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A Quantitative Concept of the Permeability to Hydrogen of Passivating Layers on a Metal at the Apex of the Crack in the Corrosion-induced Cracking of Constructional Materials

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A general theoretical and methodological approach to the determination of the role of the local anodic dissolution and hydrogen-induced embrittlement in the corrosion-induced cracking of various constructional materials is examined. The possibility of the quantitative estimation of the role of the hydrogen-induced embrittlement in the corrosion-induced cracking of high-strength steels and titanium, aluminium, magnesium, and zirconium alloys is demonstrated. A quantitative concept of the permeability of hydrogen of passivating layers on a metal at the apex of a crack, which has made it possible to determine quantitatively for the first time the relation between the critical concentration of hydrogen and the stress intensity coefficient in the hydrogen-induced embrittlement of steels and titanium and aluminium alloys, has been developed on the basis of several postulates. Two new methods for the investigation of the adsorption of hydrogen and anions at the apex of the crack in corrosion-induced cracking, based on this concept, are proposed.
The bibliography includes 47 references.

CONTENTS

I. Introduction 428
II. Relation between the critical concentration of hydrogen and the critical stress intensity coefficient in the hydrogen-induced embrittlement of constructional materials 429
III. The permeability to hydrogen of passiviting layers on a metal at the apex of the crack in corrosion-induced cracking 431
IV. The degree of surface coverage of the passivating film on a metal at the apex of the crack by adsorbed hydrogen atoms 436
V. Hydrogen-induced embrittlement in corrosion-induced cracking at positive potentials 438

I. INTRODUCTION

There is at present no unique concept concerning the mechanism of the growth of cracks in corrosion-induced cracking (CIC) on any specific alloy–electrolyte system. There is an even greater lack of a generally accepted theoretical and methodological approach to the determination of the mechanism of the growth of cracks which would be applicable to any constructional materials regardless of their composition and structural state. The majority of studies have been characterised by a one-sided approach to the determination of the CIC mechanism—whilst justifying the leading role of one of the possible mechanisms, the authors fail to consider or reject the possibility of the growth of cracks via other, competing mechanisms. An attempt has been made[1-3] to develop a general electrochemical method for the determination of the CIC mechanism using the following initial postulates. At the apex of the crack there is a possibility of the simultaneous occurrence of two main processes–local anodic dissolution (LAD) and hydrogen-induced embrittlement (HIE), the role of each of which depends on the composition of the alloy and the electrolyte, the heat treatment of the alloy, the potential, etc. and also on the rate of growth of the crack V and the stress intensity coefficient K. The coefficient V is regarded as an index of the extent to which the properties of the metal at the apex of the crack approach those of a freshly formed surface and defines the permeability of the passivating films to hydrogen. The different types of influence of cathodic polarisation on the growth of cracks observed in the study of high-strength martensite steels[1] serve as an experimental basis of the ideas concerning the CIC mechanism developed in the above studies.[1-3] This phenomenon consists in the fact that, other conditions being equal, the same cathodic polarisation retards the growth of cracks if the initial V and K at the corrosion potential are below certain critical values and accelerates the growth of cracks if they are above such values. The physical significance of the concept of the "critical rate of growth of the crack" is as follows. With increase of V, the time required for the formation of passivating layers on the metal at the top of the crack, which constitute barriers to the penetration of hydrogen into the metal, diminishes. Regardless of the value of V, cathodic polarisation increases the rate of the electrochemical evolution of hydrogen. However, for coefficients V below the critical value, the films formed on the metal hinder the penetration of hydrogen into the latter, the attainment of the critical concentration of hydrogen, and the onset of the HIE. On the other hand, cathodic polarisation suppresses the LAD and, as shown by experiment, reduces V. When the critical and higher values of V are µreached, passivating films can no longer effectively prevent the penetration of hydrogen into the metal and for this reason cathodic polarisation accelerates the growth of cracks via the HIE mechanism although it does reduce the rate of local dissolution.

The critical rate of growth of the crack V_{cr} and the corresponding critical stress intensity coefficient K_{HIE} are quantitative indices of the role of the LAD and HIE in the growth of the cracks; for $V < V_{cr}$ and $K < K_{HIE}$, the main CIC mechanism involves the LAD; for $V > V_{cr}$ and $K > K_{HIE}$, the mechanism is based on the HIE. The values of V_{cr} and K_{HIE} depend on the composition of the alloy and the electrolyte, the cathodic polarisation potential, etc. Changes in the alloy–electrolyte system reducing the stability of the passivating layers at the apex of the crack or the critical concentration of hydrogen should diminish V_{cr} and K_{HIE}, i.e. should enhance the role of the HIE in the CIC. This hypothesis was confirmed experimentally in the determination of the dependence of V_{cr} and K_{HIE} in the CIC of high-strength steels on the content in the electrolyte of chlorides, agents promoting such saturations with hydrogen, and oxidants and also the dependence of these quantities on the heat treatment of the steels.[1,2]

Although the ideas which we have developed[1-3] about the CIC mechanism suffer from no limitations associated with the composition of the alloy or the electrolyte, they cannot be transferred mechanically to all materials without demonstrating experimentally that cathodic polarisation exerts different types of influence on the growth of cracks in the CIC of these materials, as for high-strength steels. As the above ideas were generalised, they were subjected to tests. In particular, it was assumed *a priori* that, when any alloy (or group of alloys with a specific base) tends to undergo HIE in the absence of a corrosion medium but at the same time cathodic polarisation always has the same effect on its CIC, it is possible to alter the CIC conditions in such a way that cathodic polarisation exerts different types of effect on V for this alloy. For example, it is known that austenite steels and titanium, zirconium, magnesium, and alluminium alloys tend to undergo internal HIE but, in CIC in 0.5 M NaCl solution, cathodic polarisation only retards the growth of cracks in these materials.[2] This means that in the NaCl solution the main CIC mechanism involves LAD, while HIE does not play an appreciable role although it can occur. On the other hand, one can postulate the existence of conditions for these materials such that HIE plays an appreciable or main role in the CIC. Indeed electrolytes have been selected in which cathodic polarisation in the CIC of the above materials influenced the growth of cracks in different ways; for V and K below their critical values, it reduced V, increasing it after the attainment of such values.[2-4]

The agreement between the theoretical prediction and the experimental fact of the different types of influence of cathodic polarisation on the growth of cracks in the CIC of austenite high-strength steels and titanium, zirconium, magnesium, and aluminium alloys[2-4] suggests that this feature is common to all CIC processes and makes it possible to formulate a general theoretical and methodological approach to the determination of the role of LAD and HIE in the CIC of constructional materials regardless of their base and the composition of the electrolyte. According to this approach, the unambiguous influence of cathodic polarisation (i.e. only retardation or only acceleration of the growth of cracks regardless of the values of V and K) should be regarded as a special case of its varying influence on V, reflecting the independence of the leading CIC mechanism of V and K. More detailed arguments in support of this postulate can be found in another communication.[2]

The ideas about the CIC mechanism developed in a series of studies[1-4] are mainly qualitative. In the present review a quantitative concept of the permeability to hydrogen of passivating layers on a metal at the apex of the crack, which makes it possible to establish a relation between the electrochemical CIC conditions, the coefficients V_{cr} and K_{HIE}, and the critical concentration of hydrogen in the HIE, has been formulated on the basis of the extension and analysis of these ideas.

II. RELATION BETWEEN THE CRITICAL CONCENTRATION OF HYDROGEN AND THE CRITICAL STRESS INTENSITY COEFFICIENT IN THE HYDROGEN-INDUCED EMBRITTLEMENT OF CONSTRUCTIONAL MATERIALS

The fundamental concepts of the theory of the HIE of constructional materials are the critical concentration of hydrogen c_{cr} and the critical stress intensity coefficient in HIE, K_{HIE}. The value of K_{HIE} can be determined experimentally both in the HIE in gaseous hydrogen and in electrolyte solution under CIC conditions. However, none of the methods of physicochemical analysis and none of the HIE theories have so far been developed sufficiently to permit the experimental or computational determination of the absolute values of c_{cr} (there is no generally accepted physical model of the HIE; models of the distribution of stresses ahead of the apex of the crack are in the state of development; the configuration of the apex of the crack and the location of the breakdown zone in the HIE relative to the top of the crack are unknown, etc.[2,5]). The question of the relation between c_{cr} and K_{HIE} is extremely important for the theory of HIE and was frequently discussed previously.[2,5-9] However, at the present time only the following qualitative relation can be regarded as established: the higher K_{HIE}, the lower c_{cr} and conversely.

The method for the investigation of the relation between c_{cr} and K_{HIE} proposed by the present author[10] follows from general ideas about the CIC mechanism[1-4] and is based on the possibility of the quantitative estimation of the role of HIE in CIC by means of the experimental determination of the values of V_{cr} and the corresponding critical stress intensity coefficients K_{HIE}. These values depend on the electrolyte composition, the heat treatment and the structure and strength of the alloy, the pH of the medium, the presence of agents promoting saturation with hydrogen, the process temperature, the potential of the specimen, and also the nature and the ratio of the concentrations of the corrosive and passivating ions. The last factor is particularly important because this ratio defines, like V, the permeability to hydrogen of the film of the metal at the top of the crack.

The main postulate of the HIE theory states[2] that the crack grows when the critical hydrogen concentration c_{cr} is established ahead of its apex and the critical value of the stress intensity coefficient K_{HIE} has been attained. Having supplemented this condition by stating that c_{cr} decreases with increase of K_{HIE}, one can formulate the equation

$$c_{cr}K_{HIE}^{n} = \text{const.} \qquad (1)$$

This relation, proposed in Ref.11, is one of the possible formulations of the criterion of breakdown in HIE and is not based on any specific physical model of HIE. Formally it is close to the power relation examined by Van Leeuwen[9] within the framework of the decohesive theory of HIE.[8]

The penetration of hydrogen into the metal ahead of the apex of the crack growing under the CIC conditions includes several successive steps:

(1) The occurrence of an electrochemical reaction as a result of which a definite concentration (degree of surface coverage) of adsorbed hydrogen atoms θ is established on the surface of the passivating film.

