# ON THE USE OF THE CONCEPT OF CYCLIC CORROSION-CRACKING THRESHOLD AS A BASIC CHARACTERISTIC OF STRUCTURAL MATERIALS IN THE MECHANICS OF CORROSION FRACTURE

## I. P. Gnyp and V. I. Pokhmurs'kyi

UDC 620.194.23: 669.14: 621.039.5

We investigate the similarities and differences in the processes of static and cyclic corrosion cracking of alloys. It is shown that the threshold amplitude of the stress intensity factor of cyclic corrosion cracking  $\Delta K_{\rm Iscfc}$  can serve as a basic characteristic of materials that are not susceptible to static corrosion cracking have two basic characteristics  $K_{\rm Iscfc}$  and  $\Delta K_{\rm Iscfc}$  with different natures. As an exception, the values of these characteristics coincide for high-strength alloys. We suggest a model for description of the influence of environment on the fatigue-crack growth rate in alloys according to the mechanisms of hydrogen embrittlement and anodic dissolution of a metal at the crack tip as well as a procedure for its practical implementation. We justify the analysis by evaluation of the service life of structural members).

Static corrosion cracking of structural alloys and its distinctive features have been fairly well studied [1-3] and the threshold of the stress intensity factor (SIF) of corrosion cracking  $K_{Iscc}$  is used as a standard parameter in engineering analysis [4]. Although the cyclic corrosion crack-growth resistance of materials has been investigated quite extensively [5-19], it is not customary to use the threshold of cyclic corrosion cracking as its basic characteristic. A large body of data has been accumulated on the influence of the SIF amplitude ( $\Delta K$ ) [5-10], frequency (f) [11-15], and asymmetry coefficient (R) [7, 8, 16-18] of loading cycles on the fatigue-crack growth (FCG) rate in various structural alloys under the influence of various environments at different temperatures [6-9,12, 13, 18, 19]. The dependence of the profiles of kinetic corrosion diagrams of fatigue fracture (KDFF) of metals on the parameters of cyclic loading (f, R) is much more complicated than that for the diagrams of corrosion cracking [1-3]. For constant values of f and R, the dependence of the FCG rate in alloys on  $\Delta K$  in corrosive media is nonlinear in the central segment of the KDFF [5-10], which is not typical of media that are inert with respect to metals. Where the values of  $\Delta K$  and f are constant, the FCG rate is a nonlinear function of the testing frequency [11-15]. If the values of  $\Delta K$  and f are kept constant, then the FCG rate is a nonlinear function of the asymmetry coefficient of loading cycles [7, 8, 16, 18]. This means that, under the influence of media with fixed compositions, the FCG rate ( $v_{cf}$ ) in structural alloys is a function of three variables, i.e.,  $v_{cf} = v_{cf}(K, f, R)$  [5].

To describe the influence of the media on the FCG rate in alloys as a function of the parameters of cyclic loading, it is necessary to clarify the physical nature of the interaction between metals and media and reveal the characteristics of this interaction responsible for the intensity of the effects induced by the media. The threshold of the amplitude of the SIF of cyclic corrosion cracking of alloys ( $\Delta K_{Iscfc}$ ), whose existence has never been denied, can be regarded as a characteristic of this sort [3, 5–18]. Unlike corrosion fatigue, the mechanism of cyclic corrosion cracking involves static cracking of a metal subjected to repeated plastic deformation. This mechanism is realized for low loading frequencies and the intensity of the effect of the medium on the FCG rate increases with the asymmetry coefficient of loading cycles. In KDFF of alloys, the effect of the threshold  $\Delta K_{Iscfc}$  manifests itself as an abrupt acceleration of fatigue-crack growth as compared with high-frequency corrosion tests; furthermore, the second segment of KDFF becomes terrace-like. Unfortunately, the parameter  $\Delta K_{Iscfc}$  is ignored in engineering analysis and terrace-like KDFF are described by equations of linear fracture mechanics [16, 20–25].

Karpenko Physicomechanical Institute, Ukrainian Academy of Sciences, L'viv. Translated from Fiziko-Khimicheskaya Mekhanika Materialov, Vol. 30, No. 6, pp. 7–24, November – December, 1994. Original article submitted February 1, 1994.

The goal of the present work is to justify the use of the threshold of the amplitude of the SIF of cyclic corrosion cracking in scientific investigations as a basic physical characteristic of a metal (independent of other parameters) and to demonstrate the possibility of its application to the engineering analysis of the service life of structural members.

#### Analysis of the Effect of Environment on the Profiles of KDFF of Metals

- By convention, all metals and alloys can be split into the following groups:
- (a) nonsusceptible to static corrosion cracking but susceptible to cyclic corrosion cracking;
- (b) susceptible to static corrosion cracking and, hence, to cyclic corrosion cracking;
- (c) nonsusceptible to both cyclic and static corrosion cracking.

