

CORROSION AND TEMPERATURE EFFECTS ON CRACK KINETICS IN STEELS

O.M.ROMANIV*

Overview of environment effects on the crack propagation in structural steels under static and fatigue loading is presented. Crack kinetics is not only a function of environmental mechanisms but also undirect mechanical factors which are determined with the crack branching, the changes of morphology of crack tip, crack closure etc. The real contribution of adsorbational effect, peculiarities of local electrochemical situation in the crack tip are discussed. The changed influence of high temperature water environment during fatigue crack growth in terms of combined processes of repassivation phenomena and thermal aging is interpreted.

INTRODUCTION

The fracture mechanics created not only new approaches to the evolution of strength and serviceability of materials but also discovered the series of new phenomena which were out of eyesight in studies of materials on smooth specimens and machine parts. Considerable quantity of such new phenomena is connected with the influence of environments.

One of the first very interesting results in this field concerned to experimental quantitative confirmation of Rebinder effect which was intuitively formulated after observations of brittle fracture of rocks and alloys under the influence of liquid metals [1]. Such confirmation was received by Panasyuk and Kovchyk [2] on polymers and steels during studies of stable equilibrium of plates with a specially loaded crack. The drop of effective fracture energy for carbon steel (0.8% C) under the influence of metanol is equal to 15% and in the distilled water 25%. Such experiments did not answer on the question as this drop has a pure adsorbational nature but they gave quantitative instruments for evaluation of the environmental effects during short time testings of materials with cracks, and were in disagreement with conclusions of Johnson, who denied the

* Department of Structural Mechanics, Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine, Lviv

influence of corrosive environment on fracture toughness of structural steels [3]. Romaniv et al. [4] gave quantitative evaluation of K_{Ic} drop in steels under the influence of distilled and sea water and showed fractographically that this effect is connected with losses of barrier functions of the process zone on the front of crack tip with evidences of short-time subcritical crack growth.

Indeed subcritical crack growth under the influence of static and cyclic loading belongs to the specific phenomena which demand serious generalizations in this part of discipline which is named corrosion fracture mechanics [5]. Some results in this field which were received in the Karpenko Physico-Mechanical Institute in Ukraine are presented in this paper. The studies were performed on various standard East European steels under the influence of water environment (distilled and sea water, the water of boron regulation in BWR).

SUBCRITICAL CRACK GROWTH IN STEELS UNDER THE INFLUENCE OF CORROSION ENVIRONMENTS. GENERAL CONSIDERATIONS.

Phenomena of subcritical crack growth in steels under the influence of static and cyclic loading and corrosion mild environments are well studied and reduce to next considerations [5]. Corrosion environment (distilled and sea water - 3% water solution of NaCl) provokes subcritical crack growth (SCCG) on the precracked high strength steels and accelerates SCCG under the cyclic loading. Schematically the velocity (V) - stress intensity factor (SIF) (K) curves receive features as in Fig.1.

For durable static loading are characteristic middle terrace like sections which testify nonsingle-valued character of V - K dependence in a certain interval of SIF values (Fig.1a). Such plateau are not typical for fatigue but they can be provoked with some factors especially under the influence of large static part of loading in regime of low frequency testing and under the influence of cathodic polarization (Fig.1b,c).

The strength level of steels determined by metallurgical content (esp. carbon % and thermal treatment) is of principle significance for SCCG. For high strength martensitic steels maximal drop of thresholds and crack acceleration are observed. Such influence weakens with a drop of strength and when a metal structure nearests to the equilibrium state of steels from martensite to troostite and finally to the perlite-ferrite mixture (Fig.2). For low strength steels under the influence of environment sufficient increase of corrosion fatigue thresholds ΔK_{thc} is observed. Such effects can be evaluated using influence factors

$$\beta_{th} = \frac{\Delta K_{thc}}{\Delta K_{th}} \quad \text{and} \quad \beta_{\Delta K} = \frac{\Delta K_c^*}{\Delta K^*} \quad (1)$$

Here β_{th} testifies relation between amplitude ΔK^* values which provide the middle region of the crack growth velocity $V=10^{-7}$ m/cycle. Some generalizations concerning of strength of steels ($\sigma_{0,2}$) and frequency of testing in the distilled water on factors β_{th} and $\beta_{\Delta K}$ are presented in Fig.3 [5]. The showed data demonstrate that transition from high strength to low strength state in steels brings to the opposite tendency: the corrosion fatigue thresholds become higher than on air and retardation of crack velocity is observed. Time factor transformed by frequency values enhances negative influence of corrosive environment in high strength state and positive influence for steels in low strength conditions.