(2) The penetration of the hydrogen adsorbed on the surface of the film through the latter and the establishment of a certain concentration c_{ms} of hydrogen in the surface layer of the metal at the apex of the crack at the metal–film boundary. This concentration is determined by the permeability of the film to hydrogen: $c_{ms} = \theta\alpha$. The dimensionless quantity shows what proportion of the hydrogen adsorbed on the passivating film penetrates through the latter and is responsible for the HIE.

(3) The attainment of a critical concentration of hydrogen $c_{cr} = c_{ms}\xi = \theta\alpha\xi$ directly at the apex of the crack ($\xi = 1$) or at a certain distance from it ($\xi < 1$), the distance being unimportant, since the given formal treatment is not associated with any specific physical model of HIE. The requirements that the HIE mechanism remains unaltered when the experimental conditions are changed (for example, when the cathodic polarisation potential or the concentration of chloride ions are changed) and that the transport coefficient ξ remains constant are significant.

The HIE mechanism is determined by the properties of the metal–hydrogen system and is independent of the electrochemical conditions at the apex of the crack which influence

the HIE kinetics in CIC. The coefficient ξ depends on the diffusion coefficient of hydrogen in the metal, the distance of the breakdown zone from the apex of the crack, and the diffusion time, i.e. on the duration of the cathodic polarisation in the determination of the values of K_{HIE}. For a constant cathodic polarisation time, ξ = const. for the given alloy.

The constancy of the cathodic polarisation time is ensured by the method used to determine K_{HIE},[10] which consists of the following steps. The specimen in the electrolyte at a certain initial potential E_i (for example the corrosion potential E_{cor}) is stressed until the attainment of an arbitrary coefficient K, is maintained in this state for 300 s, and is then subjected to cathodic polarisation until the attainment of the potential E_{cp}. If the cathodic polarisation induces an acceleration of the growth of the crack up to 150 s, the specimen is again polarised to E_i, K is reduced by 3–5%, and, after being maintained at E_i the specimen is polarised to E_{cp}. If the cathodic polarisation does not accelerate the growth of the crack in the course of 150 s, then K is increased by 3–5% and the above operations are repeated. Thus, using the method of successive approximations, K_{HIE} is determined as the minimum value of K for which cathodic polarisation to E_{cp} accelerates the growth of the crack up to 150 s. The relative errors in the determination of K_{HIE} and V_{cr} are 4 and 10% respectively.[10]

The quantities θ and α depend on the compositions of the alloy and the electrolyte, the pH, temperature, the potentials E_i and E_{cp}, etc. Other conditions being equal, the permeability to hydrogen is proportional to the rate of growth of the crack and the concentration of the corrosive anion, for example the chloride ion $[Cl^-]$, adsorbed on the film at the top of the crack. It is assumed that the adsorption of chloride ions from solution is described by the Langmuir isotherm at low coverages: $[Cl^-] = \beta(Cl^-)$, where β is the adsorption coefficient and (Cl^-) and $[Cl^-]$ are the concentrations of chloride ions in solution and adsorbed on the film respectively. It is also assumed that, when $V \leq 0.01$ mm h^{-1}, the permeability of the film to hydrogen is independent of the rate of growth of the crack and, when $V > 0.01$ mm h^{-1}, it is proportional to V.[10]

These ideas about the permeability to hydrogen of passivating films on the metal on top of the crack growing under CIC conditions are based on the present author's data;[2,3] in the absence of halide ions, it proved impossible to induce the HIE of aluminium, titanium, and zirconium alloys under CIC conditions even for $K \cong K_{IC}$ (where K_{IC} is the critical stress intensity coefficient in the absence of corrosion medium) and a cathodic polarisation potential E_{cp} up to −4 V (relative to n.h.e.†), while for certain ratios of the concentrations of passivator and depassivotor ions optimal for each material the acceleration of the growth of cracks under cathodic polarisation (i.e. HIE and CIC) is observed for $K_{HIE} \leq 0.03$, K_{IC}, and $E = -0.7$ V. For the materials investigated previously,[2,3] the quantity α can be neglected in the absence of corrosive ions, but, for high-strength steels this cannot be done in the general case, since their CIC via the HIE mechanism can occur, for example, in distilled water. However, even for high-strength steels it is possible to establish conditions (by selecting the composition of the electrolyte and the cathodic polarisation potential) under which the permeability of the film to hydrogen is determined by the concentration of the corrosive ions in the electrolyte also at the top of the crack. In this Section only such conditions will in fact be considered; the permeability of steels to hydrogen is discussed in greater detail in Section III.

Taking into account the above assumptions concerning the critical parameters describing quantitatively the role of HIE in CIC (V_{cr} and K_{HIE}, the criterion for the HIE in the alloy–hydrogen system (1) can be used also as the criterion of the HIE in CIC having formulated it in the form

$$\theta\alpha\xi K_{HIE}^n = \text{const}, \tag{2}$$

$$\theta\xi\beta(Cl^-)V_{cr}K_{HIE}^n = \text{const}, \tag{3}$$

$$\lg[(Cl^-)V_{cr}] = \text{const} - n\lg K_{HIE}. \tag{4}$$

The constant coefficients ξ and β in Eqn.(3) are unknown and it is therefore impossible to determine the permeability of the film to hydrogen in absolute units. However, the exponent n in the power relation (1) between the critical concentration of hydrogen and the stress intensity coefficient can be determined from the slope of the linear plot in terms of the variables of Eqn.(4).

In conformity with the assumptions made, the power exponent n in Eqns.(1)–(4) characterises the HIE in the alloy–hydrogen system and is in no way related to the corrosion stability of the alloy in any particular electrolyte. Hence it follows that n may depend on the composition, structure, and the conditions of the heat treatment of the alloy and on temperature but should be independent of any electrochemical parameters of the electrolyte.[10] The experimental test of these conclusions shows that the assumptions made in the derivation of Eqns.(1)–(4) are valid. In particular, the observed value of n should be independent of the method of introduction of hydrogen into the specimen: for the same material, the exponent n should be identical for HIE under CIC conditions and in an atmosphere of gaseous hydrogen. For HIE in CIC, the exponent n should not be influenced by the nature of the solvent, the concentrations of the passivator and depassivator ions, the pH, the cathodic polarisation potential, and similar factors, although variation of these parameters does influence significantly V_{cr}, K_{HIE}, θ, and other terms in Eqns.(2)–(4).

Since n is independent of the electrochemical parameters of the solution, all the data obtained for one material in different solutions may be plotted on a single curve. In each series of experiments where only the concentration (Cl^-) is varied, the solution with the maximum value of (Cl^-) is selected as the standard.[10] Then, for this series, Eqn.(4) is transformed into

$$\lg\frac{[V_{cr}(Cl^-)]_x}{[V_{cr}(Cl^-)]_{st}} = \lg\frac{\alpha_x}{\alpha_{cr}} = -n\lg\frac{K_{HIE,x}}{K_{HIE,st}}, \tag{5}$$

where the subscripts "st" and "x" correspond to the standard in variable concentrations (Cl^-).

The validity of Eqn.(5) was tested in a study[10] in which the dependence of K_{HIE} and V_{cr} on the concentrations of chloride, bromide, and sulphate ions was obtained in various buffer solutions in the CIC of aluminium and titanium alloys and four high-strength martensite steels. These data, treated in accordance with Eqn.(5), are presented in Fig.1; it is seen that, despite the considerable scatter, the experimental points for each material do indeed fit on a straight line. The slopes of the straight lines (i.e. the power exponents n) for the aluminium alloy, the titanium alloys, and the high-strength steels are respectively 2.1, 3.0, and 5.5. As assumed, n for each material is independent of the electrochemical parameters associated with the electrolyte; however, within the limits of experimental error, it was impossible to

†Here and henceforth the potentials are given throughout relative to the normal hydrogen electrode (n.h.e.).

observe the dependence of n not only on the conditions in the heat treatment of the steel but also on the composition, structure, and strength of titanium α-alloys and the high-strength martensite and martensitically ageing steels.

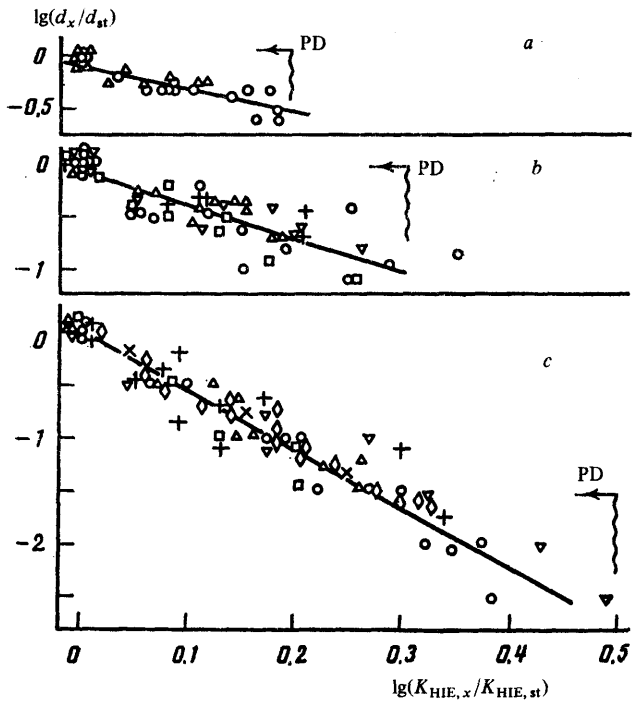


Figure 1. Dependence of K_{HIE} in the CIC of aluminium (*a*), and titanium (*b*) alloys and high-strength steels (*c*) on the permeability to hydrogen of the passivating films at the apex of the crack; PD—planar deformation boundary. The different symbols correspond to different alloys, different heat treatment conditions, and different electrolyte compositions.[10]

One can apparently conclude that the exponent n in Eqn.(1) is a characteristic parameter of the HIE of the alloys and depends solely on the nature of the metal on which the alloy is based. One cannot rule out the possibility that the different values of n for aluminium and titanium alloys and high-strength steels reflect different mechanisms of the HIE of these materials. We may note that, with increase of the tendency of the materials towards HIE in the series aluminium alloys–titanium alloys–high-strength steels, the exponent n also increases. Unfortunately, there are no data concerning the influence of the type of lattice on n; such data can be obtained by studying with the aid of the method described titanium β-alloys and high-strength austenite steels.

