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

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Peculiarities of kinetics of the development of construction material (first of all concrete and steel) deformations placed in substance medium which is surface active (SAS) with regard to given material (substance) are researched in the work. We identified new phenomenon of such type which is based on the fact that the majority of solids placed in external medium having surface-active features with regards to its substance have unique feature to develop deformations under the effect of external stresses: stage of nonlinear reversible deformation (NRD). Such research is necessary for further detail elaboration of the proposals (at the stage of future applied researches) aimed at the improvement of operational performance of such materials.

Key words: *physicochemical mechanics, surface-active substance, creep, concrete, solids.*

A lot of forms of demonstration of Rehbinder Effect, i.e. phenomena of the media effect on solids' mechanic properties conditioned by the reduction of solid's free surface energy on its interface with media are known in physical-chemical mechanics.

We identified new phenomenon of this type which is based on the fact that most of the solids placed in external media having surface-active properties with regard to its substance have special feature of the deformation development under the effect of the external stresses – stage of nonlinear reversible deformation (NRD). In achieving this stage the dimensions of deformable object continue to change in time under constant applied external voltage. This nonlinear deformation stops when it achieves some limiting value. In case of removing the surface-active media and maintaining the effect of the external stress, the deformation will return to the value expected at the stage of elastic deformation when SAM is absent. In removing the stress, the object dimensions return to initial values as in classical (linear) elastic deformation case. The solid in SAM can be subject to such NLD many times each time returning to the initial dimensions.

We offered the mechanism of the described phenomenon. We explain it with new form of demonstration of Rehbinder Effect initiated in SAM in microcracks present on the surface and within the solid volume. These very microcracks reversibly change their dimensions under the effect of the external stress. We researched the dependence of NLD motion in time and in such dependence we discovered the presence of separate components connecting with the microcracks on the surface and within the material volume.

It is suggested to run thorough research of the above phenomenon specifically for the construction materials for the purposes to describe it is a suggested way. Such research will allow to identify the expected dependence of function parameters describing the time motion of NLD on the external characteristics of deformable solids (for instance, their dimensions, surface condition, etc.) and physical-chemical parameters of their interaction with media for each material. The values of such dependences will allow to predict the time motion of NLD of particular objects and in future this, in its turn, can be used in the applied researches associated with the operation of the constructions in SAM under the stresses sufficient for the NLD development (for instance, for the design of pipelines, boilers, high pressure vessels, etc.).

Rehbinder Effect. 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.

Since the year 1928 – since the time of the first publication of P. A. Rehbinder [1] about his discovery of the phenomena of physical-chemical influence of the surface-active media on solid's mechanical properties [2], 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 its specific features allowed the industrial application of the surface-active substances during mechanical treatment of the materials [3-5], during drilling rocks [6], fine grinding [7], protecting the machinery details from early damage [8]. Significant role of the effect during fatigue damage of the metals [9], friction and tear and wear [10-11] and behavior of geological processes [12] was shown. We managed to obtain varied and a lot of 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 [1, 14, 15], covalent crystals – germanium covered by the film of gold or other metals [16]; ionic single and polycrystals – salts, oxides, hydroxides; rocks being in contact with water, water solutions of SAM and electrolytes, ionic alloys [17-19]; graphite [20]; molecular single and polycrystals of organic compound (naphthalene, anthracene, etc.) in contact with various polarity organic liquids and their water solutions [21]; thermoplastic polymers [13, 22].

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 (figure 1). This enabled to compare the breaking strength and measured or calculated interfacial power values on the boundary of solid – media (liquid or gaseous) [16, 23, 24]. In all the studied cases Griffith relation was maintained, i.e. Φ would appear proportional to square root from value γ of interfacial power.

$$\sigma = a\sqrt{G\gamma / c}\,, \tag{1}$$

where G – modulus of elasticity; c – size of failure of crack nucleus; α – dimensionless factor close to the one.

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 (figure 2). 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.

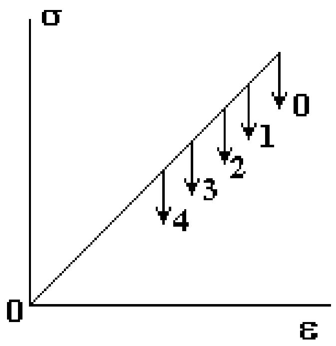

Figure 1. Typical diagram of the deformation of elastic-brittle solid in the absence (0) and presence of surface-active media (1-4). The activity of SAM increases from 1 to 4.