Some interesting peculiarities of SCCG of structural steels in corrosive environment (distilled and sea water) in conditions of static loading should be marked. For some systems metal-environment the various path of V - K curves was observed which is dependent on the starting value of SIF K_{I0} (Fig.4). Fig.5 demonstrates various types of time to rupture diagrams for precracked specimens which depend on the initial level of SIF K_{I0} . In presented case we observe really two different rupture diagrams which coverage two different levels of strength, in both cases we observe specifically different mode of fracture [5].

CRACK GROWTH MECHANISMS UNDER THE INFLUENCE OF CORROSION FACTOR.

Influence of environment on the crack growth kinetics is attributed to the changes in the fracture mechanisms. From the first stage of interaction of environment with metal changes of fracture mechanisms induce also changes of the crack morphology. The specific phenomena of micro- and macrobranching are observed, the anodic corrosive blunting of the crack tip is also possible which some time disply together with plastic blunting of the crack. Changes on fracture surfaces are also connected with changes of crack closure (CC) which is very important on the near threshold interval of crack velocities V .

Environmental mechanisms. The stable opinion exists [5] that the mentioned phenomena of the crack growth kinetics in constructional low alloyed steels under the influence of water environment are connected with action of hydrogen (at first hydrogen embrittlement) or with typical corrosive mechanism of anodic dissolution of stressed crack tip. Mentioned both mechanism can interact together but prevails view about the dominant (alternative) role of one of the

named mechanisms [5]. As a dominant reason of the crack growth resistance drop in high strength steels the hydrogen embrittlement is considered. Such mechanism is confirmed with additional influence of cathodic polarization accordingly to the indicative concept of Marichev [6]. On the other hand the main factor of kinetics changes in low strength steel is anodic dissolution which intensifying crack blunting can retard crack growth.

Manifestation of dominant environment mechanism depends strongly on various mechanical factors [7] as the amplitude ΔK , frequency, size of specimen which influence on the stress-strain state in the vicinity of main crack. Reinforcement of the tendency for domination of one of the mentioned two mechanisms can be good described with the mechanical-electrochemical analogy which was deduced comparing hydrogen-anodic transition with brittle-ductile transition which is well studied in classical courses of mechanical behaviour of iron and steels [7].

Adsorbational factor. Taking into account dominant action of hydrogen or anodic mechanism of the acceleration (or retardation) of crack growth it is very important to take account of the adsorbational origin of environment influence, which is practically undivided from both other mentioned groups of factors. Using static crack growth tests of high strength steel in special chamber under the influence of aprotone medium dymethylsulfoxide (DMSO) Romaniv et al. [8] showed the possibility of pure adsorbational lowering of strength and its accelerating influence on the crack growth (Fig.6). Such influence was denied by Nicols and Rostocker [9] in their discussion with Karpenko which postulated adsorbational drop of the fatigue strength in metanol. Protodonoric admixtures to dymethylsulfoxide increase the crack kinetics and strength drop but the pure adsorbational influence also can be significant factor of strength diminishing of metals and alloys.

Corrosive crack branching of cracks. For various metal-environment systems the crack growth especially under the static loading is connected with crack branching [10]. The microbranching is attributed at first with the intergranular crack growth which is connected with preferential hydrogen migration during the grain boundaries and consequently with hydrogen embrittlement of material. Some time, especially for the stainless steels, intergranular rupture can be connected with intergranular corrosion [10]. On the second hand macrobranching is the consequence of crack growth along the slip bands. This phenomenon depends on sizes of specimens and initial loading stages. Macrobranching is the main reason of undefinitiveness of $V-\Delta K$ curves presented in Fig.4. Romaniv et al. [7] showed that such diagrams can be brought to single curve after calculations of nominal

values of K taking into account branching and blunting of the crack. From the similar position data presented in Fig.5 can be interpreted from the point of two dominant types of branching: macrobranching (curve 1) and microbranching (curve 2).

Local electrochemical situation in the crack tip. Panasyuk et al. [11] mansided investigated phenomena of nonconformity of electrochemical parameters of corrosive in the crack tip and on the bulk of the specimens (Fig.7). The unconformity of electro potential φ_s and φ_T and hydrogen value pH_s and pH_T depends on the initial conditions and history of loading, crack branching conditions and other factors. Ratych and Dmytrakh [7] also showed that such unadequacy can be also a reason of various situation of $V-K$ curves. Taking into account history of loading exists a system of $V-K$ or $V-\Delta K$ curves (Fig.8). They are enveloped from the left by the basic curve which determines the conditions of maximal guaranteed safety. Such approach is important in the problem of safety of BWR.

