Instability of boundary regions and formation of zigzag interdomain and interfacial walls

A. L. Roĭtburd
I. P. Bardin Central Scientific-Research Institute of Ferrous Metallurgy

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The long-range field of an interfacial or interdomain wall can disrupt the stability of the region near the wall and cause it to break up into a system of periodically alternating domains. The wall acquires a zigzag shape in the process.

The so-called zigzag walls between ferroelastic and ferroelectric domains have recently attracted research interest. Although zigzag walls were discovered almost 15 years ago,[1] it is still not clear just why such walls form, with an exceedingly developed surface and with a corresponding surface energy which is several orders of magnitude higher than the energy of a smooth wall of the same average crystallographic orientation. In the present letter we show that a zigzag wall between domains, like the corresponding periodic heterophase structures observable at interfacial walls in the course of ferroelastic[2] and martensitic[3] transitions, is of the same physical nature as the intermediate state of a superconductor. Its appearance is a consequence of an instability of a single-phase state when it is subjected to the long-range field set up by an interfacial wall.

1. For definiteness, we consider the appearance of a zigzag wall between ferroelastic domains (twins). Figure 1 shows the free energy of a ferroelastic substance as a function of the transition parameter: the uniform shear strain. Equilibrium states of unstressed domains correspond to strains ϵ_0^1 and ϵ_0^2. States in the spinodal region $\epsilon_1^* < \epsilon < \epsilon_2^*$, for which the condition $\partial^2 f/\partial\epsilon^2 < 0$ holds, are unstable. If the external stress causes domain 1 to reach the stability boundary ϵ_1^*, this domain collapses into a state of stable domain 2. If the system is loaded through the application of an external deformation, it will convert into a mixture of plane-parallel domains in a barrier-free fashion inside the spinodal region.[4]

2. Interfacial and interdomain walls may serve as a source of long-range fields—elastic, magnetic, or electric—which propagate away from the wall a distance on the order of the size of the wall. In the case at hand, of a strain transition, the source of the stress field is the inconsistency of the intrinsic (equilibrium) strains of the domains, $\hat{\eta} = \mathbf{n}\times(\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0)\times\mathbf{n}$, where $\mathbf{n}$ is the normal to the domain wall.[5] If the domains border each other along a twinning plane, this inconsistency is zero, no stress arises, and the jump in the strain values between domains is $\Delta\epsilon = \epsilon_2^0 - \epsilon_1^0$ (Fig. 1b). If the orientation of the wall deviates from a twinning orientation, the inconsistency grows, and the jump in the strain decreases. There is a certain critical orientation of the wall for which the jump in the strain reaches the width of the spinodal region, $\Delta\epsilon^* = \epsilon_2^* - \epsilon_1^*$. Figure 1c shows a wall with a "supercritical" orientation. The elastic interaction between domains causes the jump in the strain to decrease to

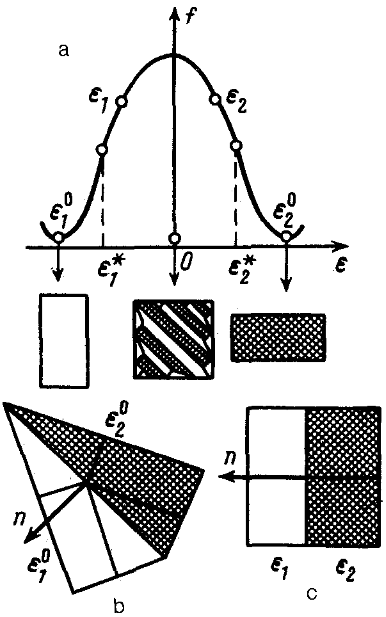

FIG. 1. a—Free energy as a function of the order parameter (the strain); b,c—mutual deformation of phases for various orientations of the wall. Shown in part a below the ϵ axis are the states ϵ_1^0 and ϵ_2^0, which correspond to the equilibrium domains, and the polydomain system which arises in the decay of an unstable state with $\epsilon = 0$.

$\Delta\epsilon = \epsilon_2 - \epsilon_1 = \nu(\epsilon_2^0 - \epsilon_1^0) < \Delta\epsilon^*$ (ν is the Poisson ratio), and both domains are in an unstable state. (The impossibility of supercritical orientations was exploited by I. M. Lifshitz[5] in determining the equilibrium shape of a twin.)

