PHYSICAL-CHEMICAL MECHANICS OF DEFORMATION OF CONSTRUCTION MATERIALS IN SURFACE-ACTIVE MEDIA

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The purpose of the research is a detailed study of features of kinetics of development the deformation of constructional materials (concrete and steel in the first place), placed in the medium of substances, which are surface-active with respect to the given material (substance). This kind of study is necessary for further detailed development of the proposals (on the stage of applied research), intended for growth of performance characteristics of these materials.

We have found out new phenomena of this category, which consists in the following, that most of the solid bodies, placed in external medium, and having surface-active features with respect to its substance, have characteristic in development of deformation under external stress: - stage of nonlinear reversible deformations. During reaching this stage, the sizes of deformable object continue changing with the lapse of time, under constant, appurtenant external stress. This nonlinear deformation stops, when it reaches some limiting value. If the surface-active features are removed, and an action of external stress is kept, than the deformation will be returned to the value, expected in case of elastic deformation in absence of surface-active features. In case of removal of stress, the sizes of object returns to datum value, like in case of linear elastic deformation. The body in the medium of SAW (surface acoustic wave) can be undergone by such nonlinear reversible deformation iteratively, which each time returns to the ingoing size.

Such research will give a possibility to reveal for each material the proposed dependence of parameters of function, describing time dependence of nonlinear reversible deformation from external characteristics of deformable bodies (for example their sizes, condition of surface etc) and physicochemical parameters of their onteraction with the medium.

Rehbinder Effect takes special place in the variety of the types of solid interaction with liquid or gaseous media. In some cases it is difficult to identify the boundary separating this group of phenomena from the others as well as to distinguish it per se from the resultant action of the media. Under Rehbinder Effect we will be able to understand group of phenomena associated with the effect of media on solid's mechanical properties conditioned by the reduction of solid's free surface energy on its interface with the media.

The discovery of new phenomenon by P. Rehbinder is about physical-chemical influence of the surface-active media on solid's mechanical properties. Large volume of material about the regularities, mechanisms and nature of such phenomena was accumulated at a lot of laboratories of Russia, Ukraine, USA, Germany, France and other countries. These works showed wide extension of Rehbinder Effect in the nature and technology. Number of specific features of this fact conditioned the introduction of the surface-active substances in the industry, for instance during mechanical treatment of the materials, during drilling rocks, fine grinding, protecting the machinery details from early damage. Significant role of the effect during fatigue damage of the metals, friction and tear and wear and behavior of geological processes was shown. We managed to obtain various data on the solids behavior when contacting the surface-active melts, solutions and gases. Common thermodynamic nature and kinetic peculiarities of Rehbinder Effect which under particular conditions can be observed in solids of any composition and structure – in metals and alloys, substances with covalent, ionic or molecular compound, blank and porous solids, poly- and mono-crystalline solids, polymers and glasses was determined.

Reduction of strength and increase of brittleness of solids are studied on many systems: metal single and polycrystals being in contact with or covered from the surface by thin film of more fusible hot metal, covalent crystals – germanium covered by the film of gold or other metals; ionic single and polycrystals – salts, oxides, hydroxides; rocks being in contact with water, water solutions of SAM and electrolytes, ionic alloys; graphite; molecular single and polycrystals of organic compound (naphthalene, anthracene, etc.) being in contact with various polarity organic liquids and their water solutions; thermoplastic polymers.

Besides, the following picture is observed: for brittle solids damaged before achieving yield point, the effect of the surface-active media leads to the brittle failure under minor stress and deformation, and modulus of elasticity, i.e. inclination of the straight line in "stress-deformation" coordinates practically does not change.

Failure of elastic-plastic materials occurs under minor stresses and deformations. In case of significant decrease of the surface energy as a result of contacting the active medium, they become brittle and less elastic

$$\sigma = \alpha\sqrt{G\gamma c}\,. \qquad (1)$$

Within the plastic failure field, the equation (1) is replaced by the analogous equation:

$$\sigma' = a'\sqrt{G\gamma^*} + c\,, \qquad (2)$$

where now γ^* - work of new surface formation and plastic deformation accompanying it or <u>effective</u> surface energy which is normally once or twice more that the true one.

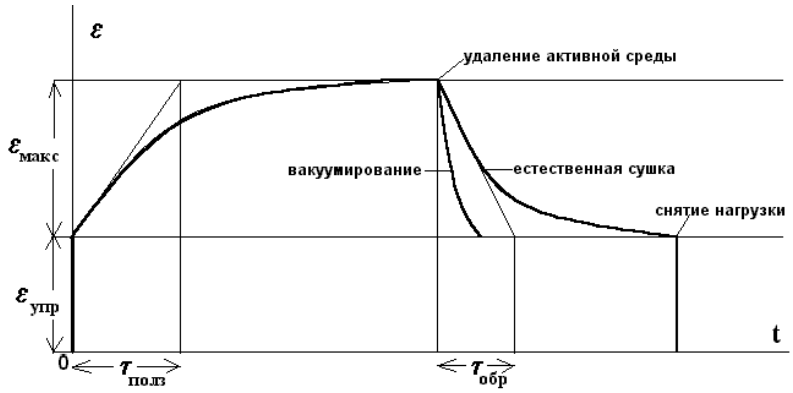
Another possible mechanism to explain the reasons of water effecting the glass strength was suggested by Charles and Hilling. They put forward their view about the corrosion character of media effect – demonstration of "corrosion under stress". This mechanism is based on the possibility of dissolution of crack tip having (due to large overstress as a result of stress concentration) excess chemical potential and therefore having significant solubility. This hypothesis was widely spread for a long time and even the attempts were made to apply it for the description of metal brittleness under the effect of metal melts. However, later the authors themselves revoked these views. In thorough work of Bernstein it is shown with great cogency that we are dealing with the reduction of the energy of damage activation in the glass on the account of hydrolytic decomposition of bonds. Basically, it is possible to talk about total equivalency of the concepts of acceleration of chemical reaction under the effect of mechanical stress and facilitation of mechanical breaking of chemical bond under the effect of chemical reaction (physical-chemical interaction).

