Topological approach to studying mechanochemical effects in the processes of corrosion of metals under stress

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Abstract. It is hereby suggested to use a topological approach based on the principles of synergetics and the theory of catastrophes to describe some aspects of the mechanochemical effect of the sign of deformation in stress corrosion phenomena. It was found that a steel plate being located in an aggressive environment and subjected to additional force impact may be informatively considered as a synergistic system. It has been established that the concept of sensitivity to imperfection can be applied to the interpretation of the deformation sign effect. It has been demonstrated that the violation of the symmetry of the sides of a bent plate is made provision for by the structure of standard models - catastrophes of the «ruffle» type. Possible scenarios for the development of mechanochemical effects are considered, taking into account Maxwell's principles and maximum delay principles. Topological models which describe both the above-mentioned mechanochemical effect of the deformation sign at small times (within 50 s) and its reversal with time are constructed and analyzed. Further possible directions of investigation of mechanochemical effects in the processes of corrosion of metals under stress are formulated.

1. Introduction

As you know, stress corrosion is a process which occurs under conditions when a material experiences external loads and deformation. It should be noted [1] that from the standpoint of mechanochemistry with making allowance for presence of the initial stress in the surface layer of any hard body in the form of surface tension, any naturally occurring corrosion is stress corrosion. As a result of the application of external forces to a body and its subsequent deformation, an additional surface stress is formed, which significantly affects the speed of the physicochemical dissolution process and, therefore, the rate of destruction of the material (in particular, metal structures). In this regard, finding of the laws of this phenomenon is not only of scientific, but also of practical interest.

It was experimentally established [2] that the applied mechanical stress accelerates corrosion. In order for the effect to be clearly expressed, sufficiently large stresses are needed. This result is most easily achieved through bending samples, in particular metal plates. In the thesis [3], it was for the first time experimentally discovered that the corrosion rate for the concave side of the plate is higher than for the convex side. Since the opposite sides of the curved plate differed in the sign of deformation, this phenomenon was called the mechanochemical effect of the sign of deformation in the phenomena of corrosion. It should be noted that for the first time the mechanochemical effect of the sign of deformation was recorded [4] in experiments on the dissolution of curved plates of single-crystal calcium chloride. In [3], it was also established that over time, the deformation sign effect reverses.

As follows from [1], the mechanochemical effect of the sign of deformation is inherent not only in stress corrosion processes, but also to any solid-body surface reactions. Thus, the effects discovered in [3] can be interpreted as universal and obeying a limited number of laws of nonlinear development of complex systems.

In connection with the above, the purpose of this research is to establish the regular patterns of the development of the processes of metals corrosion under stress. The research program provides for...
solving problems associated with the description and analysis of the phenomena, in which an increase in the influence leads to a qualitatively different behavior of the system.

2. Statement of the Basic Material

Some aspects of the mechanochemical effect of the sign of deformation in the phenomena of stress corrosion are proposed [5] to be interpreted from the standpoint of synergetics [6, 7] and catastrophe theory [8, 9]. In particular, it is assumed that a steel plate placed in an aggressive environment and subjected to additional force is recommended to be interpreted as a synergistic system, since within the framework of this approach, much attention is paid [6, 7] to the understanding of the fundamental significance of symmetry and violation of symmetry. In this aspect, the violation of symmetry (i.e., the manifestation of internal differentiation between different parts of the system or between the system and its environment) embodies one of the first preconditions of complex behavior and is accompanied by the emergence of new properties.

In turn, various symmetry violations (including spatial symmetry) are taken into account [6, 8] in the structure of standard models — catastrophes: canonical equations contain a term playing the role of a «symmetry violator» or the imperfection parameter, which is geometrically represented by the asymmetric bifurcation diagram. According to catastrophe theory, a «ruffle» type catastrophe corresponds to such an evolutionary picture. In accordance with this theory, whatever character the system imperfections may have, while it in the absence of imperfections is described in canonical form by means of a function:

$$V_c(x) = \frac{1}{4}x^4 + \frac{1}{2}c_2x^2,$$  \hspace{1cm} (1)

then, if imperfections are available, by the function:

$$V_c(x) = \frac{1}{4}x^4 + \frac{1}{2}c_2x^2 + c_1x.$$  \hspace{1cm} (2)