Under periodic loading, structural alloys nonsusceptible to static corrosion cracking in a given medium [5, 7, 10–12, 26] are susceptible to cyclic cracking. As soon as the amplitude of SIF exceeds a certain threshold value, the KDFF of alloys display a sharp acceleration of FCG. Qualitative changes in the kinetics of FCG for the indicated values of  $\Delta K$  mean that the investigated material becomes susceptible to corrosion cracking. By analogy with the parameter  $K_{Iscc}$ , we say that the amplitude of SIF characterized by a sharp acceleration of FCG is the threshold of cyclic corrosion cracking of metals and denote it by  $\Delta K_{Iscfc}$ .

Materials susceptible to static corrosion cracking are characterized by the presence of a region of sharp acceleration of FCG for  $\Delta K_{\text{Iscfc}} < K_{\text{Iscc}}(1-R)$  [22, 27–29]. Thus, for low-carbon steel tested in hydrogen  $\Delta K_{\text{Iscfc}}/(1-R) \cong 0.25 K_{\text{Iscc}}$  [22, 27], at the same time, for high-strength alloys  $\Delta K_{\text{Iscfc}}|_{R=0} \rightarrow K_{\text{Iscc}}$ . Therefore, materials susceptible to static corrosion cracking or hydrogen embrittlement have two different (both in magnitude and in nature) characteristic parameters, namely  $K_{\text{Iscc}}$  and  $\Delta K_{\text{Iscfc}}$ . Consequently, for structural materials that do not suffer static corrosion cracking in a given medium and are susceptible to cyclic corrosion cracking, the characteristic  $\Delta K_{\text{Iscfc}}$  is necessary because it enables one to detect qualitative changes in the effect of media on the FCG rate. For materials susceptible to static corrosion cracking, it reflects the changes in the intensity of the effect of media on cyclically deformed metals.

The profiles of the KDFF of alloys placed in either hydrogen [22, 27-29] or hydrogenating media [3, 5, 6, 10, 18] or subjected to electrolytic hydrogenation [3, 6, 30] are qualitatively similar, which means that the indicated media affect the crack-growth rate according to the same mechanism of hydrogen embrittlement of a metal in the prefracture zone [1-3, 6, 18, 27-29, 31-34]. Depending on the intensity of the effect of the media, the KDFF of alloys susceptible to cyclic corrosion cracking can be split into two regions according to a value of  $\Delta K_{\text{Iscfc}}$  that is definitely larger than the threshold amplitude of SIF in air  $\Delta K_{\text{th}}$ . For  $\Delta K$  lower than  $\Delta K_{\text{Iscfc}}$ , the influence of the medium on the FCG rate is mainly governed by the anodic mechanism of corrosion fatigue; for  $\Delta K \ge \Delta K_{\text{lscfc}}$  one should additionally take into account the mechanism of cyclic corrosion cracking, which is accompanied by an abrupt acceleration of FCG. This part is followed by a low-angle segment of the values of FCG rate explained by the competition between the effects of mechanical and corrosion factors. The second part of the KDFF of alloys is always terrace-like; it is characterized by different slopes of the low-angle part of the curve whose end practically coincides with the FCG rate in air at  $\Delta K \rightarrow \Delta K_{fc}$  (Fig. 1a-d). Let us now dwell upon the typical profiles of KDFF because they are not always correctly explained in the literature [3, 35, 36]. In [37], one can find three types of KDFF similar to those depicted in Fig. 1a, b, d. In the first part of KDFF (Fig. 1a), we observe an increase in the influence of the medium on the FCG rate and a decrease in the threshold values of the amplitude of SIF ( $\Delta K_{thc}$ ) as the loading frequency decreases. This is typical of alloys that do not undergo passivation in the medium under investigation when mechanical loading activates corrosion processes and the FCG is accelerated as a result of anodic processes. It is clear that the lower the loading frequency, the greater the time of reaction between the metal at the tip of an activated crack and a solution and the greater its influence on the FCG rate [37, 38]. As soon as the amplitude of SIF attains the critical value  $\Delta K_{\text{Iscfc}}$ , the mechanism of cyclic corrosion cracking starts working and FCG accelerates. In the second part of KDFF, the mechanisms of corrosion cracking and anodic dissolution operate simultaneously and can be formally separated (dashed lines in Fig. 1). In this case, the value of  $\Delta K_{\text{Iscfc}}$  is independent of the loading frequency.



Fig. 1. Typical profiles of diagrams of cyclic corrosion fracture of alloys.

The diagrams displayed in Fig. 1b are typical of metal-medium systems characterized by predominance of the processes of corrosion cracking and hydrogen embrittlement (passivating or gaseous environments) [3, 35, 36], but the values of the x-coordinate that separate the indicated parts of KDFF are not necessarily equal to  $K_{Iscc}$ . Similar KDFF are observed for alloys subjected to electrolytic hydrogenation (Fig. 1c). Cathodic polarization inhibits anodic processes and hydrogen embrittlement remains predominant in the effect of the media.

