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ON THE APPLICABILITY OF SYNERGISTIC APPROACHES TO THE CONSTRUCTION OF A GENERAL MODEL OF CORROSION CRACKING

T. S. Esiev[1]

Corrosion cracking (CC) is one of the most dangerous kinds of damage of metallic materials in many branches of industry. Its ambiguity and complexity is a result of the cooperative interaction of the factors of the ambient, the stress state, and the structure of the metal. Despite the great practical importance of the problem and the considerable achievements in theoretical and experimental research the nature of CC has not yet been fully comprehended and we still lack a general theory of corrosion cracking of steels and alloys.

It becomes more and more obvious that the possibilities of study of the causes and mechanisms of CC within traditional concepts of continuum mechanics, the physics of metals, and the theory of electrochemical reactions have virtually been exhausted. It seems the methods for analyzing the problem of CC should be revised cardinally and it is time to search for new ideas and methods based on concepts of general physics.

At the present time the processes of deformation and fracture of materials are often described with the use of the principles of synergetics, i.e., a scientific direction investigating the general laws of formation, stability, and decomposition of time and space structures in composite nonequilibrium systems of various natures [1, 2].

In the present work we made an attempt to use the approaches of synergetics for explaining the dynamics of the CC process under the conditions of hydrogen charging. It is known that in addition to adsorption decrease in the strength and anode dissolution, hydrogen embrittlement is one of the three mechanisms of interaction between a corrosive medium and a "stressed" metal [3]. In some practically important cases (for example, in sulfide corrosion cracking) the mechanism of hydrogen embrittlement plays the dominant role.

The synergistic model of damage and fracture considers the deformed body as an open nonequilibrium system that develops with a hierarchic change of dissipative structures self-organizing with the aim of the most efficient energy (and substance) exchange with the ambient [1, 2]. In the given case the term "self-organization" is used to define dynamic ordered structures that appear in plastic deformation and fracture of materials, i.e., it is implied that the self-organization is dynamic. In correspondence with the principle of minimum production of entropy the self-organization of dissipative structures becomes possible under the condition that

$$\mathrm{d}_e S < 0; \ |\mathrm{d}_e S| > \mathrm{d}_i S,$$

where $\mathrm{d}_e S$ is the increment of the entropy flux through the boundaries of the system and $\mathrm{d}_i S$ is the increment of the entropy due to its production inside the system.

In the process of active loading the removal of the entropy ($\mathrm{d}_e S < 0$) from the system and, consequently, the preservation of conditions for the existence of dissipative structures, is provided by continuous arrival of mechanical energy from the ambient (i.e., from a loading device).

Under corrosion cracking the deformed body experiences the action of long-term static stresses that are lower than the yield strength. Therefore, in the given case no mechanical energy arrives from the outside. According to the principles of classical thermodynamics, a solid body under the conditions of passive loading is a closed system. Such systems are able to evolve. However, the accompanying processes inevitably increase the production of entropy $\mathrm{d}_i S$ (at $\mathrm{d}_e S = 0$) due to the decrease in the heterogeneity acquired by the material in the stage of fabrication and assembling. The transition to an equilibrium state is realized through various degradation processes that develop in the material during a long period of service. Then the working capacity (endurance) of the body under load, which is determined by the temperature-and-force conditions, obeys the thermal fluctuation model due to S. N. Zhurkov, namely,

$$\tau = \tau_0 \exp \frac{U_0 - \gamma\sigma}{kT},$$

where U_0 is the initial activation energy of the fracture process, τ_0 is a constant, γ is a structurally sensitive parameter, and σ is the stress.

[1] I. M. Gubkin Russian State University for Petroleum and Gas, Moscow, Russia.

However, it turns out that as applied to CC the dependence between τ and γ often differs from the presented one rather substantially. For example, cracking of high-strength steels in hydrogen-charging media occurs in a much shorter time than it follows from Zhurkov's formula even under very low stresses.

Modern concepts of the nature of strength are based on the assumption that any infinitely brittle fracture is preceded by plastic deformation (PD), the occurrence of which is connected with a certain expenditure of energy. In those cases when energy is not supplied to the considered body in the process of its long-term hold under load, fracture ("free fracture" in terms of E. I. Shemyakin [1]) is possible due to the energy of elastic deformations accumulated in the body. Analyzing the conditions of "free fracture" researchers concluded that there exists a critical size of the body below which the potential energy accumulated in the body is insufficient for fracture. However, we know of many examples when specimens of extremely small size broke in the process of CC tests. These and other facts show that CC cannot be realized only due to the "internal energy resources." At the same time, by definition, a deformed body does break finally, which means that virtually from the moment of its loading it undergoes kinetically irreversible processes. Consequently, there should be a source of additional energy that feeds the fracture process from the outside of the "metal – loading device" system. Taking into account that a passively loaded body is in a state of mechanical equilibrium with the loading device, we can infer that the additional energy can appear only as a result of electrochemical reactions on the surface of the corroded metal, and the direct transfer of this energy into the volume of the body is performed through a flow of hydrogen.