This approach enabled new methods of theoretical determination of K_{ISCC} values, and also served as a basis for correction of our view on the inhibitory protection of alloys, taking into account local electrochemical situation but not the nominal parameters of electrolyte [11].

Crack closure of the corrosive-mechanical cracks. In the near threshold region the crack growth kinetics depends often on the CC [7]. Crack closure can change sufficiently under the influence of corrosive and temperature factors. Microcracking connected with the intergranular rupture can sufficiently increase crack closure induced with crack roughening (CCR) [7]. Supplementary effect can be provoked due to formation of corrosion products on the crack surface (CCC). Corrosive build up of ferrum oxides becoms very stable in high temperature conditions, which is typical for WWR systems. Our evaluation showed that supplementary growth of CC connected with corrosive environment can growth up DKth more than on 30% [7].

Near threshold behaviour — interrelation of various factors. Comparison of influence on the corrosion fatigue behaviour of various factors can be done very clear during determination of fatigue thresholds DKth. As it was proposed in our paper [7] the approximate formula for evaluation of DKth can be presented as follows:

$$\Delta K_{th} = \Delta \bar{K}_{thc} + \frac{1}{2} \bar{\sigma}_m \sqrt{\rho_{th}} \quad (2)$$

In this expression $\Delta \bar{K}_{th}$ - component which takes into account the level of CC connected with its various parts (roughness, branch-

ing, corrosion products); factor α should be determined as correction of SIF on the branching and after transformation of the natural crack into modelling system with a sharp single branched crack [5] ρ_{rh} – the adjusted radius of crack tip blunted with the joint action of anodic dissolution and plastic blunting [7].

The most physically undetermined part in expression (2) $\bar{\sigma}_m$ - threshold stress, this characteristic can be interpreted as some invariant value very similar to fatigue stress on smooth specimens. Beside of outcoming influence on this parameter of interatomic bonding in material C, the level of parameter $\bar{\sigma}_m$ depends on the level of bonds degradation (adsorbition, hydrogen embrittlement etc.). The last conditions are after Panasyuk also connected with the local electrochemical parameters φ_T and pH_T

$$\sigma_{rh} = F(C, \varphi_T, pH_T) \quad (3)$$

Indicative meaning of acoustic emission. In literature exist some attempts to use acoustic emission (AE) for evaluation of the accelerating influence of corrosion environment on the crack growth in metals [7]. Comparison of AE effects in high and low strength steels brings to the following conclusions. AE is a very sensitive instrument of determination of the crack growth kinetics changes in water environment connected with intergranular crack propagation in high strength steels [12]. Such a phenomenon can be manifested as a growth of acoustic events connected with intergranular cleavage (Fig.9). On the second hand during the striation crack growth in the low strength steels hydrogen reducing plasticity also weakens acoustic effects of development of striations [13].

INFLUENCE OF HIGH TEMPERATURES. COMBINED ACTION OF CORROSIVE ENVIRONMENT AND OF INCREASED TEMPERATURES.

The increase of testing temperature can sufficiently influence on the kinetics of crack growth in steels and other alloys. Such factors can influence on the crack behaviour of alloys:

- a) structural changes in materials under the action of long thermal influence (temperature aging, for example formation of precipitations on barriers created on inside slip bands [14]);
- b) thanks to tendency to form pores in vicinity of the crack tip which is stimulated by creep damages;
- c) due to the temperature changes in CC. The last aspect deserves on supplementary remarks.

When the testing temperature rises due to the intensification of cross slip the roughness of fracture surface diminishes the CCR drops and accordingly drop of the nominal ΔK_{th} values. But the following rise of temperature induces the autocatalytic processes of oxide formation. Romaniv et al. showed [7] that originally the growth of temperature is connected with diminishing of oxide film but later its thickness growth and this is connected with a growth of ΔK_{th} (Fig.10).