An increase in the threshold amplitude of the SIF of crack nonpropagation  $\Delta K_{\text{thc}}$  as compared in its value in air or inert media ( $\Delta K_{\text{th}}$ ) and a deceleration of FCG in the first part of KDFF are typical of steels and alloys in hightemperature aqueous media that form dense elastic-brittle oxide films on the metal surface (Fig. 1d) [39]. These films increase the value of  $\Delta K_{\text{thc}}$  due to the Roscoe effect, i.e., to an increase in the resistance to the exit of dislocations to the surface and the effect of crack closure [36]. Oxide films formed on steels are very dense and, therefore, high-temperature aqueous media practically do not interact with the metal itself. Thus, in the first part of KDFF, crack growth is mainly caused by mechanical loading (Fig. 1d). At a certain amplitude of SIF  $\Delta K_{\text{por}}$  (protective oxide rupture), an uncovered newly-formed metal surface appears as a result of oxide film rupture [41, 42]. The relationship between the kinetic parameters of electrochemical reactions and the loading frequency (or its rate of increase) determines the intensity of the effect of high-temperature aqueous media on the FCG rate in steels in the second part of KDFF (Fig. 1d).

The threshold amplitude of the SIF of cyclic corrosion cracking of alloys is clearly visible in the diagrams displayed in Fig. 1(a-d) but not in the KDFF presented in Fig. 1e. The explanation of the profiles of corrosion KDFF of high-strength steels by corrosion cracking for SIF lower than  $\Delta K_{\text{th}}$  [3, 35, 36] requires additional justification. For  $\Delta K < \Delta K_{\text{th}}$ , the processes of adsorption softening and anodic dissolution of a metal are predominant [1, 32]. Therefore, one can assume that, in this case, the anodic dissolution of the metal is so intense that conditions favorable for hydrogen embrittlement are never formed in the prefracture zone [43]. In this case, the fact that  $\Delta K_{\text{thc}}$ decreases with a decrease in the loading frequency can be explained by an increase in the characteristic time of the reaction between the metal and the medium, while the presence of plateaus [3, 35, 36] is explained by the competition between the crack-growth rates caused by pure mechanical loading and anodic dissolution. Actually, the profiles of the first parts of KDFF are basically the same (see Fig. 1a and Fig. 1e) and, hence, one can assume that their dependences on the loading frequency are governed by the same mechanisms of the influence of the media as can be corroborated by numerical analysis [44]. Thus, one can assert that no indication of the effect of cyclic corrosion cracking can be detected in the KDFF presented in Fig. 1e. In all other diagrams displayed in Fig. 1(a-d), the threshold amplitude of the SIF of cyclic corrosion cracking is pronounced and its value is independent of the loading frequency, i.e., it can be regarded as a characteristic of a material in a given medium.

# Principal Hypotheses and Computation Models for the Evaluation of the Influence of Media on the FCG Rate in Metals

The introduction of the characteristic  $\Delta K_{\text{Iscfc}}$  is also necessary because, up to now, the influence of the media and, in particular, of high-temperature aqueous media on the FCG rate in steels whose KDFF contain pronounced indications of cyclic corrosion cracking (Fig. 1d) has been explained and analytically described on the basis of the model of anodic dissolution of the metal at the crack tip [45]. Analysis performed in the framework of this model demonstrates that the threshold of cyclic corrosion crack-growth resistance decreases as the loading frequency increases in contradiction with experimental data [11–15]. Actually, the mechanism of cyclic corrosion cracking is not even mentioned in the work [45] and the dependence of the parameter  $\Delta K_{\text{Iscfc}}$  on the loading frequency is reflected only in the graphic data. This and some other shortcomings of the model suggested in [45] for the description of the influence of high-temperature aqueous media on the FCG rate in steels were analyzed earlier in [42, 46].

The mechanisms of both static and cyclic corrosion cracking are, as a rule, realized under the influence of hydrogen but have different kinetics of the processes of its accumulation in the prefracture zone. In the case of static corrosion cracking, hydrogen is delivered to the prefracture zone (a zone of maximum tensile stresses) by diffusion under the gradient of tensile stresses [22–27, 47]. In the prefracture zone, it interacts with structural microdefects and embrittles the metal. High-strength alloys are more sensitive to the embrittling influence of hydrogen because their crystal structure contains more defects than the structure of medium-strength and low-strength alloys. Under cyclic loading, one observes a rapid increase in the number of line defects (dislocations) and the appearance of bulk defects (microcavities), which accumulate hydrogen transferred both by diffusion [48] and by a more efficient mechanism of dislocation transport [49, 50]. These factors create a situation in which the threshold values of the SIF of corrosion cracking are lower than  $K_{Iscc}$  and the parameter  $\Delta K_{Iscfc}|_{R=0}$  can be equal to  $K_{Iscc}$  only for the limiting defectiveness of the original structure of the investigated metals.

Materials may be nonsusceptible to static corrosion cracking either due to the absence of conditions favorable for the hydrogenation of the prefracture zone in a given medium or due to the low defectiveness of their structure, which is characterized by a small number of nonmetallic inclusions, an energetically balanced crystal lattice slightly distorted by interstitials, and low stresses on the grain boundaries. Cyclic plastic deformation is accompanied by an increase in the number of dislocations by 3–4 orders of magnitude. The processes of hardening and loosening of a metal make it more sensitive to the action of hydrogen [51]. Passivating oxide films at the crack tip periodically fracture under cyclic loading, thus creating favorable electrochemical conditions for hydrogen release and penetration into the metal [39, 46, 52]. Note that hydrogen is actively transported by dislocations into the pre-fracture zone up to the initiation of corrosion cracking [43]. This happens when secondary microcracks appearing in the prefracture zone join the main crack and the length of the latter increases abruptly.

