of the film, decreasing with an increase in the thickness of the layer, so that there is no evolution of oxygen in the transpassive region. Coulomb measurements using current–time curves gave a value, independent of the potential, of less than nine elementary charges per surface atom up to the appearance of a quasi-steady state in the passive region.

In alkaline fluoride- and chloride-containing solutions, the anode behavior of titanium has been investigated under galvanostatic conditions using a mechanical interrupter [64]. With currents $i \leq 1$ mA/cm^2, passivation was not observed. In neutral chloride solutions, after the evolution of chlorine, pitting corrosion appeared.

Taking account of the special characteristics of titanium in electrolytic technology, a study was made of its corrosion in contact with aluminum and copper in a 10% solution of sulfuric acid, as well as with high-alloy steel X8CrNiTi 18.10, with a ratio of areas equal to 1 : 1 [103].

In a couple with aluminum, titanium behaves like a corroding anode. With the imposition of anode polarization on both metals, the passivation of titanium sets in, which is in agreement with the above-mentioned results [63].

In contact with copper, the corrosion process of titanium is characterized by a strong cathode inhibition (the reduction of O_2 by Cu).

The corrosion of chrome–nickel steel in contact with titanium decreases considerably without any substantial reinforcement of the dissolution of titanium.

On zirconium, galvano- and potentiostatic polarization measurements in H_2SO_4, HCl, $HClO_4$, and HF [65, 66] gave somewhat different results. Thus, in HCl and $HClO_4$, with polarization there was active dissolution and pitting. The data on the mechanism of the conductivity of an oxide coating are in agreement with those obtained for titanium [65]. Special studies were made of the fluctuation of the nonconduction potential in weak solutions of fluoric acid [64, 66]. Their frequency, amplitude, and total duration depend on the composition of the electrolyte and, in a disk-type electrode, also on the rate of its rotation. They are connected with the presence of dissolved oxygen, with the decisive role being played by undissociated molecules of fluoric acid. The scheme proposed to explain them, involving interconnected

electrochemical and chemical reactions, satisfies the conditions for the development of periodic vibrations formulated in the theory of Bonhoeffer [67].

Periodic vibrations have been recorded also with the galvanostatic anode polarization of zirconium in solutions of $NaF + N_2F_2$ [66]. The change in their frequency and amplitude with irradiation, in accordance with previous data [65], bears witness to electron conductivity of the film.

Investigations on Metals with Salt Passivity. The theory of the formation of passivating salt layers is discussed briefly below, in connection with the kinetic concept of passivation. It has been shown experimentally that it is characteristic for metals of the side subgroups I and II of the periodic system (Cu, Ag, Zn) with anode polarization in saturated salt solutions. The system $Zn/ZnSO_{4\,satur}$ has been the most studied in this regard [68-74].

According to Hönicke [71], the dissolution of zinc in an acid solution of $ZnSO_4$ is inhibited not by an oxide but by a salt layer, with whose irradiation there is no increase in the anode current (characteristic for a layer with electron conductivity, formed with passivation in alkaline solutions).

In subsequent work [59, 72], a detailed study was made of the connection between the water content in the layer and its passivating action. Using T_2O, it has been shown that (as in layers of γ-Al_2O_3), there is electroosmotic dehydration. In addition, Ferse [73] found that the dehydration counteracts the diffusion of water from the solution, which creates the possibility of a stationary passive state. It was established using a spiral contractometer that, when anode polarization is switched on, leading to the absorption of water by the layer, the mechanical stresses in the protective layer change sharply. Experiments with zinc and zinc sulfate tagged with radioactive isotopes (Zn^{65}, S^{35}) [74] showed that, after covering of the anode by hydrated zinc sulfate (formed mainly by separation from a supersaturated solution) and the start of the current drop, the transition of tagged zinc into the solution ceases. The inhibition of the dissolution itself, as has been established subsequently, is due to the direct formation of a very thin non-porous layer of $ZnSO_4$ in accordance with the reaction $Zn + SO_4^{2-} \rightarrow ZnSO_4 + 2e$. In this layer, transport of ions is effected by their movement through the crystal lattice; there, its resistance is several orders of magnitude greater than that of the thick external hydrated layer. Iron and nickel are also subject to salt passivation in electrolytes in which oxide passivation is impossible, for example, in saturated solutions of their own chlorides [75], or in concentrated sulfuric acid (> 15 M), in which this has been demonstrated by Ritter for nickel [20, 85-87]. This is explained by the desorption of water molecules from the surface of the metal and by favorable conditions for the reactivation reaction. With the passivation of nickel by a layer of $NiSO_4$, it is characteristic that, with an increase in the temperature, the current density does not increase, as with oxide passivity, but falls.

