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Abstract

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THE INFLUENCE OF DISLOCATIONS ON THE TEMPERATURE CHARACTERISTICS OF THE POLYMORPHIC TRANSFORMATION OF CRISTOBALITE

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Defects of the crystal lattice, in particular dislocations, have a substantial effect on the kinetics and temperature characteristics of a polymorphic transformation. Thus, in zinc sulfide whiskers having the most perfect crystal structure, an increase in the phase-transition temperature by 350° was found ([1]). True, in other cases this effect is not observed (cobalt whiskers) or amounts to only 10–20° (iron whiskers) ([2]).

It is possible to determine the conditions whose fulfillment is necessary in order for the influence of dislocations on the temperature characteristics of a polymorphic transformation to be sufficient for experimental observation. First of all, dislocations must be the principal structural defects. The dislocation density must vary within sufficiently broad limits, and the heat of transition must be comparable with the energy of the stresses associated with the dislocations. The transformation temperature is also important: at comparatively low temperatures the rates of diffusion processes are small, and therefore dislocation climb and relaxation phenomena may be neglected. Finally, all other conditions being equal, the most favorable objects for studying the role of dislocations are those in which the transformation proceeds by the martensitic type. Cristobalite satisfies these conditions.

It is known ([3]–[5]) that the polymorphic transformation in cristobalite is a purely temperature function and is accompanied by large volume changes with a comparatively small heat of transition ($\sim 3 \cdot 10^7$ erg/cm^3). This transformation belongs to the martensitic type and proceeds in temperature intervals near 250°. Depending on the crystallization temperature, varieties of cristobalite are obtained that differ from one another in the number of stacking faults of the planes of silicon-oxygen tetrahedra ([4], [6], [7]), which, in accordance with the theory of structural polytypism ([4], [8]), accounts for the noncoincidence of the temperature intervals in cristobalite samples crystallized at different temperatures. Since the stacking faults are bounded by a semipinned edge dislocation ([9]) with Burgers vector $1/3\,a\,[111]$, samples (of cristobalite) with substantially different disloca-

Fig. 1

Figure 1: Fig. 1

tion densities can be obtained. To estimate the dislocation density one may use the data of works (^{6}, ^{7}), in which it is indicated that in cristobalite obtained at comparatively low crystallization temperatures, stacking faults occur on the average after 10-20 planes of silicon-oxygen tetrahedra. Taking into account that the dimensions of individual blocks are $\sim 10^{-4}$ cm, we obtain a dislocation density $\rho \sim 10^{10}$ cm^{-2}. At such dislocation densities, they naturally may be regarded as the principal defects of the crystal lattice.

The influence of dislocations on the character of a polymorphic transformation is connected, above all, with the nucleation process (^{10}). In the direct transformation the phase transition is accompanied by an increase in volume, and formation of a nucleus in a region of tension is thermodynamically favorable. The reverse transition is accompanied by a decrease in volume, which determines the preferential formation of a nucleus in a "compressed" region. Then the gain in energy must

leads to a lowering of the temperature of the $\alpha \to \beta$ transformation and to an increase in the temperature of the $\beta \to \alpha$ transformation, the more strongly the more this cristobalite differs from the ordered 3C type, since at a high dislocation density the probability increases of forming a dislocation cluster that ensures the appearance of a nucleus of sufficiently large dimensions. The considerations presented show that the transformation hysteresis, equal to the difference between the temperatures at the onset of the forward and reverse transitions $(P - T^* - T_1^*)$, may assume zero and even negative values.

The role of dislocations in a polymorphic transformation is not limited to the nucleation process. Dislocations, distorting the crystal lattice, make a substantial contribution to the magnitude of its internal energy. This may also lead to a displacement of the entire transition curve because of a change in the temperature of the "true" allotropic transformation, approximately determined by the formula:

$$T_0 = T^* - P/2 = T_1^* + P/2;$$

P is the hysteresis.

Fig. 1. Temperature-concentration curves for cristobalite specimens obtained at different crystallization temperatures: a –1600°, 10 h; b –1300°, 14 h. Different symbols refer to repeated experiments; light symbols –heating, dark symbols –cooling.

The dependence between the temperature characteristics of the polymorphic transformation and the dislocation density can be obtained by means of thermodynamic relations. Let us represent the specific free energy of the crystal as:

$$\varphi = U_0 + \rho\omega - TS, \tag{1}$$

where ρ is the dislocation density; ω is the energy referred to unit length of a dislocation line; $\rho\omega$ has the meaning of the energy associated with a unit volume of the crystal.

If the transformation belongs to the martensitic type and proceeds at sufficiently low temperatures, then it may be assumed that the number of dislocations in the crystal is conserved. Then we obtain:

$$(\rho\omega)_2 = (1-k)(\rho\omega)_1, \tag{2}$$

where the subscript "2" refers to the phase with the larger specific volume; $k = \Delta V/V$ is the volume jump upon transformation.

Using (1) and (2), we determine the temperature of the "true" allotropic transformation from the condition $\varphi_2 - \varphi_1 = 0$:

$$\Delta U_0 - k\rho\omega - T_0\Delta S = 0. \tag{3}$$

Hence

$$T_0 = \frac{\Delta U_0 - k\rho\omega}{\Delta S} = \tau_0 - \frac{k\rho\omega}{\Delta S}, \tag{4}$$

where $\tau_0 = \Delta U/\Delta S$ has the meaning of the temperature of the "true" allotropic transformation in a dislocation-free crystal.

