On the Analysis of the Activation Volume

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The stress and temperature dependence of the activation volume is often explained by a similar dependence of the measured stress sensitivity. This explanation cannot be reconciled with the nonconservative motion of dislocations, with dislocation climb, nor with the intersection mechanism. It is in contradiction with the results obtained in direct dislocation velocity measurements as well.

It is now shown that when the backward movement of the dislocations is taken into consideration an explanation, consistent with the rate theory and with the dislocation mobility observations, can be developed. The analysis shows that with constant activation volume the stress sensitivity is stress and temperature dependent, in agreement with the corresponding measurements and mechanisms.

The determination of the activation volume associated with the rate controlling mechanism is of great importance in the analysis of thermally activated processes. It is usually assumed that the experimental, or Arrhenius, rate equation

\[ \dot{\gamma}_p = A \exp \left[ - \frac{\Delta E_e - V_e (\tau_{eff}) \tau_{eff}}{kT} \right] \] (1)

describes the observed dependence of the plastic deformation rate on the stress and temperature. In Eq. (1) \( \dot{\gamma}_p \) is the plastic shear strain rate, \( \Delta E_e \) is the experimental activation energy, \( V_e \) is the experimental activation volume, \( \tau_{eff} \) is the effective stress, \( k \) is the Boltzmann constant, \( T \) is the temperature in K, and \( A \) is an experimental preexponential factor.

In deformation theory \( V_e \) is defined as

\[ V_e = \left( \frac{d \Delta E_e}{d \tau_{eff}} \right)_{T, \text{structure}} \]

By definition \( V_e \) is related to the stress sensitivity \( m \) as

\[ m = \left( \frac{d \ln \dot{\gamma}}{dT} \right)_{T, \text{structure}} \]

\[ = \frac{V_e (\tau_{eff}) + \frac{\tau_{eff}}{kT} dV_e (\tau_{eff})}{kT} \]

When the activation volume is independent of the stress then

\[ \dot{\gamma} = A \exp \left[ - \frac{\Delta E_e - V_e \tau_{eff}}{kT} \right] \]

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and because

\[ m = \left( \frac{d \ln \dot{\gamma}}{d \tau_{eff}} \right)_{T, \text{structure}} = \frac{V_e}{kT}, \quad (3) \]

the experimental activation volume \( V_e \) is proportional to the stress sensitivity \( m \).

In Fig. 1 typical experimental results are represented schematically. The stress sensitivity increases indefinitely with decreasing stress and approaches asymptotically to a finite value at large stresses. Two alternative conclusions are usually drawn from the observed stress and temperature dependence of the stress sensitivity: Either it is considered that the behavior reflects the dependence of the activation volume on the stress and temperature, or that the variation of the stress sensitivity reflects structural changes. Because of the difficulties involved in separating these two alternatives, the third possibility, that both the activation volume and the structure change with the stress and the temperature, is usually avoided.

Although \( V_e \) may indeed vary with the stress, temperature, and structure, these conclusions present logical inconsistencies as generalized statements and lead to contradictions. In direct dislocation velocity measurements, carried out at constant structure, the stress sensitivity is typically of the type shown in Fig. 1: Consequently, the typical stress and temperature dependence of \( m \) cannot be considered as the experimental expression of structural changes. It follows then, that if the activation volume is stress dependent at constant structure, the last term in Eq. (2) is not zero and Eq. (3) cannot be used for the evaluation of the true activation volume.

It is the purpose of this paper to present a consistent explanation of the typical stress sensitivity.
behavior and to develop a method for the analysis of the activation volume.

Discussion

Following the pioneering work of Eyring and Orowan, Alefeld has suggested that Eq. (1) is incomplete because in the evaluation of the activation volume the backward movement of the dislocation has to be considered also. In his analysis, Alefeld has assumed that the energy barrier is symmetrical. Accordingly, the rate equation is expressed as

\[ \dot{\gamma} = 2A \sinh \left( V \tau_{\text{eff}} / kT \right), \]

and the stress sensitivity as

\[ m = \left( \frac{d \ln \dot{\gamma}}{d \tau_{\text{eff}}} \right)_{T, \text{structure}} = \left( \frac{V}{kT} + \frac{dV}{dT} \frac{\tau_{\text{eff}}}{kT} \right) \coth \frac{V \tau_{\text{eff}}}{kT}. \]

Assuming, as before, that the activation volume is independent of the stress, that is

\[ dV/d\tau_{\text{eff}} = 0, \]

it follows that for a symmetrical energy barrier

\[ m = \frac{V}{kT} \coth \frac{V \tau_{\text{eff}}}{kT}. \] (4)

The analysis showed that Eq. (4) is represented by a family of curves similar to that obtained experimentally (Figure 1). This is an important conclusion because it indicates a way to resolve the contradictions arising with the use of Equation (3).

In the last few years direct dislocation velocity and stress relaxation measurements, that were carried out at constant structure, indicated that very often mechanisms with a linearly stress dependent apparent activation free energy

\[ \Delta G = \Delta G^\ast - V \tau_{\text{eff}} \]

cannot be associated with symmetrical energy barriers: It has been shown that in many covalent, ionic and metallic crystals the rate controlling mechanism is associated with non-symmetrical energy barriers. The stress and temperature dependence of the dislocation velocity \( v \) was described well with the rate equation derived from the absolute rate theory, as

\[ v = \delta_t \frac{kT}{h} \exp \left\{ -\frac{\Delta G_t^\ast}{kT} \right\} \exp \left\{ \frac{V_t \tau_{\text{eff}}}{kT} \right\} \]

\[ -\delta_b \frac{kT}{h} \exp \left\{ -\frac{\Delta G_b^\ast}{kT} \right\} \exp \left\{ -\frac{V_b \tau_{\text{eff}}}{kT} \right\}, \] (5)

where \( \delta \) is the distance travelled by the dislocation after each activation, and \( h \) is Planck’s constant. The deformation kinetics expressed by Eq. (5) removes the restrictions imposed by the symmetrical barrier model and is a satisfactory description for the analysis of the activation volume for a large variety of crystalline materials.

It follows from Eq. (5) that the relation between the stress sensitivity and the activation volume is expressed as

\[ m = \left( \frac{d \ln \dot{\gamma}}{d \tau_{\text{eff}}} \right)_{T, \text{structure}} = \left( \frac{d \ln v}{d \tau_{\text{eff}}} \right)_{T, \text{structure}}. \]
According to Eq. (6) $m$ is stress and temperature dependent at constant activation volume. Figure 2 illustrates the stress sensitivity calculated for typical activation volume values. The figure shows that the stress and temperature dependence of the calculated stress sensitivity is similar to the usually observed behavior. The very good agreement is further demonstrated by a characteristic diagram for germanium, shown in Figure 3. Similar results were obtained for LiF, NaCl, Si, Al, Fe, etc. Figures 2 and 3 show that at high stress level all curves approach asymptotically to a finite value, defined by Eq. (6) as

$$m = \frac{V_f}{kT}$$

and that the increase of $m$ at low stress level is due to backward activation over the energy barrier and not to the increase of the activation volume.

2. E. Orowan, Z. Phys. 98, 386 [1936].