

Review

Principles of identification of the physical processes caused by variation of thermodynamic parameters in solids

Yu. V. KORNYUSHIN, L. N. LARIKOV

Institute of Metal Physics, Academy of Sciences of the Ukrainian SSR, Kiev, USSR

A method is proposed which permits identification of the reversible and irreversible thermodynamic processes occurring in solids as thermodynamic conditions vary, and definition of the contribution of each process to the whole. Theoretical values have been obtained of the ratio of the rates of change of enthalpy and volume as well as the ratio of the total heat and volume effects for a series of processes in solids. The method is applied to some actual special cases.

1. Formulation

Variation in the thermodynamic parameters of a solid may cause various physical processes, classified as follows:

(1) Processes which are reversible at a limiting low transformation rate (e.g. phase transformations in a region where the phase equilibrium curve exists).

(2) Irreversible processes which in principle can be made reversible at other values of the thermodynamical variables, pressure P , and temperature T ; e.g. $\beta \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ transformations in solid gallium [1] belong to this class.

(3) Processes which in principle cannot be reversible; e.g. formation, motion and annihilation of dislocations.

Processes that arise due to variation of thermodynamic parameters in solids usually occur in succession, but some appear simultaneously. In order to investigate the processes caused by such variation, use is generally made of the heat and volume effects produced by temperature variation, the pressure being held constant (atmospheric or zero). It turns out that more complete information is obtained by measuring the heat and volume effects simultaneously, for example, during the annealing of hardened metals [2, 3].

This mode of investigation is based on the experimental regularity founded on the fact that each elementary thermodynamic process is related to a narrow range of heat Q , and volume ΔV , effect ratios [2, 3]. The width of this range is defined by conditions under which the process develops and is usually less than the error of measurement. It should be noted that these ranges do not overlap for the majority of processes.

The processes are of two types:

(a) Those where \dot{Q}/\dot{V} does not depend on the stage of development of the process, but depends on the conditions under which this development occurs (\dot{Q} is the rate of enthalpy change, \dot{V} is the rate of change of body volume). If the pressure and temperature remain constant during the process this ratio also remains constant throughout the process and is equal to $Q/\Delta V$. This type of process includes, for example, a series of diffusional phase transformations, as well as an annihilation of point defects and dislocations.

(b) Those where \dot{Q}/\dot{V} depends on the stage of development of the process. To this type belong, for example, formation and healing of defects.

Knowing Q , ΔV , \dot{Q} , \dot{V} , $Q/\Delta V$ and \dot{Q}/\dot{V} for various processes one can identify these processes by such characteristic features as the absolute

value of total heat and volume effects and their signs; agreement of nonagreement of the signs of $Q(T, P)$ and $\Delta V(T, P)$; the ratios $Q/\Delta V$ and \dot{Q}/\dot{V} , and equality or nonequality of their values; the reversibility of the process; the presence or absence of hysteresis when the process is reversible; and finally, the dynamics of heat evolution and the change in the body volume, i.e. the shape of the two families of curves $\dot{Q}(T, P)$ and $\dot{V}(T, P)$. The process rate $-\dot{\phi}$ is determined by the values of \dot{Q} and \dot{V} . If one of these values is known it is possible, for example, to evaluate how many defects participate in the process per unit time. The stage of development of the process $-\Delta\phi$, that is, e.g. the number of defects participating in the process, is determined by the values of Q and ΔV . Indeed for the general case, when the body goes from one thermodynamically nonequilibrium state to another at constant pressure and temperature, the rate of heat absorption is given by the formula

$$\dot{Q} = -T^2 \frac{\partial}{\partial T} \left[\frac{\dot{\phi}(T, P)}{T} \right], \quad (1)$$

where $\phi(T, P)$ is the Gibbs free energy. The rate of change of body volume may be defined from the relation

$$\dot{V} = \frac{\partial \dot{\phi}(T, P)}{\partial P}. \quad (2)$$

In the majority of actual cases, the temperature and the pressure vary during the process but slowly enough for an appreciable part of the process to occur at almost unchanged values of T and P . It means that Equations 1 and 2 are applicable at very small time intervals, during which the values of T and P remain constant while the process itself makes marked progress.

Let us now consider \dot{Q}/\dot{V} and $Q/\Delta V$ for the various elementary processes responsible for hardness in solids. Those most important are as follows: phase transformation; formation, annihilation and motion of point defects (vacancies and interstitials); formation, annihilation and motion of dislocations (including dissociated ones); formation and annihilation of dislocation walls; formation and relaxation of dislocation tangles or pile-ups; motion and redistribution of impurities in the crystal; formation, annihilation and motion of the grain boundaries; formation, development, motion and healing of non-uniformities (pores and cracks). Each of these processes is connected with certain peculiarities of the rate of heat evolution and the rate of change of volume.

2. Phase transformations

The effective and reliable way to study phase transformations is to measure the heat evolution and volume change rates (with pressure and temperature) simultaneously. If a phase transformation occurs in the course of experiment, peculiarities in these rates arise.

During a first order phase transformation, the latent heat of the phase transition is evolved (or absorbed). A second order phase transformation (as well as a first order one) is accompanied by abrupt jumps in the compressibility, heat capacity and thermal expansion coefficient. A first order phase transformation may be simply and reliably identified by the rate of heat evolution and volume change, as well as by heat and volume effects. A second order phase transformation may also be identified by the rates of the enthalpy and volume change since these rates (at definite rates of pressure and temperature change) depend on the compressibility, the heat capacity and on the thermal expansion coefficient which are different for different phases. Let us consider a phase transformation of the first order.

2.1. Reversible first order transformations

In the case of a reversible first order phase transformation, where there exists a phase equilibrium curve, $P_0 = P_0(T_0)$ (P_0 and T_0 are the co-ordinates of the points of the phase equilibrium curve) one may neglect the effects caused by the presence of the interphase boundary and, taking into account the following relations

$$\dot{\phi}(P_0, T_0) = 0, \quad dp_0 = \frac{dp_0}{dT_0} dT_0, \quad (3)$$

one may define from Equations 1 and 2 the ratio of the heat evolution and volume change rates

$$\frac{\dot{Q}}{\dot{V}} = T_0 \frac{dp_0}{dT_0}. \quad (4)$$

Equations 1 to 3 yield, for the ratio of the heat and volume effects, the Clapeyron–Clausius equation

$$\frac{Q}{\Delta V} = T_0 \frac{dp_0}{dT_0}. \quad (5)$$

It follows, from the comparison of Equations 4 and 5, that a reversible first order phase transformation should be considered as a type (a) process, neglecting the effects due to the presence of the interphase boundary. It is noteworthy that a finite

rate of phase transformation is not the only cause of the deviation of the ratio of heat content and volume change rates from the Clapeyron–Clausius equation. Phase transformations in solids are accompanied by rather small heat evolution and volume changes, so that initially the interphase boundaries contribute greatly to the volume and enthalpy change rates of the transformation. The relative interphase boundary contribution decreases during the later development of the transformation, and the ratio of rates approaches the Clapeyron–Clausius equation.

2.2. Actual diffusional first order phase transformations

A first order phase transformation is usually a non-equilibrium irreversible process. There are two limiting cases:

(1) The time required for the temperature to be uniformly spread throughout the specimen is much longer than that needed for the nucleus to be formed and the phase transformation to occur. In this case the rate of the phase transformation is limited by heat conductivity (the rate of the heat input and output). This case corresponds to low transformation rates. The temperature of the initial phase is that of the phase transition, T_0 . If the transition $1 \rightarrow 2$ occurs, e.g. endothermally, the surface temperature of the solid will have $T > T_0$ and the ratio of heat to volume effects may be written as

$$\left(\frac{Q}{\Delta V}\right)_T = \left(\frac{Q}{\Delta V}\right)_{T_0} \frac{1 + Q_0^{-1} \int_{T_0}^T C_P^{(2)} dT}{1 + \Delta V_0^{-1} \int_{T_0}^T d_2 V_{02} dT} \quad (6)$$

where Q_0 , ΔV_0 and $(Q/\Delta V)_{T_0}$ are the heat and volume effects and their ratio at the limiting low transformation rate, $C_P^{(i)}$ the heat capacity at constant pressure, $\alpha_i = V_{0i}^{-1} \partial V_i / \partial T$ is the coefficient of thermal expansion, and V_{0i} is the volume of material in the i th phase at temperature T_0 .

For the reverse transition $2 \rightarrow 1$, $T < T_0$ and

$$\left(\frac{Q}{\Delta V}\right)_T = \left(\frac{Q}{\Delta V}\right)_{T_0} \left[1 + Q_0^{-1} \int_T^{T_0} C_P^{(1)} dT \right] \times \left[1 + \Delta V_0^{-1} \int_T^{T_0} \alpha_1 V_{01} dT \right]^{-1} \quad (7)$$

It may be seen that in this limiting case, the heat and volume effects and their ratios are different for the direct and reverse transformation.

(2) The time required for the temperature to become uniform is much shorter than the time needed for the nucleus to be formed and the phase transformation to occur. Here the phase transformation rate is restricted by the kinetic processes (the nucleus formation and the diffusion), and this corresponds to high transformation rates. As the temperature is almost uniform this process resembles to some degree an equilibrium process, and the transformation temperature depends on the transition rate. When the pressure remains constant but the phase transformation temperature are different, T_1 and T_2 , the heat and volume effect ratios are related by the expression

$$\left(\frac{Q}{\Delta V}\right)_{T_2} = \left(\frac{Q}{\Delta V}\right)_{T_1} \times \frac{1 + Q^{-1}(T_1) \int_{T_1}^{T_2} (C_P^{(2)} - C_P^{(1)}) dT}{1 + \Delta V^{-1}(T_1) \int_{T_1}^{T_2} [\alpha_2 V_2(T_1) - \alpha_1 V_1(T_1)] dT} \quad (8)$$

where V_i is the volume of the substance in the i th phase.

It should be noted that if, for example, the transition $1 \rightarrow 2$ is endothermic at the transition temperature $T_2^* > T_0$, then for the reverse transition $2 \rightarrow 1$, we have $T_1^* < T_0$. Thus the heat and volume effects, as well as their ratios, are different in this case for the direct and reverse transitions, contrary to the case of reversible transformation.