As stated above, in the model considered the exponent n should not be influenced by the method of introduction of hydrogen into the alloy. The validity of this postulate can be tested by comparing the value $n = 5.5$ obtained[10] for high-strength steels (under the conditions of HIE in CIC) with the value of n under the conditions of gas-phase HIE. There are fairly numerous literature data on the dependence of the K_{HIE} of high-strength steels on the hydrogen pressure, but they are unsuitable for the determination of n, because they refer mainly to the range of high (in excess of 1 atm) pressures at which one can postulate the maximum degree of surface coverage by adsorbed hydrogen atoms. Virtually the only study in which the dependence of K_{HIE} (for high-strength martensite steel 4340) on hydrogen pressure was determined (in the range 0.1–1000 mmHg) is that of Oriani and Josephic.[8] The data from this investigation, treated in terms of Eqn.(5), are designated in Fig.1c by rhombuses; they fall within the scatter band of the HIE data in the CIC of other high-strength steels. The exponent n, determined independently from the results of the above investigation,[8] is 5.1 and is virtually identical with the value $n = 5.5 \pm 0.5$ found for HIE in CIC.[10]

Despite the fact that Eqns.(1)–(5) are empirical and are not based on any specific physical model of HIE, the values of n obtained[10] can be useful in the development of physical ideas about the mechanism of the HIE of various materials. In particular, the identity of the values of n for the HIE in the CIC of high-strength steels and for their HIE in a gaseous medium makes it possible to assume that the HIE of these materials has the same mechanism.

The derivation of Eqns.(1)–(5) is based on several postulates (the applicability of the proposed criterion of breakdown in HIE, the direct proportionality of the permeability to hydrogen to the rate of growth of the crack and to the concentration of chloride ions adsorbed on the film, and the independence of θ of $[Cl^-]$, which do not conflict with the known theoretical ideas but cannot be justified analytically or tested experimentally. For example, it is impossible to test by an independent procedure the values of n obtained,[10] because only qualitative ideas about the relation between c_{cr} and K_{HIE} have been developed in the HIE theory. Nevertheless the concept of the permeability of passivating layers on the metal to hydrogen at the top of the crack, developed by Marichev,[10] permits predictions for certain values of n which can be tested experimentally (see Sections III and IV).

III. THE PERMEABILITY TO HYDROGEN OF PASSIVATING LAYERS ON A METAL AT THE APEX OF THE CRACK IN CORROSION-INDUCED CRACKING

The permeability to hydrogen α was formally introduced above dimensionless quantity showing which part of the hydrogen adsorbed on the passivating film penetrates through it onto the metal–film interface and is responsible for the occurrence of HIE. The mechanism of the permeability to hydrogen has not yet been fully elucidated but one can assume that the diffusional transport of hydrogen through the passivating film does not play the main role. Thus in the CIC of aluminium and titanium alloys for $K > K_{HIE}$ the acceleration of the growth of the cracks after the cathodic polarisation has been switched on takes place after 1 s, while for $K < K_{HIE}$ under the same CIC conditions acceleration was not observed even after more than 10^4 s. Furthermore, the occurrence of the CIC of these alloys via the HIE mechanism, for example, in 1 M CrO_3 has not been observed even for $K \cong K_{IC}$, but, when 0.01 M NaCl is introduced, HIE takes place at a high rate for low values of K. It appears unlikely that such small amounts of added chloride ions, which do not alter significantly the corrosion potential and do not cause the breakdown of the passive state of the alloys in 1 M CrO_3 solutions, should increase by several orders of magnitude the diffusion coefficient of hydrogen in the passivating film.

Since θ and the constant coefficients (except n) in Eqns. (2) and (3) are unknown, the absolute values of the permeability to hydrogen cannot be determined from data obtained

in tests on the CIC (i.e. the quantities V_{cr} and K_{HIE}). However, having adopted $\alpha = 1$ for certain arbitrarily selected standard experimental conditions, it is possible to determine the relative changes in α_x when, for example, the concentration of chloride ions in the electrolyte is altered:

$$\alpha_x = \frac{V_{st}}{V_x}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n. \quad (6)$$

It is assumed that small changes in the composition of the electrolyte (as a rule by not more than 0.05 M of activator or passivator ions) do not affect the surface coverage θ of the film by adsorbed hydrogen, which depends mainly on the potential of the specimen and the pH of the electrolyte.[12]

The most complete information about the dependence of the permeability to hydrogen α of passivating layers on a metal at the top of the crack on the electrolyte composition can be obtained for high-strength steels, since in the course of their CIC the growth of cracks via the HIE mechanism at sufficiently negative cathodic polarisation potentials takes place in water and NaOH solutions not containing activating ions.[2] The following standard experimental conditions have been selected[13] for high-strength steels: NaOH solution at pH 10, cathodic polarisation potential for the determination of V_{cr} and K_{HIE} amounting to $E_{cp} = 0.8$ V, and the period from the instant when the cathodic polarisation is switched on to the instant of the acceleration of the growth of cracks via the HIE mechanism amounting to 150 s. This choice was dictated by the necessity to keep constant the pH of the electrolyte as its composition is changed (for example, the 0.03 M Na_2HPO_4 solution has pH 9.9), the appreciably insignificant corrosion of the steels investigated, and also the fact that in this electrolyte the critical HIE stress intensity coefficient is small for $E_{cp} = -0.8$ V. The latter significantly extends the possible limits of variation of the electrolyte composition, especially on introduction of passivators, since the increase of K_{HIE} induced by them should not lead to the breakdown of the passive planar deformation state of the specimens.[14] The corrosion potential of the steels studied was approximately 0.2 V in NaOH solution at pH 10 and −0.15 V in 0.03 M Na_2HPO_4 solution, changing insignificantly (by ±0.05 V) after the introduction of activator or passivator ions into these electrolytes at a concentration of 0.05 M.

Fig. 2 shows that the introduction of additional NaOH at a concentration of 0.03 M into the standard NaOH solution increases the permeability to hydrogen of the passivating films at the apex of the crack by a factor of 6, while the additional introduction of 0.01 M NaCl causes a further increase by a factor of 2. The addition of nitrate ions to these solutions lowers sharply the permeability to hydrogen, the decrease being more pronounced the lower the initial permeability. Thus, when 0.001 M $NaNO_3$ is introduced into the standard solution, the permeability to hydrogen diminishes by a factor of 15 (curve *1*), but it hardly changes when the solution contains also 0.01 NaCl (curve *3*).

We must emphasise that not only nitrates but also other anions, mainly oxidants (chromates, nitrites, nitrobenzoates, etc.) can reduce α, but there is no correlation between the strength of the oxidant and the degree of its influence on the permeability to hydrogen. For example, the strongest oxidants investigated by the present author,[13] namely H_2O_2 and $Na_2S_2O_8$, at concentrations up to 0.1 M do not reduce α in the CIC of steel in the presence of 0.03 M Na_2HPO_4 (the latter actually increases significantly α, since its reduction entails the formation of sulphate, which, like the chloride ion, increases the permeability to hydrogen). The introduction into the same solution of 0.05 M $NaNO_3$, which is an appreciably weaker oxidant but effectively displaces chloride ions from the surface of the steel as a result of competitive adsorption,[13,15] lowers α by three orders of magnitude.

It is of interest to compare the role of phosphates and nitrates. Phosphates are assumed to be corrosion inhibitors; indeed in the presence of 0.03 M Na_2HPO_4, the corrosion potential increases by 0.05 V compared with the potential in NaOH and the corrosion of the specimens is almost fully suppressed but the permeability to hydrogen of the passivating layers at the top of the crack increases by 5–6. On the other hand, nitrates are believed to behave as corrosion activators (although there have been studies[16,17] demonstrating their inhibiting effect on the CIC process and corrosion fatigue), but they reduce α very markedly in solutions containing chlorides and sulphates and fully suppress the CIC of high-strength steels in a standard NaOH solution. In a series of prolonged (up to one month) experiments, it was shown that not only K_{HIE} but also K_{ISCC} (critical coefficient of the density of stresses in CIC) increases appreciably in the presence of nitrates.[13]

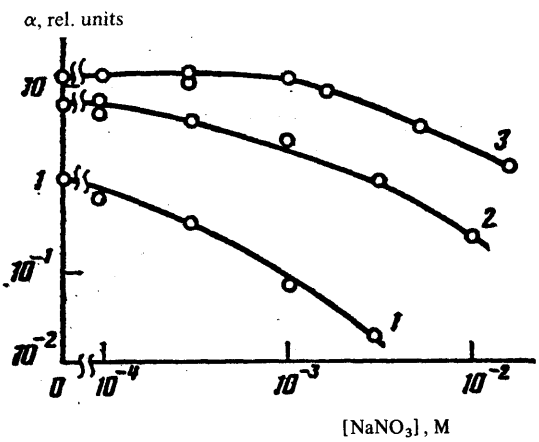


Figure 2. Dependence of the permeability to hydrogen, α, of passivating layers on a metal at the apex of the crack on the concentration of added $NaNO_3$ in the CIC of the steel 33Kh3NMFA in solutions at pH 10: *1*) NaOH; *2*) NaOH + 0.03 M Na_2HPO_4; *3*) NaOH + 0.03 Na_2HPO_4 + 0.01 M NaCl. The permeability to hydrogen in the NaOH solution was adopted as unity; $E_{cp} = -0.8$ V.[13]

It was subsequently established[15] that, when HIE conditions in distilled water are chosen as standard, all the anions investigated—the phosphate, acetate, borate, nitrate, hydroxide, and especially chloride and sulphate ions—increase the permeability of passivating films to hydrogen, i.e. they function as activators of the HIE of high-strength steels. The activating effect of anions on the HIE process depends significantly on the steel composition. Nitrates and other oxidants lower the permeability to hydrogen and increase HIE and hence they function as inhibitors of the HIE process only when they are introduced into solutions containing other anions, for example, chloride or sulphate ions, which activate the HIE of steel to a greater extent than nitrate ions.