The distinctive features of static and cyclic corrosion cracking described above were not taken into account in the model of linear superposition of the effect of mechanical loading and the factor of static corrosion cracking on the FCG rate [53]. The investigation carried out in [3] demonstrated that this model is valid only in certain exceptional cases. In view of the fact that the hydrogenation of the prefracture zone leads to a decrease in the incubation period of spasmodic crack propagation, mechanical and corrosion-hydrogenation factors enhance each other and, hence, their joint effect cannot be adequately described by linear summation. Later, this was recognized by R.P. Wei [54] — one of the authors of the model under consideration. Thus, the hypothesis of linear superposition is quite dubious. The approach of Gerberich [28] who distinguished the characteristic  $\Delta K_{Iscfc}$  from  $K_{Iscc}$ , was aimed at improvement of the Wei–Landes model [53] but failed to remove its evident disadvantages [3], because it was also based on the hypothesis of additivity of mechanical and corrosion processes. The other models discussed in [3] and, in particular, the Rhodes model of the process of interaction [55] are mechanistic and, thus, unsuitable for the analytical description of KDFF of alloys, because they do not take into account the presence and nature of the threshold amplitude of the SIF of cyclic corrosion cracking.

# Functional Model of the Influence of Media on the FCG Rate

The characteristic  $\Delta K_{\text{Iscfc}}$  was first used for the analytical description of KDFF in [38]. Later, this characteristic was used as a basis of our model of functional-additive influence of the parameters of loading and corrosion factors on the FCG rate in steels under the action of high-temperature aqueous media suggested and developed in [39, 41, 42]. Let us now dwell upon the fundamentals of this model to clarify the advantages of using the parameter  $\Delta K_{\text{Iscfc}}$  for the description of the processes of interaction between metals and media and for the construction of the function of influence of the parameters of cyclic loading on the FCG rate. For  $\Delta K$  greater than  $\Delta K_{\text{Iscfc}}$ , the mechanism of cyclic corrosion cracking is no longer negligible and its intensity increases with the amplitude of SIF in the region  $\Delta K > \Delta K_{\text{Iscfc}}$  but only up to a certain limit. As  $\Delta K$  increases, FCG induced by mechanical loads becomes more rapid, the plastic domain of a cyclically deformed metal enlarges, and the distance  $x_{p,d}$  to the domain of maximum tensile stresses (prefracture zone) increases [22, 27, 47, 48] (Fig. 2). Under these conditions, the amount of hydrogen accumulated in the prefracture zone decreases even as  $\Delta K$  increases; in this case, the intensity of the influence of a medium on the FCG rate decreases [43]. Correlation between the indicated factors manifests itself in the slopes of the second parts of KDFF of alloys [see Fig. 1(a-d)].



Fig. 2. Diagram of the domains of cyclic (1) and static (2) plastic deformation and the distribution of tensile stresses in the vicinity of the crack tip ( $x_{p.d.}$  is the distance between the crack tip and the prefracture zone).

The environmentally-assisted acceleration of FCG with a decrease in the loading frequency at constant  $\Delta K$  in the second part of KDFF is explained by the intense transport of hydrogen into the prefracture zone by dislocations. The energy of binding of hydrogen protons to dislocation cores is small [50-52] and, in the case where dislocations move sufficiently rapidly, hydrogen breaks the bond with the core and its transport terminates. A decrease in the loading frequency promotes an increase in the amount of hydrogen in the prefracture zone but only for frequencies greater than a certain critical frequency  $f_c$  that depends on the test temperature. As the frequency decreases further and becomes less than  $f_c$  ( $f < f_c$ ), hydrogen kept in the prefracture zone only by the gradient of tensile stresses escapes from this zone into the surrounding metal due to the gradient of its concentration. The competition between the processes of accumulation and escape of hydrogen weakens its influence on the crack-growth resistance of metals in the prefracture zone. Hence, the maximum of the frequency dependence of the FCG rate in hydrogen-containing [22, 27] and hydrogenating media [13–15] is attained at the critical loading frequency  $f_c$ .

The influence of the asymmetry coefficient of loading cycles on the FCG rate in alloys for constant values of f and the amplitude of SIF in the region  $\Delta K_{\rm Iscfc} < \Delta K < \Delta K_{\rm fc}$  is governed by two factors, namely, by the mean level of tensile stresses and by the amplitude in a cycle. The size of the domain of static plastic deformation increases with the mean level of stresses but the size of the domain of cyclic plastic deformation and crack opening are determined by the amplitude of SIF (Fig. 2) [56, 57]. As R increases but remains lower than  $R_{\circ}$  the influence of the medium becomes more pronounced. At the same time, as  $R \rightarrow 1$ , the FCG rate decreases because steels are not susceptible to static corrosion cracking under the influence of high-temperature aqueous media [41, 42].