In practice, the onset of transformation usually occurs as the first limiting case mentioned above, while the end of transformation occurs as the second. Different shapes of the hysteresis constitute special features of first order phase transitions of the first class.

As is well known, when some parameters (e.g. the pressure) are changed, second order phase transitions may be turned into first order ones. The point where the curves on the P – T diagram corresponding to various transitions make the continuation from one to the other is known as the Curie point.

It should be noted that phase transformations in solids are often treated as second order, since the accompanying heat and volume effects are so small that they cannot be measured or are zero at zero (or nearly zero) pressure; that is the phase

transitions are second order only at an isolated point on the P - T diagram.

If the differences between the heat capacities, coefficients of thermal expansion and compressibilities of the phases near the transition point do not obey Ehrenfest's relations, then the transition latent heat and transformation volume effect depend on temperature and pressure; that is they vary along the phase equilibrium curve. It may be shown that in this case, heat and volume effects, undetectable at the atmospheric pressure, increase with pressure and attain measurable values. At high pressures, the increment (due to pressure) of heat and volume effects at the transition is proportional to the discrepancy between, on the one hand, the relations of differences of thermal capacity, compressibility and the thermal expansion coefficient in the phases near the transition point, and on the other, Ehrenfest's relations.

Thus investigation of total heat and volume effects on phase transformation under high pressure greatly helps the identification of the true order of the transition. Comparison of the heat and volume effect ratios with the Clapeyron-Clausius equation opens the way to answering questions about the degree of irreversibility of a first order transformation of the first class.

Now let us turn to first order phase transitions of the second class. We shall assume that at some pressure P_0 and temperature T this phase transition is reversible (that is, P_0 and T lie on the phase equilibrium curve) and the ratio of heat to volume effects is $(Q/\Delta V)_{P_0, T}$.

If at the same temperature T and the pressure $P \neq P_0$, one of the phases, for instance phase 1, may exist only in a metastable state, then the transition can occur only in one direction; from metastable to the stable state, $1 \rightarrow 2$. For this transition the ratio of heat to volume effect is given as

$$\begin{aligned} \frac{Q}{\Delta V} = & \left(\frac{Q}{\Delta V} \right)_{P_0, T} \left[1 + \frac{P - P_0}{Q(P_0, T)} \Delta V(P_0, T) \right. \\ & + \frac{V_1(P_0, T)}{Q(P_0, T)} \int_{P_0}^P dP' \int_{P'}^{P_0} \frac{dP''}{\kappa_1(P'')} \\ & - \frac{V_2(P_0, T)}{Q(P_0, T)} \int_{P_0}^P dP' \int_{P'}^{P_0} \frac{dP''}{\kappa_2(P'')} \\ & \left. + \frac{TV_1(P_0, T)}{Q(P_0, T)} \int_P^{P_0} \alpha_1 dP' + \frac{TV_2(P_0, T)}{Q(P_0, T)} \int_{P_0}^P \alpha_2 dP' \right] \end{aligned}$$

$$\times \left[1 + \frac{V_2(P_0, T)}{\Delta V(P_0, T)} \int_P^{P_0} \frac{dP'}{\kappa_1(P')} + \frac{V_2(P_0, T)}{\Delta V(P_0, T)} \int_{P_0}^P \frac{dP'}{\kappa_2(P')} \right]^{-1}, \quad (9)$$

where $\kappa_i = -V_i(P_0, T)(\partial V_i/\partial P)^{-1}$ is the bulk modulus of the i th phase.

2.3. Second derivatives of thermodynamic potentials at reversible phase transitions

In the case of an equilibrium reversible transition from phase 1 into phase 2, one of the equilibrium conditions along the curve of the transition points requires equality between the Gibbs free energies in the two phases.

$$\phi_1(P_0, T_0) = \phi_2(P_0, T_0). \quad (10)$$

Here the pressure P_0 is not an independent variable but depends on the temperature; $P_0 = P_0(T_0)$.

Differentiation of the Equation 10 with respect to temperature yields the Clapeyron-Clausius equation

$$S_2 - S_1 = \Delta S = \Delta V \frac{dP_0}{dT_0} \quad (11)$$

Let the jump of volume along the transition point curve be a known temperature function;

$$V_2 - V_1 = \Delta V = f(T_0) \quad (12)$$

(in the special case of transition of the second order $f(T_0) \equiv 0$). Then it follows from Equations 11 and 12 that the entropy jump along the transition point curve is

$$\Delta S = f(T_0) \frac{dP_0}{dT_0} \quad (13)$$

Differentiation of Equations 12 and 13 with respect to temperature yields

$$\Delta \left(\frac{\partial V}{\partial T} \right)_{P_0} + \frac{dP_0}{dT_0} \Delta \left(\frac{\partial V}{\partial P} \right)_{T_0} = \frac{df}{dT_0} \quad (14)$$

$$\begin{aligned} \frac{\Delta C_P}{T_0} - \frac{dP_0}{dT_0} \Delta \left(\frac{\partial V}{\partial P} \right)_{P_0} = \\ \frac{df}{dT_0} \frac{dP_0}{dT_0} + f(T_0) \frac{d^2 P_0}{dT_0^2} \end{aligned} \quad (15)$$

In the special case of a second order phase transition order, where $f(T_0) \equiv 0$, Equations 14

and 15 acquire the form of relations derived by Ehrenfest in 1933.

Now let us consider the formulae for the jumps of the other second derivatives of thermodynamic potentials. At an equilibrium phase transition the pressures in both phases remain unchanged;

$$P_1 = P_2 = P \quad (16)$$

where we take P_1 and P_2 to be functions of volume and temperature while the volume of each phase, V_1 and V_2 may be treated as a function of the temperature along the transition point curve in the P - T diagram. Differentiation of Equation 16 with respect to temperature with the aid of Equation 12 gives

$$\Delta \left(\frac{\partial P}{\partial T} \right)_V + \frac{dV_1}{dT_0} \Delta \left(\frac{\partial P}{\partial V} \right)_{T_0} + \left(\frac{\partial P}{\partial V_2} \right)_{T_0} \frac{df}{dT_0} = 0 \quad (17)$$

This may be rewritten as

$$\Delta \left(\frac{\partial P}{\partial T} \right)_V + \frac{dV_2}{dT_2} \Delta \left(\frac{\partial P}{\partial V} \right)_{T_0} + \left(\frac{\partial P}{\partial V_1} \right)_{T_0} \frac{df}{dT_0} = 0 \quad (18)$$

Similarly, assuming that the left side of Equation 13 is a function of volume and temperature, while the volume of each phase, V_1 and V_2 , along the curve of the P - T diagram is a temperature function, and differentiating Equation 13 with respect to temperature with the aid of Equation 12, we get

$$\begin{aligned} & \frac{df}{dT_0} \frac{dP_0}{dT_0} + f \frac{d^2 P_0}{dT_0^2} \\ &= \frac{\Delta C_V}{T_0} + \frac{dV_1}{dT_0} \Delta \left(\frac{\partial P}{\partial T} \right)_V + \left(\frac{\partial P}{\partial T} \right)_{V_2} \frac{df}{dT_0} \\ &= \frac{\Delta C_V}{T_0} + \frac{dV_2}{dT_0} \Delta \left(\frac{\partial P}{\partial T} \right)_V + \left(\frac{\partial P}{\partial T} \right)_{V_1} \frac{df}{dT_0} \quad (19) \end{aligned}$$

In the special case of a second order phase transition, $f(T_0) \equiv 0$ and $V_1 = V_2 = V$. Due to the coincidence between Equation 17 and 18, as well as Equation 19, we get the same result as that obtained by Landau in 1937.

2.4. Martensite transformation identification

Martensite transformations are accompanied by often significant inner stresses. This leads to an essentially thermodynamically irreversible character for martensite transformations, even under very low heating and cooling rates. As a result we have a finite difference between temperatures of the beginning of direct and reverse transformations. Elastic energy is often an essential part of the balance during martensite transformation, and this leads to a significant difference between Q/V and $Q/\Delta V$ during transformation. Therefore the martensite transformations usually belong to the process of type (b).

3. Point defects

Let us now discuss the case when the concentration of point defects is small and the interaction of point defects can be ignored, a condition which is usually satisfied. Let $g = g(P, T)$ be the change in the Gibbs free energy per defect. Then the atomic equilibrium concentration of point defects is

$$C_0 = \exp \left(-\frac{g}{kT} \right) \quad (20)$$

where k is Boltzmann's constant.

In course of plastic deformation, excess non-equilibrium point defects can appear, which are able to move and to annihilate. For the annihilating vacancies, the following relation holds [2];

$$V \frac{Q_v}{\Delta V_v} = \frac{E_v}{\alpha_v}, \quad (21)$$

where E_v is the work required for the formation of one g-atom of vacancies ($E_v = 17.9 \text{ kcal (g-atom)}^{-1}$) for copper at atmospheric pressure [4]), V is the volume of one g-atom of the specimen substance, and α_v is the atomic volume fraction occupied by a vacancy.

For interstitials we have, by analogy with Equation 21,

$$V \frac{Q_i}{\Delta V_i} = \frac{E_i}{\alpha_i - 1} \quad (22)$$

Here E_i is the work required for the formation of one g-atom of interstitials, and α_i is the atomic volume fraction occupied by one interstitial.

The work required for formation of one g-atom

of point defects is related to g by the expression

$$E = -N_L T^2 \frac{\partial}{\partial T} \left(\frac{g}{T} \right), \quad (23)$$

where N_L is the Loschmidt number.

At small concentrations of point defects, when their interaction may be neglected, the above annihilation of excess point defects is a process of the type (a). However the ratio of heat effects to volume ones, Equations 21 and 22, varies a little at different temperatures. The temperature at which the main part of the excess defects annihilates depends on the process kinetics (in particular, for example, on the temperature change rate during the annealing).

Hence we can somewhat alter the ratio of heat effects to volume ones by changing the conditions under which the process is developed (e.g. the rate of temperature change during annealing), but all the possible values of these ratios are confined in a narrow range.