One of the consequences of the concept of the permeability of passivating films to hydrogen has been the development of a method of study *in situ* of the adsorption of chloride ions (or other activator ions) on the film at the apex of the crack in the CIC of constructional materials.[15] The method consists in the experimental determination of K_{HIE} and V_{cr} under standard and real conditions and in the calculation of

the relative changes in the concentration of chloride ions $[Cl^-]$ at the top of the crack. The standard condition is assumed to be $[Cl^-]_{st} = 1$. The real conditions differ in the concentrations of chloride or nitrate ions in the solution. It has been suggested that the constant coefficients in Eqns.(2) and (3) are identical for standard and real conditions. It follows from Eqns.(2) and (3) that

$$[Cl^-]_x = \frac{V_{st}}{V_x}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n. \qquad (7)$$

Within the framework of the assumptions made above, Eqn. (7) makes it possible to calculate the isotherms for the adsorption of chloride ions on the surface of the passivating film at the top of the crack growing in the CIC and also the decrease of $[Cl^-]$ as a result of competitive adsorption after the introduction of various extraneous anions, especially corrosion inhibitors, into the standard solutions.[15] This method can be used to investigate the adsorption of not only chloride ions but also of other anions in the presence of which the CIC of the alloy proceeds via the HIE mechanism. In the CIC of high-strength steels, it is possible to investigate by this method, for example, the adsorption of sulphate, phosphate, and other ions and the influence of inhibitors on the latter. For different constructional materials, the research technique is the same, but the exponent in Eqn.(7) varies (see above). The standard conditions (i.e. the material, the electrolyte composition, and the cathodic polarisation potential) are also different in the determination of the critical HIE parameters.

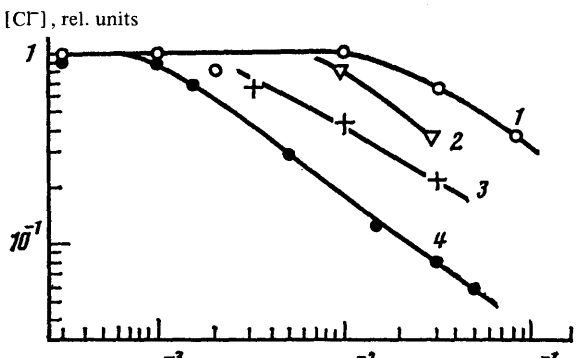


Figure 3. Dependence of the concentration of chloride ions adsorbed on the passivating film at the apex of the crack in the CIC of the steel 33Kh3NMFA in 0.03 M Na_2HPO_4 + 0.01 M NaCl solution on the concentration of inhibitors: *1*) $NaCrO_4$; *2*) hexamethyleneammonium 3,5-dinitrobenzoate (G-4); *3*) $NaNO_3$; *4*) $NaNO_3$; $[Cl^-] = 1$ in solution in the absence of inhibitors; $E_{cp} = -0.8$ V.[15]

Fig.3 presents certain results of a study of the competitive adsorption of chloride ions in the region of the apex of the crack in the presence of inhibitors in the CIC of different materials.[15,19] It shows that the introduction of oxidant anions into the standard solution hinders the adsorption of chloride ions, the nitrate ion, which has come to be regarded as an activator rather than an inhibitor of corrosion, being the most effective. Under the CIC conditions, this anion displaces chloride ions from the surface of the passivating film at the top of the crack much more vigorously than the known general corrosion inhibitors such as chromates, nitrites, and the organic G-4 inhibitor. This influence of nitrate is characteristic of the CIC of not only high-strength steels but also titanium and aluminium alloys.[19]

In this connection, mention should be made of the study[17] in which the CIC of high-strength steel was investigated in distilled water and it was shown that at high rates of growth of the crack nitrates are more effective as CIC inhibitors than nitrites, while chromates do not exhibit an inhibiting activity (at concentrations of 0.01 M). We may also mention a study[16] in which the possibility of the inhibition by nitrate of the corrosion fatigue of the high-strength aluminium alloy 7075 in a solution of chloride was demonstrated. It may be that the adsorption processes in the CIC exhibit a definite specificity which is in fact responsible for the highest adsorption capacity of the nitrate ion and the most effective displacement by the latter of chloride ions from the surface of the passivating film at the apex of the crack. As stated above, this is not associated with either the charges of the anions or with their oxidising capacity.

The above specificity has apparently no direct relation with oxo-ion reduction processes either, because the chromate ion influences the permeability to hydrogen less strongly than nitrate although it is not only reduced on the surface of iron but also enters into the composition of the passivating film in the form of Cr^{3+}.[18] In the CIC of aluminium alloys, the effectiveness of chromate is also greater than that of nitrate, vanadate, and molybdate,[19] although it has been established by electronic X-ray spectroscopy (ESCA) that it also enters into the composition of the film. The specificity of the adsorption processes in CIC affects also the behaviour of phosphate: being a general corrosion inhibitor, it increases the permeability to hydrogen of passivating films at the apex of the crack (Fig.2). The method for the study of adsorption at the apex of the crack examined above makes it possible to discover similar differences in the behaviour of oxo-ions in CIC and general corrosion; however, the formal ideas about the permeability to hydrogen, constituting its basis, proved insufficient to explain the specificity of the adsorption in CIC. The development of a physical model of the permeability to hydrogen is necessary for this purpose.

The competitive adsorption of chloride and nitrate ions in the CIC of steel A in solutions having the composition (0.001–0.01) M NaCl + (0–0.01) M $NaNO_3$ has been investigated in detail,[15] the results being presented in Fig.4. Fig.4*a* shows that an increase in the concentration of chloride ions in solution reduces sharply K_{HIE}, while an increase of the concentration of nitrate ions increases it. The higher the HIE activator (chloride ion) concentration, the higher the concentration of the HIE inhibitor (nitrate ion) inducing an increase of HIE. Under standard conditions, 0.01 M NaCl with $[Cl^-] = 1$, the relative changes in $[Cl^-]_x$ under real experimental conditions accompanying the changes in the chloride and nitrate ions in solution were calculated from the data in Fig.4*a* with the aid of Eqn.(7). The results of the calculations are presented in Fig.4*b* (curves *2–6*): evidently in the absence of nitrate ions the degree of adsorption of chloride ions increases in direct proportion to their concentration in solution, i.e. in the experimental concentration range the adsorption saturation on the surface of the passivating film at the top of the crack is not attained (curve *1*).

Assuming, as was done above in the derivation of Eqns. (2) and (7), that the adsorption of chloride and nitrate ions is described by the Langmuir isotherm, it is possible to calculate from curves *2–6* in Fig.4*b* the ratio *R* of the adsorption

coefficient β of the chloride ions to the adsorption coefficient γ of the nitrate ions. If, following the introduction into the chloride solution at a certain concentration (Cl^-) of a definite amount of nitrate ions up to the concentration (NO_3^-), the initial concentration of the adsorbed ions [Cl^-] = 1 diminishes by a factor m, then it follows from the formal ideas about competitive adsorption[21] that

$$[Cl^-]_x = \frac{1}{m} = \frac{\beta(Cl^-)}{1+\beta(Cl^-)+\gamma(NO_3^-)},$$
$$[NO_3^-]_x = 1 - \frac{1}{m} = \frac{\gamma(NO_3^-)}{1+\beta(Cl^-)+\gamma(NO_3^-)}, \quad (8)$$
$$R = \beta/\gamma = \frac{(NO_3^-)}{(m-1)(Cl^-)}.$$

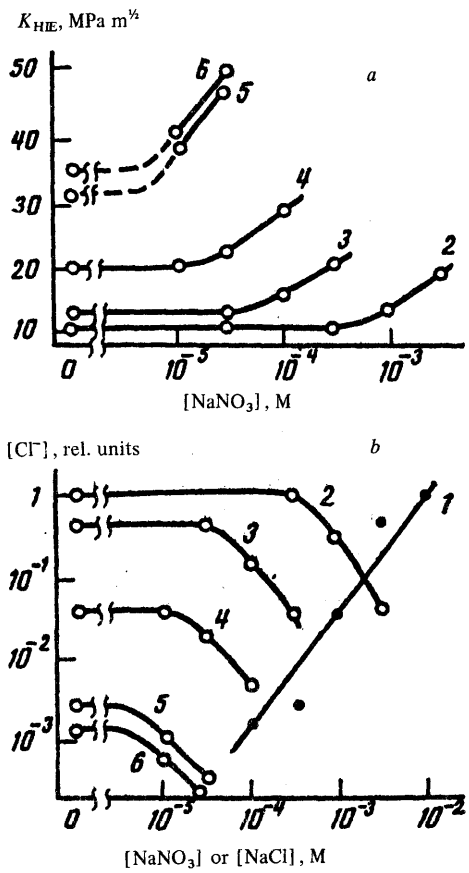


Figure 4. *a*) Dependence of K_{HIE} for the steel 02N18K9M5T on the $NaNO_3$ concentration in NaCl solutions at different molarities; *2*) 0.01; *3*) 0.003; *4*) 0.001; *5*) 0.0003; *6*) 0.0001; *b*) calculated dependence of the concentration of chloride ions adsorbed on the surface of the film at the apex of the crack on the $NaNO_3$ concentration in NaCl solutions: *1*) pure NaCl solutions; as in Fig. 4*a* above.[15]

It must be emphasised that, within the framework of the assumptions made, the absolute ratio of the adsorption coefficients of the HIE activators and adsorption is determined from Eqn.(8), although the change in the concentration of the adsorbed HIE activator ions can be determined from Eqn.(7) only in terms of relative units. The following adsorption coefficients of chloride and nitrate ions on the passivating film at the top of the crack in the CIC of steel in neutral solutions have been calculated from the data in Fig. 4*b* by Eqn.(8)[15] (in order of increasing initial NaCl concentrations): 0.06, 0.03, 0.03, 0.03, 0.07, i.e. $R = 0.04 \pm 0.01$. Similar calculations have been made for all the steel–electrolyte systems investigations in the above study;[15] it was established that the strongest inhibitor of HIE in the CIC of steels is the nitrate ion and that the adsorption coefficient ratios depend not only on the nature of the coadsorbed anions but also on the composition of the steel.

