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Variation of activation volume with temperature for Fe, Si, and Ge

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Abstract

In this paper, a new approach is presented to calculate the activation volume, which is based on Eyring absolute reaction rate theory. Emphasis is placed on the determination of activation volume from the indentation creep microhardness data measured using Vickers indentor at constant load for various dwell times and temperatures. Different materials like Fe (with metallic bonding), Si, and Ge (with covalent bonding) are chosen for the study. The results serve to validate the approach outlined here because direct comparison can be made with the data obtained through a conventional creep test of specimens. The result obtained also shows that activation volume increases with increasing homologous temperature.

Keywords: Activation volume; Indentation; Vickers; Microhardness

1. Introduction

The deformation of crystalline materials at elevated temperatures is a thermally activated process. A crystal contains a distribution of obstacles of activation energy (Q) towards the motion of dislocation during the deformation. Each obstacle is characterized by critical stress σ_0, which means that at 0 K, these obstacles are overcome by the dislocation under an applied stress $\sigma = \sigma_0$. If a constant stress σ is applied to the crystal, obstacles with $\sigma_0 < \sigma$ will be overcome at once by the dislocation, giving rise to instantaneous strain. When the measuring temperature is greater than 0 K, obstacles with $\sigma_0 > \sigma$ may be overcome due to thermal activation with a probability proportional to $\exp\left(-Q/(k_B T)\right)$. Hence, at higher temperatures, as soon as the dislocation is arrested at an obstacle with σ_0 slightly higher than σ, the thermal energy predominates the small value of Q. This enables the dislocation to overcome the obstacle, resulting in rapid strain.

2. Model

Under the thermally activated process, the dislocation can jump over the barrier with frequency v^+ [1], which is given by Eyring equation:

$$v^+ = v_0 \exp\left(\frac{-Q + V_a \sigma}{k_B T}\right) \tag{1}$$

where v_0 is the attempt frequency, V_a is the activation volume, k_B is the Boltzmann constant, and T is

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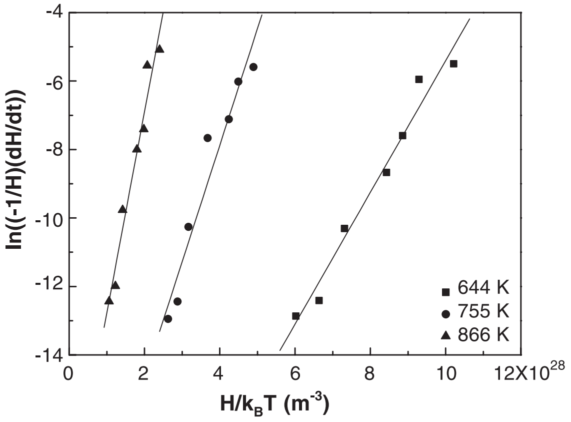

Fig. 1. Variation of $\ln((-1/H)(\mathrm{d}H/\mathrm{d}t))$ with $H/(k_\mathrm{B}T)$ for Fe.

temperature [in K]. Once the barrier has been overcome and the dislocation segment has fallen into the next trough, it acquires new energy to overcome the following barrier in a purely random process. Thus, there will be a chance to jump back with frequency:

$$\nu^- = \nu_0 \exp\left(\frac{-Q - V_\mathrm{a}\sigma}{k_\mathrm{B}T}\right). \tag{2}$$

Thus, the net forward reaction rate is given by:

$$\nu = \nu^+ - \nu^- \tag{3}$$

$$\nu = \nu_0 \sinh\left(\frac{V_\mathrm{a}\sigma}{k_\mathrm{B}T}\right)\exp\left(\frac{-Q}{k_\mathrm{B}T}\right).$$