The complicated character of the influence of the parameters of cyclic loading on the FCG rate in alloys affected by environments can be described by an analytic function with the help of which it would be possible not only to approximate experimental KDFF but also to predict the changes in the FCG rate induced by variation of the parameters  $\Delta K$ , f, and R.

We now consider a procedure used to construct the function of influence of high-temperature aqueous media on the FCG rate in steels and demonstrate the possibility of using this function for some other metal-medium systems. In high-temperature aqueous media, the surface of low-carbon low-alloy steels is covered with dense magnetite films, guaranteeing absolute protection of metals against the influence of the media [58]. An ST-1 specimen of 15Kh2NMFA steel tested continuously for six months in an autoclave with reactor water at a temperature of 300°C exhibited no changes in size. Moreover, its surface was still bright with signs of grinding and polishing. Therefore, 15Kh2NMFA-type steels without detrimental impurities do not suffer cracking under static loading in hightemperature aqueous media. In the course of cyclic tests, the protective brittle oxide film periodically ruptures as the cyclic load increases and, as a result, a galvanic couple is formed by a newly-formed surface at the crack tip and passivated surfaces of the crack lips. Earlier, it was established that the duration of electrochemical reactions leading to the complete repassivation of the newly-formed surfaces  $\tau_r$  is a decisive factor of the influence of high-temperature aqueous media on the FCG rate [39, 41, 46, 59–61].

Anodic processes on the newly-formed surfaces lead to the losses of the metal, and it is natural to assume that these losses should be regarded as a linear addend to the FCG rate caused by mechanical loading. Electrolytic hydrogenation of the material in the course of electrochemical reactions is not connected with direct losses of the metal. Accumulated in the prefracture zone, hydrogen embrittles the metal and its effect is reduced to the acceleration of crack growth induced by mechanical loading. Thus, on the basis of the analysis of the influence of anodic and cathodic processes at the crack tip, one can write the following equation for the environmentally-assisted FCG rate in steels [38]:

$$v_{\rm cf} = v_{\rm c} + v_{\rm f} h_{\rm cf},\tag{1}$$

where  $v_c$  is the rate of pure corrosion growth of the crack,  $v_f$  is the FCG rate induced by mechanical loading, and  $h_{cf}$  is a function that reflects the influence of hydrogen embrittlement of the metal in the prefracture zone on the FCG rate induced by mechanical loading.

Methods for evaluation of the influence of media on the FCG rate according to the mechanism of anodic dissolution ( $v_c$ ) are well known [44, 62–64] and we do not consider them here.

The function  $h_{cf}$  is given by the formula [41, 42]

$$h_{\rm cf} = \left[ \frac{\left(\Delta K_{\rm eff} - \Delta K_{\rm por}\right)^2}{\left(\Delta K_{\rm eff} - \Delta K_{\rm Iscfc}\right)^2 + B\Delta K_{\rm thc}^2} \right]^m,\tag{2}$$

where  $\Delta K_{\text{eff}}$  is the effective amplitude of SIF in a cycle ( $\Delta K_{\text{eff}} = K_{\text{max}} - K_{\text{op}}$  if  $K_{\min} \leq K_{\text{op}}$  and  $\Delta K_{\text{eff}} = \Delta K$  if  $K_{\min} > K_{\text{op}}$ , where  $K_{\text{op}}$  is the SIF of crack opening), B is a parameter that takes into account the susceptibility of the metal to cyclic corrosion cracking, and m is a function that reflects the level of hydrogen occlusion by the metal. For  $\Delta K_{\text{eff}} < \Delta K_{\text{por}}$ , the crack is arrested and, hence, no influence of the medium is observed. The maximum

influence of the medium according to the mechanism of hydrogen embrittlement is attained for  $\Delta K_{\text{eff}} > \Delta K_{\text{Iscfc}}$ . For  $\Delta K_{\text{eff}} \le \Delta K_{\text{fc}}$ , the influence of hydrogen embrittlement becomes negligible and we can write

$$\lim_{\Delta K \to \infty} h_{\rm cf} = 1. \tag{3}$$

The maximum intensity and the type of the effect of the medium on the FCG rate according to the mechanism of hydrogen embrittlement are governed by the parameter B, which is determined experimentally.

The dependences of the parameters of cyclic corrosion crack-growth resistance on the asymmetry coefficient of loading cycles are described by the following relations [3, 39, 63]:

$$\Delta K_{\rm Iscfc}(R) = (\Delta K_{\rm Iscfc}|_{R=0} - \Delta K_{\rm por})(1-R) + \Delta K_{\rm por}$$

$$\Delta K_{\rm thc}(R) = (K_{\rm thc} - \Delta K_{\rm por})(1-R) + \Delta K_{\rm por}.$$
(4)

The formula obtained by inserting relations (4) in the expression in the square brackets in (2) adequately describes the influence of the parameters  $\Delta K$  and R on the environmentally-assisted FCG rate according to the mechanism of hydrogen embrittlement and does not contradict any known experimental data [3, 5–23, 26, 27, 34–37, 45, 55, 63–68].