The method examined above can be used to investigate the theoretically and practically important question of the dependence of the adsorption of anions on the potential. This question has been examined comprehensively in theoretical electrochemistry but it is far from clear in corrosion theory. The point is that electrochemical studies are carried out on objects which are not corroded in the course of the experiment and which do not form passivating films—on noble metals, mercury, and amalgams. The dependence of the degree of adsorption on the potential under such conditions is determined by the φ potential (on a reduced scale), which characterises the charge of the electrode relative to the solution and the structure of the electrical double layer.[22]

Ideas about the adsorption of anions on noble metals are sometimes used in the study of the role of anions in the corrosion processes occurring on real constructional materials. This is apparently insufficiently justified, since no account is taken of the specificity of the interaction of the anions with the passivating films present inevitably on the surface of real alloys in weakly acid, neutral, and alkaline electrolytes on dissolution in the passive and active states and also in pitting, in the growth of cracks in the CIC and HIE, etc. As a rule, the increase of the surface activity of the anions in the sequence $F^- < Cl^- < Br^- < I^-$, observed in adsorption on mercury,[22] is not observed in the corrosion of iron, titanium, and aluminium alloys. For example, the activating capacity of anions in pitting on iron increases in the sequence $F^- < I^- < Br^- < Cl^-$ [23] and anions are adsorbed not only on the passivating film but are also incorporated in the latter.[24] The fluoride ion, which exhibits no surface activity at the mercury–aqueous solution interface, depassivates aluminium alloys most strongly although it does enter into the composition of the film.[25]

There are very few literature data for specific adsorption (especially for the dependence of the degree of adsorption on the potential) on metals of practical importance owing to the lack of a method for the investigation of adsorption in electrolytes *in situ*. The method of adsorption-enhanced Raman scattering (Raman spectroscopy) developed in recent years has been used successfully in the study of adsorption on noble metals.[26] The data obtained by this procedure for iron have been criticised.[27]

As stated above (see Section I), the K_{HIE} for each alloy–electrolyte system depends significantly on the duration and potential of the cathodic polarisation E_{cp} in the determination of K_{HIE} and also on the initial potential E_i at which the passivating layers are formed at the apex of the crack. Therefore, in the determination of the dependence K_{HIE} on the electrolyte composition, these values were constant. The present author[28] investigated the influence of E_{cp} and E_i on the competitive adsorption of anions in the CIC of martensitically ageing steel. The dependence of K_{HIE} on E_{cp} for E_i = const. and the dependence of K_{HIE} on E_i for E_{cp} = const. were determined experimentally for several solutions in which the concentration of the HIE inhibitor ions was varied

at a constant concentration of HIE activator ions. Fig.5 shows that an increase of both the concentration of nitrate ions and of the potential E_{cp} increases K_{HIE} (curves *1–4*). The influence of the increase of the $NaNO_3$ concentration is caused by the decrease of the adsorption of the HIE activator (the chloride ion) as a result of competitive adsorption and the influence of the increase of E_{cp} is associated with the decrease of the degree of surface coverage by adsorbed hydrogen atoms at the apex of the crack. For each potential E_{cp}, the dependence of the concentration of the chloride ions adsorbed in the region of the apex of the crack (Cl^- on the concentration of nitrate ions in solution was calculated by Eqn.(7); it was shown that E_{cp} in the range from −0.4 to 1.0 V does not affect the adsorption of anions. The decrease of $[Cl^-]$ with increase of $[NO_3^-]$ for different values of E_{cp} is described by the same curve *5* from which the ratio of the adsorption coefficient of chloride and nitrate ions $R = 0.04$, independent of E_{cp}, was determined with the aid of Eqn.(8). An analogous conclusion can be reached on the basis of a study of the adsorption of $[B_4O_7^{2-}]$, namely that R virtually does not change when E_{cp} is varied in the range from −0.2 to −1.0 V for a constant value $E_i = E_{cor}$.

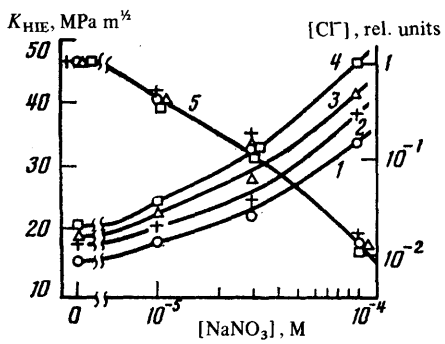


Figure 5. Dependence of K_{HIE} for the steel 02N18K9M5T in 0.0003 M NaCl solution (curves *1–4*) and of the concentration of chloride ions adsorbed on the film at the top of the crack (curve *5*) on the $NaNO_3$ concentration in solution at different cathodic polarisation potentials E_{cp} (V): *1*) −0.4; *2*) −0.6; *3*) −0.8; *4*) −1.0.[28]

The dependence of K_{HIE} on the cathodic polarisation potential E_{cp} and the absence of such dependence of R are not in conflict, because different standard values of K_{HIE} for a given E_{cp} for a solution not containing HIE inhibitor ions are used in the calculation of R for different values of E_{cp}. Brief cathodic polarisation does not apparently alter the composition and properties of the passivating film formed at the corrosion potential.

The initial potential E_i, at which the passivating film at the apex of the crack is formed, exerts a significant influence on the competitive adsorption of anions. At the constant potential $E_{cp} = -0.6$ V, the increase of E_i from zero to +0.8 V entails a marked decrease of the degree of adsorption of $B_4O_7^{2-}$ from solutions with identical concentrations of tetraborate and nitrate ions; the ratio of the adsorption coefficients of these anions R diminishes from 0.03 to 0.003.[28] Fig. 6 presents the dependence of R on the potentials E_{cp} and E_i for all the electrolytes investigated in the above study.[28]

Evidently, for constant values of E_i, E_{cp} (curves *1* and *2*) hardly influences R, which depends mainly on E_i. This dependence is different for different pairs of competing anions. With increase of E_i, the ratio R for the $B_4O_7^{2-}/NO_3^-$ pair diminishes (curve *3*), that for the pair OH^-/CrO_4^{2-} hardly changes, while that for the pair OH^-/NO_3^- decreases in the range −0.2–*0.4 V and increases with increase of E_i to +0.7 V.

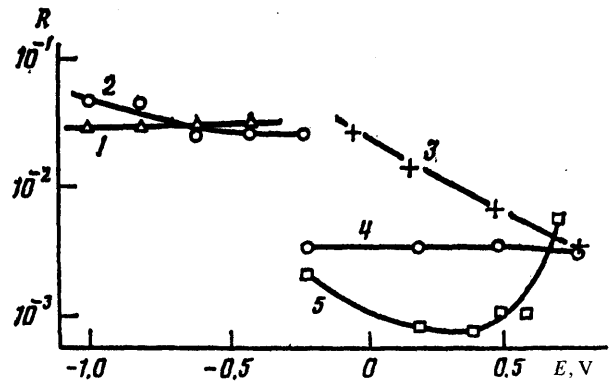


Figure 6. Dependence of the ratio R of the ion adsorption coefficients on E_{cp} (curves *1* and *2*) and E_i (curves *3–5*): *1*) Cl^-/NO_3^- pair; *2*) and *3*) $B_4O_7^{2-}/NO_3^-$ pair; *4*) OH^-/CrO_4^{2-} pair; *5*) OH^-/NO_3^- pair.[28]

The method described above makes it possible to calculate the ratio of the adsorption coefficients of two anions when they are present simultaneously in solution but it does not permit the calculation of the absolute adsorption coefficients of individual anions. Nevertheless, the activating or inhibiting capacity of different anions in relation to the HIE process at different potentials E_i in which the passivating film has been formed can be inferred qualitatively from data for the variation of K_{HIE} for the same steel in solutions with different concentrations of such anions. Thus it is seen from Fig.7 that, over the entire experimental range of potentials, the anion $B_4O_7^{2-}$, which does not activate the general and pitting corrosion of steels, increases the permeability of passivating films to hydrogen just as much as the chloride ion—the most active of the halide ions. The joint adsorption of $B_4O_7^{2-}$ and halide ions enhances their activating effect on the HIE process and the differences in the activating effects of different halide ions are virtually abolished. The ability of anions to activate the HIE process at potentials from −0.8 to +0.1 V increases in the sequence $F^- \ll I^- \cong Br^- < Cl^- \cong B_4O_7^{2-}$, while at a potential of +0.5 V it increases in the sequence $F^- \ll I^- \ll Br^- < B_4O_7^{2-} < Cl^-$ (Fig.7, curves *1–5*), i.e. halide ions increase the permeability of passivating films to hydrogen in the same sequence in which they activate pitting on iron and which is not the same as the sequence based on the increase of their surface activity and adsorption capacity on mercury.