Entropy is one of the most important thermodynamic functions for both reversible and irreversible processes. In the case of one point defect it consists of two parts, configurational and nonconfigurational.

$$\begin{aligned} \text{Configurational entropy} = \\ -k \left[\ln C + \frac{1-C}{C} \ln (1-C) \right], \end{aligned}$$

where C is the point-defect concentration (equilibrium or not). Nonconfigurational entropy (for both equilibrium and nonequilibrium defects) may be defined from

$$s = \frac{E}{N_L T} + k \ln C_0 = kT \frac{\partial \ln C_0}{\partial T} + k \ln C_0. \quad (24)$$

The motion of point defects within an homogeneous crystal is not accompanied by the evolution of heat or by body volume change. The redistribution of point defects in a crystal containing sources of inner stresses (e.g. dislocations) may be described in the same way as that of impurities. The heat evolution and body volume change resulting from impurity redistribution will be treated in Section 5.

Frenkel pairs may be formed in solids during irradiation. A Frenkel pair is a vacancy bound to

an interstitial, so if Frenkel pairs annihilate,

$$V \frac{Q_F}{\Delta V_F} = \frac{E_F}{\alpha_v + \alpha_i - 1} \quad (25)$$

where E_F is the work required for the formation of one g-atom of Frenkel pairs, which includes interaction energy and so it depends on the distance between the defects in a pair and orientation of the pair. Formation of a Frenkel pair leads to a volume change, which according to the linear elasticity theory is a sum of volume changes due to the formation of a vacancy and an interstitial.

4. Dislocation processes

4.1. Dislocation contribution to the crystal volume and enthalpy

It turns out that the main contribution in the dislocation energy is from long-range elastic fields, dislocation cores contribute no more than 10 to 15% [5]. Numerical calculations [6] also show that the contribution of dislocation cores to the change in crystal volume is also no more than 10 to 15% of the total volume change due to the dislocation's presence. Therefore we shall ignore the dislocation cores henceforth, and only consider their elastic fields.

The volume change for a crystal containing dislocations may be described only within the framework of nonlinear elasticity theory.

Zener [7] was the first to study the volume change in case of an elastically isotropic crystal containing dislocations. He deduced a formula similar to that for the elastic energy stored during the deformation of isotropic continuum.

Seeger and Stehle [8] have developed the microscopic theory of volume effects for an isolated screw dislocation situated in a crystal of definite shape, and this has been applied to particular types of dislocations [11, 12]. Their results may be obtained rather simply by the thermodynamic method [9]. A consistent nonlinear theory of volume effects in anisotropic crystals containing dislocations was developed by Toupin and Rivlin [10].

It can be shown that in the general case, when a cubic crystal belonging to one of the most symmetrical subgroups, O , O^h or T^h is subjected to the action of an arbitrary high hydrostatic pressure, the change in the crystal volume due to the presence of dislocations is given by the

formula

$$\begin{aligned} \Delta V &= a \int_{(V)} u_{ik} u_{ik} d\tau + b \int_{(V)} u_{ii}^2 d\tau + c \int_{(V)} (u_{11}^2 + u_{22}^2 + u_{33}^2) d\tau, \\ a &= -\frac{2C_{166} + C_{144} + C_{11} + 2C_{12} + 4C_{44} - 2P}{C_{11} + 2C_{12} + P} \\ b &= -\frac{C_{112} + 0.5C_{123} - 0.5C_{11} + C_{12} + P}{C_{11} + 2C_{12} + P} \\ c &= -\frac{0.5C_{111} - 0.5C_{123} - 2C_{166} - C_{144} + 2C_{11} - 2C_{12} - 4C_{44}}{C_{11} + 2C_{12} + P} \end{aligned} \quad (26)$$

Here V is the crystal volume, C_{ik} and C_{ikl} are the crystal elastic moduli of the second and third orders, respectively, u_{ik} is the tensor of linear deformations caused by the presence of dislocations in a hydrostatically compressed crystal. This tensor may be obtained from the linear deformation tensor for dislocations in the crystal without external pressure. The procedure is as follows: we substitute $b(P)$ for the Burgers vectors \mathbf{b} , and the resolved moduli for the elastic moduli of the second order,

$$\begin{aligned} C_{iklm} \rightarrow \bar{C}_{iklm} &= C_{iklm}(P) \\ &+ P(\delta_{ik}\delta_{lm} - \delta_{il}\delta_{km} - \delta_{im}\delta_{kl}) \end{aligned} \quad (27)$$

Equations 26 and 27 are in accord with the results obtained for the corresponding special cases in the references cited.

The dislocation contribution to the crystal enthalpy is

$$Q = \frac{1}{2} \bar{C}_{iklm} \int_{(V)} u_{ik} u_{lm} d\tau \quad (28)$$

which in the case of a cubic crystal gives

$$\begin{aligned} Q &= \frac{1}{2} \bar{C}_{44} \int_{(V)} u_{ik} u_{ik} d\tau + \frac{1}{2} \bar{C}_{12} \int_{(V)} u_{ii}^2 d\tau \\ &+ \frac{1}{2} (\bar{C}_{11} - \bar{C}_{12} - 2\bar{C}_{44}) \int_{(V)} (u_{11}^2 + u_{22}^2 + u_{33}^2) d\tau \end{aligned} \quad (29)$$

4.2. Heat to volume effect ratio

Equations 26 and 29 yield

$$\frac{Q}{\Delta V} = \frac{2\bar{C}_{44} + \bar{C}_{12}\beta + (\bar{C}_{11} - \bar{C}_{12} - 2\bar{C}_{44})\delta}{2a + 2b\beta + 2c\delta}, \quad (30)$$

where

$$\delta = \frac{\int_{(V)} (u_{11}^2 + u_{22}^2 + u_{33}^2) d\tau}{\int_{(V)} u_{ik} u_{ik} d\tau} \quad \beta = \frac{\int_{(V)} u_{ii}^2 d\tau}{\int_{(V)} u_{ik} u_{ik} d\tau} \quad (31)$$

and for dislocations [13]

$$0 \leq \delta, \delta \leq 1 \quad (32)$$

One can see from Equations 30 and 31 that for different types of dislocation or for different distributions in the crystal there are specific ratios of heat to volume effects. The values of these ratios may differ by no more than 30% at usual magnitudes of elastic moduli [13] but may also be exactly the same [14] (e.g. in the case of randomly distributed dislocations and dislocations gathered in the polygonal walls).

For the elastically isotropic medium we may write

$$\begin{aligned} \bar{C}_{11} - \bar{C}_{12} &= 2\bar{C}_{44} \\ 8C_{456} + C_{123} + 6C_{144} &= C_{111} \\ 2C_{144} + C_{123} &= C_{112} \\ 2C_{456} + C_{144} &= C_{166} \end{aligned} \quad (33)$$

and the coefficients before δ in Equation 30 are zero.

That is why knowledge of one structural factor β is enough for the model of the elastically isotropic medium. In the case of anisotropic crystal we may estimate both β and δ from the approximation of the elastic isotropic medium, e.g. for the screw dislocations we have in this approximation $\beta = \delta = 0$. For the straight edge dislocations in the unlimited crystal we may write

$$\beta = \frac{2(1-2\sigma)^2}{1+(1-2\sigma)^2}, \quad \delta = \frac{1+2(1-2\sigma)^2}{2+2(1-2\sigma)^2}, \quad (34)$$

where σ is the Poisson's ratio.

If the dislocation distribution is not uniform, the values of heat and volume effects may differ greatly from those for the case of uniformly distribution [14]. However, their ratio varies little after redistribution of the dislocations. Thus, e.g. for pile-ups in the Stroh model [15]

we get, according to the approximation adopted in [16],

$$\beta = \frac{16(s_{11} + 2s_{12})^2}{13s_{11}^2 + 29s_{12}^2 + 6s_{11}s_{12} + 5s_{44}^2}$$

$$\delta = \frac{13s_{11}^2 + 29s_{12}^2 + 6s_{11}s_{12}}{13s_{11}^2 + 29s_{12}^2 + 6s_{11}s_{12} + 5s_{44}^2}, \quad (35)$$

where s_{ik} are the elastic constants. It turns out [16] that for the piled-up dislocations the values of heat and volume effects may be an order of magnitude higher than those for randomly distributed dislocations, but the value of their ratio differs little in these two cases.

4.3. Dissociated dislocations

Let us now take the case where a dislocation with Burgers vector \mathbf{b}_3 dissociates into two partial Shockley dislocations with Burgers vectors \mathbf{b}_1 and \mathbf{b}_2 [17].

Here the volume effects get contributions not only from each partial dislocation but also from the overlapping of their fields. The complete volume effect is

$$\Delta V = (\Delta V_1 + \Delta V_2) \left[1 + \frac{1}{4} \left(\ln \frac{L}{r_0} \right) \left(\ln \frac{Lq}{2\pi} \right) \right] \quad (36)$$

where ΔV_1 and ΔV_2 are the volume effects due to each of the partial linear dislocation, r_0 the space between partial dislocations L the crystal grain size and q_D is the limiting value for the wave vector of the phonons in the Debye theory of heat capacity. The total energy of the dissociated dislocation, including the stacking fault energy, is

$$\mathcal{E} = (\mathcal{E}_1 + \mathcal{E}_2) \left[1 + \frac{1}{4} \left(1 + \ln \frac{L}{r_0} \right) \left(\ln \frac{Lq_D}{2\pi} \right) \right] \quad (37)$$

Here \mathcal{E}_1 and \mathcal{E}_2 are the energies of each partial dislocation.

The ratio of heat to volume effect for dissociated dislocations $(Q/\Delta V)_{\text{dd}}$ is directly related to that for perfect dislocations $(Q/\Delta V)_d$ by the formula

$$\left(\frac{Q}{\Delta V} \right)_{\text{dd}} = \left(\frac{Q}{\Delta V} \right)_d \left[1 + \left(4 \ln \frac{Lq_D}{2\pi} + \ln \frac{L}{r_0} \right)^{-1} \right]. \quad (38)$$

Since as a rule $\ln(Lq_D/2\pi) \approx 5$, it may be concluded that the heat to volume effect ratio for

perfect dislocations differs from that for dissociated ones only by a few percent.