Brief Exposition of Theoretical Concepts. The theoretical concepts with respect to passivation processes expounded in this section should be regarded as generalizations of a great number of experimental investigations carried out in East Germany during the last 15 years; these have, in great measure, been touched upon above.

The main role in the retardation of corrosion, both with passivation and with inhibition [76], is assigned in these concepts to the boundary between the metal and the oxide phase, which is regarded as a chemisorption bond between the metal and oxygen, and which constitutes the principal barrier to the reaction $Me \rightarrow Me^{z+} + ze$.

Starting from the usual models of chemisorbed layers of oxygen on the pure surface of a metal, Schwabe and Weissmantel [77-79] developed new model concepts. Instead of a model of localized metal –oxygen bonds, which did not explain the experimental data, there was assumed the formation of bonds between the electrons from one or several surface layers of the metal and adsorbed atoms, with the possibility of the existence of several forms of disposition of the oxygen. In the case of dense packing of the chemisorbed oxygen atoms, interaction between them must lead to the formation of mesomeric compounds which strengthen the bond between particles.

With anode polarization in aqueous solutions, the principal role in the formation of the chemisorption layer and the oxide phase lying above it is played by adsorbed water. Of the other components of the electrolyte, protons and anions can exert a considerable effect on passivation processes. Therefore, the passivation process is regarded as a system of competing reactions taking place simultaneously [80-92], including active dissolution (1), the passivation reaction (2), processes of reactivation under the effect of chemical dissolution of the passivating layer (3), and its breakdown as a result of the specific adsorption of anions.

Reactions (1-3) can be written, as is shown below, retaining the necessity for individual stages of the reactions. It has been found also that the sequence of the processes taking place with passivation presented here may change in different cases [35-37].

Active dissolution:

$$Me(OH_2)_{ad} \rightleftharpoons MeOH_{ad} + H^+ + e \quad (1.1)$$

$$MeOH_{ad} \rightarrow MeOH^+ + e \quad (1.2)$$

$$Me(OH_2)_{ad} \rightarrow MeOH^+ + H^+ + 2e \quad (1.3)$$

$$MeOH^+ + H^+ \rightarrow Me^{2+} + H_2O \quad (1.4)$$

$$Me \rightarrow Me^{2+} + 2e \quad (1.5)$$

Passivation:

$$Me(OH_2)_{ad} \rightleftharpoons MeOH_{ad} + H^+ + e \quad (2.1)$$

$$MeOH_{ad} \rightarrow MeO_{ad} + H^+ + e \quad (2.2)$$

$$Me(OH_2)_{ad} \rightarrow MeO_{ad} + 2H^+ + 2e \quad (2.3)$$

Both mechanisms differ considerably in the reactions into which enters the chemisorption compound $MeOH_{ad}$, formed in one of the anode stages of the interaction between surface atoms of the metal and sorbed molecules of water. On the one hand, the compound $MeOH_{ad}$ can pass into solution anodically (reaction 1.2); on the other hand, under appropriate conditions, it can be converted into the oxide, without the formation of soluble intermediate products. This two-dimensional oxide must be regarded as a chemisorbed layer. In contrast to this primary layer, which is of decisive importance for passivation, the oxide phase whose formation is connected with a finite current in the passive region exerts only a supplementary, secondary protective action against corrosion.