The following facts are striking. The dependence of the adsorption of different anions on steel on the potential E_i (Figs.6 and 7) exhibits no anomalies at the zero-charge potential of iron (−0.4 V). The anions F^-, SO_4^{2-}, and NO_3^-, which are inactive or weakly active on the mercury–aqueous solution interface, are powerful activators of the corrosion

of iron and steels. The adsorption capacity series for halide ions on mercury, which breaks down appreciably in corrosion, pitting, CIC, and HIE of constructional materials in neutral solutions,[15,23] holds in the corrosion of nickel in highly acid solutions at a high rate of dissolution,[29] where passivating films, constituting a separate phase, have apparently not formed on the electrode surface. These facts lead to the conclusion that concepts of the zero-charge potentials of the metals and of the ϕ potentials on the reduced scale (in the form in which they have been formulated in theoretical electrochemistry[22]) are inapplicable to corrosion processes occurring on the surfaces of passivating films. Indeed the zero-charge potential characterises the clean surface of the metal in the absence of specifically adsorbed ions and not the surface with a layer of oxides or hydroxides, which are always formed in the corrosion of technical metals and alloys in weakly acid, neutral, and alkaline solutions.

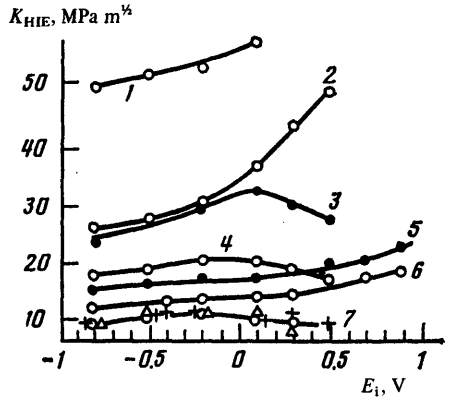


Figure 7. Dependence of K_{HIE} for steel A on the formation potential of the passivating film in solutions of different salts (concentration 0.001 M); *1*) NaF; *2*) NaI; *3*) NaBr; *4*) NaCl; *5*) $Na_2B_4O_7$; *6*) $Na_2B_4O_7$ + NaF; *7*) $Na_2B_4O_7$ + NaCl (or NaBr or NaI); $E_{cp} = -0.8$ V.[28]

Hoar[30] emphasises the disagreement between the zero-charge potentials on clean and oxidised metals in aqueous solutions and suggests that the zero charge potential of the oxidised metal is close to the pitting potential. The concept of the "pH of the zero charge potential (pH_0)* is used in the study of adsorption on oxide and oxidised metallic electrodes. It has been shown that anions are adsorbed on the surfaces of oxides at pH < pH_0 and that their adsorption is independent of the polarisation of the electrode over a wide range of potentials.[31] A tendency to use the concept of pH_0 in corrosion studies has arisen recently. For example, it has been shown[32] that in a chloride solution a decrease of pH_0 of aluminium ($pH_0 = 9.1$) when the latter is alloyed with molybdenum ($pH_0 = 1.95$) increases the pitting potential from −0.7 to −0.5 V.

The method for the investigation of adsorption on a passivating film proposed by the present author[15,28] makes it possible to obtain information *in situ* about the adsorption processes at the apex of the crack in the CIC at different potentials and is fairly sensitive (up to 10^{-5} g-ion litre^{-1} for chloride and nitrate ions). It can be used to study any constructional materials in the CIC of which HIE plays an important role. Some of the results of the calculations by this method, for example, data for the adsorption of chloride ions on the surface of a passivating film at the apex of the crack in the CIC of the AL27-1 aluminium alloys have been tested by the ESCA method. It follows from the calculated data that,[19] when $NaNO_3$ is introduced into the 0.5 M CrO_3 + 0.01 M NaCl solution at a concentration of 0.01 M, the concentration of chloride ions adsorbed on the passivating film diminishes by a factor of five. It has been established by the ESCA method that [Cl^-] is 1.5 at.% in the initial solution, while after the introduction of 0.01 M $NaNO_3$ it is not more than 0.5 at.%. This confirms the more general conclusion of the above study that, in the simultaneous presence of chloride and nitrate ions at equal concentrations (in the range 0.01–0.1 M) in 0.5 M CrO_3 solution, the adsorption of chloride ions on the passivating film is almost completely suppressed.

The competitive adsorption of anions in the CIC of the AL27-1 aluminium alloy and the study of adsorption by the ESCA method have been described in detail in studies[19,20] where it was shown, in particular, that the adsorption isotherm of chloride ions, calculated by Eqn.(7), is very close to the experimental isotherm obtained by the ESCA method. Extensive possibilities for experimental tests (by studying the adsorption, saturation with hydrogen, and permeability to hydrogen of thin films, etc.) have arisen as a result of the investigation of high-strength steels because in these materials it is possible to select conditions for the determination of K_{HIE} in the absence of the growth of the crack, i.e. when $K_{HIE} < K_{ISCC}$. The state of the surfaces of the model specimens, investigated, for example, by the ESCA method, is closer to the state of the real surface at the top of the stationary crack than under the conditions of its growth.

IV. THE DEGREE OF SURFACE COVERAGE OF THE PASSIVATING FILM ON A METAL AT THE APEX OF THE CRACK BY ADSORBED HYDROGEN ATOMS

The first two stages in the HIE process (the discharge of hydrogen ions and the adsorption of hydrogen atoms on the surface of the passivating film at the top of the crack until the attainment of a degree of surface coverage θ with subsequent transport of hydrogen through the film to the film–metal interface) are especially important, because each of them may become the rate-limiting stage in the HIE accompanying the CIC under certain conditions. It must be specially emphasised that the degree of such coverage of the film–solution interface by adsorbed hydrogen atoms can significantly exceed the degree of coverage of the nickel–metal interface, because passivating films are barriers to the penetration of hydrogen to the metal both in CIC and in gas-phase HIE, so that the boundary conditions for the diffusion of hydrogen in the metal are determined to a very large extent by the permeability of the film to hydrogen. For example, the presence of 2–3 monolayers of the oxide on the surface of tantalum reduces the rate of adsorption of hydrogen by a factor of 10^{10}.[33] The role of passivating films as barriers to the penetration of hydrogen into the metal is one of the few questions in the theory of CIC for which there is virtually no disagreement (in its qualitative treatment), but in the few studies[12,34,35] which have been devoted to the determination of θ for adsorption on iron, steel, and nickel the role of films is as a rule not considered.

The method for the determination of the degree of surface coverage θ by adsorbed hydrogen atoms of the film at the top of the crack in CIC[36] is based on the quantitative concept of the permeability of passivating films to hydrogen. In the

study of the dependence of K_{HIE} and V_{cr} on the cathodic polarisation potential E_{cp} for the same alloy–electrolyte system, the coefficients in Eqns.(2) and (3), namely ξ, α, and β, can be regarded as constant; the dependence is then determined solely by the dependence of θ on the potential. Since the above constant coefficients in Eqns.(2) and (3) are unknown, the determination of the absolute values of θ from the results of corrosion-mechanical tests is impossible. However, having adopted $\theta = 1$ for certain standard conditions (the compositions of the alloy and the electrolyte and the potential E_{cp}), it is possible to determine the relative changes in θ_x as the potential is varied. It follows from Eqns.(2) and (3) that

$$\theta_x = \frac{V_{cr,st}}{V_{cr,x}}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n. \quad (9)$$

The standard potential for each alloy–electrolyte system is chosen arbitrarily (as a rule, this is the most negative potential in the series of experiments).

The dependence on the potential E_{cp} on the degree of coverage θ by hydrogen atoms of the surface of the passivating film on the metal at the apex of the crack in the CIC of the high-strength steels N18K9M5T, 40Kh13, and 38N4MFA and the VT20 titanium alloy has been investigated.[36] All the steel specimens and some of the titanium specimens were tested in the state of planar deformation (the exceptions where the thickness of the titanium specimens did not satisfy the formal requirements[14] will be noted below). The relative error in the experimental determination of K_{HIE} was 4%, while the error in the calculation of θ by Eqn.(9) was about 40%.

Fig.8 presents the dependence of the surface coverage by hydrogen atoms of the passivating film at the top of the crack on E_{cp} in the CIC of the steel 02N18K9M5T in different solutions at pH 10. Thus, in view of its high tendency to undergo HIE, this steel is particularly convenient for the investigation of such dependence, since its HIE under CIC conditions in alkaline solutions at $E_{cp} = -(0.2–0.8)$ V can be induced for $K \leq K_{ISCC}$, i.e. in the absence of the growth of cracks at the corrosion potential. This extends the range of the potentials investigated and reduced significantly the scatter of the values of θ, because in the calculation of θ one can disregard the critical rates of growth of the cracks and hence the errors in their measurement. The cathodic polarisation potential $E_{cp} = -0.8$ V was selected as standard for electrolytes. It must be emphasised that the adoption of $\theta = 1$ for standard conditions does not imply the assumption of the complete surface coverage of the film by adsorbed hydrogen, since the method employed does not permit the determination of the absolute values of θ. Presumably the coverage at $E_{cp} = 0.8$ V is close to the maximum, because at more negative potentials (down to −1 V) it hardly changes in all the electrolytes investigated. For the 0.03 M Na_2HPO_4 + 0.1 M NaCl solution (Fig.8, curve *1*), the region of weak dependence of θ on the potential ranges from −0.4 to −0.8 V. For electrolytes without chloride ions and for the solution having the composition 0.03 M Na_2HPO_4 + 0.05 M $NaNO_3$ + 0.1 M NaCl, in which the adsorption of chloride ions is significantly suppressed by nitrate ions, the decrease of θ with the increase of the potential can be described by the general curve 2, for which $\Delta E/\Delta \lg\theta$ in the range from −0.3 to −0.8 V is 0.25 V. In the solution 0.03 M Na_2HPO_4 + 0.1 M NaCl, the decrease of θ with increase of the potential from −0.8 to −0.4 V is not quite so intense (curve *1*), but in the range from −0.4 to −0.2 V the rate of decrease of θ accelerates and curves *1* and *2* have approximately equal slopes.