Mentioned example is only a partly case of the influence of external environment on the high temperature crack growth behaviour. Special significance in the frame of mentioned problem have the investigations of reactor steels in the high temperature water environment. The series of investigations in this direction were performed by Scott [15] and Ford [16]. In the Karpenko Physico-Mechanical Institute Pokhmurski et al. [17] investigated fatigue crack behaviour of the perlitic 0.15C-1Cr-2Ni-1Mo-1Va steel and stainless 0.08C-18Cr-10Ni-1Ti steel in reactor water of high parameters ($T=300^{\circ}\text{C}$, $p=18\text{ MPa}$). Sufficient acceleration of crack growth in the environmental conditions was discovered (Fig.11). The formation of plato sections on the diagrams was revealed which testifies the stress corrosion cracking of perlitic steel. The local electrochemical investigations also were conducted. They showed that the increase of repassivation time of newly regenerated surfaces is accompanied by the increase of water influence upon fatigue crack growth rate. The authors proposed the calculation model which confirms and gives proof the mentioned concept of surface repassivation influence on the crack growth.

CONCLUDING REMARKS

On these days the main generalization of the corrosion influence on the SCCG of alloyed steels at ambient temperature are well established. At higher temperatures the conducted investigations concern only to the behaviour of steels in pressurized water reactors.

New investigation methods of local electrochemical studies in the crack tip open now new possibilities for explanation of the influence of environments in a crack tip, and they should be used in high temperature conditions.

Temporary understanding of the processes of interaction of materials with environments demands formation of the calculating models in which environment acts not only as factor of debonding of elementary particles but also as important indirect factor of changes of mechanical situation in enclave of the crack (by means of branching, tip blunting, crack closure changes etc.).

The question of interrelation of factors of high temperature creep of material and electrochemical action of corrosive environment in the problems of high temperature corrosive mechanical behaviour are only on the initial stage of investigations and they demand at first careful experimental studies.

References

- (1) Rebinder, P.A., Report on the VI Congress of Russian Physics, M., 1928. (in Russian)
- (2) Panasyuk, V.V., Kovchyk, S.E., Applied Mechanics, V.9, N 2, 1963, pp. 183-189. (in Ukrainian)
- (3) Johnson, H.H., "Fracture", Academic Press, N.Y. and London, V.3, 1971.
- (4) Romaniv, O., et al., Physico-Chemical Mechanics of Materials, N 1, 1974, pp. 16-20. (in Russian)
- (5) Romaniv, O.N., Nykyforchyn H.N., "Corrosion Fracture Mechanics of Structural Alloys", Metallurgia Publishers, Moscow, 1986. (in Russian)
- (6) Marichev, V.A., Physico-Chemical Mechanics of Materials, N 2, 1975, pp. 14-17. (in Russian)
- (7) Romaniv, O.N., et al., "Fracture Mechanics and Strength of Materials", Kyiv, Naukova Dumka Publishers, V.4, 1990. (in Russian)
- (8) Romaniv, O.M., et al., *Bullet. of Electrochem.*, 3(6), 1987, pp. 547-551.
- (9) Nichols, H., Rostocker W., "Environment Sensitive Mechanical Behaviour", Gordon and Breach, 1967, p. 237.
- (10) Speidel, M.O., "Spannungsrissskorrosion von Stahl in Wasser", Band 2, Verlag "Thubal-Kain", 1988, pp. 117-143.
- (11) Panasyuk, V.V., "Mechanics of Quasibrittle Fracture of Materials", Naukova Dumka Publishers, 1991, pp. 229-336. (in Russian).
- (12) Romaniv, O.N., et al., Physico-Chemical Mechanics of Materials, N 2, 1987, pp. 51-55. (in Russian)
- (13) Wang, Z.F., et al., *Fatigue and Fracture of Engineering Materials and Structures*, Vol. 16, N 4, 1993, pp. 441-452.
- (14) Koterazawa, R., "Creep-Fatigue Crack Growth of Metallic Materials at Elevated Temperatures" in: *Advances in Fracture Resistance and Structural Integrity*. Edited by V.V.Panasyuk et al., Pergamon, 1994.
- (15) Scott, P.H., "Environmental Assisted Cracking in Alloy 600 Components in PWR Primary Water", in: *Advances in Fracture Resistance and Structural Integrity*, Edited by V.V.Panasyuk et al., Pergamon, 1994.
- (16) Ford, F.R., "The Development and Use of Environmentally-Assisted Cracking Models for Light Water Reactors", in *Fracture Mechanics: Successes and Problems*, Lviv, 1993.