The net forward reaction determines the macroscopically observed creep strain rate of specimen subjected to external loading at a specified temperature; hence, steady strain rate $\dot{\varepsilon}_\mathrm{s}$ is given by [2,3]:

$$\dot{\varepsilon}_\mathrm{s} = AT\left(\frac{V_\mathrm{a}\sigma}{k_\mathrm{B}T}\right)\exp\left(\frac{-Q}{k_\mathrm{B}T}\right) \tag{4}$$

where A is a constant. For moderate stress and narrow temperature range, Eq. (4) is simplified to the exponential form as [4]:

$$\dot{\varepsilon}_\mathrm{s} = A\exp\left(\frac{-Q + V_\mathrm{a}\sigma}{k_\mathrm{B}T}\right). \tag{5}$$

In an indentation creep test, the experimental data are in the form of microhardness variation with dwell time, where hardness itself is calculated from the applied load and the indentation size. For Vickers indenter with an included angle of 136°, microhardness (H) is given by [4]:

$$H = 2\sin 68^\circ \frac{P}{D^2}\ \mathrm{MPa} \tag{6}$$

where P is applied load [in N] and D is length of the indentation diagonal [in mm]. The strain rate was defined as [5]:

$$\dot{\varepsilon}_\mathrm{s} \propto \frac{1}{D}\frac{\mathrm{d}D}{\mathrm{d}t} \tag{7}$$

using Eqs. (6) and (7), the strain rate may be written as:

$$\dot{\varepsilon}_\mathrm{s} \propto -\frac{1}{2}\frac{1}{H}\frac{\mathrm{d}H}{\mathrm{d}t}$$

$$\dot{\varepsilon}_\mathrm{s} = -K_1\frac{1}{H}\frac{\mathrm{d}H}{\mathrm{d}t} \tag{8}$$

where K_1 is a proportionality constant. Following Roebuck and Alomand [5] and Evans and Goetze [10], stress σ is related to microhardness by the relation

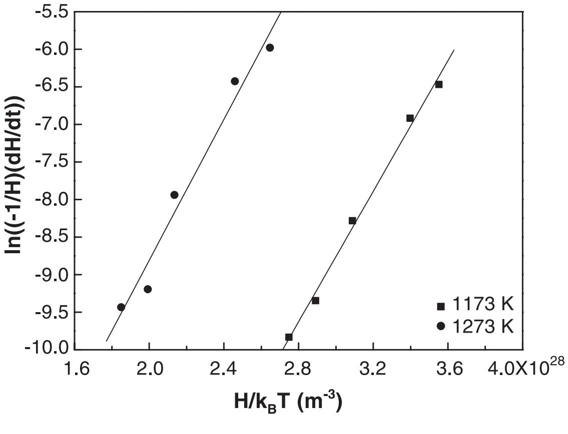

Fig. 2. Variation of $\ln((-1/H)(\mathrm{d}H/\mathrm{d}t))$ with $H/(k_\mathrm{B}T)$ for Si.

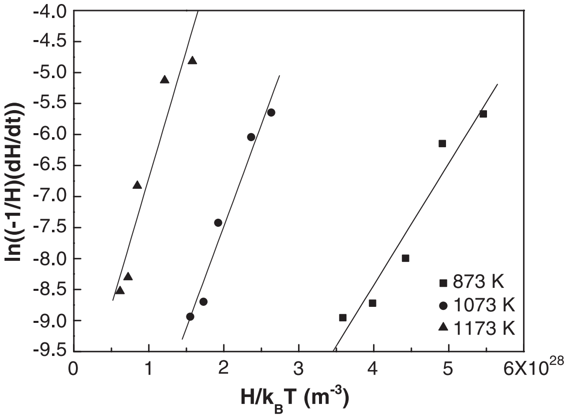

Fig. 3. Variation of $\ln((-1/H)(\mathrm{d}H/\mathrm{d}t))$ with $H/(k_{\mathrm{B}}T)$ for Ge.