The exponent *m* is a function of the ratio of the time of repassivation of the newly-formed surface at the crack tip  $(\tau_r)$  to the growth rate of the SIF in a cycle and reflects the influence of the loading frequency and the shape of loading cycles on the FCG rate in alloys [39, 41, 42]. In fact,

$$m = \sqrt{\frac{\Delta K_{\text{por}} \tau_l}{\Delta K_{\text{eff}} \tau_r}},$$
(5)

where  $\tau_l$  is the duration of the part of a cycle where loading increases. Relation (5) describes the acceleration of FCG as the frequency of continuous loading decreases because the exponent *m* increases from zero to one as the influence of the medium according to the mechanism of hydrogen embrittlement becomes maximal. It is clear that the loading frequency must be decreased as  $\Delta K_{eff}$  increases to guarantee the maximum possible influence of the medium on the FCG rate. This theoretical conclusion made in [38, 41] was corroborated by the experimental data obtained in [69]. This means that relation (2) is applicable not only for the description of experimental KDFF but also to the evaluation of the influence of the medium is maximal can be found as follows [39, 42]:

$$f_{\rm c} = \frac{1}{\Delta K_{\rm eff} \,\Delta K_{\rm por}^{-1} \,\tau_{\rm r} + \tau_{\rm ul}},\tag{6}$$

where  $\tau_{ul}$  is the duration of the part of a loading cycle where the value of SIF is held at a given level or decreases. In passing, we note that the use of a constant loading frequency of 17 MHz in standard specifications is groundless. For  $f < f_c$ , FCG induced by the influence of high-temperature aqueous media decelerates as the loading frequency decreases [13, 14, 67, 70]. The causes of this phenomenon are described above; in relation (2), this is taken into account by the substitution of the inverse quantity  $m^{-1}$  for the exponent m [42]. Equation (2) also reflects the effect of the shape of loading cycles. Thus, for II-shaped cycles and sawtooth cycles with inverted (Japanese) teeth, the influence of the medium on the FCG rate is negligible [5, 7, 26]; in relations (2) and (5), this case corresponds to the limit as  $\tau_l \rightarrow 0$ ,  $m \rightarrow 0$ , and  $h_{cf} \rightarrow 0$ . The highest intensity of the influence of the medium is observed in the case where the growth rate of the SIF in a cycle is constant, i.e.,  $\Delta \dot{K} = \Delta K_{por} \tau_r^{-1}$ . Hence, to reduce the duration of autoclave tests, we used sawtooth loading cycles with slowly increasing and rapidly decreasing loads [5, 7, 71]. The dependences of the FCG rate on the parameters of cyclic loading  $\Delta K$ , f, and R in planes calculated according to relation (2) are well known and have been carefully compared with experimental data [38, 39, 41, 42, 64, 68]. In Fig. 3, we present spatial dependences of the maximum influence of the media on the FCG rate according to the mechanism of hydrogen embrittlement for the following cases:

(a)  $h_{cf} = h_{cf}(\Delta K, R)$  and m = 1 [the growth rate of the SIF in a cycle is constant and equal to  $\Delta K = \Delta K_{nor} \tau_r^{-1}$  and the loading frequency is given by relation (6)];

- (b)  $h_{cf} = h_{cf}(\Delta K, f)$  and R = 0.7;
- (c)  $h_{cf} = h_{cf}(R, f)$  and  $\Delta K$  is found from the condition  $\frac{\partial}{\partial f} \frac{\partial h_{cf}}{\partial R} = 0$ .



Fig. 3. Spatial dependences of the maximum influence of the parameters of cyclic loading on the FCG rate in steels affected by high-temperature aqueous media according to the mechanism of hydrogen embrittlement.

The changes in the FCG rate in a given alloy under the influence of a medium according to the mechanism of hydrogen embrittlement are described by the collection of values of the function  $h_{cf}$  in the space between the plane  $\log h_{cf} = 0$  and the planes  $\log h_{cf}(\Delta K, f, R)$  [Fig. 3(a-c)]. It is clear that it is practically impossible to acquire this collection experimentally. For this reason, dependences similar to those depicted in Fig. 3 have not yet been constructed for any type of alloy placed in the same medium of fixed chemical composition and at a constant temperature [66, 67].

# The Method for the Analytical Description of KDFF Used in Standard Specifications

Up to now, many researchers and engineers [5-8, 10, 15, 16, 18-23, 25, 27, 34, 35, 37, 63-67, 69-73] have used simplified mathematical models instead of the model given by Eq. (1) and relations (2) and (5). The maximum and minimum values of experimental data are traditionally limited by broken lines described by the Paris equation

$$v = C\Delta K^n \tag{7}$$

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In the ASME (American Society of Mechanical Engineers) Standards [23], engineering analysis is based on the data obtained at loading frequencies that do not exceed 17 MHz. The maximum FCG rate is limited by the upper envelope of the collection of values obtained for R = 0.65, while the minimum FCG rate is limited by the lower envelope of the collection of values obtained for R = 0.25.



Fig. 4. Extrapolation of KDFF by the Paris equations suggested in the ASME Boiler Code [23].