In the thermodynamic aspect it is just the specific nature of the interaction between the metal and hydrogen that determines the possibility of transformation of the considered system into an open one. Penetrating into the crystal lattice hydrogen distributes in it very nonuniformly and is chiefly accumulated in "traps" of various kinds. Under the conditions of intense hydrogen charging directed diffusion flows begin to function in the metal, "pumping" energy into the regions of the traps. As the excess energy accumulates in localized regions, the body itself (together with the loading device) becomes an ambient with respect to the mentioned regions and together they form an open strongly nonequilibrium system. According to the data of [2] new dynamic states can appear in systems far from thermodynamic equilibrium, namely, dissipative structures capable of numerous stability – instability transformations in the course of spontaneous self-organization. In our case the striving of a solid body for removing the excess energy also causes formation of dissipative structures of various scales in local volumes of the material. The leading mechanism of the energy dissipation is the succession of nonequilibrium phase transformations, i.e., plastic deformation (I) → microfracture (II) → macrofracture (III).

In this chain of events fracture is a particular case of the mentioned transformation that occurs at the highest structural level, when the possibilities of the dissipation of the energy fed to the material have been fully exhausted.

Virtually all CC models known today treat plastic deformation as a very important component of the process. However, the mechanism of CC in these models is represented in a simplified form as the loss of the shear stability by the crystal lattice without allowance for the multilevel nature of the deformation. According to the concept of [4], PD is a local structural transformation that occurs as a multilevel dissipation process. The hierarchy of the structural levels of the deformation is based on the hierarchy of the physical carriers of PD. At the microlevel the local structural transformation manifests itself as nucleation and motion of individual dislocations. As the PD continues, the dislocation density increases with the appearance of collective forms of motion of an ensemble of interacting dislocations, which cause a new quality, i.e., volume structural elements begin to move in a continuous medium. There follows a transition from the microscopic level to the mesoscopic one, in which the carriers of the deformation are larger-scale mesodefects. At the mesolevel the motion of the mentioned elements occurs by the "shift-rotation" scheme causing a vortex mechanical field and providing the organization of new channels of energy dissipation, which are more effective than the motion of individual dislocations. When the mesodefects penetrate the entire cross section of the specimen, it fails, and the failure is the final stage of the single process of the evolution of the vortex mechanical field at the microlevel.

The notion of the vortex nature of plastic flow in solid bodies involves a necessary appearance of localization of strain in stress concentrators, which also have a hierarchy of scales. The localization of PD is caused by many factors and is observed at virtually any degree of deformation at all scale and structural levels. In any type of localization of PD we observe a very important feature, i.e., the appearance of a strongly excited state in the zones of local flow. Under the conditions of strong excitation new allowed states appear in the space of the interstices, which are inherent in the electron-energy spectrum of the crystal. As the strongly excited crystal moves to equilibrium, it can acquire intermediate structures that generate additional channels of energy dissipation upon their appearance. Therefore, any type of defect in an actual crystal should be treated as a local metastable structure inevitably arising upon the action of external fields on the crystal, when it passes through the stages of a strongly excited state. Localization of PD will finally disturb the continuity and cause failure of the material. The generation of microcracks in local volumes that have fully exhausted their plastic possibilities is preceded by a crystal → amorphous phase transformation. Further development of the microcracks, their interaction and merging into a through crack are also controlled by PD. In the plastic zone forming in front of

the crack tip we can observe the same stages of the evolution of the dislocation structure as in the mentioned local volumes.

At the present time, the mechanism of CC is very often described within the models of crack growth in hydrogen-charged metals, which allow for the role of microscopic PD [5]. The essence of these models can be briefly reduced to the following. It is assumed that hydrogen is able to diminish the resistance of the material to microscopic PD, promoting the motion of individual dislocations in the most favorably oriented zones. The moving dislocations are inevitably decelerated near certain barriers (grain and phase boundaries, inclusions, and other stoppers) and accumulate high stresses at these places. As a result, the structure of the material acquires the so-called regions of volume extension that are powerful hydrogen traps. The enrichment of these regions with hydrogen, the accumulation of elastic stresses, and the exhaustion of their relaxation by the plastic mechanism cause the formation and propagation of microcracks and fracture of the specimen. Thus, the known models, quite rightfully assign the decisive role in the development of CC to microplastic deformation. At the same time, the physical nature of the hydrogen-promoted PD remains unclear. In addition, the described mechanism is not quite suitable for the description of the cases of CC in low-strength steels, in which fracture is preceded by a quite considerable PD.

Let us consider the occurring events with the use of a synergistic approach to the description of the CC model.

