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The Influence of Substances Reducing the Surface Energy of Naphthalene Single Crystals on Plastic Flow

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The effect of surface active substances on plastic flow of naphthalene single crystals is considered. The role of normal and shear stresses is revealed. Rates of single crystals flow in different glide systems under constant stress are compared. The stress of plastic flow in single crystals can be decreased in active media by as much as 50 %.

The most pronounced manifestation of surface phenomena in solids is their deformation in surface active environments, i.e. in media reducing the surface energy of solids. The effect of adsorption plasticizing plays an important role in a variety of processes, such as pressing and cutting of metals, boundary friction and lubrication (particularly its initial stages). In this view molecular crystals are convenient materials with very appropriate physico-chemical properties. However, the presence of several glide systems in one single crystal makes it difficult to find the conditions under which only one type of dislocations would move. Aromatic hydrocarbon crystals are of this type. The "easiest" glide systems, namely the (001)[010] (I) and the (001)[110], (II), appear to meet the requirements of individual one-system glide¹⁻⁴ We find however, that the resulting glide depends on the orientation of the glide plane towards the stress direction. Glide in the I or II system is individual, i.e. does not involve any other glide system in the deformation process, only in a certain range of angles χ_0 between the extension axis and the glide plane.

Data on normal and shear stresses of elastic-brittle fracture of single crystals vs. glide planes orientation have shown that in the I glide system at angles $\chi_0 > 50^\circ$ a second system is involved in the deformation process,

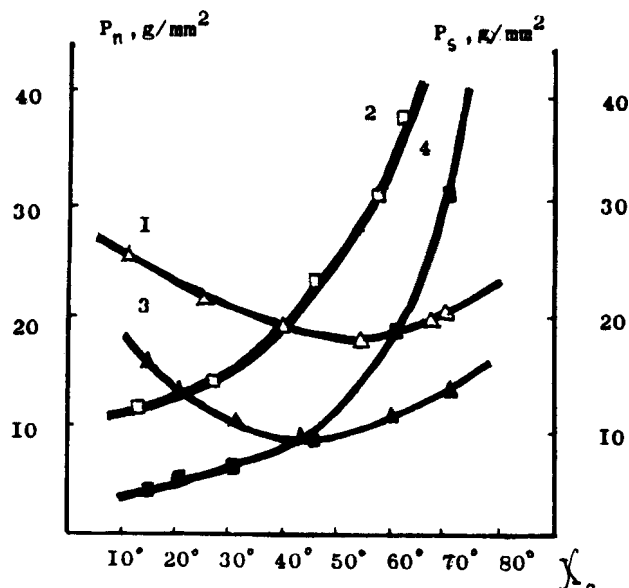


FIGURE 1

i.e. (010)[001]. Intersection of (001)[010] and (010)[001] dislocations which are moving in different planes strengthens the crystal, so that the shear stresses increase (Figure 1).

A similar picture is observed in the II glide system, where plastic flow occurs on account of (001)[110] dislocations. At $\chi_0 > 30^\circ$ the stress is high enough to make the (001)[010] dislocations move. The complex plastic flow which involves intersection of dislocations moving in one crystallographic plane weakens the crystal so that the stresses of brittle-plastic failure at $\chi_0 < 30^\circ$ decreases appreciably (Figure 2).

The stresses $P_{s\bar{a}}$ and $P_{n\bar{a}}$ at which plastic flow begins at the crystallographic shear rate $\lg \dot{a} = -4$ depend on the orientation of the glide planes in the same manner (Figures 3, 4).

In surface active environments the yield point decreases, and so does the fracture stress. For example, in α -chlornaphthalene P_n and P_s are half the values found for the I glide system (Figures 1, 3 curves 3 and 4). For the II glide system the decrease is smaller (Figures 2, 4, curves 3 and 4) due to the inconvenient geometry of the system. The environment seems likely to affect all the types of dislocations in the same manner under the same conditions.