A «trident»-type graph which is of frequent occurrence in bifurcation theory corresponds to the «perfect» system (1). The geometry of this diagram regulates the absence of catastrophic jumps, while in system (2) they necessarily occur when moving from one stable branch to another with increasing control parameter $c_2$. In this case, parameter $c_1$ is interpreted as initial imperfection. It should be noted that not only various defects (structural, geometric, etc.) are permissible to be considered as imperfections, but also the effects of external fields.

In light of the foregoing, it seems possible to use the above approaches in describing and analyzing both the previously indicated effect of deformation sign (Figure 1) and the case of its reversal over time (Figure 2).

For a more complete picture of the representation of the process under study at short time periods (Figure 1), two variables (control variables in terms of catastrophe theory) are additionally introduced: the load $P$ on the sample and deformation $\varepsilon$ of the sample (in [3] these parameters are constant). Accordingly, the mass loss of the sample (%) is interpreted in accepted terminology as a state parameter.

Catastrophe theory rigorously proves that the only type of model surface in such systems with one state parameter and two control parameters is «ruffle» (Figure 3). Qualitatively different system behavior is determined by various combinations of control parameters. In the case under consideration, the parameter $P$ is called splitting parameter, since when its critical value is exceeded, the model surface splits into two sheets, i.e. its variation regulates the very probability of ambiguity of the dependence (%) on the sign $\varepsilon$ and the occurrence of jumps. The normal parameter $\varepsilon$ is directed along the normal (perpendicular) to the splitting factor.
Figure 1. Dependence of sample mass decrease per a surface unit (in mg/cm$^2$) on the time $\tau$ for the concave (1) and convex (2) sides of a curved steel plate in a 35% hydrochloric acid solution. The slope of the lines represents the corrosion rate.

Figure 2. Inversion of the deformation sign. Curves of dependence of the sample mass loss (%) on the time $\tau$ for the concave (1) and convex (2) sides of a curved steel plate in a 35% hydrochloric acid solution.

An analysis of the scheme of distribution of deformations of a curved steel plate and curves of the dependence of the weight loss of the sample for its concave and convex sides in a 35% solution of hydrochloric acid at short time periods revealed [3], that the effect under consideration may be satisfactorily described by a model which geometry obeys the Maxwell's principle. In this case, a situation [6, 8] occurs, similar to the formation of a shock wave (gap) or phase transition of the first order in the areas of coexistence of different phases. In the absence of an external load ($P = 0$), the mass loss (%) is the same for the opposite sides of the sample. After passing through some value $P_{cr}$ a manifestation of the deformation sign effect begins, which increases as the load increases. The structure of the model is designed with consideration to the fact that the dissolution rate is higher for the concave side than for the convex side. The upper sheet of the assembly corresponds to the mechanochemical dissolution effect for the compressed side of the curved plate, and the lower sheet – for the stretched side.

The position of the topological model in Figure 3 (a) at an angle to the axis (%) illustrates the well-known fact of acceleration of corrosion under stress, regardless of the sign of deformation [3]. Thus, all the points of the model surface are above the value of the parameter of state in the absence of external influence. For better visualization of the image of the quality situation being observed, the bottom sheet of the assembly is conditionally torn off.

The projection of the flat sector of manifold of the catastrophe «ruffle» onto the plane of control parameters is the so-called Maxwell's set (dashed line in Figure 3). According to this bifurcation scheme, movement from one sheet to another occurs whenever the control parameter $\varepsilon$ crosses the set (structure of the shock wave), i.e. changes its sign to the opposite.
Figure 3. Topological model of the mechanochemical effect of deformation sign in the phenomena of corrosion under stress (catastrophe «ruffle», Maxwell’s principle): (a) – three-dimensional surface in coordinates (%), $\varepsilon$ and $P$ (1 – cross section of the model); (b)–projection of the model onto the plane of the control parameters $\varepsilon$ and $P$ (2 – Maxwell’s set).