$\sigma = H/3$. We substitute Eq. (5) into Eq. (8) and rearrange:

$$\ln\left(-\frac{1}{H}\frac{\mathrm{d}H}{\mathrm{d}t}\right) + B = \frac{V_{\mathrm{a}}H}{3k_{\mathrm{B}}T} \tag{9}$$

where B is defined as:

$$B = \ln K_1 - \ln A + \frac{Q}{k_{\mathrm{B}}T}. \tag{10}$$

The plots of $\ln((-1/H)(\mathrm{d}H/\mathrm{d}t))$ versus $H/(k_{\mathrm{B}}T)$ represent a straight line with intercept B and slope $V_{\mathrm{a}}/3$, where slopes directly measure the activation volume.

3. Results and discussion

Indentation creep response is analyzed using the data of iron [6], silicon, and germanium [7]. The variations of $\ln((-1/H)(\mathrm{d}H/\mathrm{d}t))$ versus $H/(k_{\mathrm{B}}T)$ are shown in Figs. 1–3 for Fe, Si, and Ge, respectively. The test materials, their melting point, Burger vector, crystal structure, and nature of bonding are given in Table 1 [8], while the activation volumes of the test materials determined from the graph are given in Table 2 in terms of $\boldsymbol{b}^3$ (where $\boldsymbol{b}$ is the Burger vector).

Table 1
Test materials, their melting points, Burger vectors (***b***), crystal structures, and their bonding

SN	Test materials	Melting point (K)	Burger vector (A)	Crystal structure	Type of bonding
1	Fe	1530	2.48	bcc	Metallic
2	Si	1687	3.83	fcc (diamond type)	Covalent
3	Ge	1211	3.99	fcc (diamond type)	Covalent

Table 2
Activation volumes of test materials at different temperatures

SN	Test materials	Test temperature (K)	T/T_{m}	Activation volume ($\boldsymbol{b}^3$)
1	Fe	644	0.42	37.8
2	Fe	755	0.49	66.6
3	Fe	866	0.56	115.2
4	Si	1173	0.70	23.4
5	Si	1273	0.75	25.4
6	Ge	873	0.72	9.0
7	Ge	1073	0.88	14.4
8	Ge	1173	0.96	18.0

The results indicate that activation volume generally increases with increasing test temperature. For iron, the activation volume is $37.8\boldsymbol{b}^3$, $66.6\boldsymbol{b}^3$, and $115.2\boldsymbol{b}^3$ at a homologous temperature of 0.42, 0.49, and 0.56 K, respectively, which is consistent with the earlier observed value [9]. The activation volume for silicon is $23.4\boldsymbol{b}^3$ and $25.4\boldsymbol{b}^3$ at a homologous temperature of 0.70 and 0.75 K. The activation volume for germanium $9.0\boldsymbol{b}^3$, $14.4\boldsymbol{b}^3$, and $18.0\boldsymbol{b}^3$ at 0.72, 0.88, and 0.96 K, respectively.

4. Conclusion

The temperature and time dependence of Vickers microhardness data of test materials are the result of plastic flow by glide process. This is a consequence of thermally activated motion of dislocations. Silicon and germanium have an 'fcc' structure and each atom has four nearest neighbours to which it is linked by four purely covalent bonds. On the other hand, iron possesses a 'bcc' structure at the temperature under consideration and has metallic bond. The iron, silicon, and germanium microhardness data are measured at the same stress. It is observed that the activation volume of silicon ($23.4\boldsymbol{b}^3$, $25.4\boldsymbol{b}^3$) and germanium ($9.0\boldsymbol{b}^3$, $14.4\boldsymbol{b}^3$, and $18.0\boldsymbol{b}^3$) even at extremely high homologous temperatures is lower than that of iron ($37.8\boldsymbol{b}^3$, $66.6\boldsymbol{b}^3$, and $115.2\boldsymbol{b}^3$). This is due to the highly directional covalent bond of silicon and germanium in comparison to the weak metallic bond of iron.

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