Figures 1-4 show that the minimum shear stress to make dislocations move in air is 8 g/mm². A geometric estimate of the dislocation movement

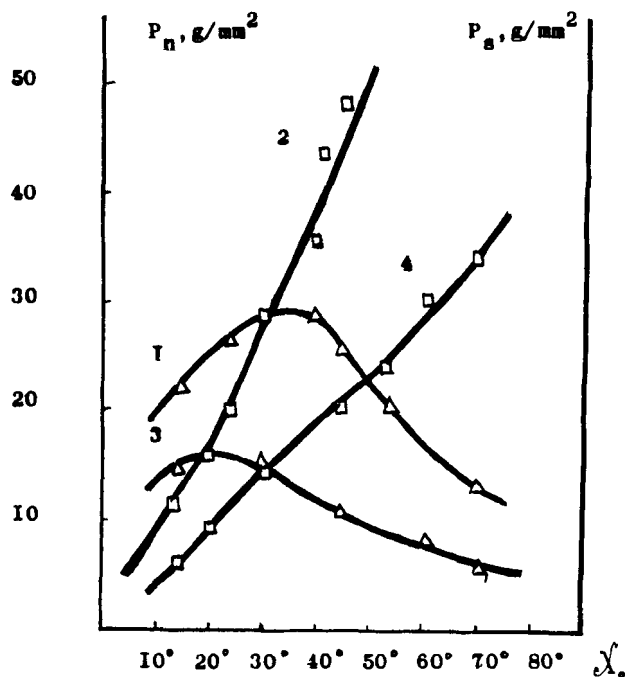


FIGURE 2

stress gives for the narrow Peierls dislocation in an ideal crystal at $\nu = 0.3$ the following:

$$P_s = \frac{2\mu}{1-\nu} e^{-2\pi/(1-\nu)} = \frac{E}{1-\nu^2} e^{-2\pi/(1-\nu)} = \frac{10^{11}}{1-0.09} e^{-9}$$

$$\approx 5 \cdot 10 \frac{\mu \text{ dyn}}{\text{cm}^2} \sim 0.5 \text{ gr/mm}^2$$

This value is almost an order of magnitude lower than the experimental one, the difference being due to various obstacles and to the intersection of climbing dislocations with those of the network.

A dislocation source, say Frank-Reed source, in naphthalene single crystals operates at lower stresses than those for dislocation movements through the perfect lattice

$$P_{sF} = \frac{2T}{Cl} = \frac{\mu C}{l} = \frac{10^{11} \cdot 10^{-7}}{2.6 \cdot 3 \cdot 10^{-1}} = 10^{\mu} = 0.1 \text{ gr/mm}^2, \quad l = 3 \cdot 10^{-3} m$$