Let us write the free energy of a crystal in which nuclei of the new phase of volume v have formed, assuming that the dimensions and arrangement of the nuclei relative to the dislocations are such that, in the volume proportional to v, stresses are absent:

$$F = \varphi_1(1-v) + \varphi_2 v - \gamma v\rho\omega. \tag{5}$$

The temperature at which the formation of such nuclei is energetically favorable is found from the condition $F = \varphi_1$:

$$T_0' = \tau_0 - \frac{k\rho\omega}{\Delta S} - \frac{\gamma\rho\omega}{\Delta S}. \tag{6}$$

Analogously for the reverse transition:

$$T_0'' = \tau_0 - \frac{k\rho\omega}{\Delta S} + \frac{\gamma\rho\omega}{\Delta S}. \quad (7)$$

Substituting (6) and (7) into the formulas for the temperatures of the onset of the direct and reverse transitions ($T^* = T_0' + R/\Delta S$ and $T_1^* = T_0'' - R/\Delta S$, where R is a quantity associated with the existence of hysteresis in a dislocation-free crystal and dependent on the volume jump during the transition, the elastic constants, and the interphase surface tension), we then obtain

$$T^* = \tau_0 + \frac{R - \gamma\rho\omega - k\rho\omega}{\Delta S} \quad \text{and} \quad T_1^* = \tau_0 - \frac{R - \gamma\rho\omega + k\rho\omega}{\Delta S}, \quad (8)$$

and also, for the hysteresis:

$$\Pi = 2\,\frac{R - \gamma\rho\omega}{\Delta S}. \quad (9)$$

In accordance with ($^{11-13}$), $\rho = \Delta D/D$, where D is the density. Since $\Delta D/D = -3\Delta d/d$, substituting $\rho = \alpha\,\Delta d/d$ into (4), (8), and (9), we obtain an expression of the type

$$A - Bd, \quad (10)$$

which denotes a linear correlation between the temperature characteristics of the polymorphic transformation and the spacing between the close-packed planes.

The validity of the above considerations was checked in studying the polymorphic transformation of cristobalite samples obtained at different crystallization temperatures. The temperature-concentration curves of the transformation in samples crystallized at the highest and lowest temperatures are shown in Fig. 1.

Comparison of the temperature characteristics of the transformation (Table 1) confirms the data available in the literature (^{5}) on an increase in the transformation temperature and hysteresis with increasing firing temperature.

The same Table 1 gives the spacings d_{222} (quasi-cubic unit cell) between the close-packed planes. As is seen, d_{222} depends substantially on the crystallization temperature. Since all impurity ions (Al, Fe, Ca, Na) have sizes larger than the silicon ion, then with an increase in the firing temperature, and consequently in solubility as well, the interplanar spacings should increase. Therefore, the observed decrease in interplanar spacings is caused by a decrease in the dislocation density with increasing crystallization temperature.

This circumstance makes it possible to interpret the correlation between the temperature characteristics of the polymorphic transformation and the spacing between packing planes (Fig. 2) as confirmation of the above considerations concerning the influence of dislocations on these characteristics. Indeed, the relation between the magnitude of the hysteresis (Fig. 2a) and the temperature of the onset

Fig. 2. Correlation between the temperature characteristics of the polymorphic transformation of cristobalite and the interplanar spacing d_{222}—quasi-cubic unit cell. Π°—hysteresis; T^{*}—temperature of the onset of transformation; T_0—temperature of the "true" allotropic transformation.

of the transformation T^{*} (Fig. 2b) with the value d_{222} has, in accordance with formula (10), the form $A - Bd$. The same dependence is also observed for the temperature of the "true" allotropic transformation (Fig. 2c). This shows that dislocations affect not only the process of nucleation, but also alter the heat of transition. It follows from this that the transformation-onset temperature, determined by both causes (formula 8), must change with increasing dislocation density (and, consequently, with interplanar spacing) more steeply than T_0, which is in agreement with experiment (compare Figs. 2b and 2c).

Table 1

Heat-treatment conditions: temp., °C	Heat-treatment conditions: time, h	Onset temperature of transformation, °C	Hysteresis	Width of the transformation interval	Temperature of the true allotropic transformation, °C	d_{222}, in X	Heat-treatment conditions: temp., °C	Heat-treatment conditions: time, h	Onset temperature of transformation, °C	Hysteresis	Width of the transformation interval	Temperature of the true allotropic transformation, °C	d_{222}, in X
1650	10	250	8	20	246	2.0155	1550	11	238	4	16	235	2.0176
1600	10	243	7	19	238	2.0169	1500	14	230	0	22	232	2.0195
1600	2	242	6	19	238	2.0169	1300	14	210	−6	26	213	2.0220

Confirmation of the correctness of the considerations set forth is also provided by the good agreement between the value of the dislocation density given by the estimate according to relation (4) and the value cited above ($\rho \sim 10^{10}$ cm^{-2}), obtained by counting the number of defects in the crystal. Indeed, substituting into (4) the experimentally found values $\tau_0 - T_0 \sim 10^{\circ}$; $\Delta S = q/T \sim 10^{5}$ erg/cm$\cdot$deg; $k \sim 5 \cdot 10^{-2}$ and the value $\omega \sim 10^{-3}$ erg/cm estimated according to Cottrell (^{9}), we obtain $\rho \sim 10^{10}$ cm^{-2}.

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