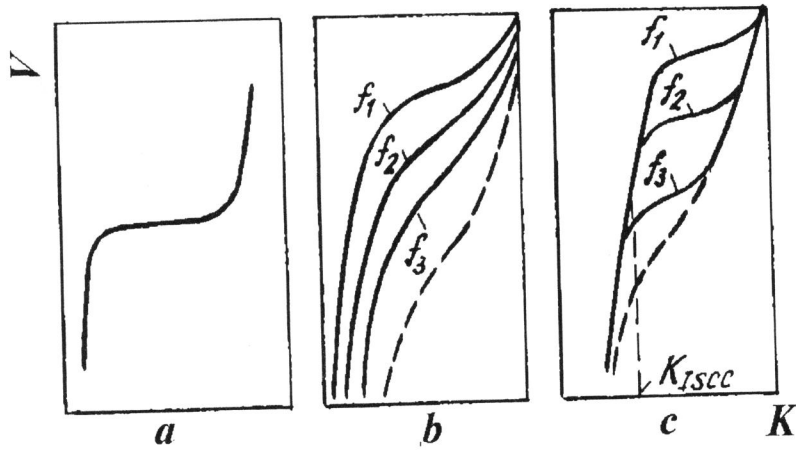


Figure 1. Examples of typical subcritical crack growth curves: a – static loading; b-c – fatigue loading with various frequencies f .

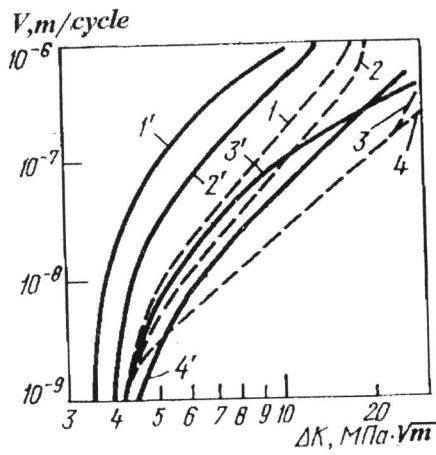


Figure 2. SCCG kinetics in 60CHS steel after quenching under loading in water (solid line) and in air (dotted line): 1-1' – tempering at 200°C; 2-2' – at 300°C; 3-3' – at 400 °C; 4-4' – at 500°C

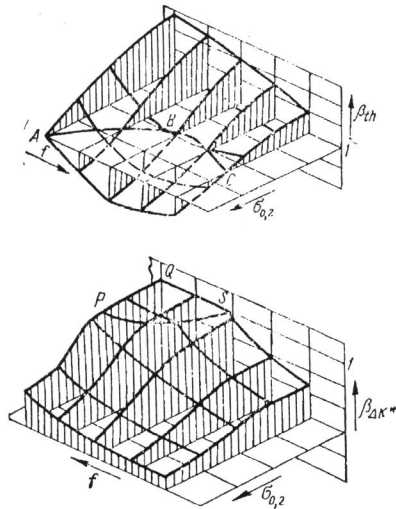


Figure 3. Diagrams which demonstrate influence of strength $\sigma_{0,2}$ and frequency f on β_{th} and $\beta_{\Delta K^*}$.

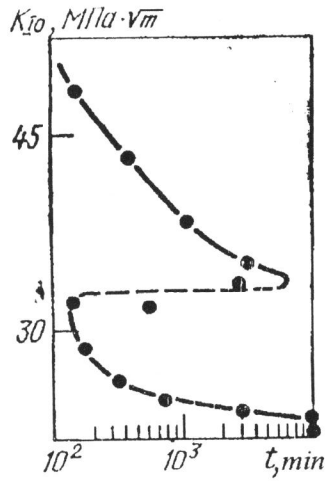


Figure 5. Diagrams of durability of precracked specimens (20Ch13 steel, testing under static loading in sea water).

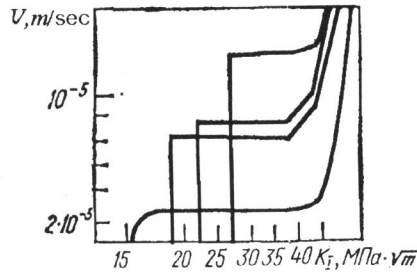


Figure 4. Kinetic diagrams for static loading (50Ch steel), testing in metanol.