The most likely limiting stage of single crystal plastic flow is the movement

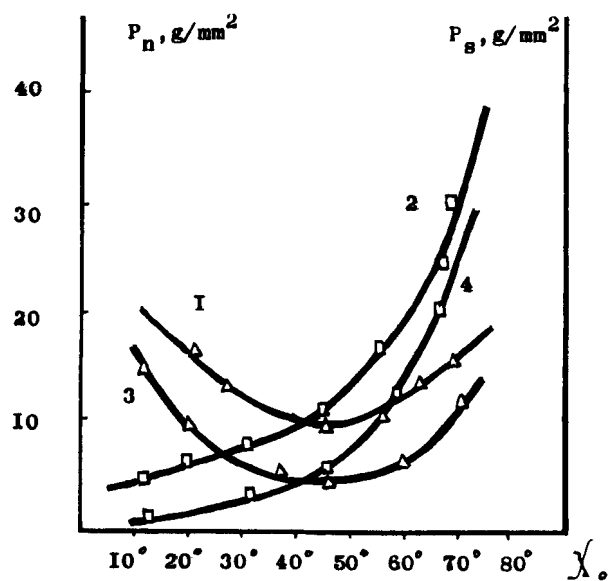


FIGURE 3

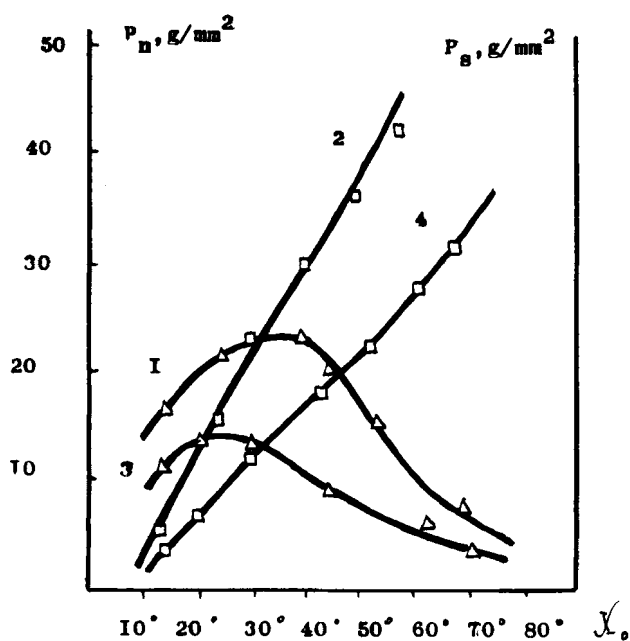


FIGURE 4

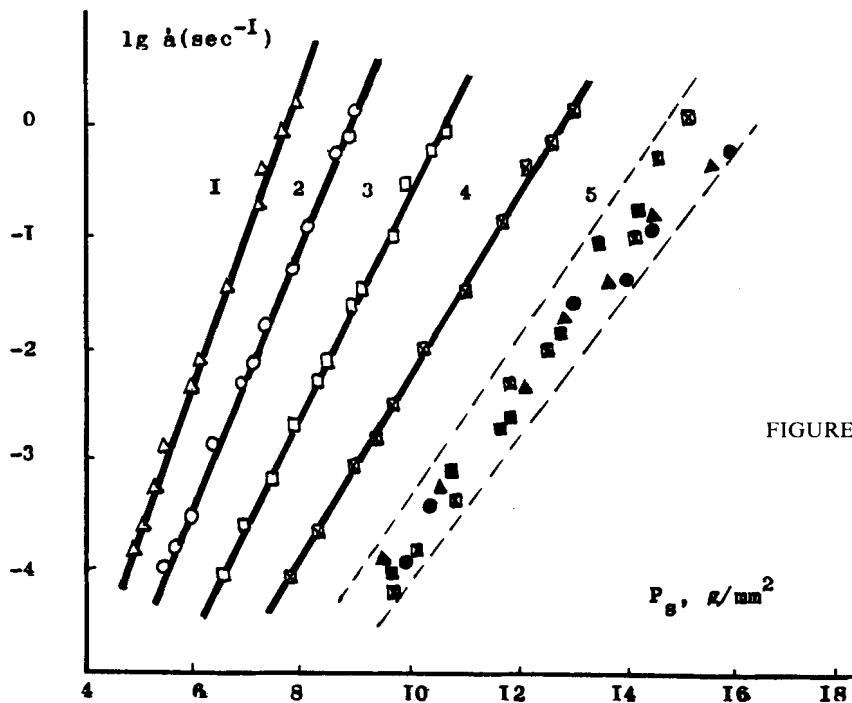


FIGURE 5

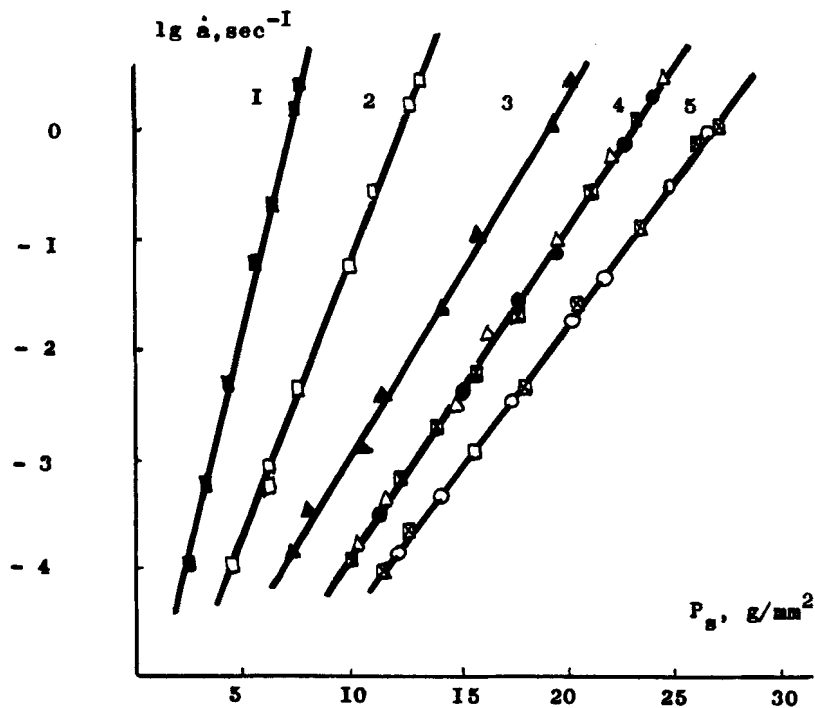


FIGURE 6

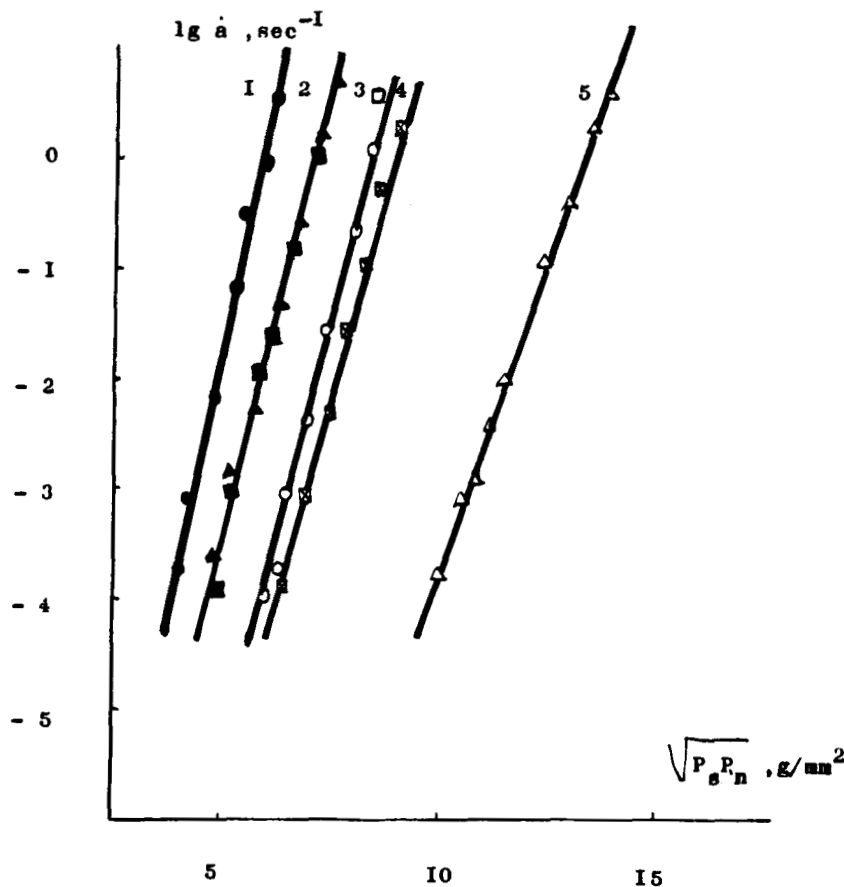


FIGURE 7

of dislocations when they emerge at the surface rather than when they are moving in the bulk. Thus the most important factors are the imperfection of the surface, the concentration of sinks and the surface barrier of the crystal.

Using the experimental data on creep (plastic flow under constant stress) in the I and in the II glide systems and taking into account the changing glide geometry during deformation we have estimated how the rate of pure shear depends on shear and normal stresses. Pure shear was estimated as

$$a = \frac{1}{\cos \phi_0} [\sqrt{(1 + \varepsilon)^2 - \sin^2 \lambda_0} - \cos \lambda_0]$$

where ε is deformation, $\phi_0 = 90^\circ - \chi_0$.