The results given above show that such processes as polygonization, dislocation annihilation and relaxation of approximately one-type dislocation clusters may be accurately regarded as processes of type (a). In the case when the main contribution to the change of the enthalpy and the crystal volume on recrystallization is provided by the dislocation annihilation, the recrystallization itself may also be regarded accurately as the process of type (a).

It should be noted that, just as in the case of vacancy annihilation, the change in the annealing rate leads to a shifting of the temperature intervals of the dislocation processes and thus to a small variation of the heat and volume effects ratio.

5. Redistribution of point imperfections

Let us begin with redistribution of point imperfections (point defects, impurities) in the field of elastic stresses. The point imperfections have an inhomogeneous equilibrium distribution [5] which depends on the interaction energy between point imperfections and deformation. Calculations carried out within the framework of the linear elasticity theory [5] represent the point imperfection as either a singularity [18], or a continuous inclusion whose volume is not equal to that of the cavity in the matrix and whose elastic properties differ from those of the matrix. According to these calculations the interaction of the point imperfection with deformation may be described by the formula

$$\Delta\phi = -\bar{K}v_0u_{11} \quad (39)$$

where $\Delta\phi$ is the variation of the Gibbs free energy from the interaction between the point defect and deformation, \bar{K} is the reduced bulk modulus of the cubic crystal, v_0 is the crystal volume change caused by the introduction of the cubically symmetric point imperfection, u_{11} is the dilatation due to internal deformation of the point imperfection.

The elasticity theory fails in the region near the point imperfection as well as in the imperfection itself, so that Equation 39 may be inaccurate. When smooth deformations are considered, the expansion of the addition* to Equation 39 into a

*This addition is due to the fact that the local Gibbs free energy in and near the point imperfection deviates from the value predicted by the elasticity theory.

series, by deformation and the symmetry of the problems, result in the following expression;

$$\Delta\phi = -(\bar{K}v_0 + \epsilon)u_{II} + \dots \quad (40)$$

It appears that $\epsilon = 0$. To prove this let us consider the special case where deformation, u_{II} , is due to a change in the pressure from P to $P + \Delta P$. From Equation 40,

$$\Delta\phi = (\bar{K}v_0 + \epsilon) \frac{\Delta P}{\bar{K}} \quad (41)$$

On the other hand, if $\phi(P, T)$ is the Gibbs free energy of the crystal containing imperfections, subjected to the external pressure P , then the system Gibbs free energy will be altered with the pressure change by $\phi(P + \Delta P, T) - \phi(P, T)$. This variation consists of the changes caused by the interaction between deformations and imperfection, Equation 41, and changes in the Gibbs free energy of the ideal crystal caused by the pressure variation $\phi_0(P + \Delta P, T) - \phi_0(P, T)$. Therefore it may be written

$$\Delta\phi = \phi(P + \Delta P, T) - \phi(P, T) - [\phi_0(P + \Delta P, T) - \phi_0(P, T)] \quad (42)$$

Expanding Equation 42 into a series for small ΔP , and considering only the first term of the series, a comparison of the result with Equation 41 gives $\epsilon = 0$, (here the following thermodynamic relations were used:

$$\left(\frac{\partial\phi}{\partial P}\right)_T = V, \quad \left(\frac{\partial\phi_0}{\partial P}\right)_T = V_0$$

where V and V_0 are the volume of the crystal containing a point imperfection and of the ideal crystal, respectively; $V - V_0 = v_0$).

Thus Equation 39, although derived by means of the models (inadequate for a point imperfection) of the elasticity theory, turned out to be correct.

If a single point defect reaches the dislocation axis, the existing kink in the dislocation line is shifted by one atomic unit; a pair of point defects can give rise to formation of new kinks and hence to changes in the crystal Gibbs free energy and in the volume (according to the formulae given in the preceding sections).

Penetration of the impurity into the dislocation core results in heat and volume effects. Dislocation cores are very important for such effects in some cases of dislocation ageing [19]. The dislocation

ageing is generally a type (b) process. However at low impurity concentrations, when the main contribution to heat and volume effects is provided by terms proportional to the first degree of the impurity concentration, the values Q and ΔV are proportional to the amount of impurity, and an approximation treating the dislocation ageing as the type (a) process is not so bad. If the annealing rate is varied, the temperature interval of the dislocation ageing is shifted, changing the heat to volume effects ratio.

6. Grain-boundary contribution to heat and volume effects

6.1. Contribution to the enthalpy

First of all we evaluate the energy of non-dislocation boundaries which are not the stress sources in the material. Let every thousandth crystal atom belong to the boundary, so that the general boundary area amounts to $\sim 10^5 \text{ cm}^{-1}$ (per cm^3). The total boundary energy is about 10^8 erg cm^{-3} for a density of boundary surface energy $\gamma = 10^3 \text{ erg cm}^{-2}$. This approximately corresponds to the dislocation stored energy for a density of dislocations of nearly 10^{11} cm^{-2} . It follows from such an evaluation that in the case of a fine-grain structure, the boundary energy can contribute greatly to the crystal's total energy and this contribution should be taken into account for each special case. In a coarse-grain material of sufficiently high dislocation density the boundary contribution to the total energy is insignificant.

There is one more mechanism by which the grain-boundary energy of a polycrystal may be increased; the stresses due to the interaction between the adjacent grains. Let τ_0 denote a typical stress value, and μ be the shear modulus. The order of magnitude of the energy associated with these stresses is $\mathfrak{E} \approx \mu^{-1} \tau_0^2$.

If $\tau_0 = 3 \times 10^{-3} \mu\text{m}$, $\mu = 10^{12} \text{ erg cm}^{-3}$, we get $\mathfrak{E} = 10^7 \text{ erg cm}^{-3}$, an order of magnitude below the boundary energy in a fine-grain material. In particular, the stresses τ_0 in the noncubic crystal may be of thermal origin and in the case of a rapid cooling (from $\sim 10^3 \text{ K}$ to room temperature) may contribute considerably to the distortion energies (up to 10^9 erg cm^{-3}).

Let us now consider the case when the grain boundaries serve as the stress sources (e.g. dislocation boundaries). If the dislocation density in the crystal is high (of the order 10^{11} cm^{-2} or more) the number of dislocations in the grain boundaries

is at least several times smaller than the total number of dislocations in the crystal. If the boundary stresses vanish rapidly with increasing distance from the boundary, the boundary dislocation contribution to the energy is at least several times smaller than that from the crystal dislocations.* Thus in crystals with a high dislocation density, such boundary dislocations contribute to the total distortion energy of the crystal much less than randomly distributed crystal dislocations. If in such cases dislocation boundaries and crystal dislocations disappear at recrystallization, the main contribution to the heat effect is provided by the annihilation of randomly distributed dislocations.

If the crystal dislocation density is not high, the equidistant dislocation boundary contribution to the energy may be significant and should be considered in each special case. Boundaries which consist of randomly situated dislocations have energy which is an order of magnitude (or more) higher than that of equidistantly situated dislocation boundaries of the same number of dislocations.

6.2. Contribution to the volume

Let us now evaluate the grain-boundary contribution to the polycrystal solid volume. We first consider the case of nondislocation boundaries when the boundaries are not stress sources in the material.

Let each thousandth crystal atom belong to the boundary. Assuming that the substance density in the boundary is not less than in the melted metal, then for copper one finds that the relative volume effect created by the boundaries does not exceed 5×10^{-5} . This is an order of magnitude less than the volume effect caused by randomly distributed dislocations of 10^{11} cm^{-3} . The volume effect due to interaction of adjacent grains of the order $\Delta V/V \approx 5(\tau_0/\mu)^2$ and is 5×10^{-5} at $\tau_0 = 3 \times 10^{-3} \mu$. When a polycrystal consisting of non-cubic crystallites is cooled rapidly from T to T_0 we have, since the coefficient of thermal expansion α depends on direction

$$T_0 \approx (\alpha_{\max} - \alpha_{\min})(T - T_0)\kappa \approx 10^{-2}\kappa.$$

at $\alpha_{\max} - \alpha_{\min} = 10^{-5} \text{ K}^{-1}$ $T - T_0 \approx 10^3 \text{ K}$, and $\Delta V/V$ is approximately 5×10^{-4} .

The thermal stresses are low at recrystallization, since it tends to relax the inner stresses;

*We have such a situation when the boundary consists of equidistantly situated dislocations.

the boundaries do not contribute significantly to the volume effect. Therefore the main contribution to the volume effect during recrystallization is provided by dislocation annihilation.

Let us now consider the case when the grain boundaries are the sources of inner stresses. Since the formulae describing the enthalpy in the deformed crystal are of the same structure as those derived for the volume change, the relative contribution from the dislocation boundaries to the volume effects will be the same as that to the heat effects.

Thus during recrystallization the main contribution to the volume effects, in the case when the equidistant dislocation boundaries are obliterated, is provided by the annihilation of random crystal dislocations as in the case when nondislocation boundaries are obliterated. The contribution of the randomly situated dislocations on the boundaries ought to be taken into account.