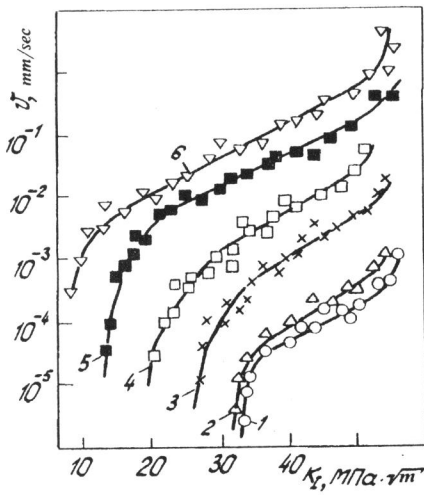


Figure 6. Kinetic diagrams of static fracture of 45ChNMFA steel: 1—in pure DMSO; 2—DMSO+1% H₂O; 3—DMSO+10% H₂O; 4—DMSO+40% H₂O; 5—H₂O.

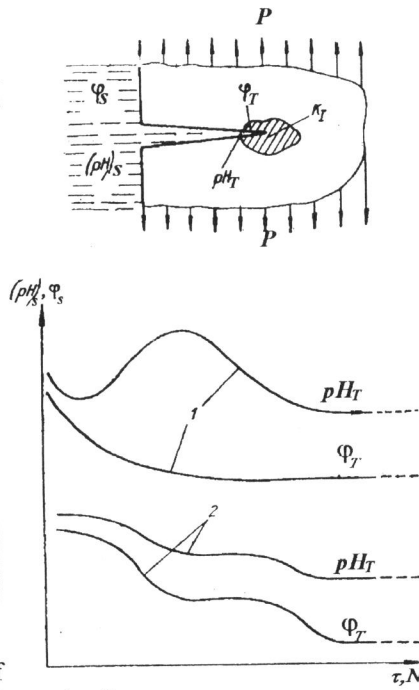


Figure 7. Variation of ϕ_T and pH_T during propagation of two various cracks.

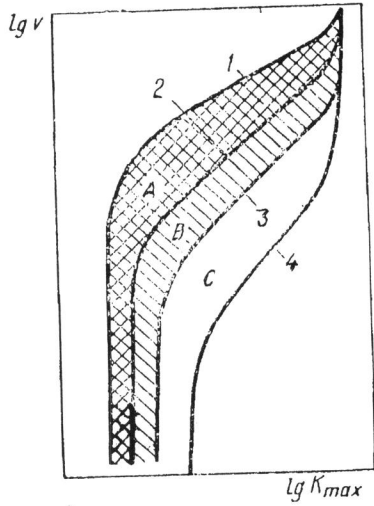


Figure 8. Basic diagrams for various possible combinations of φ_T and pH_T [11].

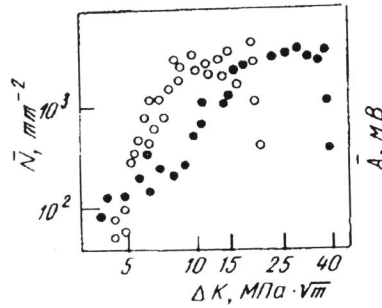
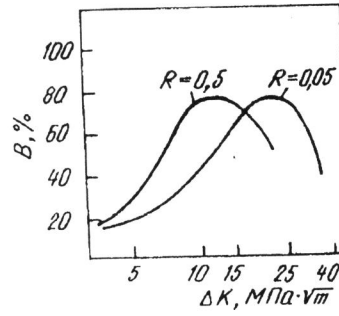


Figure 9. Number of acoustic events N and % of cleavage facets B during testing in water of 40Ch steel

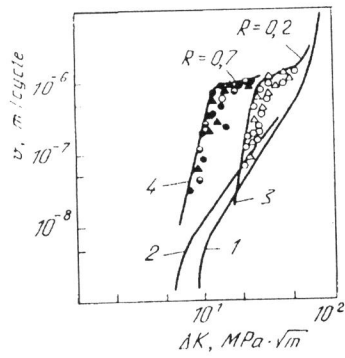


Figure 11. Kinetic diagrams of fatigue fracture of 15Ch2NMFA steel in the air (1,2) and high temperature water environment [3,4]

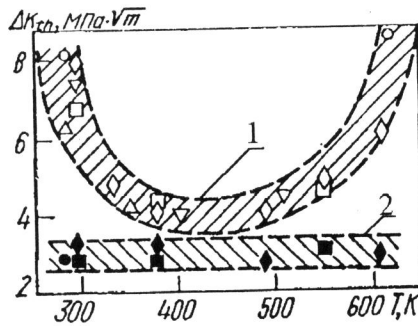


Figure 10. Temperature dependence of ΔK_{th} for carbon (1) and stainless steels (2).