INFLUENCE OF SLIGHT MECHANICAL ACTIONS ON THE REACTIVITY OF ENERGETIC MATERIALS AND ANOTHER METASTABLE SYSTEMS

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The new aspect of theory of mechanical activation of chemical processes in condensed metastable systems has been elaborated. The influence of uniaxial and biaxial deformations of the medium containing homogenious micronuclei on the frequency of their appearance and formation was established. Such mechanism is realised, in particular, at intensive heating in liquid and viscous-elastic explosive and another metastable reactive systems at homogenious nucleation.

INTRODUCTION

A week mechanical actions (vibrations, impacts, sound, etc.), causing no considerable dissipative heating of a substance, can be the reason for intense spontaneous boiling or thermolysis of chemically unstable liquid or solid reagent, if it takes place in overheated systems. The chief cause of such process is variation in the average curvature of the new phase nuclei surface [1,2]

$$H=1/R_1 + 1/R_2$$

where R_1 and R_2 are the principal radii of curvature.

The deformation of the nuclei leads to decreasing of the work of their formation and increases frequency of their appearing. Such processes take place not only in volatile but and in unvolatile chemically unstable systems, which are in metastable state, for example, in solutions and melts of polymers, olygomers, low-molecular weight substances, explosives etc. The main aim of this report is to find quantitative relationships, which allow to predict the metastable's systems sensitive to outside mechanical actions. A solution of this problem in the general case of nuclei form changes during load have some mathematical problems which are connected with analysis of the stressed state of medium in the vicinity of micronuclei by methods of elastic and viscous-elastic theory.

However, even so the most ordinary physical model of nucleus in a sphere form which going in uniaxis-symmetrical ellipsoid offers to get some practical results. Let us suppose that the pliability of nuclei with gaseous products is considerably smaller than rigidity of its environment medium (matrix) and makes not resistance to its deformation. That is why we will consider longitudinal and cross deformations of nucleus will be equal to the average longitudinal and cross of the medium.

GEOMETRIC MODEL

Two variants of deformation of isotropic medium with isolated micronucleus sphere have been considered. In the first case nucleus transforms from initial sphere to elongate ellipsoid with the semi-axes a, b, c where b = c, a more than b. In the second case nucleus goes to compressed axial-symmetrical ellipsoid, i.e. spheroid with semi-axes a, b, c = b, b more than a.

The surface area of the stretched ellipsoid (variant 1) equals

$$S = 4\pi r^2 K, \qquad (1)$$

where r is the radius of initial sphere, the coefficient $K = (1 + 0.25\epsilon)$ takes account of the nucleus surface's deformation into incompressible medium (Poisson coefficient v = 0.5).

In particular case when relative axial deformation is absent ($\varepsilon = 0$), we have: K = 1, and S = $4\pi r^2$ (sphere form of micronucleus). The area of the compressed ellipsoid's surface (variant 2) also is S = $4\pi r^2 K$, but in this case K = $1 - 0.5 \varepsilon$

Proceeding in the same manner, we transformed the expression for the ellipsoid volume into

$$V = (4/3) r^3 N,$$
 (2)

where the coefficient N has different values which are depended from load's kind of medium : for a stretched ellipsoid $N = (1+\epsilon)(1-\epsilon) = 1 - \epsilon^2$; for a compressed ellipsoid $N = (1-\epsilon)(1+\epsilon) = 1 - \epsilon^2$

By virtue of smallness of relative deformations ε , it is safe to put $N \cong 1$ for the both load kinds.

THE WORK OF THE NUCLEUS FORMATION

Let us assess the work of the formation of an ellipsoidal nucleus by analogy with the work required to form a spherical bubble in an initially homogeneous medium:

$$\Delta G = 4\pi r^2 K\sigma - (4/3)\pi r^3 N \Delta G_v$$
(3)

The nucleus of critical size is stable and its ΔG reaches extreme value. The extremum's condition is $d(\Delta G)/dr = 0$. Then $r_{cr} = 2\sigma K/(\Delta G_v)N$. For spherical nucleus K = N = 1 and $r_{cr} = 2\sigma/\Delta G_v$. On the other hand the values of ΔG must satisfy a condition of equilibrium of the surface in every point of nucleus surface:

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \sigma H,$$

where Δp is the pressure drop at the surface of the nucleus.