Thus, deformation of the sample $\varepsilon$ in this case should be interpreted as the initial imperfection with making allowance for presence in the initial (undistorted) state of surface tension which is added to the applied stress when the plate is stretched and subtracted from it when the plate is compressed. In other words, this symmetry-breaking single control parameter of geometric imperfection is adequate to the balance of all stresses in a bent sample. Consequently, the effect of the sign of deformation in the phenomena of corrosion under stress may be interpreted (in the terminology of the involved theory) as sensitivity to imperfection.

To simulate the reversal of the deformation sign effect (Figure 2) it also seems appropriate to use a catastrophe of the «ruffle» type, but under condition of observing the principle of maximum delay (Figure 4). According to this scenario, the system jumps into another state only when it has no other choice.

The investigated phenomenon is proposed to be described using two control parameters: $P$ (as in the first case) and the time $\tau$. As the state parameter, the difference in mass loss $\Delta$ (%) of the concave and convex sides of the curved sample was chosen:

\[
\begin{align*}
\text{if } (\%)_{\text{concave}} & > (\%)_{\text{convex}} \quad \text{then } (\%)_{\text{concave}} - (\%)_{\text{convex}} = + \Delta(%) ; \\
\text{if } (\%)_{\text{concave}} & < (\%)_{\text{convex}} \quad \text{then } (\%)_{\text{concave}} - (\%)_{\text{convex}} = - \Delta(%) .
\end{align*}
\]

Thus, the top sheet of the surface corresponds to the realization of the effect of the sign of deformation, and the bottom sheet corresponds to the fact of its reversal. Since in the absence of external influence the symmetry of the sides of the plate is not broken, i.e. $\Delta(%) = 0$, thus the corresponding section of the assembly coincides with the axis $\tau$.

The most interesting property of this surface is the presence of two fold lines starting at the so-called assembly point $B$ which form a bifurcation curve with a tip at point $B_1$ on the plane of the control parameters $\tau$ and $P$ (Figure 4). These points correspond to the $P_{\varepsilon}$ value (in presence of the time coordinate), which, if reached, after some time [3] causes occurrence of cracks, which initiate the
phenomenon of reversal of the deformation sign effect. It should be noted that when constructing the topological model, the acceleration of the onset of crack formation according to increase in load (i.e., a decrease in withstanding) is to be taken into account.

Figure 4. Topological model of reversing the effect of the deformation sign (catastrophe «ruffle», the principle of maximum delay): (a) – three-dimensional surface in the coordinates $\Delta(\%)$, $\tau$ and $P$ (1 – cross section of the model; 2 and 3 – fold lines; $B$ – assembly point); (b) – projection of the model onto the plane of the control parameters $\tau$ and $P$ (4 – bifurcation curve, i.e. bifurcation set; $B_1$ – bifurcation point).

In the general case, the bifurcation curve divides the control space into areas which are adequate to the various modes of the system functioning. Qualitative changes in its behavior occur only when the «trajectory», formed by a combination of control parameters, leaves the region inside this curve. It is in such a situation the state parameter $\Delta(\%)$ jumps.

3. Conclusions and propositions
Qualitative features of behavior (signs of catastrophe) of the under study make it possible to simulate the general picture of the ongoing mechanochemical processes. If the sample mass loss (%) is presented as a function of two properly selected control parameters, then gap changes in the state of the system under study are described quite clearly with the help of a catastrophe of the «ruffle» type. In particular, the interpretation of the effect of the sign of deformation as sensitivity to imperfection does not contradict the provisions of mechanochemistry. In addition, expanding the scope of the experiment (due to the directed variation of the qualitative and quantitative composition of the aggressive environment, the type and value of external influences, etc.) will make it possible to use synergetic ideas for further research of these nontrivial effects, which have been first discovered in laboratory systems [3].

According to Poston and Stewart, the catastrophe theory approach should be seen as predicting what would be useful to look for, rather than what should certainly be seen. At present, only
experiment may serve for determining which aspects of the considered phenomena may be effectively described using this approach, and which may not [8].

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