7. Heat and volume effects in crystals containing cracks

A crack may be described in terms of dislocations if the structure of the dislocation core is considered. The nature of the dislocation core was studied by several authors [15, 20–28], and the results of these investigations are summarized in [29]. It is shown that when the Burgers vector is equal to 3 to 4 interatomic spaces or more, the superdislocation core becomes hollow and a wedge-like crack appears. The energy of the unit length of the wedge crack with Burgers vector νb is given by [30]

$$\frac{\mathcal{E}}{L} = \frac{\mu\nu^2 b^2}{4\pi(1-\sigma)} \ln \frac{L}{2h_\nu} + \gamma(\nu b + \sqrt{(\nu^2 b^2 + 4h_\nu^2)}) \quad (43)$$

Here h_ν is the altitude of the wedge-crack. The first term in Equation 43 gives the contribution of the deformation around the wedge-crack to the crystal elastic energy, the second the surface energy of the crack cavity. The volume change of the crystal due to the wedge-crack is, per unit length,

$$\frac{\Delta V}{L} = f\nu^2 b^2 \ln \frac{L}{2h_\nu} + \frac{1}{2}\nu_b h_\nu. \quad (44)$$

Here f is a factor of the order of 10 and depends on the crystal elastic moduli of the second and

third order; the first term in Equation 44 is the crystal volume of the crack cavity. The entropy contribution for the cracks is small enough so that the Gibbs free energy of the unit length of a crack coincides with the enthalpy and is

$$\frac{Q}{L} = \frac{\phi}{L} = \frac{\bar{\mu} \nu^2 b^2}{4\pi(1-\bar{\sigma})} \ln \left(\frac{L}{2h_v} \right) + \gamma(\nu b + \sqrt{(\nu^2 b^2 + 4h_v^2)}) + \frac{P}{2} \nu b h_v, \quad (45)$$

where $\bar{\mu}$ and $\bar{\sigma}$ are the reduced shear modulus and the Poisson's ratio respectively. The equilibrium altitude of the wedge-crack is defined by the condition

$$\frac{\partial}{\partial h_v} (\phi/L) = 0 \quad (46)$$

From this condition we have

$$P b \nu h_v + 8\gamma h_v^2 (\nu^2 b^2 + 4h_v^2)^{-1/2} = \frac{\bar{\mu} \nu^2 b^2}{2\pi(1-\bar{\sigma})} \quad (47)$$

If pressure is not extremely high, so that $h_v \gg \nu b$, Equation 47 may be simplified to

$$h_v = \frac{\bar{\mu}}{2\pi(1-\bar{\sigma})} \frac{\nu^2 b^2}{4\gamma + P b \nu}. \quad (48)$$

At extremely high pressure conditions we may run into a case when $h_v \ll \nu b$. For this case, Equation 47 yields

$$h_v = \frac{\bar{\mu}}{1-\bar{\sigma}} \frac{\nu b}{2\pi P}, \quad \frac{\bar{\mu}}{1-\bar{\sigma}} \ll 2\pi P. \quad (49)$$

The surface energy γ may be estimated as $\mu b / 4\pi(1-\sigma)$ [30]. In this case, at $P=0$, instead of Equation 48 we have $h_v = \frac{1}{2} \nu^2 b$. Using this value and Equation 44, we get that the crack cavity volume is larger than the elastic deformations volume effect if

$$\nu > \nu_0 = 4f \ln \left(\frac{L}{\nu_0^2 b} \right). \quad (50)$$

For $f=5$, $\ln(L/\nu_0^2 b) = 5$ we get $\nu_0 = 100$.

The ratio of heat content and volume change rates during the processes of crack-alteration (formation, growth and healing) depends on the degree of development; that is, such processes belong to the type (b). In addition, the relation mentioned above certainly depends on temperature and pressure and hence varies with the process rate since the temperature and pressure intervals of the process development are shifted.

8. Heat and volume effects in the crystals containing pores

Vacancies may form complexes which may grow into pores. For the case of annihilation of excess vacancies in copper, the heat to volume effects ratio is 1.75×10^{11} erg cm⁻³. According to G. Vineyard's calculation [31] the heat to volume effects ratio in copper makes up 2.3×10^{11} erg cm⁻³ for annihilation of divacancies, and 1.3×10^{11} erg cm⁻³ for annihilation of trivacancies. Vineyard's calculations for tetra-, penta- and heptavacancies are widely scattered, following the general rule that the higher the number of vacancies in the complex, the lower the heat to volume effects ratio on the annihilation of the complex. The ratio is the highest for divacancies as expected, since divacancies are elongated in one direction most.

The energy evolved when the next vacancy joins the complex decreases with the growth of the complex size, until it becomes energetically unfavourable for a vacancy to enter a complex made up on N^* vacancies. Complexes whose number of vacancies is larger than N^* may be conventionally regarded as pores.

Let us consider the case when external pressure is much less than the crystal elastic moduli. According to the continuum theory it is energetically unfavourable for the vacancy to join a pore of the radius

$$r < r^* = 2\gamma V [E_v - P(1-\alpha_v)V]^{-1}$$

because such attachment would be accompanied by the heat absorption. The radius r^* corresponds to the number of vacancies constituting this pore,

$$N^* = 32 \frac{\pi}{3} \left[\frac{\gamma V}{E_v - P(1-\alpha_v)V} \right]^3 N_0, \quad (51)$$

where N_0 is the number of atoms per crystal unit volume.

For copper at $P=0$, we get $N^* \approx 7$. These estimations are beyond the limits of applicability of the continuum theory and therefore can be considered as qualitative only. Since the pore is a thermodynamically nonequilibrium defect it can be healed, in which case, just as with the healing of vacancies and their complexes, the volume of the body is decreased and heat is evolved. Here the following relation is valid

$$\frac{Q}{\Delta V} = \frac{3\gamma}{r} + P. \quad (52)$$

If the specimen contains pores of various radii then, in Equation 52,

$$r = (\sum_i r_i^3) (\sum_j r_j^2)^{-1} \quad (53)$$

with the summations carried out over all the pores.

At a definite pore size r_1 , the heat to volume effects ratio at healing is the same as for vacancies,

$$r_1 = 3\gamma\alpha_v V [E_v - \alpha_v P V]^{-1}. \quad (54)$$

The number of vacancies making up such a pore is

$$N_1 = 36\pi\gamma^3\alpha_v^3 V^3 N_0 (E_v - \alpha_v P V)^{-3}. \quad (55)$$

For copper at $P = 0$, we get $N_1 = 20$. For $N > N_1$, the heat to volume effects ratio is lower than for vacancies, while for $N < N_1$ it is higher.

If the specimen contains a large enough number of excess vacancies, complexes can be formed which are able to grow into pores. The growth of the pore due to coagulation of excess vacancies is possible when the total vacancy concentration dominates the local equilibrium vacancy concentration near the pore C , which is higher than the equilibrium vacancy concentration C_0 :

$$C \approx C_0 \exp \left[\frac{2\gamma}{rkTN_0} + P \frac{1 - \alpha_v}{kTN_0} \right]. \quad (56)$$

It is easy to see that large pores will grow first, the finer the pore, the more difficult and slow is its growth. Equation 55 yields $C = 1.53 C_0$ for copper at $P = 0$, $kT = 8 \times 10^{-4}$ erg, and $r = 10^{-6}$ cm.

However, there may be another cause for pore growth. Let us assume that the specimen contains an impurity gas, insoluble or badly soluble in the metal. The gas atoms will evolve into the pores or their nuclei, thus stimulating pore growth. The heat and volume effects ratio for the vacancy coagulation into the pore is

$$\frac{Q}{\Delta V} = \frac{3\gamma r^{-1} + P_0 \left(\frac{5}{2} - \frac{\mathcal{E}}{kT} \right) - E_v V^{-1}}{1 - \alpha_v - \beta P_0 (N_0 kT)^{-1} + (P_0 - P - 2\gamma r^{-1}) \kappa^{-1}} + P$$

where P_0 is the gas pressure in pores. If this pressure differs from pore to pore then

$$P_0 = (\sum_i P_{0i} r_i^3) (\sum_j r_j^3)^{-1}. \quad (58)$$

r is defined by Equation 53, \mathcal{E} is the interaction

energy of the impurity gas atom and the metal, β is the atomic volume fraction occupied by gas atoms in the metal.

It follows from Equation 57 that for

$$r_1 = r_2 = 2\gamma \left(\frac{3}{2} - \frac{P}{\kappa} \right) \left[E_v V^{-1} + P_0 \left(\frac{\mathcal{E}}{kT} - \frac{5}{2} \right) + P \left(\alpha_v + \beta \frac{P_0}{N_0 kT} + \frac{P - P_0}{\kappa} - 1 \right) \right]^{-1}, \quad (59)$$

Equation 57 reduces zero; its sign is positive when $P = P_0 = 0$ and $r < r_2$, and negative when $r > r_2$. The physical reason for the fact that Equation 57 reduces to zero is that when the pores of the radius r_2 are formed, the system neither evolves nor absorbs the heat, although its volume is changed. The number of vacancies constituting this pore at $P = P_0 = 0$ is

$$N_2 = N_1 \alpha_v^{-3}, \quad (60)$$

For the copper $N_2 = 95$.

When the vacancy coagulation into pores occurs without gas evolution into the pores, the volume of the body will always increase. Heat is evolved if $r > r_2$, but absorbed if $r < r_2$.

All the processes which are accompanied by the change in the pore state belong to type (b). The ratios $Q/\Delta V$ and \dot{Q}/\dot{V} for these processes are somewhat different for various rates of the processes.

9. Simultaneous development

Preceding sections were concerned with the ratio of enthalpy and volume change rates in solids, and the ratio of heat and volume effects for various processes that occur in solids when thermodynamical parameters are changed. Fig. 1 shows the curves of the heat evolution rate and volume change for a sample of high purity plastically deformed nickel [32]. The first peak corresponds to vacancy annihilation, the second to recrystallization. Fig. 2 compares \dot{Q}/\dot{V} and $Q/\Delta V$ for both processes; one can see that both processes prove to be of type (a) within the limits of experimental error.

In preceding sections it was found that the ratios under study depend on various parameters of the solid. These parameters are at present considered as independent, and it is no surprise that the ratios under study are very different in one and the same metal. This difference can be used to identify elementary processes and

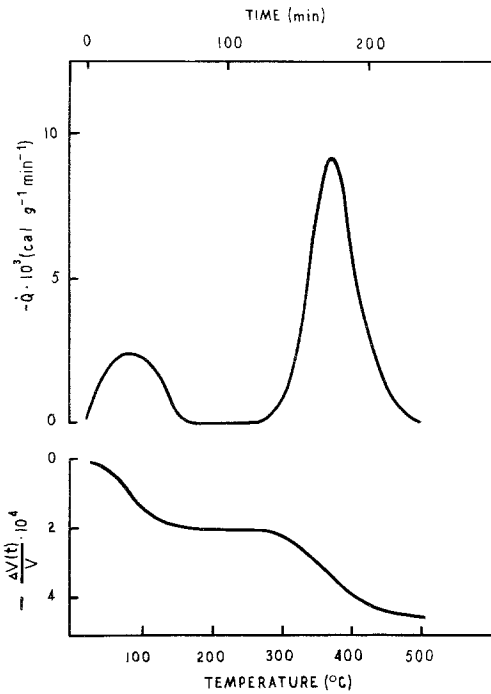


Figure 1 Heat evolution rate $-\dot{Q}$ and volume change $\Delta V(t)/V$ during annealing at $2^\circ \text{C min}^{-1}$ of high purity twist-deformed ($nd/l = 0.6$) nickel [32].

