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THERMAL DRAG OF THE ANTIPHASE DOMAIN BOUNDARY MOTION

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Abstract—The antiphase domain boundary is a region in materials where ordering of atoms changes from one structural variant to another. The influence of the internal energy excess on the dynamics of such a boundary is considered in the framework of the Onsager theory of linear response. The internal energy transport entails a temperature hump in the transition region and causes a drag effect. An evolution equation that takes into account the finite thermal conductivity is derived. An experimental setup to reveal the thermal drag is suggested. © 1998 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

Symmetry breaking order–disorder transitions in alloys generally are characterized by a loss of orientational or translational symmetry elements when different structural variants are possible in a transformed material. They may appear as a result of *continuous* ordering below the critical temperature T_C . If the alloy is quenched from the disordered phase into the ordered one, both variants should nucleate at random at the initial stage of transformation and the configuration of the crystal may be described as a *fractal structure* of two or more self-entangled, interwoven macrodomains which is characterized by a wide range of length scales. The antiphase domain boundaries (APB) or domain walls are interfacial layers of thickness w that separate domains with opposite relative displacements of atoms and otherwise identical physical properties. Near T_C they are so wide that they actually become visible under the microscope. APBs constitute a network of structural defects of a crystal and, because of the surface tension σ of the interfaces (surface free energy), they are in global disequilibrium with the crystal: in later stages of material evolution this structure will coarsen by the mechanism of APB migration [1]. It is important to analyze all the forces that govern coarsening of the network of APBs because the latter is a ubiquitous process. Usually APBs are encountered in binary or multi-component metallic alloys, as is the case for Cu–Au [2], Fe–Co–V [3] and Fe–Al [4], and the role of alloying elements on their dynamics is relatively well elucidated [5]. However, APB motion is also subjected to different thermal effects, that stem from transmission of energy together with the interface. These effects have not received any attention in the literature; their study is long overdue.

In this paper we derive an evolution equation for APB motion that takes into account energy transfer in materials with different magnitudes of the thermal conductivity λ . We look at a system that has been quenched from the disordered state down to temperature $T_0 < T_C$, undergone second-order transition and held isothermal at T_0 . Notice that during isothermal annealing only the outer surface of the sample is actually held isothermal at T_0 , which does not exclude a possibility of creating short-range temperature humps in the bulk.

2. THEORY

Away from equilibrium, each thermodynamic system should be characterized by one or a few internal parameters that unambiguously describe the state of the system. The motion of a piece of a spherical interface of given solid angle Ω separating two variants of the same phase may be described by the change in the radius of curvature R . The appropriate flux in the present problem is then defined as the rate of displacement of the interface ΔR in the direction of the center of curvature:

$$J_V = V_n \equiv \frac{\Delta R}{\Delta t} \quad (1)$$

where Δ refers to differences of quantities after and before the interface motion and V_n is the normal velocity of the latter.

Irreversible thermodynamics gives a simple recipe for the choice of the conjugate driving force: the product of the flux and force should be equal to the entropy production in the system due to the process in question [6]. As the interface is an open system, the heat transferred into or out of the system ΔQ must be taken into account in the expression of the entropy production due to relocation of an interface

on ΔR . Then, denoting by Φ the driving force of the interface motion (per unit area), and calculating the entropy production during Δt , one obtains

$$J_V \Phi \Omega R^2 \Delta t = T \Delta S - \Delta Q \quad (2)$$

where T is the average temperature of the interface. Since the interface does not exchange any work with the surrounding material, the first law of thermodynamics yields that the amount of heat transferred ΔQ is equal to the internal energy change ΔE . Recalling that $F = E - TS$, the driving force may be represented as follows:

$$\Phi = -\frac{\Delta F + S \Delta T}{\Omega R^2 \Delta R} \quad (3)$$

where E , F , S are the internal energy, free energy and entropy of the transformed material in excess to that of the homogeneous material and $\Delta T = T - T_0$. The driving force Φ represents the resultant of intermolecular forces exerted on a piece of interface and is equal to the work done by these forces per unit of interface displacement. Equation (3) may also be derived utilizing the concept of the chemical potential which, in the first place, has been introduced by Gibbs to simplify the calculation of the work done by or on the system [7]. In this case, the $S \Delta T$ term in equation (3) follows from the Gibbs–Duhem relation and may increase or decrease the driving force Φ as compared to the traditional ΔF . The “Gibbs–Duhem force” may even drive the *first-order* transformation, e.g. solidification, in the direction opposite to ΔF [8].