As was shown in [1,2], $\Delta p=(p_s - p')(1 - v'/v'')$, where p_s is equilibrium pressure, p' is ambient pressure, v' is specific volume of the matrix, v'' is specific volume of the nucleus contents. Equating of the right sides of the last equations gives $p' = p_s - (2\sigma n)/r(1 - v'/v'')$ where $n = r(1/R_1 + 1/R_2)/2 = rH$, n is coefficient of nucleus form, which is depended from the degree of surface's curvature in the given point of surface. Then after transpose we have

$$W = \Delta G_{cr} = (16\pi\sigma^{3}K^{3})/(3\Delta G_{v}^{2}N^{2})$$
(4)

In particular case for the spherical nucleus K = N = 1. Then $W = W_0 = (16 \pi \sigma^3)/(3\Delta G_v^2)$ what comply with the traditional value of the work W_0 for the spherical nucleus form [1].

Substitution of the values ΔG_v into equation (4) yields

$$W = (16\pi\sigma^3 K n^2) / [3(p_s - p')(1 - v'/v'')]$$
(5)

The value of n in this equation correlates to the most loaded points of the nucleus surface where the average curvature is minimum.

The work of nucleus formation in accordance with Gibbs equation [1] is $W = (1/3) S_{cr}\sigma$, where S_{cr} is the surface area of critical nucleus. Since for the ellipsoidal nucleus $S_{cr} = 4\pi r^2 K$ we have $W = (4\pi/3)r_{cr}^2\sigma K$. Eq. (5) have another form: $W = W_0 \Psi$, where coefficient $\Psi = Kn^2$.

For the points on the equator of nucleus surface at its tension $R_1 = a^2/b$, $R_2 = b$. Than $n = (r/2)(b/a^2+1/b)$, (a>b). After substituting of values of a and b for a small deformations we have $n = 1 - \epsilon$.

For spheroid's poles of nucleus in case of its compression R $_1 = R_2 = b^2/a$, where b is the great semi-axe. In this case for small deformations at v = 0,5 $n = 1 - 2\epsilon$. If we take in account the found values of K and n we get:

for axial stretching $\Psi = Kn^2 = (1 + 0.25\epsilon)(1 - 2\epsilon) \cong 1 - 1.75\epsilon;$ for axial compression $\Psi = Kn^2 = (1 - 0.5\epsilon)(1 - 4\epsilon) \cong 1 - 4.5\epsilon.$

A strained state arising in simple shift is represented as a combination of compression and stretching of elementary volume in two mutually perpendicular directions. Therefore, for simple shear, coefficient Ψ can be taken equal to the average value of two above-indicated values: $\Psi = 1 - 3,12\varepsilon$, where $\varepsilon = \gamma/2$, γ is the shearing angle.

THE KINETICS OF NUCLEATION IN A DEFORMED MEDIUM

The both homogeneous and heterogeneous frequencies of nucleation are connected with work nucleus formation [1]

$$k_{\text{hom}} = N_0 \text{Bexp}(-W/k_B T), \tag{6}$$

where $N_0 = 10^{28} \text{ m}^{-3}$ is the number of molecules per unit volume of the material, $B \cong 10^{10} \text{ s}^{-1}$ is the kinetics factor, k_B is the Bolzmann constant, and $k_{het} = N_{het}Bexp(-W_{het}/k_BT)$ where W_{het} is the work of the heterogeneous nucleus formation, N_{het} is the number of centres of heterogeneous nucleation. In so far as $W = W_0 \Psi$ we have

$$k_{\text{hom}} = N_0 \text{Bexp}(-W_0 \Psi(\epsilon)/k_B T)$$
(7)

The rate constant of the overall reaction of thermolysis with one stage nucleation process is

$$\mathbf{k} = \mathbf{A} \, \mathbf{k}_{\mathrm{n}}^{\beta} \, \mathbf{k}_{\mathrm{ch}}^{\lambda} \tag{8}$$

where $k_n = k_{hom} + k_{het}$; k_{ch} is the rate constant of the surface chemical reaction, $k_{ch} = k_o \exp(-E/RT)$, E is the activation energy, β , λ are parameters.

In the case of the mostly homogenious nucleation ($k_{hom} >> k_{het}$) at $\beta = 1$ and $\lambda = 1$ for uniaxial stretching

$$k = AN_{o}Bexp\{[-W_{o}(1 - 1,75\epsilon) + E_{o}]/k_{B}T\}$$
(9)

It's clearly to be seen that according to (9) the mechanical action (uniaxial deformation) leads to the increasing of the overall reaction rate due to increasing of nucleation frequency.