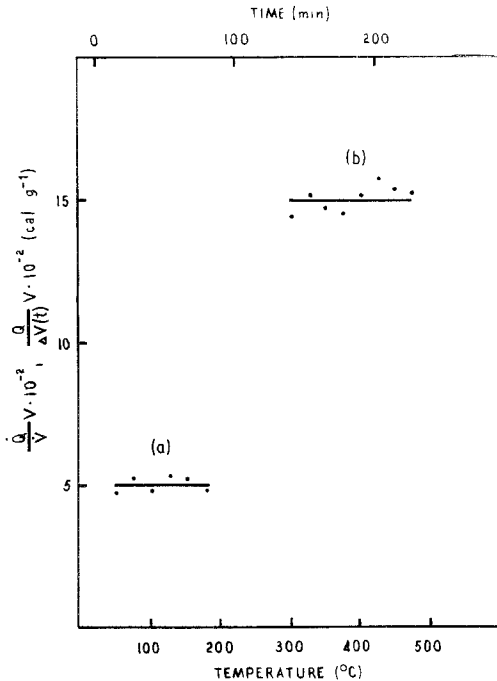


Figure 2 Enthalpy to volume change ranges ratio $V\dot{Q}/\dot{V}$ (dots), and heat to volume effects ratio $VQ/\Delta V$ (line), for (a) vacancy annihilation and (b) recrystallization (data of [32]).

separate of their various contributions. To the authors knowledge, there are no cases of coincidence of heat to volume effects ratios for different processes in any metal. Fig. 3 shows a typical scheme of heat and volume effects ratios for various elementary processes occurring during strengthening and softening of solids.

We now consider the case when several processes take place simultaneously. For example, if there are two simultaneous type (a) processes whose ratios $\dot{Q}_1/\dot{V}_1 = A_1(P, T)$, $\dot{Q}_2/\dot{V}_2 = A_2(P, T)$ are known, one may determine their contribution, to the observed heat effects $Q(t)$ and volume $\Delta V(t)$ effects (the time dependences of temperature and pressure are also to be measured). For example, the first process contribution to the heat effect is

$$Q_1(t) = \int_0^t \frac{A_1(P, T)}{A_1(P, T) - A_2(P, T)} [\dot{Q} - A_2(P, T)\dot{V}] d\tau \quad (61)$$

(it should be remembered that $P = P(t)$, $T = T(t)$). Similar formulae may be deduced for $Q_2(t)$, $\Delta V_1(t)$ and $\Delta V_2(t)$. It is noteworthy that the degree of process development (both of the types (a) and (b) is determined by the ratio $Q_i(t)/Q$ or by another ratio, connected with the first, $\Delta V_i(t)/\Delta V$. The elementary process contribution to a composite process is given either by the fraction Q_i/Q or by the fraction $\Delta V_i/\Delta V$ connected with the first.

Thus the combined and simultaneous measurement of the enthalpy and volume changes rates in solids can provide information for identification of not only a single type (a) process but also two simultaneous type (a) processes, and allows evaluation of their relative contributions to heat and volume effects. If more than two processes of type (a) occur in a solid simultaneously, contributions can be distinguished by means of simultaneous measurement of \dot{Q} , \dot{V} and other physical parameters (e.g. electrical resistance and other transport characteristics).

To follow the development of one process of the type (b) it suffices to measure \dot{Q} and \dot{V} simultaneously. Here the degree of the process development is determined by the ratio \dot{Q}/\dot{V} , and by each of the parameters $Q(t)$ and $\Delta V(t)$, while the process rate is described by \dot{Q} and \dot{V} . If this process is accompanied by others, additional

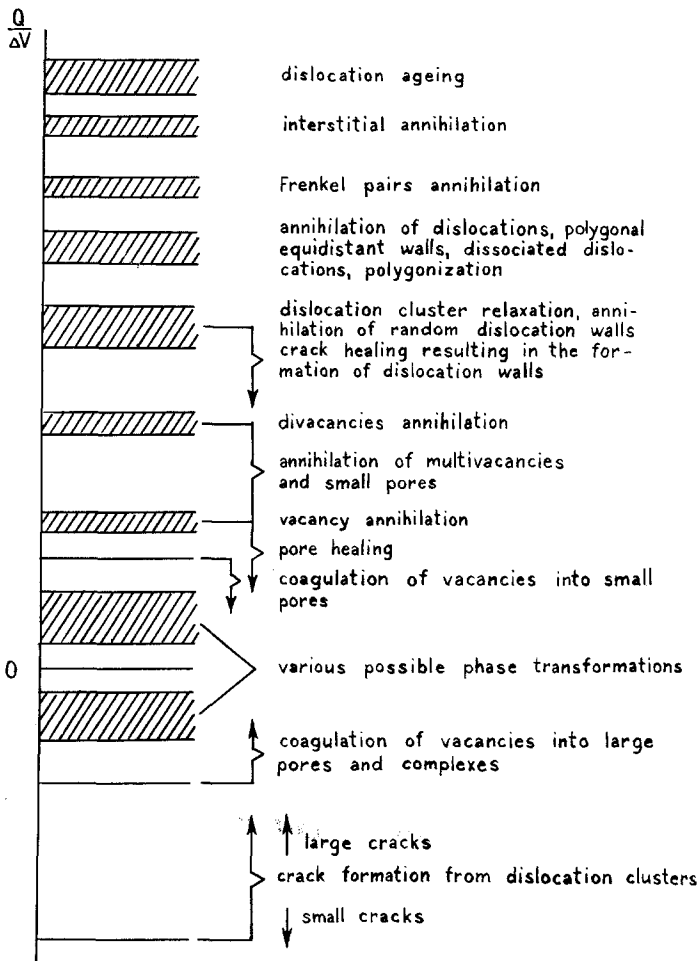


Figure 3 Typical scheme of heat and volume effects ratios $Q/\Delta V$ for various elementary processes.

measurements of other physical parameters become necessary to interpret the picture.

In both general case and the case when ratios coincide (the case of degeneration), the following features should be used for identification:

- (1) absolute values of total heat and volume effects,
- (2) the sign of each effect,
- (3) the signs of \dot{Q} and \dot{V} which may be coincident or not,
- (4) the value of ratios $Q/\Delta V$ and \dot{Q}/\dot{V} ,
- (5) coincidence or noncoincidence of $Q/\Delta V$ and \dot{Q}/\dot{V} ratios,
- (6) possibility of direct and reverse transitions,
- (7) presence or absence of the hysteresis in this case.

10. Application to real processes

Mechanical and thermal treatments of metals and alloys give rise to a series of processes (phase transformations, formation, interaction and anni-

hilation of defects in the crystal structure). Solid-state physics has proposed methods for investigating phase transformations and various types of defect (separately or in combinations), when their concentration is not too high. Diffraction methods have helped immensely in the investigation not only of phase transformations but also of linear defects in weakly strengthened metals, while the auto-ionic microscope made it possible to observe single defects and the true structure of grain boundaries in metals. However, neither of these methods provides quantitative information about the nature of processes that arise during high strengthening of commercial alloys under real conditions.

During the last two decades new methods were developed (solid state calorimetry and the volumetric method) to study the variety of structural and phase transformations that occur at high strengthening and thermal softening of metals and alloys. As late as the fifties, attempts were

made in Australia and the USA to determine the general quantity of vacancies and dislocations created during deformation of various metals. The authors used both volumetric and calorimetric measurements, and theoretical evaluations of energy and volume of single defects (without consideration of their interactions). Boas [33] in his report at the Lake Placid Conference, 1956, gave data on the dislocation density in highly deformed nickel. These data were calculated on the basis of calorimetric and volumetric measurements carried out at Melbourne University and showed a discrepancy of an order of magnitude. It was pointed out during the discussion of this report that the measure chosen for evaluation of the volume change per dislocation was rather rough, cracks and pores could be formed, and that dislocation ageing took place in the samples with high impurity content.

Clarebrough *et al.* [34] compared the results of calorimetric measurements obtained by Australian and American authors with the results obtained by the English authors who measured the dislocation density by the method of diffraction electron microscopy on samples of moderately deformed metals [35, 36]. The conclusion was drawn that the results for silver and nickel were in a good agreement, results for copper gave three times the discrepancy. Large deviation (by the order of magnitude) was found for aluminium, and this was attributed to the fact that a great number of dislocations disappeared from this metal during the preparation of thin foils. The authors of the report also compared data on the change of macroscopic density in samples of silver, copper and nickel (highly deformed by compression, $\epsilon = 70$ to 75%) with data on dislocation densities in the same metals obtained by the comparison of the results from calorimetric and electron microscopic measurements. The authors have found that the change in the crystal volume due to dislocations makes up 0.8 the atomic volume per atomic plane for nickel, 1.9 for silver and 3.7 for copper. Such a result for Ni and Ag varies little from the theoretical evaluation [8], which gives about 1.5 atomic volumes per atomic plane for edge dislocation and 0.75 for screw. The agreement for copper is much worse, perhaps because of the difference between calorimetric and electron microscopic measurements for this metal.

Investigations carried out in 1963 in the Insti-

tute of Metal Physics in Kiev (Academy of Sciences of the Ukrainian SSR) [1, 2] demonstrated that the processes occurring during heating of metals subjected to mechanical or thermal hardening might be analysed more successfully in terms of heat and volume effects ratios. It was shown, in particular, that such an approach made it possible to separate reliably the point defect annihilation from the linear defect annihilation, and to distinguish both these processes from the carbide phase transformations in steels. Later, these investigations were extended to a series of metals [2, 32, 37] (results are summarized in [38]). The new approach also allowed investigation of the physical nature of high strength resulting from low-temperature thermo-mechanical treatment and from patenting [39–42].