Along with these simultaneous reactions which depend on the potential, account must also be taken of the above-mentioned reactivation processes, which lead to the appearance of a stationary state with a fully established current density. As follows from the reaction scheme presented above, protons inhibit passivation, and can break down the passivating layer chemically in accordance with the reaction

$$MeO_{ad} + 2H^+ \rightarrow Me^{2+} + H_2O \quad (3)$$

The reactivating action of the anions may be a result of competing adsorption and, probably, of complex formation reactions.

In the development of the concept of passivation, as of a kinetic phenomenon, calculations were made in the publications of Ebersbach [88-92] which make it possible to express the connections between the current density and the time, and the current density and the potential analytically and graphically, on the basis of the assumption of physically reasonable parameters.

In the calculation, account is taken of the effect of the duration of the polarization, the given potential, and the activities of the protons and anions on the degree of filling and, by the same token, on the measured total current density. Together with a number of other necessary simplifications with respect to the actual passivation conditions [88, 89], it is assumed that a monomolecular coating completely stops the passage of the current. Thereby, the increase in the oxide phase is not taken into account, although the latter of course has an effect on the behavior of the passive anode. Under the assumption that at the moment of time $\tau = 0$ there is no coating on the surface, calculation gives the following result:

$$i = (i_1 + i_2)\left[1 - \frac{1}{1 + \frac{K+B}{Ci_2}}\left(1 - e^{-(Ci_2 + K + B)\tau}\right)\right] \quad (4)$$

The dependence on the potential enters here through the quantities i_1 and i_2, which correspond to reactions (1) and (2), and, if the reaction is limited by transfer of the charge, it is expressed by an ordinary exponential equation. The values of K + B are a measure of the rate of the dissolution reactions of the layer, while the quantity C is the amount of monomolecular coating per unit quantity of electricity.

From Eq. (4), with determined parameters, we can calculate the potential—current density curves corresponding to measurements under potentiostatic conditions at electrodes whose surface is renewed for each experiment. It is also possible to plot curves obtained with a stepwise or continuous change in the potential; in this case, for each potential, account is taken of the previously formed coating.

For the case of potentiostatic passivation with potentials somewhat more positive than the passivation potential, with small values of τ, Eq. (4) can be replaced by the approximate formula:

$$i=(i_1+i_2)\exp(-Ci_2\tau) \quad (5)$$

With the use of passivation processes, this calculation makes it possible to determine their kinetic parameters, in spite of the parallel course of the dissolution reaction [33-37].

Comparison with experiment attests to the agreement in principle between the theory expounded and experiment. The different behavior of metals with passivation can be explained by the difference in the parameters which characterize anode dissolution and the passivation reaction.

We denote the equilibrium potentials of the anode dissolution and passivation reactions by u_1 and u_2, and the corresponding densities of the exchange currents by i_1^0 and i_2^0. Then, the following limiting cases can be distinguished:

1) $U_2-U_1 \ll 0$. The passivation reaction is so much more preferable that the corresponding metal, in aqueous solutions in the pH interval within which the oxide is stable, always forms a passivating layer. This type of behavior is characteristic for Al, Ti, Zr, Ta, W, and others.

2) $U_2-U_1 \approx 0$. In this case the metal is at first active. The metal can be passivated anodically the more easily the less the difference U_2-U_1, and the lower the ratio of the exchange currents, i_1^0/i_2^0:

a) $i_1^0/i_2^0 > 1$. This case is observed for Fe, Co, and Ni, in solutions not containing halogens. Passivation can be attained only with a relatively high anode polarization.

b) $i_1^0/i_2^0 \ll 1$. Passivation is facilitated, case of chromium.