Curve in Fig. 4	R	С	n	
1	≥0.65	$5.39 \cdot 10^{-9}$	1.95	
2	≥ 0.65	$1.74 \cdot 10^{-13}$	5.95	
3	≤ 0.25	$2.13 \cdot 10^{-9}$	1.95	
4	≤ 0.25	$1.48 \cdot 10^{-14}$	5.95	
5	0.25 < R < 0.65	$2.13 \cdot 10^{-9}$	1.95	
6	0.25 < R < 0.65	$1.48 \cdot 10^{-14}$	5.95	
7	0.5	$4.77 \cdot 10^{-13}$	3.73	

Table 1

The dependence of the FCG rate on the parameter R within the range of 0.25-0.65 is described by the following linear equations:

$$v_5 = 2.13 \cdot 10^{-9} \Delta K^{1.95} (3.75R + 0.06),$$

$$v_6 = 1.48 \cdot 10^{-14} \Delta K^{5.95} (26.9R - 5.75),$$

although the dependence  $v_{cf}(R)$  is actually nonlinear (see Fig. 3c). To estimate the service life of a structural member under loads with R > 0.65 or R < 0.25, it is customary to use the values of  $v_{cf}$  for R = 0.65 or R = 0.25, respectively. It is clear that the corresponding estimates are simplified and conservative, and, therefore, the specifications of [23] should be revised.

Modern computers make analysis of the service life of structural members according to relations (1), (2), and (5) fairly feasible. Moreover, if the procedure and scope of autoclave tests are well designed, then the required parameters of cyclic crack-growth resistance, i.e.,  $\Delta K_{1scfc}$ ,  $\Delta K_{por}$ ,  $\tau_r$ , B, and  $\Delta K_{tho}$  can be measured relatively easily.



Fig. 5. Sequence of autoclave tests for determination of the characteristics of cyclic corrosion crack-growth resistance of steels [see Eqs. (1), (2), (4), and (5)].

#### **Experimental Determination of the Parameters Appearing in Equation (2)**

As a starting point, we choose the KDFF of an alloy in air for R = 0.2 (1) and R = 0.7 (2) (Fig. 5a) to increase the accuracy of further calculations [41]. On the basis of the results of autoclave investigation of the influence of the amplitude of SIF on the FCG rate as the asymmetry coefficient R = 0.7 and the loading frequency f = 17 MHz (or the relevant rate of increase of the SIF) remain constant, we plot the dependences presented in Fig. 5a, which enable us to determine  $\Delta K_{Iscfc}$ . The influence of the loading frequency (rate of increase) on the FCG rate is studied in the region of  $\Delta K_1 > \Delta K_{Iscfc}$  where the growth of a crack is more stable (Fig. 5a); the corresponding plot is displayed in (Fig. 5b). Having found the maximum value of  $v_{cf}$ , we determine  $f_c$ . Further, using Eq. (7), we compute the product  $\Delta K_{por} \tau_r^{-1}$  for m = 1 without performing autoclave electrochemical tests. The point C in Fig. 5 is then plotted in Fig. 5a and the value of the function  $h_{cf1}$  is determined according to the difference between the rates of FCG in the medium for m = 1 and in air (Fig. 5a, segment AC). To construct  $v_{cf}$  as a function of R (Fig. 5c) and determine the asymptotic value of  $R_0$  we gradually increase the asymmetry coefficient of loading cycles for constant  $\Delta K = \Delta K_1$  and  $f = f_c$ . The condition

$$R_0 = \frac{(K_{1\max} - \Delta K_{por})}{K_{1\max}}$$

enables us to find  $\Delta K_{\text{por}}$ . By decreasing the asymmetry coefficient to R = 0.2 ( $\Delta K = \Delta K_1$ ,  $f = f_c$ ), we obtain the true value of  $v_{cf}$  (Fig. 5c, point D). Then we plot the point D in Fig. 5a and determine the difference between the FCG rates in the medium for m = 1 and in air  $h_{cf2}$  (Fig. 5a, segment ED). The equations

$$h_{cf1} (R = 0.7, \Delta K_1, f_c) = AC,$$

$$h_{cf2} (R = 0.2, \Delta K_1, f_c) = ED,$$
(8)

are used to compute  $\Delta K_{\text{thc}}$  The parameter B is found from relation (2). Here,  $\Delta K_1$  is necessarily equal to  $\Delta K_{\text{eff}}$ .

It is easy to see that the experimental procedure described above allows one to obtain all characteristics of cyclic crack-growth resistance necessary to describe the entire collection of data by testing, in fact, a single CT-type specimen (see Fig. 3). This is especially important for high-temperature low-frequency tests in view of their long duration and high power consumption [5, 7, 10, etc.].

We have already considered a model of functional-additive influence of high-temperature aqueous media on the FCG rate in steels such that the parameter  $\Delta K_{por}$  is decisive for high R and the influence of anodic dissolution is negligible [39]. For metal-medium systems that do not form rigid and relatively thick oxide films, the Roscoe effect is not observed and  $\Delta K_{por} \rightarrow 0$ . Therefore, the experimental determination of the parameters  $\Delta K_{Iscfc}$ ,  $\Delta K_{thc}$ , and B according to the scheme outlined above becomes significantly simpler. At the same time, to compute the function m according to (5), one must undertake an additional investigation because its physical nature is subject to changes; the corresponding results will be published elsewhere. If the metal in a metal-medium system is susceptible to static corrosive cracking, then the condition  $\lim_{f\to 0} h_{cf} \rightarrow 1$  is not satisfied and, hence, to predict the service life of structural members, one must have an analytic expression that describes kinetic diagrams of static cracking (KDSC).

