Estimation of activation parameters for materials in sclerometric tests

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The present work is concerned with the kinetics of the scratching process on polymethylmetacrylate (PMMA) and LiF single crystals. It is shown that the scratching may be described in terms of a thermally activated process. The activation parameters are estimated for both PMMA and LiF.

1. Introduction

Sclerometric tests of materials, i.e. scratching hardness tests are one of the most conventional techniques of hardness and microhardness control [1]. At the present time the scratching technique is widely used, the scratching of solid surfaces by abrasive grains being the basis of any mechanical treatment [2]. Therefore, the investigation of deformation around the indentor during the scratching process is essential. It appears that with the introduction of a kinetic parameter τ^* (a measure of the contact time) one can quantitively describe the relation between τ^* , temperature and scratching hardness as the average stress on contact.

The form of this dependence is analogous to those describing the kinetics of processes of deformation and disintegration under different means of mechanical tests [3]. The values of the activation parameters appear to be nearly the same allowing some conclusions to be drawn about the mechanism of the phenomenon.

The results of the investigation of the kinetics of the scratching process on polymethylmetacrylate (PMMA) and LiF single crystal are given in the present paper.

2. Experimental methods

The studies were carried out on PMT-3 especially equipped for the sclerometric tests [4]. The scratching was done in all experiments using the tip of Vicker's pyramid indentor. The microhardness was calculated from the formula [5]:

$$H_{\rm s} = 3.708 \, P/d^2, \tag{1}$$

where P is the load on the indentor, d is the width of the scratch averaged by 8 to 10 scratches. The microhardness obtained from Equation 1 may be identified as the acting contact stress.

The scratching velocity, V was varied between 9×10^{-7} and 8×10^{-2} cm sec⁻¹ with the help of two SD-54 type motors with reductors. The test temperature was varied between room temperature and 400° C, and the loads were 10g for PMMA and 100g for LiF.

The time τ^* necessary for the indentor to pass a distance equal to the track width, d, was chosen as the principal kinetic parameter

$$\tau^* = d/V \tag{2}$$

This time could be identified as the "life-time" of the frictional bond [6]. It should be noted that this parameter is commonly used in the physics of friction [7]. The analysis of stress and temperature dependences of this parameter enabled the following conclusions to be drawn concerning the nature of the process.

3. Results and discussion

The dependence of track width upon the scratching velocity for LiF and PMMA shown in Fig. 1 was used as the experimental basis for the analysis of τ^* (H_s , T) curves. It is seen that increasing the velocity results in a decrease in the track width. This result seems to be connected with the fact



Figure 1 Dependence of scratch width upon scratching velocity.



Figure 2 Dependence of "life-time" τ^* upon acting stress H_s (microhardness).

that increasing the sliding velocity, V, decreases the "life-time" τ^* of the frictional bond. The resistance of scratching is increased simultaneously. The effect of τ^* on H_s on a semilogarithmic scale, is shown in Fig. 2. The number of experimental points on the steep line is generally increased with temperature and those on the sloping line are decreased. The extensions of the steep and sloping lines intersect forming two fans. In the case of PMMA it is possible to draw two fans, but with a limited number of points on the steeper fan.

A plot of $\log \tau^*$ versus 1/T (by the sectional method) again reveals the two fans for $\log \tau^*$ versus 1/T for each material (Fig. 3). The tops of the fans are the same ordinates τ_0^* ($\log \tau_0^* = -12-13$). The values τ_0^* could be defined within the accuracy only of two to three orders of magnitude because of the long extrapolation. The abscissas of the fan tops (poles) are equal to zero for the steep fans, and not equal to zero for the sloping fans, i.e. a deviation of the poles is observed [8].

The dependences of $\log \tau^*$ on H_s and on 1/T998



Figure 3 Temperature dependence of "life-time" τ^* .