Recently the priority is given to such mechanisms of the crack development by the affect of the surface-active media which allows computer calculations with the effect of molecular dynamics. Such calculations were run by Shukin and Jushenko for two-dimensional model. They clearly showed the attenuation and relief of bond breakage in virtual solids with the participation of surface-active atom.

Scientific novelty is that in researching the carrying capacity of some materials, we discovered that as a result of their loading along with elastic deformation, the delayed nonlinear reversible deformation (NRD) damping in time gradually develops. This phenomenon was very thoroughly studied for concrete deformable under regular heat-humidity conditions. According to the experiments, such NLD is conditioned exceptionally

by the effect of the surface-active media and has reversible nature including total disappearance of additional deformation when removing the surface-active media. The study of the materials of various composition and structure (concrete, tuff, gypsum, glass, organic glass, rubber, naphthalene) showed that such inverse creep has the most common nature and can be considered as the new form of Rehbinder Effect.

The below drawing shows the describing this phenomenon.



$\gamma_{упр}$ **– elastic deformation in the absence of SAM unchangeable in time;**
. $\gamma_{макс}$ **– maximum deformation of NRD in the surface-active media;**
$\vartheta_{полз}$ **– relaxation period of NRD in the surface-active media;**
$\vartheta_{обр}$ **– relaxation period of NRD return when removing SAM.**

In order to explain the research results of the effect of NRD of the material in the surface-active media, it appeared necessary to consider the following basic original process characteristics which are common for all the researched cases:

1. when loading the specimen in the absence of the surface-active media with the stress of ultimate strength (0,5-0,8), truly elastic, totally reversible deformation which does not develop in time occurs immediately;

2. after the introduction of the surface-active media, NRD damping in time and totally reversible when removing the media starts to develop;

3. kinetics of NRD development in time in the simplest approximation is described by exponential function with the exponent value equaling to the ratio of current time of the experiment performance to some characteristic time parameter – "relaxation period". In some cases, creep at the beginning of the process is developed a bit quicker than at the end of the process. Such specific character can be explained by the sum of two exponents the second of which has longer relaxation period;

4. kinetics of the development of the reversible process in time in removing the surface-active media is also approximately described by the exponential dependence. In this case, the rate of the recovery of the researched material properties depends on the rate of the removal of the surface-active media (natural drying, vacuumization, etc.);

5. in significant loads getting close to the ultimate strength along with NRD, regular irreversible creep not damping in removing the media is observed as well. It appears to be larger than the above applied stress.

In drafting physical model of the process, we may assume that all the accumulated deformation of NRD is provided by the formation and development of subcritical (under Griffith) crack nucleus to which the views of thermodynamic theory of nucleation can be applied. In case of the stresses (excess free energy) less than those that lead to the growth of the avalanche crack (i.e. development of a new phase), fluctuation formation and spontaneous collapse of subcritical crack nucleus (nucleuses of new phase) occurs. However, if the material adsorption, surface-active to this material, occurs on the crack walls, then the reverse crack collapse becomes hampered, it is stabilized at some size less than critical and gradually increases in future.

The rate of growth of such subcritical crack can be identified by the rate of the introduction of the surface-active substance to the crack tip or by the kinetics of thermofluctuation of bond opening at its tip.

The aim of the project is the detail study of the peculiarities of the kinetics of the development of the deformation of the construction materials (first of all concrete) placed in the surface-active media with regard to this very material (substance). Such study is necessary for further detail elaboration of the proposals (at the stage of future applied researches) aimed at the improvement of the operating characteristics of these materials.

It is planned to run thorough research of the mentioned phenomenon especially for the construction materials taking into the consideration the presented view. Such research will allow to obtain the parameters of the suggested function describing the time motion of NRD on the external characteristics of deformable solids (for instance their dimensions, surface condition, etc.) for each material. Knowledge of the parameters and dependences of NRD will allow to predict the time motion of NRD of the construction materials of particular facilities which, in its term, in future can be used in the applied researches aimed at specifying the design of the structure operation in the surface-active media under the stresses sufficient for the development of NRD (for instance, for the design of pipelines, boilers, high pressure vessels, etc.).

Solid's inverse creep is the unique instrument for studying the crack formation and development to the critical size in the stressed materials as a result of the affect of the surface-active media.

Further researches of this phenomenon may contribute a lot to understanding the nature and mechanism of sudden catastrophic failure/breaking of the stressed constructions.

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