A study[34] devoted to the determination of θ by the pulsed anodic polarisation of an iron electrode in the solution 0.0001 M NaOH + 0.1 M Na_2SO_4 (pH 9.5), i.e. under conditions close to those of the present author's study[36] (Fig.8, curve *1*), showed that in the potential range from −0.3 to −0.4 V, the coverage θ varies from 0.05 to 0.12 and $\Delta E/\Delta \lg\theta =$ 0.27 V. For nickel, the main alloying component on the steel 02N18K9M5T in an alkaline solution in the region of low (up to 0.3) coverages, this coefficient is 0.20 V.[35] The similarity of the values of $\Delta E/\Delta \lg\theta$ obtained under the initial conditions by direct electrochemical methods[34,35] to those obtained by the indirect computational method described in the present study can be regarded as evidence for the validity of the assumptions underlying the computational method.

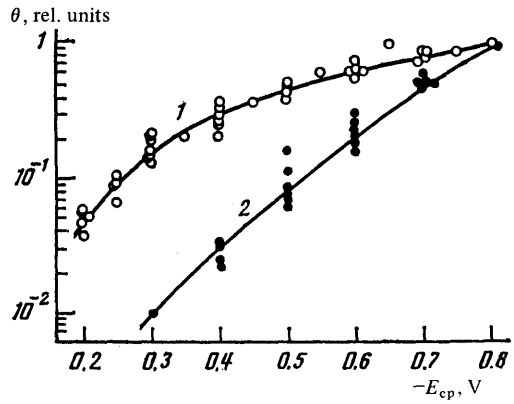


Figure 8. Dependence on the cathodic polarisation potential of the degree of surface coverage by adsorbed hydrogen atoms of the surface of the passivating film at the top of the crack under the conditions of the CIC of the steel 02N18K9M5T in solutions at pH 10: *1*) 0.03 M Na_2HPO_4 + 0.1 M NaCl; *2*) NaOH (or 0.03 M Na_2HPO_4) + 0.05 M $NaNO_3$ + 0.1 M NaCl.[36]

The concept of the permeability to hydrogen of the passivating layers on a metal at the apex of the crack in the CIC and the method for the determination of θ arising from it have no fundamental limitations associated with the nature of the material. They can be used for any alloy–electrolyte system in which there is a possibility of the growth of the crack via the HIE mechanism under CIC conditions and which is characterised by different types of influence of the cathodic polarisation on the growth of cracks, which constitutes the experimental basis for the determination of K_{HIE} and V_{cr}. Only high-strength steels satisfy these conditions in the CIC in the majority of aqueous solutions, but, by a suitable selection of the composition of the electrolyte, it is possible to extend significantly the range of such materials and to include in it austenite stainless high-strength steels and titanium, zirconium, and aluminium alloys (Section I). Their selection consists in seeking the optimum combination of the concentrations and nature of the electrolyte components—passivators and activators. The role of the passivator consists in hindering or fully suppressing the growth of cracks via the local dissolution mechanism, which increases K_{ISCC}, while the role of activators is to ensure the permeability of the passivating layers at the top of the crack to hydrogen sufficient for HIE. It has been established by means of such selection that solutions based on chromium trioxide are universal for the determination of the role of HIE in the CIC of various constructional materials. For example, different types of influence of cathodic polarisation on the growth of cracks in the CIC of high-strength steels and titanium and aluminium alloys can be observed in the solution 1 M CrO_3 + 0.1 M NaCl.[3,15,36]

V. HYDROGEN-INDUCED EMBRITTLEMENT IN CORROSION-INDUCED CRACKING AT POSITIVE POTENTIALS

Studies on HIE (in particular on the dependence of θ on E_{cp}) in solutions based on chromium trioxide are of special interest, because they make it possible to observe HIE at potentials $E_{cp} > 0$ (relative to the n.h.e.). In these solutions, the corrosion potentials of steels and titanium alloys are +(0.5–0.8) V, which permits the determination of K_{HIE} and V_{cr} over a wide range of cathodic polarisation potentials including extremely positive potentials.

It has come to be assumed that at positive potentials HIE is impossible,[37] because the electrochemical evolution of hydrogen is thermodynamically impossible. However, although in the majority of alloy–electrolyte systems HIE under CIC conditions is indeed observed at negative potentials, this view is not uncontroversial. Data have been published on HIE in the CIC of steels[38] and titanium alloys[8] at potentials in the range +(0.1–0.15) V in acid buffer solutions at pH 0–1, i.e. under conditions which rule out the additional acidification of the electrolyte in the crack owing to the hydrolysis of the corrosion products.

The theory of the hydrogen electrode deals with two consecutive electrochemical reactions: the discharge of hydrogen ions and the combination of hydrogen atoms into molecules with liberation of gaseous hydrogen via several possible mechanisms. As a result of the first reaction, absorbed hydrogen atoms capable of penetrating through the passivating layers and ultimately causing HIE, are formed on the electrode surface. This reaction is primary and is therefore most important for the HIE process. On metals which effectively adsorb and absorb hydrogen, it can lead to high surface coverages by hydrogen atoms at fairly high positive potentials (up to +0.4, 0.3, 0.27, and 0.21 V on platinum, palladium, rhodium, and nickel respectively[39]); at the zero charge potential relative to the n.h.e., the degree of surface coverage of these metals in 0.5 M H_2SO_4 solution is close to unity.[39–41] The hydrogen evolution reaction at negative potentials influences the HIE process in CIC insofar as the degree of surface coverage of the passivating film on the metal at the apex of the crack by adsorbed hydrogen atoms depends on the ratio of the rate constants for the discharge and hydrogen evolution reactions.

The hydrogen electrode theory does not take into account the adsorption energy of hydrogen atoms on the electrode surface although there are indications in the literature[40,42] that the overpotential of the hydrogen evolution reaction and the degree of surface coverage depend on the adsorption energy and on the presence of oxide layers on the metal surfaces. For example, the free energies of formation of TiH_2 and TiH are −87 and −63 kJ mol^{-1} respectively, which indicates the thermodynamic feasibility of the formation of the corresponding hydrides (and hence also of the adsorption of hydrogen atoms as the first stage in the hydride formation reaction) at potentials of +0.45 and +0.65 V respectively.[43] The enthalpy of adsorption of hydrogen on the clean iron surface ranges from −52 to −120 kJ mol^{-1} according to various data,[6,9,44] i.e. the formation of adsorbed hydrogen atoms on the iron surface when hydrogen ions are discharged in acid electrolyte is possible at potentials up to +(0.27–0.61) V (without taking into account the overpotential of the discharge reaction and the influence of passivating layers).

In connection with the question of the possibility of HIE at positive potentials under discussion, mention should be made of the increase of the sodium segregation potential in neutral and alkaline solutions on mercury:[45] the reversible sodium segregation potential is −2.71 V, but appreciable reduction of sodium ions with formation of an amalgam begins already at −1.2 V, i.e. at a potential more positive by 1.5 V than the standard value. This phenomenon, induced by the decrease of the free energy of sodium on formation of the amalgam, has apparently the same nature as the discharge of hydrogen ions at positive potentials on platinum, palladium, nickel, and other metals with a high hydrogen adsorption energy.

In the study of HIE in solutions based on chromium trioxide, the compositions and the concentrations of the solution components were selected empirically for each alloy on the basis of the following inter-related requirements:[15,36] (1) the ratio of the concentrations of the activators (NaCl and Na_2SO_4) to the passivator (CrO_3) concentration should be the maximum possible; (2) at the corrosion potential E_{cor} = +(0.5–0.8) V, the alloy must exist in a stable passive state; (3) the current density at the most negative (standard) cathodic polarisation potential should not exceed 0.3 mA cm^{-2}. The fulfilment of all these requirements ensures a high permeability of the passivating layers at the top of the crack to hydrogen, low (or zero) rates of growth of cracks via the LAD mechanism at the corrosion potential and for high values of K, as well as insignificant changes in the electrolyte composition after brief cathodic polarisation.

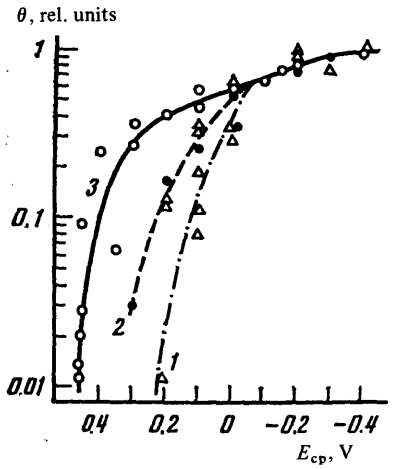


Figure 9. Dependence on the cathodic polarisation potential of the degree of surface coverage by adsorbed hydrogen of the surface of the passivating film at the top of the crack under the conditions of the CIC of the VT-20 titanium alloy in 0.1 M NaCl solutions with different amounts of added CrO_3: *1*) 2 M; *2*) 1 M; *3*) 0.5 M.[36]

For example, tests on the VT20 titanium alloy were performed in (0.5–2) M CrO_3 + 0.1 M NaCl solutions [pH 1–0, E_{cor} = +(0.75–0.85) V].[36] The dependence of K_{HIE} on E_{cp} was determined and the relative changes in θ were calculated from Eqn.(9). Fig.9 shows that in all electrolytes an increase of the potential from −0.4 to 0 V entails a smooth decrease of θ and then a sharp fall. It is noteworthy that the values of K_{HIE} corresponding to $\theta > 0.2$ were obtained under planar deformation conditions and those corresponding to a lower value of θ were obtained under the conditions of a mixed strained state of the specimen. For this reason, the values of θ in the range 0.01–0.2 in Fig.9 may be somewhat too low.