In the general case of the critical orientation of an interfacial wall, the field which it generates renders at least one of the bordering phases unstable. The result is a spinodal decay[6] of the unstable phase into alternating layers of both phases and the formation of a zigzag wall. Each section of such a wall has a subcritical orientation, and the strains of the phases do not correspond to unstable states anywhere.

3. How do the critical orientations of interfacial and interdomain walls actually arise? The diagram in Fig. 2a corresponds to the experimental formation of a twin domain in gadolinium molybdate.[7] This crystal is a ferroelastic-ferroelectric, and twinning in it is accompanied by a reversal of the polarization (the hatched part of the crystal is in an electric field). The initial stage of the polarization reversal is shown here: the formation of a single twinning layer under the electrode. The extended domain walls coincide with twinning planes and do not generate stresses (Fig. 1b). The end wall is unstable (Fig. 1c). The instability of the region beside the wall at the end of a twin cannot be eliminated by changing the orientation of the wall since it is maintained by the electric field, and the end wall converts into a zigzag wall. A situation of this sort also arises as a result of a phase transition of part of the crystal when there is a temperature gradient in the direction normal to the unstable interfacial walls (Fig. 2b). Zigzag walls may form in a similar way between oppositely directed domains of polar phases (ferromagnetic or ferroelectric) (Fig. 2c) or between polar and nonpolar phases (Fig. 2d). The thickness of a zigzag wall, i.e., the length of the teeth, is deter-

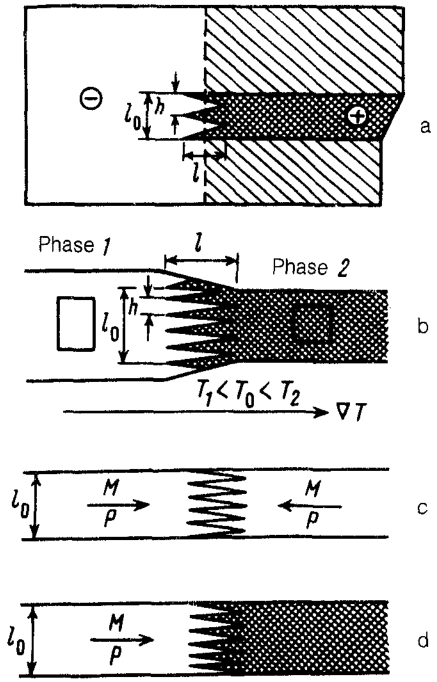

FIG. 2. Various cases of the formation of a zigzag wall. a—Twin boundary; b—interfacial wall (the unit cells of the phases and the direction of the temperature gradient are shown; T_0 is the equilibrium temperature of the phases); c—wall between oppositely directed domains; d—wall between polar and nonpolar phases.

mined by the size of the unstable region and is approximately equal to the size of the interfacial contact (l_0 in Fig. 2).

4. Let us estimate a basic geometric characteristic of a zigzag wall: the ratio of the period h to the thickness l. This ratio is determined by a competition between two factors: the elastic energy of the stress set up by the lateral sides of the teeth and the surface energy. In the case of thin teeth $(h/l \ll 1)$ the elastic stress is proportional to the deviation of the sides of the teeth from the plane for which the mutual distortion of the phases is at a minimum [in the case of a zigzag wall between ferroelastic domains, this would be a twinning plane (Fig. 2a), while for the interfacial zigzag wall in Fig. 2b it is the horizontal plane]. The elastic stresses are therefore proportional to h/l, and the elastic energy decreases with decreasing h. The surface energy, on the contrary, increases with decreasing tooth thickness h. Minimizing the free energy per unit area of the zigzag wall, $F = e(h/l)^2 l + 2\gamma(l/h)$, with respect to the period h, we find the equilibrium ratio $(h/l) = (h_0/l)^{1/3}$, where $h_0 = \gamma/e$ is a characteristic dimension. For twins, this dimension is on the order of the interatomic distance [$e \approx G(\epsilon_2^0 - \epsilon_1^0)^2$, where G is the elastic modulus], and γ is the specific surface energy. The relation between h and l which has been found is in accordance with the results of a quantitative study of zigzag walls in gadolinium molybdate.[8] The energy of an equilibrium zigzag wall, $F_0 = 3\gamma(l/h_0)^{1/3}$, with $l = 10^{-2}$ cm, is ~ 2 orders of magnitude greater than the surface energy of a smooth interfacial or interdomain wall. Comparing F_0 with the energy of an unstable smooth wall ($\sim el$), we can estimate the minimum length of a zigzag wall: $l_{0\,\min} \approx 5h_0$.

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