The interface will respond to the applied force by the change of the internal parameter. For purely resistive systems an Onsager-type relation may be established between the driving force Φ and the conjugate flux J_V through the system

$$J_V = \Gamma \Phi \quad (4)$$

where the Onsager kinetic coefficient Γ characterizes the mobility of the interface. If the temperature of the interface is equal to that of the surrounding material and does not vary during transformation then ΔF is the only contribution to the driving force Φ [1]

$$\Delta F = \sigma \Omega (R + \Delta R)^2 - \sigma \Omega R^2 \approx 2\sigma \Omega R \Delta R \quad (5)$$

and we arrive at the relation $V_n = -2m/R$ [1, 3, 4]. The interfacial diffusivity $m = \Gamma \sigma$ limits the rate of boundary migration and may be related to material parameters through microscopic modeling of the order–disorder process. As far as the temperature dependence of the interfacial diffusivity m is concerned, the irreversible thermodynamics recipe guarantees positivity of the Onsager kinetic coefficient (mobility) Γ but says nothing about its temperature dependence. Cahn and Allen [4] proved on the grounds of the mean-field theory, and confirmed experimentally, that the interfacial diffusivity $m = \Gamma \sigma$ does not exhibit any critical behavior near T_C and

contains merely an Arrhenius factor due to the activation energy of atomic motion. Hence, in the framework of the Lifshitz–Cahn–Allen theory [1, 4] the rate of APB motion does not bear any critical dependence on temperature, although the driving force ΔF does. This may be explained by the fact that the flux in our system is coupled to the surface energy so that the driving force is “expended” on the propulsion of this energy excess. Therefore, the major carrier of the critical temperature dependence, the surface tension σ , will be factored out from the Onsager relation if the latter is introduced between the free energy flux σV_n , the driving force $-2\sigma/R$ and the interfacial diffusivity m as the kinetic coefficient.

However, advection of interfacial energy along with APB generates elevation of temperature ΔT in the boundary, as follows, and alters the driving force by the amount $S \Delta T$, see equation (3). To find ΔT one needs to analyze the distribution of the internal energy density $e(\mathbf{r}, t)$ inside the interface. If the piece of interface is not curved strongly, i.e. $R \gg w$, and moves slow enough compared with the rate of ordering and heat flow, i.e. $V_n \ll m/w$ and $V_n \ll \lambda/\eta$ where η is the surface entropy, then we can assume that the steady-state regime establishes in the system. It is advantageous to look at this problem in the coordinate system that moves together with the interface because the temporal derivative of the internal energy density $e(\mathbf{r}, t)$ vanishes and the internal energy density flux J_E is constant everywhere. In this reference frame the substance moves with the velocity $(-V_n)$. Hence, neglecting viscous dissipation in the interface, the flux J_E has only two varying contributions, convective $(-e V_n)$ and conductive $(-\lambda \nabla T)$ [9]. As the temperature gradient vanishes outside the boundary we find that

$$J_E \equiv -e V_n - \lambda \nabla T = -e_0 V_n \quad (6)$$

where e_0 is the energy density in the bulk far from the interface. Averaging the varying energy density and temperature gradient over the thickness of the interface yields for the surface internal energy $\varepsilon \cong (e - e_0)w$ and temperature elevation $\Delta T \cong \nabla T w$. Thus, the steady-state condition (6) allows one to resolve for the temperature elevation:

$$\Delta T = -\varepsilon V_n / \lambda. \quad (7)$$

An equation of APB motion may be derived for an arbitrary displacement of the interface ΔR . Yet, the derivation is simplified if a displacement on the interfacial width w is considered. Then $F = \sigma \Omega R^2$, $E = \varepsilon \Omega R^2$, $S = \eta \Omega R^2$, $\Delta R = -w$ and equations (1), (3), (5) and (7) allow us to recast the Onsager relation (4) as follows:

$$V_n = -\frac{m}{1+L} \cdot \frac{2}{R}; \quad L = \frac{m \eta \varepsilon}{\lambda \sigma w}. \quad (8)$$

This is our principal result. It demonstrates that the speed of the interface is limited not only by the rate of ordering m but also by the heat conduction λ with the parameter L measuring the relative role of these processes. Significantly, this effect is of the first order in the speed of APB motion, that is essentially *nondissipative* in nature and is characterized by the effective or “dressed” interfacial diffusivity $m_{\text{eff}} = m/(1 + L)$. Thus, even gently curved pieces of APB, moving slowly towards the center of curvature, will have a speed lower than that predicted by the Lifshitz–Cahn–Allen theory [1,4]. Such slowing down may be called *thermal drag* because this effect is due to the temperature hump ΔT in the transition region and limited thermal conductivity in the material. It occurs because the Gibbs–Duhem force reduces the driving force Φ . Thermal drag is due to the excess energy in the transition region despite the fact that there is no energy difference between ordered variants, that is the *latent heat of the transition* (which causes thermal effects during first-order transformations) is zero for APB motion.