On the basis of the approach described in this paper, a method was developed for determining the plastic deformation limit within which the microcavities that have been formed do not yet contribute markedly to the strength and thermodynamic properties of the metal [16]. Here the fact was used that the heat to volume effects ratio on annealing highly deformed steels can deviate from its constant value, corresponding to the relaxation process of dislocation pile-ups, by no more than 0.1 if there are no microcavities in the crystal. Hence significant deviation of the measured ratio from this constant value

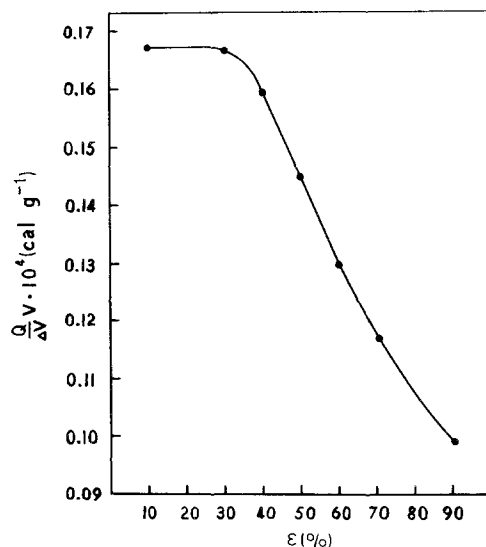


Figure 4 Heat and volume effects ratio $VQ/\Delta V$ during annealing of plastically deformed steel of 18–10 type as a function of degree of plastic deformation (data of [43]).

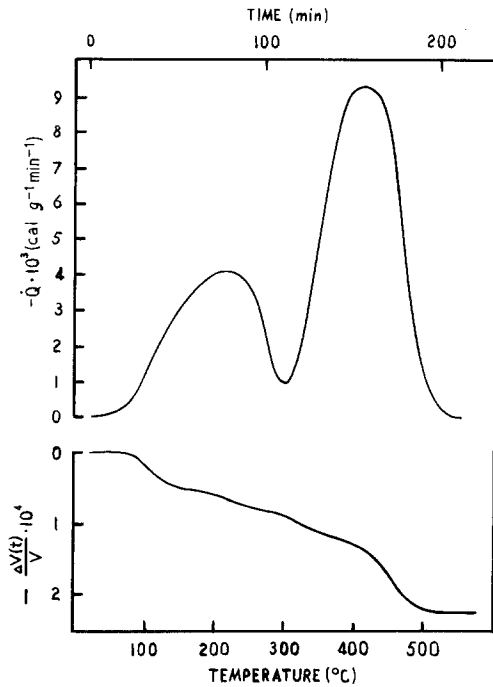


Figure 5 Heat evolution rate $-\dot{Q}$ and volume change $\Delta V(t)/V$ during annealing at 3°C min^{-1} of high purity twist-deformed ($nd/l = 0.8$) bcc iron [37].

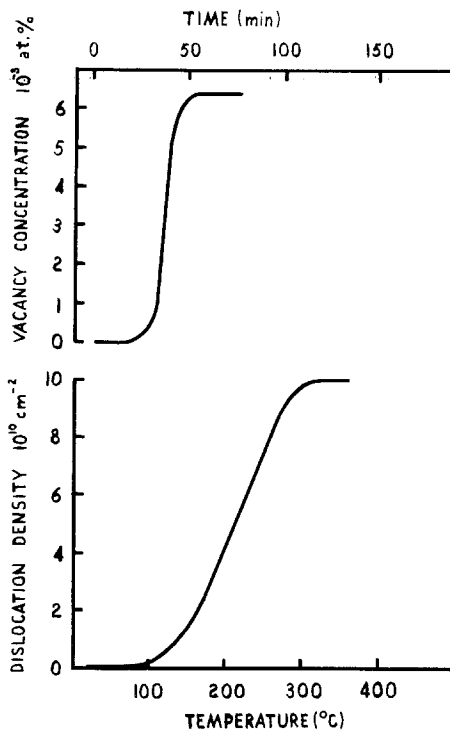


Figure 6 Atomic concentration of excess annihilating vacancies which were at equilibrium with respect to dislocations, and density of thermally mobile dislocations which have taken part in structure change and annihilation as functions of temperature (data of [37]).

indicates the appearance of microcavities in the sample. In fact, the measured change in the volume includes both the change in the microcavities' volume and the change in the volume due to dislocation pile-ups, while the measured heat effect includes both the elastic energy stored in dislocation pile-ups in the course of deformation, and the surface energy of cavities. When the cavity contributions to heat and volume effects are significant, the ratio of these effects differs from that for dislocation pile-ups.

It follows from the experimental data used in [16] that the strength of the sample decreases beyond the admitted level of plastic deformation defined by the heat and volume effects ratio. This means that microcavities affect the strength of the material and its density and heat content almost equally. Data in Fig. 4 [43] show the method described.

The methods described above were used [44] to separate thermally mobile dislocations from immobile ones; the density of the thermally mobile dislocations was determined as well as the

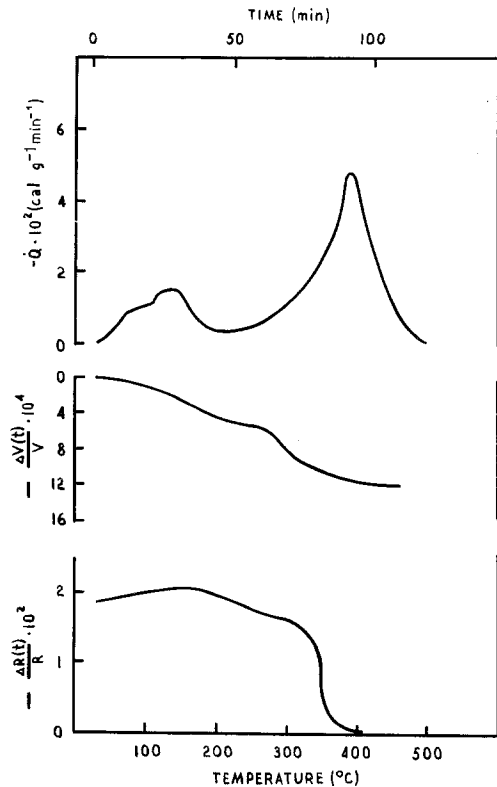


Figure 7 Heat evolution rate $-\dot{Q}$, volume change $\Delta V(t)/V$ and change of electrical resistance $\Delta R/R$, at 300 K during annealing at 4°C min^{-1} of twist-deformed ($nd/l = 0.6$) Cu-0.4 at % Zn alloy [2].

fraction of these dislocations in the total dislocation density for the case of strengthened crystals containing high dislocation densities were annealed (in this case the values cited above cannot be provided by either of the known methods). The heat and volume effects measured under conditions of annealing of deformed, highly pure iron of the bcc lattice phase were used [38] (see Fig. 5). Treatment of experimental data has shown that the immobile dislocation density amounts to about $2 \times 10^{11} \text{ cm}^{-2}$ (the corresponding heat effect makes up 0.42 cal g^{-1}), while the density of thermally mobile dislocations is about 10^{11} cm^{-2} (the thermal effect is 0.22 cal g^{-1}). The heat effect caused by vacancy processes makes up 0.03 cal g^{-1} . The mobile dislocation density was determined as the ratio of the heat effect, due to thermally activated rearrangement and annihilation of mobile dislocations, and the total heat effect of the dislocation nature. It turned out that mobile dislocations in hardened high-purity iron make up 1/3 of all the dislocations that existed before annealing.

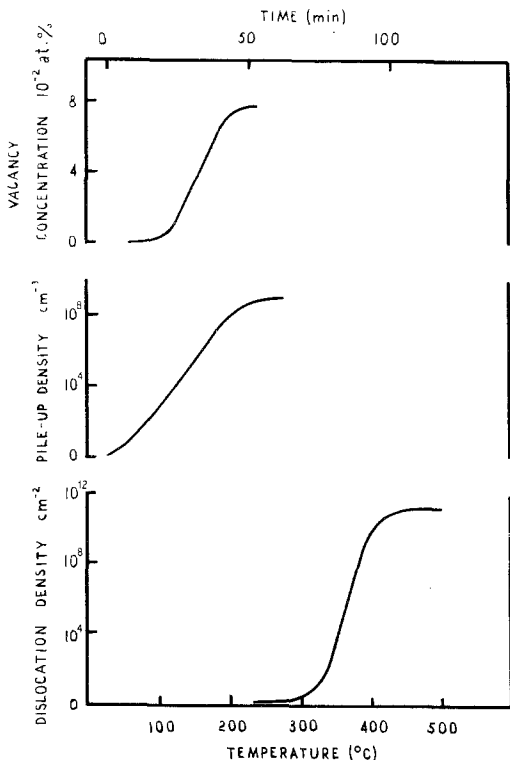


Figure 8 Atomic concentration of annihilated vacancies, change in density of relaxed dislocation pile-ups and density of annihilated dislocations density as functions of temperature during annealing at $4^\circ \text{C min}^{-1}$ of deformed Cu-0.4 at. % Zn alloy [48].

Independently, it was shown [38] on the basis of X-ray and electron microscopy investigations that thermally mobile dislocations moved by the mechanism of cross-slip. According to recent ideas, see for example p. 60 in [45], it is the mobility of dislocation screw components that determines the plasticity of bcc metals. The treatment of experimental data [44] revealed the temperature dependence of thermally mobile dislocation density (of those dislocations which participated in the rearrangement of structure and annihilation) and of the concentration of annihilated surplus vacancies to be drawn (Fig. 6).

The experimental data on heat and volume effects and on electrical resistance during the annealing of deformed dilute copper-based solid solutions [46, 47] (see Figs. 7, 9, 11 and 13), were used for a quantitative analysis of the kinetics of thermodynamically irreversible processes and for an evaluation of the contribution of each process to the heat and volume effects and to electrical resistance.