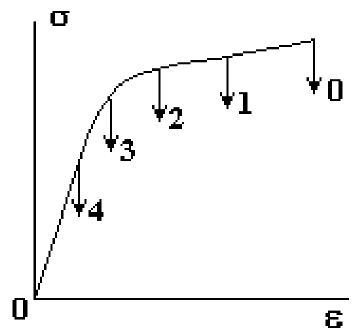

Figure 2. Typical diagram of the deformation of elastic-plastic solid in the absence (0) and presence of surface-active media (1-4). The activity of SAM increases from 1 to 4.

Arrows show failure (damage)

The first molecular-kinetic model realizing this widely distributed and multidimensional natural phenomenon was suggested by P. A. Rehbinder himself.

Such an explanation of molecular mechanism of the demonstration of Rehbinder Effect did not find further application either in his school or in other institutions. Our laboratory was an exception where the obtained data were interpreted in this particular terminology.

Another possible mechanism to explain the reasons of water effecting the glass strength was suggested by Charles and Hilling in 1962 [26]. 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 [29]. However, later the authors themselves revoked these views. In thorough work of Bernstein it is shown [27] 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).

However, one of the most preferable mechanisms to facilitate crack development under the effect of the surface-active media is still meant to be the facilitation of bond opening at the crack tip in the presence of active component which "pulls" over the energy of atom adhesion at the crack tip. Such concentration is quite well proved by the computer experiment on plane model by the method of molecular dynamics. Such researches run by Shukin and Jushenko [25] directly showed that the presence of foreign (surface-active) atom decreases the energy of atom bond at the crack tip thus facilitating its development.

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 [32, 33, 34]. According to the experiments [30, 31, 35] run together with Mr. V. K. Balavadze, 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 showed that such reversible creep has the most common nature and can be considered as the new form of the demonstration of Rehbinder Effect [1, 36-38].

Long term researches of the nature of damping NRD of solids and materials [30, 31, 35, 39] allowed to identify fundamental character of this phenomenon, in particular:

1. **occurrence and development of this phenomenon just under the conditions of solid contacting the surface-active media (liquid or gaseous providing the reduction of free surface energy of solid as a result of the adsorption, chemosorption and moistening);**
2. **reversibility of the process including gradual NRD damping under the load to the extent of removing the surface-active media.**

According to the view raised by us, the identified phenomenon of damping NRD is the new form of the demonstration of Rehbinder Effect. Characteristic species of the curve for the development and post-damping deformation when removing SAM – "nonlinear reversible deformation" – is presented on figure 3.

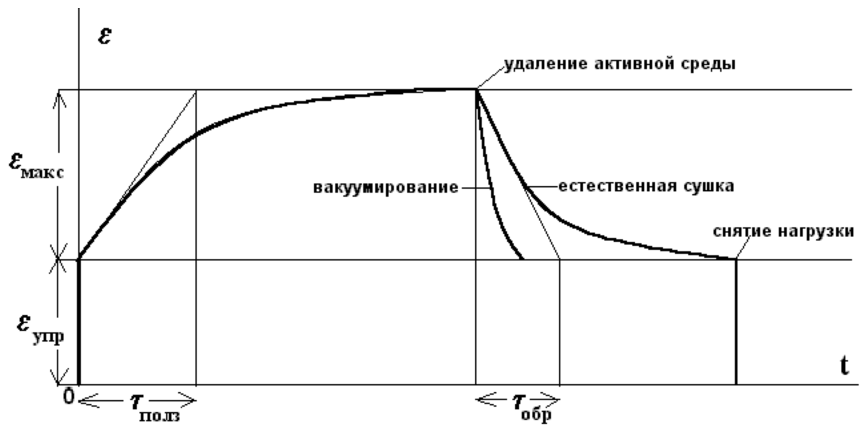

Figure 3. Characteristic species of the curves for solids' NRD:
$\gamma_{упр}$ – elastic deformation in the absence of SAM unchangeable in time;
. $\gamma_{макс}$ – maximum deformation of NRD in the surface-active media;
$\vartheta_{полз}$ – relaxation period of NRD in the surface-active media;
$\vartheta_{обр}$ – 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 expected long-term outcome as a result of implementing the project successfully
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.).

These future applied researches, after specifying the expected operating conditions in the surface-active media necessary for the industry of the construction materials can be performed by our team based on the research data and experience which will be obtained and gained during the term of this project. At the following stage of work the methods of considering the NRD phenomena in constructing the facilities which will have to be operated in the surface-active media, the method of designing the limit loads, etc. will be developed. Such works will enable to increase the reliability and efficiency of reconstructable constructions designed for the surface-active media.

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