To find the conditions when thermal drag is of importance, one has to assess the magnitude and temperature dependence of the parameter L , which is the ratio of the rates of ordering m/w and heat flow through the interface λ/η . In materials with reduced thermal conductivity the APB motion is controlled by the rate of energy transfer instead of the rate of ordering. Interestingly to note from equation (8) that if the thermal conductivity vanishes ($\lambda = 0$), i.e. the energy transfer mechanism is “turned off”, a curved APB stops cold, implying that coarsening of the APB structure is not possible without heat conduction in the material. Although the latter inference is not quite legitimate within the present thermodynamic consideration because the details of the temperature distribution inside the transition zone become important as $\lambda \rightarrow 0$, it was confirmed within the mean-field approach and will be addressed elsewhere.

As we are looking at a slowly moving interface, that is a weakly non-equilibrium thermodynamic system, the equilibrium relations between thermodynamic functions of the interface may be used as the first approximation: $\eta = -\partial\sigma/\partial T$ and $\varepsilon = \sigma + T_0\eta$. One may expect L to be large in the vicinity of the critical point, that is for small and positive $\tau = (T_C - T_0)/T_C$, because σ and w vary critically near this point. The surface tension temperature dependence near T_C can be obtained from the relation $\sigma \propto \psi^2/w$, where the order parameter $\psi \propto \tau^\beta$ varies critically with the critical exponent β and the interfacial width w is of the order of the correlation length $\xi \propto \tau^{-\nu}$ near T_C . Far from the critical point, e.g. at 0 K, the surface free energy density σ/w can be estimated as $k_B T_C/\omega$ where k_B is Boltzmann’s constant and ω is the atomic volume of the substance. Hence, for the surface free energy

and entropy this yields

$$\frac{\sigma}{w} = \frac{k_B T_C}{\omega} \tau^{2(\beta+\nu)}, \quad T_C \frac{\eta}{\sigma} = \frac{\partial \ln \sigma}{\partial \tau} = \frac{2\beta + \nu}{\tau}. \quad (9)$$

The latter expression demonstrates that the surface entropy η of APB diverges near T_C even *faster* than σ . As there is no reason to expect a critical behavior of the conductivity λ , substitution of equation (9) into equation (8) yields

$$L = (2\beta + \nu)[(2\beta + \nu)(1 - \tau) + \tau] \frac{mk_B}{\lambda\omega} \tau^{2(\beta+\nu-1)}. \quad (10)$$

According to equation (8), the thermal drag is important if $L \geq 1$. Approximately $\beta \approx \nu \approx 1/2$ [10, 11], which makes $(2\beta + \nu) \approx 3/2$ and the square bracket in the expression (10) varies between $3/2$ and 1 in the temperature region $0 < T < T_C$ ($\tau > 0$). Hence, these factors do not qualitatively alter the assessment of the thermal drag effect and may be dropped from further consideration. Thus, as follows from equation (10), the thermal drag is important if

$$m \geq m_\lambda \tau^{2(1-\beta-\nu)}, \quad m_\lambda \equiv \frac{\lambda\omega}{k_B} \approx 10^{-6} \text{ m}^2/\text{s}. \quad (11)$$

If the interface is mobile and $m \geq m_\lambda$ the thermal drag is essential in the entire temperature region $0 \leq \tau \leq 1$. If the interface is sluggish and $m < m_\lambda$, then the thermal drag manifests itself only near T_C in the temperature region

$$0 \leq \tau \leq \tau_\lambda \equiv \left(\frac{m}{m_\lambda}\right)^{1/2(1-\beta-\nu)} \quad (12)$$

In fact if $\beta + \nu < 1$ the parameter L diverges near T_C and the heat transfer causes *critical slowing down* of the boundary migration. This result is essentially different from that of the Cahn–Allen theory. The critical exponents differ for different approaches used to study the phase transition. For instance, in the framework of the mean-field theory $\beta = \nu = 1/2$ [10, 11] and the thermal region τ_λ disappears, leaving only noncritical renormalization of the interfacial diffusivity m_{eff} . However, experimental observations show that $\beta + \nu = 0.97$ [10], which creates the possibility for the thermal region near T_C with $\tau_\lambda \approx 10^{-5}$ if m is only one-half of m_λ . A quantitative estimate of the genuine interfacial diffusivity m represents a formidable task not only due to the scarcity of experimental data on the kinetics of APB but also, as will be discussed below, because m is not accessible directly from the experiment

3. SELF-SIMILARITY IN APB MOTION

A real three-dimensional surface rarely can be described by a single radius of curvature R . Rather it is characterized by two principal radii of curvature, R_1 and R_2 , with the mean curvature

$K = (R_1^{-1} + R_2^{-1})/2$ that can vanish not only for a plane ($R_1 = R_2 = 0$), but also for a “minimal surface”, for which $R_1 = -R_2$ everywhere. Such surfaces are relevant to the self-entangled fractal structures of APBs where the r.m.s. curvature

$$\bar{K} \equiv \left(\int K^2 da / \int da \right)^{1/2}$$

may be very small and does not characterize the average domain size D . Instead, the latter is inversely proportional to the total area of the surface per unit volume A_Θ , i.e.

$$D = \frac{n}{A_\Theta}; \quad A_\Theta \equiv \frac{1}{\Theta} \int da$$

where n is the spatial dimension.