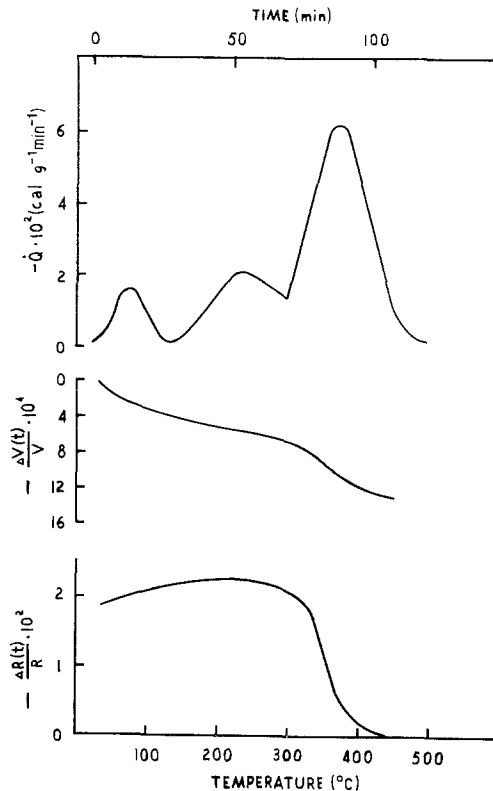


Figure 9 Heat evolution rate $-\dot{Q}$ volume change $\Delta V(t)/V$ and change of electrical resistance $\Delta R/R$, at 300 K during annealing at $4^\circ \text{C min}^{-1}$ smithing-deformed ($\epsilon = 20\%$) Cu-0.3 at. % Ga alloy [46].

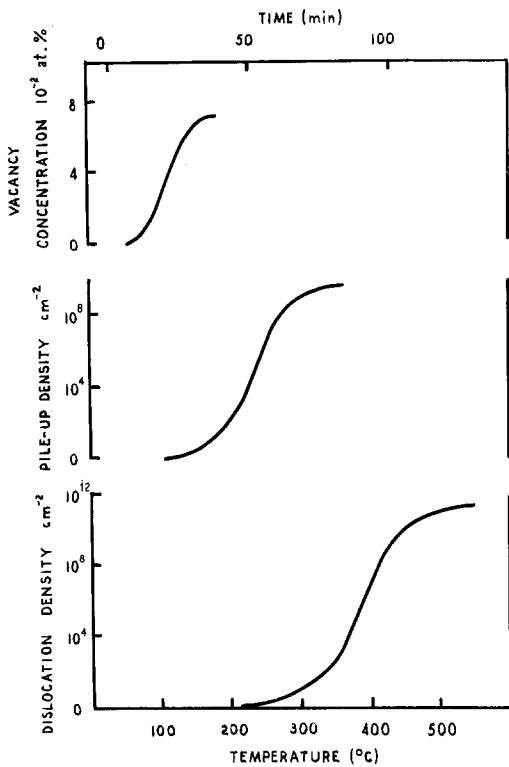


Figure 10 Atomic concentration of annihilated vacancies, change in density of relaxed dislocation pile-ups and density of annihilated dislocations as functions of temperature during annealing at 4°C min^{-1} of deformed Cu-0.3 at. % Ga alloy [48].

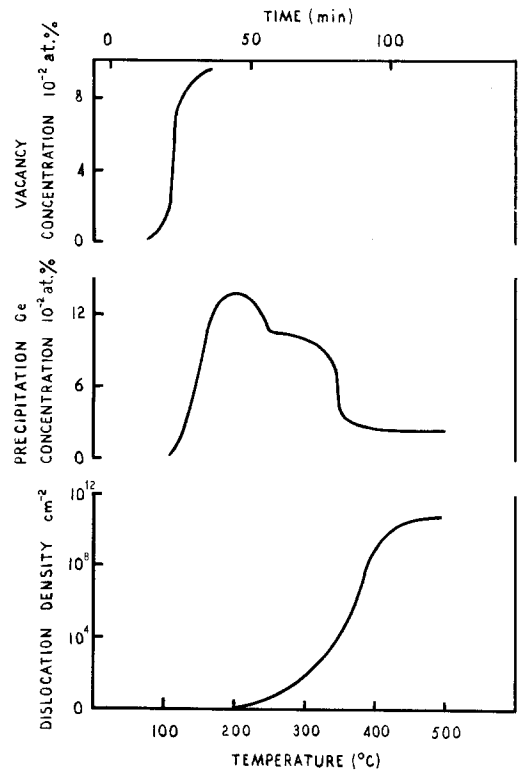
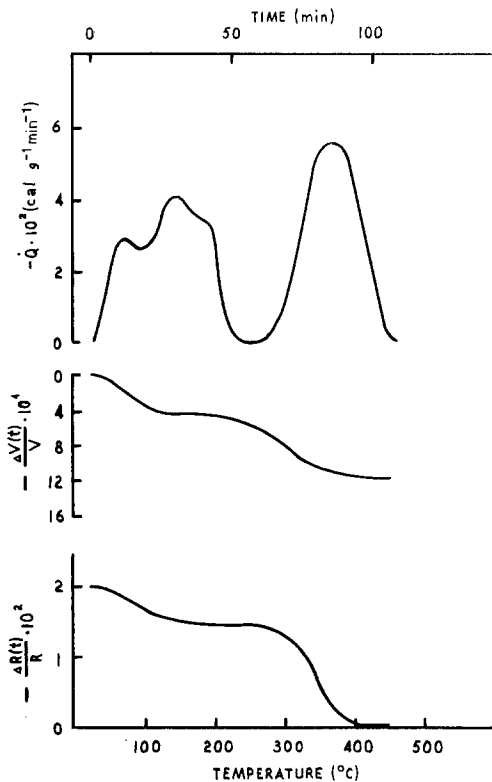


Figure 12 Atomic concentration of annihilated vacancies, atomic concentration of Ge atoms, precipitated onto dislocations and density of annihilated dislocations as functions of temperature during annealing at 4°C min^{-1} of deformed Cu-0.3 at. % Ge alloy [48].



Curves were plotted of the temperature dependence (at constant rate heating) of annihilated vacancy concentration, the density change of relaxed dislocation pile-ups, the density of annihilated dislocations, the concentration of impurity atoms segregated on dislocations and the density of rearranged and annihilated thermally mobile dislocations. In cases when two or three processes occurred simultaneously it was possible to separate their contributions into the effects under study, Figs. 8, 10, 12 and 14 show the results [48].

At present, automatic instruments are designed in the Institute of Metal Physics, Academy of Science of the Ukrainian SSR, Kiev [49] which permit one to carry out a definite time-

Figure 11 Heat evolution rate $-\dot{Q}$ volume change $\Delta V(t)/V$ and change of electrical resistance $\Delta R/R$, at 300 K during annealing at 4°C min^{-1} of smithing-deformed ($\epsilon = 20\%$) Cu-0.3 at. % Ge alloy [47].

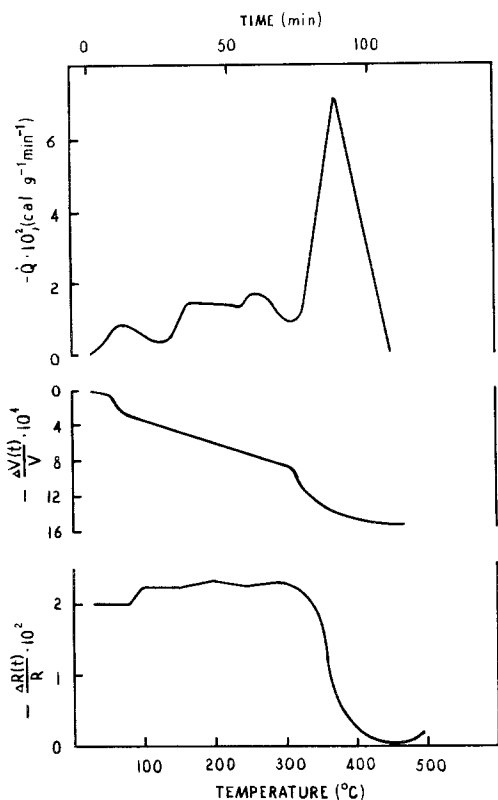


Figure 13 Heat evolution rate $-\dot{Q}$, volume change $\Delta V(t)/V$ and change of electrical resistance at 300 K $\Delta R/R$ during annealing at 4°C min^{-1} of smithing-deformed ($\epsilon = 20\%$) Cu-0.21 at. % As alloy [47].

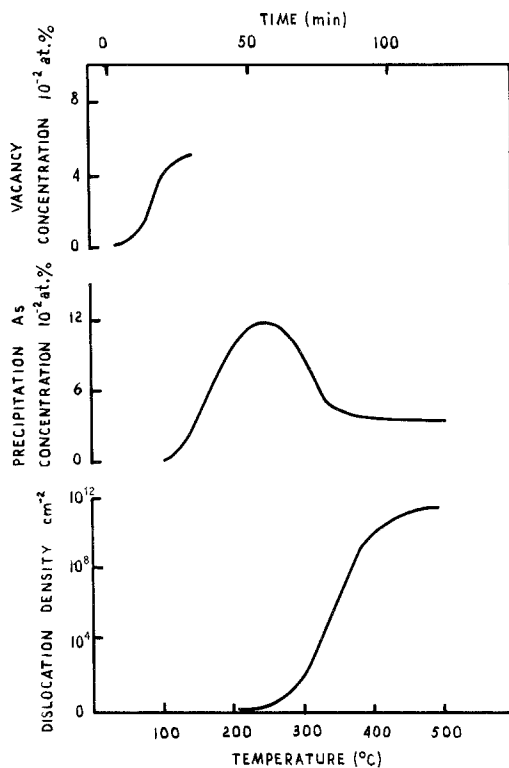


Figure 14 Atomic concentration of annihilated vacancies, atomic concentration of precipitated on dislocations As atoms and annihilated dislocations density as functions of temperature during annealing at 4°C min^{-1} of deformed Cu-0.21 at. % As alloy [48].

temperature regime, during which a simultaneous self-registration of the volume and the enthalpy change rates in the sample is made. In addition they automatically process the data obtained.

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