EXPERIMENTAL

A procedure is suggested for measuring the lifetime of matter applied onto a preheated substrate by replica technique, which is based on use of laser radiation interference in the substrate-film of matter system in combination with a fast system of photoelectric recording. The use of this procedure is of interest in case of investigation of fine effects of the kinetic of transformation of matter (thermolysis, evaporation, etc.) under condition of the overheat and under the effects of various external factors including mechanical actions (vibration of substrate, sonic, ultrasonic waves etc.) [5]. Influence of the fields of constant shearing stresses on the nucleation process in the gas and oxygenated liquids was observed in the clearance between two rotating glass cylinders coaxial inserted. The fulfilled testing allowed to confirm the above mentioned relationships. Experimental data obtained are discussed in details in the full paper.

DISCUSSION

As follows from equation (8) the decrease of the activation barrier $W_0\Psi$ for a medium's deformation is equal to the increase of some equivalent temperature T_{equ} . If $T_{equ} = T/\Psi$, so $W_0\Psi/k_BT = W_0/k_BT_{equ}$. Then

for axial stretching:	$T_{equ} = T/(1-1,75\epsilon);$
for axial compression:	$T_{equ} = T/(1-4,5\epsilon);$
for simple shift:	$T_{equ} = T/(1 - 1.56\gamma)$

If T_{equ} is equal limiting temperature T_{lim} of attainable overheat (at T_{lim} boiling and thermolysis process has a 100% chance of occurring [1-4]), the limiting deformation will be for axial stretching: $\epsilon_{lim} = (1 - T/T_{lim})/1,75;$ for axial compression: $\epsilon_{lim} = (1 - T/T_{lim})/4,5;$ for simple shift: $\epsilon_{lim} = (1 - T/T_{lim})/1,56.$

The values of the critical deformations under compression and shift for some liquids are calculated at various initial temperatures by above mentioned formulas and showed below. The temperatures of attainable superheating are taken from [1,2].

Butane , $T_{lim} = 378$ K, $\epsilon_{cr} = (1-300/378)/4, 5 = 0,0458 = 4,58\%$ (compression);

Chloromethane, $T_{lim} = 366 \text{ K}$, $\varepsilon_{cr} = (1-300/366)/4, 5 = 0,04007 = 4,007\%$ (compression).

The similar calculation for polystyrole, ($T_{lim} = 813$ K [4], the initial temperature $450^{\circ}C=723$ K), gives: $\varepsilon_{cr}=0,0246=2,46$ %. Many linear polymers have approximately identical T_{lim} [4] and thus critical deformations.

The calculated values of deformations are not large, thus the weak impact action on this volatile liquids in the case of its overheating can provoke its boiling (or fast thermolysis of polymers consequently), which pass to spontaneous explosion

The method adopted here can be used for different calculation, that apply to the influence of mechanical action on processes connected with homogenious nucleation. Among them the crystallisation of overcooled liquids, polymerisation and polycondensation of many polymers, lyophobic's sol production, cracking processes, combustion of everyday waste products etc. With the aid of developed method it is possible to calculate the values of limiting deformation of the liquid explosives which can induced its ignition at normal temperature (20^{0} C) For example, nitroglycerine ($T_{lim} = 280^{0}$ C =553K [3,4]): $\epsilon_{lim} = (1-293/553)/4,5 = 0,1 = 10\%$. In reality, the value of the critical deformation is less than 10%, because a mechanical impact partially heats the explosives.

REFERENCES

- 1. V. P. Skripov, Metastable Liquids, Wiley, New York, 1974.
- 2. P. A. Pavlov, Dynamics of Boiling of Strongly Superheated Liquids, USSR Academy of Sciences, Ural Branch, Sverdlovsk, 1988.
- 3. O. F. Shlensnky, Combustion Science and Technology, 1996, Vol. 120, pp. 383 391.
- 4. O. F. Shlensky, A. G. Shashkov and L. N. Aksenov, Thermal Decomposition of Materials, Amsterdam, Elsevier, 1991.
- 5. D. A. Rogatkin, D. N. Yundev and L. G. Moiseeva, High Temperature, 1998, Vol. 38, 1 pp.75 76.