As a result of the fractal nature of the APB structure, a self-similarity regime sets in after an initial transient. According to the hypothesis of statistical self-similarity [4, 12], consecutive in time t configurations of the structure are invariant under uniform magnification φ which plays the role of the time independent dimensionless form factor, so that $\bar{K} = \varphi A_\Theta$. Along with the local dynamic equation (8), the hypothesis of statistical self-similarity helps to resolve for A_Θ [4]. Because thermal drag does not change the functional relation between the local characteristics of APB such as V_n and K , see equation (8), it will not alter the time exponents of the structural coarsening. Therefore

$$[A_\Theta^{-1}(t)]^2 - [A_\Theta^{-1}(0)]^2 = 2(\varphi l)^2 \quad (13)$$

where

$$l = \sqrt{m_{\text{eff}} t}$$

is the time-dependent characteristic length scale of the APB structure which is affected by the thermal drag.

According to equation (13), only the rate constant $B = m_{\text{eff}} \varphi^2$ is accessible from experimental data on the temporal evolution of the total APB surface A_Θ in a specimen. This demonstrates that slow rates of coarsening may not necessarily be a result of small magnitude of the interfacial diffusivity m but due to the proximity of the APB structure to the “minimal surface” with $\bar{K} \rightarrow 0$ and $\varphi \rightarrow 0$.

Measurements of $A_\Theta(t)$ after the b.c.c. \rightarrow B2 transition in Fe-24%Al alloy give $B \approx 10^{-15} \text{ m}^2/\text{s}$ [4] which yields that thermal drag is important for this system if $\varphi \leq 10^{-4}$. Another observation can be made from the analysis of the same experimental data: coarsening of the total APB surface A_Θ in the specimen anomalously slowed down, i.e. B dropped from 10^{-15} to 10^{-17} , when the temperature was raised from 987K to 990K. This fact, which remained unexplained in the paper, may be related to the existence of the thermal region τ_λ ,

equation (12), where the APB experiences critical slowing down.

4. CONCLUSIONS

In summary, we have presented clear evidence of the thermal drag effect on APB motion which is *robust* and conceivably independent of the method employed for analysis. The thermal drag represents a nondissipative dynamic correction to the driving force ($-2\sigma/R$) due to the temperature hump ΔT generated by moving APB rather than dissipation in the latter. Dissipative correction to the evolution equation (8) has not been considered in the present paper because it is of the order V_n^2 and constitutes only a (wK) portion of the thermal drag for gently curved interfaces. Because of the thermal conduction, the hump will not stay localized within the interface but will be smeared out, thus creating a long temperature tail behind the front. The thermal waves can be imaged in infrared light through *in situ* ordering and serve as experimental verification of the thermal drag effect. This effect should be taken into account in experimental work intended to check the theory of structural evolution in materials with low thermal conductivity or high mobility, because it slows down both initial and late stages of evolution, albeit the time exponents of the latter stay unchanged. Motion of a flat APB, which may be the case in internal friction experiments, will be also accompanied by the same effect with the same parameter L , equation (8). Divergence of the “drag parameter” L at the critical point, equation (10), implies that thermal drag may even affect the continuous transition itself. Of course, one should not forget that in this region thermal fluctuations are meaningful. Temperature dependence of kinetic coefficients m and λ may give rise to another group of thermal effects that are not considered in this paper. It is naive to expect the energy transfer to be a unique process that affects continuous transitions. On the contrary, it is but one example of the whole family of transport processes (convective mass flow would be another one) that has been extensively discussed in the past with regard to the critical dynamics [13].

A network of domain boundaries may be a part of a microstructure in the variety of materials that undergo different continuous transitions, not only from the same universality class as order-disorder transition: magnetic and ferroelectric materials, liquid crystals, polymers, to name only a few. An order-disorder transition is but one example of a nondissipative drag effect. The damping of the domain wall in ferrite garnets may be dominated by the drag force due to the magnetization diffusion rather than the exchange and relativistic relaxation [14]. In the framework of the symmetry-breaking theory of the origin of cosmic structure, domain walls separating regions of different values

of the Higgs field may appear as the universe cooled passing through a series of phase transitions. Thus the present study, which gives the rate of motion of such topological defects, may be useful for the analysis of the cosmic structure formation.

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