#### Analytic Description of Kinetic Diagrams of Static Cracking

Kinetic diagrams of static cracking of alloys can also be approximated by a power function

$$v = v_0 \left(\frac{K_{\rm I} - K_{\rm Iscc}}{K_{\rm Icc} - K_{\rm I}}\right)^p = v_0 F^p,\tag{9}$$

where  $v_0$  is a constant,  $\Delta K_{Icc}$  (corrosion cracking) is the critical value of the SIF corresponding to the transition from the subcritical growth of a crack to spontaneous fracture under long-term static loading, p is a numerical exponent, and F denotes the function in parentheses. The constant  $v_0$  is determined from the KDSC for F = 1. The plot of the function F is similar to typical KDSC of alloys because the exponent p reflects the slope of the dependence of the rate of static corrosion cracking on the SIF for K somewhat greater than  $\Delta K_{Iscc}$  as well as the slope of the linear part of this curve [3] (Fig. 6a). To check the validity of relation (9), we calculated the constant  $v_0$  and the exponent p for three types of steel (Table 2) [74] and plotted the relevant functions in Fig. 6b. In Table 2, for curves 1, 2, and 3, we additionally present the values of  $\Delta K_{Icc}$  found from the KDSC of steels.

It seems possible that  $\Delta K_{Icc}$  can be regarded as a new characteristic of steels and alloys affected by corrosive media that reflects the influence of the medium on  $\Delta K_{Ic}$  according to the mechanism of corrosion crack blunting; however, this is a subject of a separate work. The calculated and experimental values of the crack-growth rate displayed in the KDSC in Fig. 6b agree well in the entire range  $\Delta K_{Iscc} \leq \Delta K_{I} < \Delta K_{Isc}$ , which means that relation (9) is indeed applicable to the computation of the service life of structural members when the mechanism of corrosion cracking is realized. Relation (9) makes the computer processing of experimental data and engineering analysis much simpler.

Both the suggested model of the influence of media on the FCG rate in alloys and the method of its practical implementation prove the necessity of using the characteristic  $\Delta K_{\text{Iscfc}}$  in scientific research and engineering analysis.



Fig. 6. (a) Plots of the function F for p = 0.1 (1), p = 0.5 (2), and p = 1.0 (3); (b) experimental values of the crack growth rate in steels as compared with the data obtained according to relation (9) (Table 2) [74].

Type of steel	t <sub>B</sub> , °C	K <sub>Ic</sub>	K <sub>Icc</sub>	K <sub>Iscc</sub>	v <sub>0</sub> ,	n	Curve
		MPa · √m		mm/sec	P	in Fig. 6	
30KhGSN2A	200	95	95	95	<b>4.2</b> · 10 <sup>−3</sup>	0.05	4
45KhN2MFA	200	33	33	50	$1.05 \cdot 10^{-1}$	1.51	2
	450	97	97	97	$6 \cdot 10^{-4}$	0.01	6
60KhS	300	18	18	28	$9 \cdot 10^{-2}$	1.68	1
	450	47	47	60	$1.2 \cdot 10^{-2}$	0.15	3
	550	60	60	60	$1.5 \cdot 10^{-3}$	0.03	5

## Table 2

### CONCLUSIONS

1. The threshold amplitude of the SIF of cyclic corrosion cracking is an independent characteristic that differs from the threshold of static corrosion cracking by the magnitude and nature of defects and the mechanism of hydrogenation of metals in the prefracture zone.

2. Alloys that are not susceptible to static corrosion cracking in a given medium may suffer cyclic corrosion cracking; in this case, they are characterized by the parameter  $\Delta K_{\text{Iscfc}}$ .

3. Alloys susceptible to static corrosion cracking in a given medium must be characterized by two parameters of different natures and magnitudes  $\Delta K_{Iscc}$  and  $\Delta K_{Iscfc}$ . As an exception, the values of these parameters may coincide for some-high strength alloys.

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4. The parameter  $\Delta K_{\text{Iscfc}}$  should be taken into account in scientific investigations because it reflects real physicochemical processes and enabled us to create a well justified analytic model for the description of the influence of high-temperature aqueous media on the fatigue-crack growth rate in steels. Unlike the existing models, our model makes it possible not only to describe the experimental KDFF but also to predict the influence of the asymmetry coefficient, loading frequency, and the shape of loading cycles on the FCG rate in broad ranges of these parameters.

5. By using the parameter  $\Delta K_{\text{Iscfc}}$  and the suggested model in engineering analysis, one can significantly reduce the number (duration) of laboratory autoclave tests and, at the same time, increase the accuracy of prediction of the service life of structural members of power plants.

The presented work was supported by the Ukrainian State Committee on Science and Technology and is published as a continuation of the discussion on the problem of protection of metals against corrosion started in the first issue of this volume [Vol. 30, No. 1 (1994)].

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