In connection with the problem formulated—the investigation of the possibility of HIE at positive potentials—it is more important to emphasise that at potentials up to +0.45 V (see curve *3* in Fig.9) the degree of surface coverage of the passivating film at the apex of the crack by adsorbed hydrogen atoms exceeds 0.01 and is sufficient to accelerate the growth of the cracks in the CIC of a titanium alloy via the HIE mechanism. The identity of the above potential with the standard potential for the formation of TiH_2 in acid solutions is apparently fortuitous and cannot be regarded as proof of the hydride mechanisms of the HIE of the VT20 alloy.

Compared with titanium, high-strength steels show a much smaller tendency to be passivated in chromium trioxide solutions and the chromate ion reduction reaction on the surface takes place more vigorously, so that the dependence of θ on E_{cp} in the HIE of high-strength steels was investigated in solutions with a lower concentration ratio $NaCl/CrO_3$ than for the VT20 alloy.[36]

Fig.10 shows that θ falls sharply with increase of E_{cp}; however, at sufficiently positive potentials in the range +(0.1–0.5) V the values of θ are in the range 0.003–0.001 and are sufficient for the growth of cracks via the HIE mechanism. The possibility of determining such low values of θ by the method proposed by the present author[36] indicates its high sensitivity, which greatly exceeds the sensitivity of the known electrochemical methods. This is because in HIE of high-strength steels—materials showing the greatest tendency towards HIE for which the degree of surface coverage by hydrogen atoms ($\theta \cong 0.0001$) exceeds by several orders of magnitude the permeability to hydrogen—was used as the indicator of the presence of adsorbed hydrogen at the apex of the crack. Evidently the sensitivity of the metal should increase with increase of the strength of the steel (i.e. with increase of its tendency towards HIE) and as the values of K in the determination of θ approach K_{IC}.

In the above study[36] no account was taken of the possibility of a change in the pH of the electrolyte in the crack owing to hydrolytic processes and of the incomplete external cathodic polarisation at the top of the crack; as a result of the above processes, the true pH and the potential E_{cp} at the apex of the crack may be other than on the surfaces of the specimen. It is therefore necessary to emphasise that the titanium alloy and high-strength steels existed in the solutions of chromium trioxide in a stable passive state (i.e. the dissolution and hence the hydrolytic processes involving the dissolution products were virtually completely suppressed) and also that, at E_{cp} = +(0.2–0.5) V, the external polarisation current density did not exceed 10 $\mu A\ cm^{-2}$. The latter implies that, under the conditions of high electrical conductivity of the solution (pH 0) and the maximum opening of the crack at high $K \cong 0.9\ K_{IC}$, such currents could induce only a slight ohmic potential drop in the crack and the true potential at the apex of the crack should be more positive than the value of E_{cp} specified by the external cathodic polarisation.

The data in Figs.(9) and (10) can be regarded as experimental proof of the HIE of titanium alloys and high-strength steels at potentials significantly greater than zero relative to the n.h.e., i.e. under conditions where the electrochemical evolution of hydrogen is thermodynamically impossible, but, as shown above, one cannot rule out the possibility of the discharge of hydrogen ions and the formation of adsorbed hydrogen atoms on the surface of the passivating film.

The results described above justify the consideration of the discharge of hydrogen ions (without subsequent evolution of hydrogen) as a possible cathodic depolarisation process together with oxygen and hydrogen depolarisation processes. Judging from the high rates of growth of cracks in the HIE during CIC, the discharge of hydrogen ions may occur at a high rate over a wide range of potentials, including high positive potentials, but the adsorption nature of this process limits its depolarising capacity: for the maximum surface coverage (one hydrogen atom per metal atom), the amount of electricity consumed in the discharge process should not exceed 160–200 $\mu C\ cm^{-2}$) depending on the lattice constant of the metal. This implies that, in the usual corrosion processes, the discharge of hydrogen ions ceases rapidly and does not play an appreciable role as the cathodic depolarisation process, but in corrosion with constant renewal of the surface it can become an important cathodic process. It was shown above that, despite the low coverages θ at positive potentials, the discharge of hydrogen ions is in fact responsible for the growth of cracks via the HIE mechanism in CIC. In corrosion fatigue, corrosion wear, and rapid anodic dissolution, for example, under electrochemical polishing conditions or in chemical milling, the discharge of hydrogen ions (without the evolution of hydrogen) can play a significant role and can lead to the saturation of the metal with hydrogen.

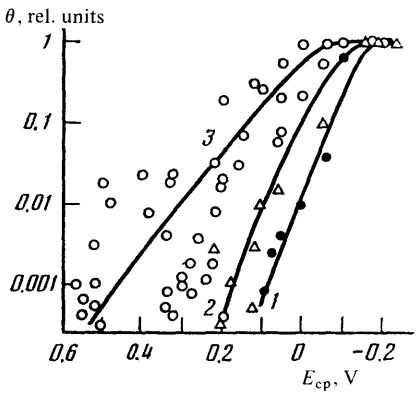


Figure 10. Dependence on the cathodic polarisation potential of the degree of surface coverage by hydrogen atoms of the surface of the passivating film at the top of the crack under the conditions of the CIC of the steels 4Kh13 (curve *1*) and 02N18K9M5T (curve *2*) in the 2 M CrO_3 + 0.1 M Na_2SO_4 + 0.003 M NaCl solution and of the steel 38N4MFA (curve *3*) in the 2 M CrO_3 + 0.02 M Na_2SO_4 solution.[36]

The role of the discharge of the hydrogen ions as the main cathodic process is apparently greatest on the freshly formed surfaces of the metal after a short (80–100 μs) time of their exposure to electrolytes. The study of corrosion and electrochemical properties of the freshly formed surfaces shows that, for many metals (iron, aluminium, titanium, etc.), the corrosion potential increases immediately after the cut and then sharply diminishes after 80–150 μs to values close to the standard potentials of the corresponding metals.[46] For lifetimes in the range 80–150 μs, the corrosion potential of the freshly formed surfaces in neutral solutions is as a rule more positive by 0.1–0.3 V than the hydrogen evolution potential and the current density of the anodic and cathodic processes reach several hundreds of $mA\ cm^{-2}$. It has been noted[46] that the nature of such an intense cathodic process is obscure because, owing to fusion-dependent limitations, this process cannot involve the reduction of the dissolved oxygen and the

electrochemical evolution of hydrogen is thermodynamically impossible. Under these conditions, the discharge of hydrogen ions at positive potentials is the most likely cathodic process. It must be emphasised that, despite these limitations associated with its adsorption nature, this process can ensure the experimentally observed cathodic current densities (up to 1 A cm^{-2}) during periods up to 200 μs. In all cases the rate of the cathodic process on the freshly formed surfaces fell sharply owing to the formation of the primary passive film after brief exposures.[46]

The adsorption nature of the cathodic discharge of hydrogen ions makes it possible to account for certain characteristic features of the CIC and HIE of constructional materials in chromium trioxide solutions. These solutions, having the composition (0.5–2) M CrO_3 + (0.01–0.1) M NaCl, possess specific properties promoting the elucidation of the role of HIE in the CIC of different constructional materials. For example, only in this medium is it possible to observe HIE in the CIC of aluminium alloys,[3] while in the CIC of titanium alloys and high-strength steels in CrO_3 + NaCl solutions, K_{HIE} is much lower than in the presence of other oxidants.[36] As a rule, at sufficiently high cathodic polarisation potentials $K_{HIE} < K_{ISCC}$, i.e. passivating layers are formed in chromium trioxide solutions in the CIC at the top of the crack. These layers effectively suppress the growth of cracks via the LAD mechanism and at the same time exhibit a fairly high permeability to hydrogen.

In contrast to other oxo-ions, chromates are reduced on the surfaces of metals, as a result of which Cr^{3+} ions enter into the composition of the passivating film.[18] Studies by the ESCA method have shown[20] that the concentration of Cr^{3+} ions on the surface of the passivating film on the AL27-1 alloy in 0.5 M CrO_3 + 0.01 M NaCl solution is 5–6 at.%. It is known[3] that hydrogen is hardly adsorbed on aluminium oxides and hydroxides. It is also known[47] that the heat of adsorption of hydrogen on chromium oxide is very high. Presumably the Cr^{3+} ions entering into the composition of the passivating layers from aqueous chromate solutions generate effective adsorption centres on which hydrogen ions are discharged. Thus the passivating films in chromium trioxide solutions, which retain effective protecting properties and suppress CIC via the LAD mechanism, can promote the penetration of hydrogen into the metal and can facilitate CIC via the HIE mechanism.

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In conclusion one should note that the quantitative concept of the permeability to hydrogen of passivating layers on a metal at the apex of the crack in the CIC of constructional materials, considered in the present review, is based on several postulates each of which separately does not conflict with known facts but cannot be fully justified theoretically or experimentally. Nevertheless, on the basis of this concept, it has been possible to reach *a priori* certain definite conclusions which have been confirmed experimentally.[10,13,15] This can be regarded as proof of the validity of the initial postulates of the concept considered and the method, arising from it, for the investigation *in situ* of the adsorption of activator ions on the passivating film at the apex of the crack in CIC, the method for the investigation of competitive adsorption, and the method for the determination of the dependence of the relative changes in the degree of surface coverage by the hydrogen adsorbed on the film on the cathodic polarisation potential. The above methods were used in the study of a wide range of processes which are of theoretical and practical importance (the development of physical ideas about the mechanism of HIE, the study of the strained state of the material at the apex of the crack, the study of inhibitors of corrosion, CIC, and HIE, the search for solutions for hydrotests, etc.).

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