We will assume that the regions of volume extension of the material, where the microscopic PD acts, possess their own stress field, have a long enough size, and therefore can be treated as volume structural elements of deformation at the mesoscopic level. We will call these local regions mesovolumes. Taking into account that the corrosion cracks commonly propagate between grains, we will suppose that the boundaries of the mesovolumes coincide with the boundaries of grains (or groups of grains). We will also assume that the hydrogen flow "charges" the mesovolumes with excess energy creating a strongly excited state in them. This provides properties not typical for the stable state of the crystal. The excited regions of the crystal begin to generate intense flows of dislocations, vacancies, and other defects [6, 7]. Under the conditions of strong excitation the motion of the dislocations accelerates to a degree that causes a kinetic phase transformation from conservative motion to climb that occurs by a diffusion-vacancy mechanism. The continuity of the action of the mentioned mechanism, which causes an outflow of entropy from the system ($d_e S < 0$), is provided by the unsteady flow of hydrogen and the local anode dissolution of metal atoms moving to the surface of the body. The active PD acquires a nature of a gas dynamic flow and promotes an increase in the stress concentration in the regions of volume extension. Simultaneously, the system tends to remove the strong excitation from the mesovolume, causing plastic relaxation of internal stresses, which occurs as a dissipative process. The competition of these two mechanisms predetermines the development of the events. When the conditions

are favorable for an unsteady hydrogen flow in the regions of volume extension, we can speak of continuing evolution of the vortex mechanical field in the studied mesovolume. The displacements of individual dislocations accompanied by rotations of the crystal lattice first form microvortexes at the lowest structural level. However, single dislocation slip cannot relax intensely the elastic stresses of such powerful concentrators as the regions of volume extension. Therefore, the next stage of the evolution of the deformation should be connected with switching to a more efficient channel of energy dissipation, i.e., the motion of mesovolumes as a whole. However, the rotation of the mesovolumes is hampered by the surrounding material, which is in a state of elastic strain. The constrained rotation of volume structural elements generates a system of mesovortexes in the crystal. In the zones of constrained deformation a high-degree strain is accumulated at the boundaries of the mesovolumes, the peak contact stresses become high, and the material in the near-boundary regions acquires a strongly excited state. With the intensification of the excitation of the crystal the role of the gas dynamic flow and fragmentation of the material increases, which indicates that the PD passes to a higher structural level. In its further evolution the fragmented structure attains a critical state in those local regions where the plastic possibilities of the material have been exhausted. Such a structure cannot resist the growing internal stresses for a long time. As the structure acquires the requisite dispersity and density of the defects, it undergoes a crystal $\rightarrow$ amorphous state phase transformation that corresponds to one more stage of self-organization of the dissipative structure.

It should be noted that hydrogen participates in the described processes. In the first phase, it promotes the fragmentation and amorphization of the structure [8]. In addition, hydrogen actively interacts with the permanently growing interfragment boundaries and the appearing defects, and therefore does not attain the state of saturation. In fact we observe a kind of autocatalytic effect that provides unsteadiness of hydrogen flow in the regions of volume extension in all stages of the evolution of PD and fracture.

The subsequent transformation of the amorphous phase into a destructive one is connected with the transformation of the energy of elastic distortions of the lattice into the surface energy of submicrocracks. The breakage of interatomic bonds that seems to have a thermofluctuation nature is necessary for further energy dissipation at a still higher structural level. The subsequent stabilization and the growth of submicrocracks is provided by the inflow of energy to mesovolumes, which is a manifestation of the interrelation between the crack formation and the PD. As the deformation continues, the concentration of the submicrocracks increases and their sizes grow until they start to combine into microcracks stochastically distributed over the volume of the metal. One more feature of the process manifests itself in this stage. The propagation of the microcracks obeys the action of two factors, namely, the plastic deformation occurring in

mesovolumes and the growth of external stresses. The latter is caused by the reduction of the cross section of the body. Whole conglomerates of grains comparable with the sizes of the body get involved in the self-similar motion. Micro- and mesovortexes of lower structural levels combine into a single large vortex at the macroscopic level, causing merging of the microcracks into a macrocrack and subsequent breakage of the body.

Thus, a full understanding of the nature of the complex and ambiguous phenomenon of corrosion cracking is possible only with the use of a synergistic approach that treats the process as an absolutely nonlinear one which occurs in an open system far from thermodynamic equilibrium. The variety of the forms of manifestation of CC is provided by numerous combinations of factors in the system "material – stress state – medium." It cannot be doubted that the fundamental laws of the development of the process are common for all of its forms. Corrosion cracking becomes possible in the presence of an inflow of additional energy to the system, which is freed as a result of electrochemical corrosion, absorbed by the material, and provides PD and fracture in localized regions together with the elastic energy stored in the system. In fact, the localized PD and fracture represent two stages of a single process of the evolution of a vortex mechanical field in the deformed body, which successively transfers from one structural level to another. The capacity of the metal to resist fracture depends more on the dynamic

structure, which is formed in the process of deformation and determines the dissipative properties of the system, rather than on its initial structure.

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