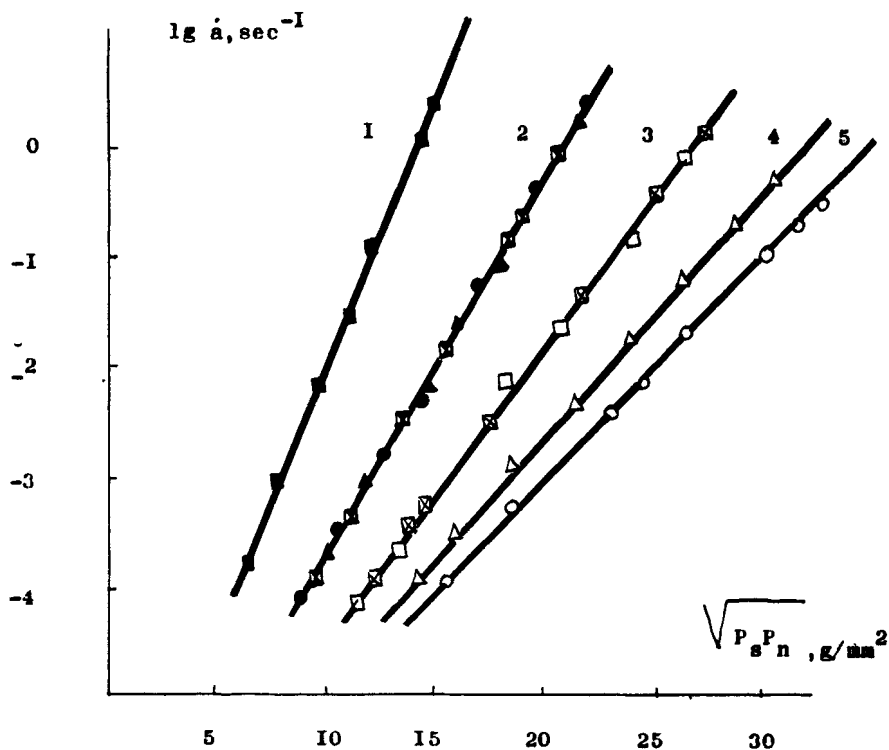


FIGURE 8

In air the pure shear rates in both the I and the II systems proved to depend primarily on shear stress, i.e. the curves for all the directions fit one narrow interval, excluding the curves where glide involves two or more systems (Figures 5, 6).

In an environment, of α -chlornaphthalene, an important role is played by normal stresses. Therefore the curves for different orientations are scattered (Figures 5, 6). If normal stress is taken into account however, the rates of pure shear in a surface active environment also fit one narrow band (Figures 7, 8).

The maximum reduction in plastic flow of naphthalene single crystals in the first glide system provided by extremely surface active environment, i.e. α -chlornaphthalene, is presented in Figure 9. If the single crystal geometry permitted pure glide of one-type dislocations, they would have probably displayed the same level of environmental effect. As seen from Figure 9, both fracture and plastic flow of single crystals are dependent on similar processes, particularly on stress concentration on microheterogeneities, so

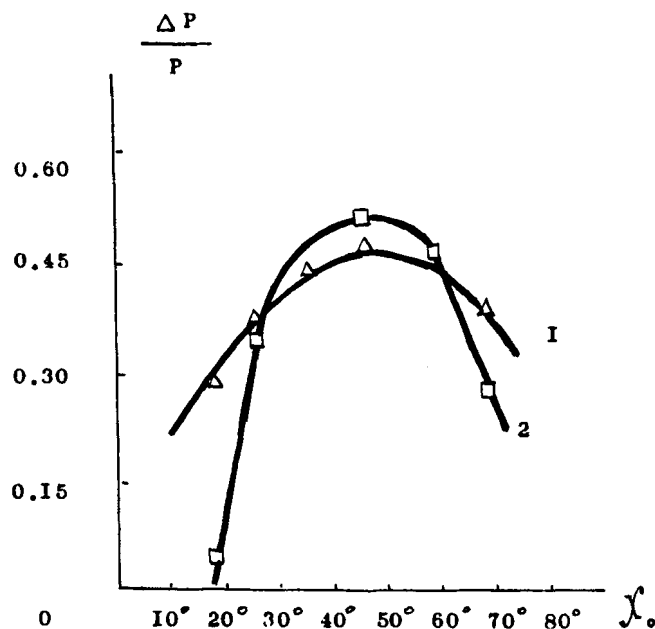


FIGURE 9

that the overstress factor responsible for the plastic flow intensity $\gamma/V_m = 8 \cdot 10^3$ appears to equal that responsible for brittle-plastic failure:

$$\frac{\gamma}{V_m} = \frac{\frac{\partial \sigma}{C}}{\frac{P_c}{P_{\text{real}}}} = \frac{P_{\text{id}}}{P_{\text{real}}} = \frac{\frac{8 \cdot 10^{10} \cdot 60}{8 \cdot 10^{-8}}}{2 \cdot 10^6} = \frac{8 \cdot 10^9}{2 \cdot 10^6} \approx \phi \cdot 10^3$$

where γ is the activation volume, i.e. the region from which the defect collects elastic energy, V_m is the volume of a molecule in the crystal.

It is quite possible that in near surface regions where dislocations accumulate, considerable microheterogeneities appear.

In presence of surface active media the size of these heterogeneities (cavities formed on dislocation pile-ups, surface defects, etc.) increases. Therefore the overstress factor increases as much as by an order of magnitude and the near-surface movement of dislocations is facilitated. The result is creep acceleration and increase in the distances covered by near-surface dislocations.

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