3) $U_2-U_1 \gg 0$.

a) $i_1^0/i_2^0 \gg 1$. If the dissolution reaction has a very high exchange current, as for example in the case of silver, the passivation potential is not attained even with large anode current densities. In this case, for passivation there is required the formation of a porous salt layer, which so far exceeds the true current density that, as a result, passivation sets in. Under these circumstances, in the system Ag/H_2SO_4 [101], in the pores of the Ag_2SO_4 deposit there is formation of Ag_2O_2.

b) $i_1^0/i_2^0 \ll 1$. If anode dissolution is strongly inhibited, passivation is facilitated. These conditions are realized, for example, for metals of the platinum group not containing halogens.

This scheme, which holds only for aqueous solutions, makes it possible to consider a variety of passivation phenomena from a single point of view.

LITERATURE CITED

1. C. L. Foley, J. Kruger, and C. J. Bechtoldt, J. Electrochem. Soc., 114, 994 (1967).
2. C. L. McBee and J. Kruger, Electrochim. Acta, 17, 1337 (1972).
3. K. Kudo, T. Shibata, G. Okamoto, and N. Sato, Corros. Sci., 8, 809 (1968).
4. J. Siejka, C. Cherki, and J. Yahalom, Electrochim. Acta, 17, 161 (1972); J. Electrochem. Soc., 119, 991 (1972).
5. J. Kruger and J. P. Calvert, J. Electrochem. Soc., 114, 43 (1967).
6. N. Sato, K. Kudo, and T. Noda, Corros. Sci., 10, 785 (1970).
7. F. C. Ho and J. L. Ord, J. Electrochem. Soc., 119, 139 (1972).
8. H. H. Uhlig, Korrosion und Korrosionsshutz, Akademie-Verlag, Berlin (1970), p. 72ff.
9. B. N. Kabanov and D. I. Leikis, Z. Fiz. Chim., 20, 995 (1946); 62, 660 (1958).
10. J. M. Kolotyrkin, Z. Elektrochem., 62, 664 (1958).
11. N. Hackerman, Z. Elektrochem., 62, 632 (1958).
12. H. G. Feller and H. H. Uhlig, J. Electrochem. Soc., 107, 864 (1960); N. D. Stolica and H. H. Uhlig, J. Electrochem. Soc., 110, 1215 (1963); F. Mansfeld and H. H. Uhlig, J. Electrochem. Soc., 115, 900 (1968).
13. G. Dietz, Dissertation TH Dresden (1956); K. Schwabe and G. Deitz, Z. Elektrochem., 62, 751 (1958).
14. K. Schwabe, Z. Phys. Chem., 214, 343 (1960).
15. K. Müller DA TH Dresden (1960); K. Schwabe, K. Müller, and A. Loge, Electrochim. Acta, 8, 193 (1963).