Figure 4 Stress dependence of scratching activation energy for LiF.

enable us to determine an analytical expression for the "life-time" of the frictional bond:

$$\tau^* = \tau_0^* \exp \left[U^*(H_s) / RT \right], \tag{3}$$

where $U^*(H_s)$ is the activation energy of scratching which may be defined from the slope of the lines $\log \tau^*$ versus 1/T [3,8] forming the fan without pole deviation

$$U^*(H_s) = 2.3R\Delta(\log \tau^*)/\Delta(1/T).$$
 (4)

The values of U^* and H_s for LiF calculated from this equation are plotted in Fig. 4. It is seen that the dependence of U^* on H_s can be approximated as a linear function:

$$U^*(H_s) = U^*_{os} - \gamma^*_{os} H_s \tag{5}$$

 $U^*(H_s)$ for PMMA from Equation (3), as long as τ_0^* is known may be

$$U^*(H_s) = 2.3RT \log{(\tau^*/\tau_0^*)}.$$
 (6)



Figure 5 Stress dependence of scratching activation energy for PMMA. Solid line – regression curve, dashed lines – the outlines of the area of reliability (probability 0.99), around the regression curve.

Using Equations 1 and 6 one can obtain independently a set of values for U^* versus H_s and H_s^* formed of 40 elements. This set is a good object for statistical treatment. The correlative and regression analysis permit us to estimate the selection correlation coefficient to be 0.95, and to obtain the linear regression equation by the least squares technique in the form of Equation 5. The results of the analysis are shown in Fig. 5.

The activation parameters for scratching U_{os}^* , γ_s^* , are given in Table I together with those for microhardness. It should be noted that the values of the activation parameters U_{os}^* and γ_s^* for LiF are in a close agreement with those obtained [9] $(U_0^* = 64 \text{ kcal mol}^{-1}, \gamma^* = 1.1 \text{ kcal mm}^2 \text{ mol}^{-1} \text{ kgf}^{-1})$ by indentation of a cylindrical rod having a flat end, if they are found from [9] using the method given by Chu and Li [10].

Combining Equations 3 and 5, one obtains the empirical formula for the "life-time" of the frictional bond as a function of stress and temperature:

$$\tau^* = \tau_0^* \exp \left[(U_{\rm os}^* - \gamma_{\rm s}^* H_{\rm s}) / RT \right].$$
 (7)

The form of this equation testifies to the thermally activated nature of the scratching process and is similar to the well-known expression for the "life-time" of solids [3] and also to the formula for the penetration velocity of the indentor [11]:

$$\tau = \tau_0 \exp\left(U_0 - \gamma\sigma\right)/RT \tag{8}$$

$$\dot{h} = \dot{h}_0 \exp - [(U_0^* - \gamma^* H)/RT].$$
 (9)

In addition to the functional resemblance of Equations 7 and 9 it should be noted that the constants τ_0^* and τ_0 are independent of the nature of the material and that their values are of the order of the average period of atomic oscillations. The initial activation energies U_{os}^* , U_0^* , U_0 appear to be almost the same value.

The last fact points to the similarity of elementary acts of the underlying processes. Although such a similarity (in the initial energies of activation) does not determine the nature of the elementary acts which control the scratching process, it makes it possible to estimate the activation parameters of strain and fracture by means of the scratching test technique.

Therefore, on the basis of the results obtained, the thermofluctuational nature of the scratching process is demonstrated. In addition, the direct correlation between the activation parameters of scratching and those of material strength has been revealed.

4. Conclusions

(1) The scratching process is thermofluctuational in nature and the principal kinetic parameter is the "life-time" of the frictional bond.

(2) The "life-time" of the frictional bond as a function of stress and temperature is expressed by Equation 7.

(3) The initial activation energies for both scratching and penetration processes appear to be nearly the same. This points to the similarity of the elementary acts underlying the processes.

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TABLE I Activation parameters of scratching and microhardness

Material	$U_{\mathbf{os}}^*$ (kcal mol ⁻¹)	$\gamma_{\rm s}^*$ (kcal mm ² mol ⁻¹ kgf ⁻¹)	U_0^* (kcal mol ⁻¹)	γ^* (kcal mm ² mol ⁻¹ kgf ⁻¹)
LiF	58	0.75	59	0.9
РММА	26.3	0.79	28	0.52

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Received 10 May and accepted 29 August 1979.