

# SELF-DIFFUSION PHASE TRANSFORMATIONS

A.L. Roitburd

Institute of Metallurgy and Metal Physics, Central Research Institute for Ferrous Metallurgy

Submitted 7 December 1970

ZhETF Pis. Red. 13, No. 2, 95 - 98 (20 January 1971)

The development of phase transitions in solids is determined to a considerable degree by the character of the contact between the initial phase and the crystals of the new phase that are created and grow in it. If the formation of the new phase occurs without violation of the continuity and without the occurrence of dislocation, i.e., without violating the compatibility of the microscopic deformations, then the interphase boundary is a transition region with a structure intermediate between the crystal structures of the phases in contact (coherent state). In the case of transitions occurring without any change of composition, the displacement of the boundary of the coherent phases, at least in certain crystallographic directions, is connected with overcoming energy barriers that are small compared with the self-diffusion activation energy, causing a high mobility of the boundary [1, 2]. At the same time, such an interphase boundary is a source of internal stresses, as a result of which the coherent state (if the dimensions of the crystals of the new phase exceeds a certain limiting value) turns out to be metastable: the energy of the system can be reduced because of the loss of contact between the phases, with complete or partial removal of the stresses. The violation of the coherence is the result of the appearance on the interphase boundary of a grid of dislocations, the elastic fields of which compensate for the proper field of the crystal, and the energy of the nuclei enters as a component part in the interphase surface tension [3]. Thus, a system of epitaxial dislocations arises, forming a singular phase-separation boundary, which is not present in the coherent state.

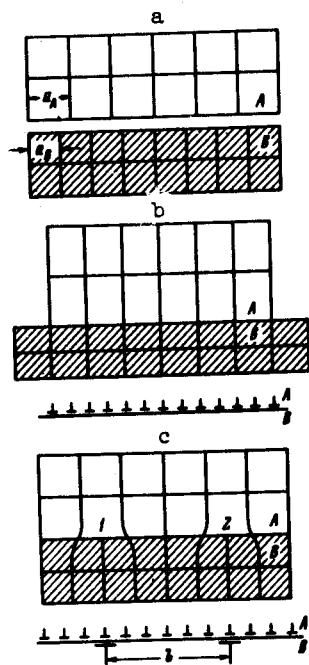


Fig. 1. Boundary cubic phases: a - equilibrium phases, b - coherent state, c - relaxed state with epitaxial dislocations. The dislocation scheme under stress is shown below.

The kinetics of the displacement of such a boundary depends strongly on the type of the epitaxial dislocations of which it is made up, which in turn is determined by the crystal-geometrical parameters of the phase transition, and also by the degree and mechanism of relaxation of the coherent state. If a conservative motion of the epitaxial dislocations is sufficient for the displacements of the interphase boundary, then the mobility of the boundary does not differ greatly from the mobility of the boundary between coherent phases. If nonconservative motion of the epitaxial dislocations is needed for the boundary displacement, then the influx (or outflow) of point defects needed for this purpose may serve as a process that limits the motion of the interphase boundary. The development of a phase transition is connected in the latter case with concentration fields and self-diffusion fluxes of point defects. By way of an example, Fig. 1 shows the boundary between two cubic phases (A and B) with different lattice parameters ( $a_A > a_B$ ). The displacement of the interphase boundary in the relaxed state (Fig. 1c) is possible without an influx of point defects to the epitaxial dislocations (1 and 3), ensuring cancellation or completion of "extra" atomic planes and climbing of the

epitaxial dislocations. For simplicity, we shall henceforth consider systems containing only one type of defects, say vacancies. From the condition for the minimum of the free energy of a two-phase system with vacancies, there follows directly the presence of a certain equilibrium concentration of the vacancies

$$c^* = c_0 \exp(-\Delta\mu \sigma^2 \ell / kT), \quad (1)$$

where  $c_0$  is the equilibrium concentration of the vacancies in the absence of an interphase boundary,  $\ell$  is the distance between the epitaxial dislocations,  $a$  is the interatomic distance, and  $\Delta\mu$  is the difference between the specific free energies of the phases, which for a flat boundary in the absence of stresses (at  $\ell = a_A a_B / (a_A - a_B)$ ) depends only on the temperature ( $\Delta\mu = \mu_A - \mu_B$ ), vanishing at the phase-equilibrium point. At a concentration  $c^* \neq c_0$ , the two-phase system is stable even upon deviation from the equilibrium point in a single-component system, and (1) can be regarded as the equation of the phase-equilibrium line on the T-c diagram of the solution of vacancies in the crystal. For a spherical crystal of the new phase, with radius R, we have