16. E. Kunze and K. Schwabe, Corros. Sci., 4, 109 (1964); E. Kunze, Dissertation TU Dresden (1965).
17. W. J. Müller, Die Bedeckungstheorie der Passivitat der Metalle und Ihre Experimentelle Begrundung, Verlag Chemie, Berlin (1933).
18. W. Schmidt, Zashchita Metal., 5, 608 (1969); K. Schwabe and W. Schmidt, Corros. Sci., 10, 143 (1970).
19. M. Jänchen, Dissertation TU Dresden (1972).
20. K. Ritter, Dissertation TU Dresden (1965).
21. J. Evers, DA TU Dresden (1968).
22. W. Leimbrock, DA TU Dresden (1970); K. Schwabe, U. Ebersbach, and W. Leimbrock, Electrochim. Acta, 17, 957 (1972).
23. C. Steinbach, DA TU Dresden (1964).
24. K. Schwabe, Chem. Techn., 13, 275 (1961).
25. Ch. Weissmantel, Dissertation TH Dresden (1958).
26. K. Schwabe, Chem. Techn., 10, 469 (1958).
27. K. Schwabe and Ch. Weissmantel, Z. Phys. Chem., 215, 48 (1960).
28. K. Schwabe, Isotopentechnik, 1, 175 (1960/61).
29. K. Schwabe, Electrochem. Acta, 6, 223 (1962).
30. K. Kermer, DA TU Dresden (1970); K. Kermer, G. Reinhard, and K. Schwabe, Werkstoffe und Korrosion, 22, 290 (1971); K. Schwabe and W. D. Arnold, 5th Int. Congress on Metallic Corrosion Ext. Abstrs., p. 439.
31. I. Krause, DA TU Dresden (1970).
32. W. Schwenk, Mannesmann-Forschungsberichte, No. 510 (1969); Schweiz. Arch. Angew. Wiss. Techn., 35, 387 (1969).
33. U. Ebersbach, K. Schwabe, and P. Kőnig, Electrochim. Acta, 14, 773 (1969).
34. W. Sutor, DA TU Dresden (1968).
35. G. Kreysa, Dissertation TU Dresden (1970).
36. G. Kreysa, U. Ebersbach, and K. Schwabe, Electrochim. Acta, 16, 1489 (1971).
37. U. Ebersbach, G. Kreysa, and K. Schwabe, Electrochim. Acta, 17, 445 (1972).
38. K. Schwabe, 2nd Int. Symposium "Reinstoffe in Wissenschaft und Technika," Dresden (1965).
39. I. Garz, Habilitionsschrift TH Magdeburg (1969).
40. E. Kunze and I. Eberlein, Neue Hütte, 16, 597 (1971); J. Sommer, Korrosion (Dresden), 1, No. 3, 33 (1970).
41. W. Nowak, Dissertation TU Dresden (1963).
42. I. Garz and U. Häfke, Werkstoffe und Korrosion, 22, 293 (1971); Corrosion Sci., 11, 329 (1971).
43. I. Garz, Abschlussbericht zur F/E-Arbeit No. 4 513 002/6-32/5, TH Magdeburg.
44. D.-D. Tschö, DA TH Dresden (1959).
45. E. Gaunitz, DA TH Dresden (1957); H. Sonntag, Dissertation TH Dresden (1958).
46. I. Garz, DA TH Dresden (1957).
47. K. Schwabe, Z. Phys. Chem., 214, 343 (1960).
48. R. Radeglia, DA TH Dresden (1961); K. Schwabe and R. Radeglia, Werkstoffe und Korrosion, 13, 281 (1962).
49. Ch. Voigt, DA TU Dresden (1962); K. Schwabe, J. Electrochem. Soc., 110, 663 (1963).
50. M. Paul, Dissertation TU Dresden (1966); Z. Phys. Chem., 237, 225 (1968).
51. J. Göllner, Dissertation TH Magdeburg (1972); J. Göllner and I. Garz, Wiss, Z. TH Magdeburg, 16, 45 (1972).
52. Le dang Anh, Dissertation TU Dresden (1972); K. Schwabe and Le dang Anh, Zashchita Metal., 9, 541 (1973).
53. R. Gressmann, Dissertation TU Dresden (1965); Corros. Sci., 8, 325 (1968).
54. I. Garz, H. Worch, and W. Schatt, Corros. Sci., 9, 71 (1969).
55. W. Schatt and H. Worch, Corros. Sci., 9, 869 (1969).
56. I. Garz and H. Worch, Z. TH Magdeburg, 14, 77 (1970).
57. K.-H. Ebert, DA TU Dresden; W. Schatt and H. Worch, Corros. Sci., 11, 623 (1971).
58. N. Schönborn, DA TU Dresden (1962).
59. Nguyen Quy, Dissertation TU Dresden (1962); K. Schwabe and Nguyen Quy, Mber. Dt. Akad. Wiss. Berlin, 5, 372 (1963).
60. H. Herold, DA TU Dresden (1963).
61. J. Nowak, Dissertation TU Dresden (1971).