$$\Delta\mu = \mu_B - \mu_A + \frac{2\lambda}{R} + \frac{\hat{\sigma} \hat{\epsilon}_0}{\sigma_0}, \quad (2)$$

where the additional terms are the Laplace pressure due to the interphase surface tension  $\lambda$ , and the work of the stress field  $\hat{\sigma}$  on the proper deformation of the phase transition  $\hat{\epsilon}_0(\ell)$ , and appear as a result of variation with respect to R of the surface and elastic free energies of the system. Since the dislocations are virtual sources (sinks) of vacancies, it can be assumed that in the vicinity of epitaxial dislocations there is established an equilibrium concentration corresponding to the curvature and the stress at the given point of an interphase surface of arbitrary form (this concentration, obviously, is not a local characteristic of the point, since the stress  $\hat{\sigma}$  is a functional of the position of the entire interphase boundary).

If the sections of the coherent boundary between the epitaxial dislocations have high mobility, then the main dissipative process for boundary displacement is vacancy diffusion. The development of the phase transition is limited by the evolution of the system of epitaxial dislocations, which can be considered exhaustively within the framework of the theory of nonconservative motion of dislocations [4, 5] in the case when the vacancy concentration in the dislocations is determined from (1) - (2). If the density of the epitaxial dislocations is sufficiently high, so that the time of equalization of the concentration on the interphase surface  $\ell^2/D$  (D is the vacancy diffusion coefficient) is much smaller than the time of the transformation, the discrete structure of the phase boundary, as a network of linear sources or sinks, can be neglected, and the kinetics of the process is described in perfect analogy with the procedure customarily used to consider diffusion phase transformations in a two-component system [6].

The fact that in this case the second component is made up of vacancies, which can be produced and vanish on the interphase surface, does not influence the formal aspect of the analysis. If a large number of new phases is present in the initial phase, then self-diffusion interaction occurs between them, via exchange of vacancies through the initial phase. As a result of the self-consistent development of the system of crystals in the vacancy field, a coalescence regime is reached [7, 5], at which the kinetics of the phase transition is controlled by relaxation of the average concentration of the vacancies as a result of diffusion to the extraneous sources or sinks (e.g., to the external surface).

The foregoing representations allow us to explain from a different point of view the existence of two qualitatively different kinetic types of phase

transformations in single-component solids [1]: the same phase transition, depending on the external conditions, can have a large (nearly sonic) velocity of the interphase boundary, with a weak dependence on the temperature (martensitic transitions), and a velocity that depends exponentially on the temperature with an activation energy close to the activation energy of self diffusion. The self-diffusion transformation kinetics in the latter case does not exclude, in accord with the foregoing, a crystallographic and morphologic connection between the initial and new phases.

- [1] G.V. Kurdyumov, Zh. Tech. Fiz. 27, 999 (1948) [sic!] Problemy metallovedeniya i fiziki metallov (Problems of Metallurgy and Metal Physics), Moscow, vol. 3, 1962, p. 9.
- [2] A.L. Roitburg, Kristallografiya 7, 291 (1962) [Sov. Phys.-Crystallogr. 7, 226 (1962)].
- [3] A.L. Roitburg, Problemy metallovedeniya i fiziki metallov (Problems of Metallurgy and Metal Physics), vol. 8, 1964, p. 235.
- [4] A.L. Roitburg, *ibid.* 9, 1968, p. 211; Fiz. Tverd Tela 7, 1142 (1965) [Sov. Phys.-Solid State 7, 916 (1965)].
- [5] A.M. Kosevich, Z.K. Saralidze, and V.V. Slezov, *ibid.* 6, 3383 (1964) [6, 2707 (1965)].
- [6] B.Ya. Lyubov, Kineticheskaya teoriya fazovykh prevrashchenii (Kinetic Theory of Phase Transitions), Moscow, 1969.
- [7] I.M. Lifshitz and V.V. Slezov, Zh. Eksp. Teor. Fiz. 35, 479 (1958) [Sov. Phys.-JETP 8, 331 (1959)].