62. J. Kunze, Corros Sci., 7, 273 (1967).
63. J. Tutschku, DA TU Dresden (1965).
64. B. Schultze, Dissertation TU Dresden (1971).
65. H. Geissler, DA TU Dresden (1965).
66. D. Rettig, Ch. Voigt, and K. Schwabe, Corros. Sci., 10, 657 (1970).
67. K. F. Bonhoeffer, Naturwiss., 40, 301 (1953).
68. W. Lorenz, Z. Phys. Chem., N. F., 20, 95 (1959).
69. F. Lohmann, DA TH Dresden (1960); K. Schwabe and F. Lohmann, Z. Phys. Chem., 215, 158 (1960/61).
70. M. Böttiger, DA TH Dresden (1960).
71. D. Hönicke, DA TH Dresden (1960).
72. K. Schwabe, Naturwiss., 49, 56 (1962).
73. E. Ferse, Z. Phys. Chem., 231, 237 (1956).
74. H.-B. Lück, Dissertation TU Dresden (1970); K. Schwabe and H.-B. Lück, Electrochim. Acta, 17, 99 (1972).
75. K. Schwabe, Habilitationsschrift TH Dresden (1933).
76. K. Schwabe, Z. Phys. Chem., 226, 1 (1964).
77. K. Schwabe and Ch. Weissmantel, Mber. Dt. Akad. Wiss., Berlin, 5, 23 (1963).
78. K. Schwabe and Ch. Weissmantel, Electrochim. Acta, 9, 991 (1964).
79. Ch. Weissmantel, Habilitationsschrift TU Dresden (1964).
80. K. Schwabe, Electrochim. Acta, 3, 186 (1960).
81. K. Schwabe, Wiss. Z. TH Karl-Marx-Stadt, 6, 27 (1964).
82. U. Ebersbach, Diplomarbeit TU Dresden (1965).
83. K. Schwabe, Angew. Chemie, 78, 253 (1966).
84. K. Schwabe, Zashchita Metal., 2, 393 (1966).
85. K. Schwabe, U. Ebersbach, and K. Ritter, Kemian Teollisuus, 23, 1073 (1966).
86. K. Schwabe, Werkstoffe und Korrosion, 18, 961 (1967).
87. U. Ebersbach, K. Schwabe, and K. Ritter, Electrochim. Acta, 12, 927 (1967).
88. U. Ebersbach, Dissertation TU Dresden (1969).
89. K. Schwabe and U. Ebersbach, Wiss. Z. TH Ilmenau, 16, 125 (1970).
90. K. Schwabe, Wiss. Z. TH Magdeburg, 14, 67 (1970).
91. K. Schwabe, Z. Chem., 11, 245 (1971).
92. U. Ebersbach, Zashchita Metal., 7, 376 (1971).
93. Zentralstelle für Korrosionsschutz, F-/E-Bericht 32/1972.
94. C. Herold, P. Schubert, and W.-D. Schulze, Korrosion (Dresden), 3, 250 (1972).
95. R. Engelhardt and H. Bondriot, Neue Hütte, 17, 366 (1972).
96. W. Meisel, Z. Chem., 11, 238 (1971).
97. W. Meisel and G. Kreysa, Z. Anorgan. und Allgem. Chem., 31, 395 (1973).
98. F. Wiedemann, Korrosion (Dresden), 1, 17 (1970).
99. J. M. Kolotyrkin, J. M. Golovina, and G. M. Florianovich, Dokl. Akad. Nauk, 148, 1106 (1963); B. N. Kabanov and V. D. Kashcheev, Dokl. Akad. Nauk, 151, 883 (1963).
100. R. W. Guard, Trans. Mat. Soc. AIME, 218, 573 (1960); R. A. Beland, Metals-Materials, 3, 53 (1963).
101. Eichler, Dissertation TU Dresden (1967).
102. K. Schwabe and Ch. Voigt, Werkstoffe und Korrosion, 16, 125 (1965).
103. M. Paul and G. Schreiter, Korrosion, 3, 30 (1972).
104. U. Ebersbach, Zashchita Metal., 10, 374 (1974).
105. C. H. Bancroft, Brit. Corr. J., 6, 119 (1971).
106. C.-G. Nestler, Dissertation TH Karl-Marx-Stadt (1971).
107. J. E. Holliday and R. P. Frankelthal, J. Electrochem. Soc., 119, 1190 (1972).