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Viewpoint Paper

The role of the triple line in solid-state microstructural evolutions: Interplay with interfaces and consequences on instabilities and pattern selection

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Abstract—The present contribution illustrates the role of the triple line in solid-state microstructural evolution. In single-phase materials, the role of the triple line in grain growth phenomena is discussed. In surface alloying, it is shown that the contact angle at the interface plays a key role on the kinetics of the process. In discontinuous precipitation, it is shown that the conditions at the triple line removes the degeneracy of the problem of spacing selection.

Keywords: Grain boundaries; Interfaces; Discontinuous precipitation

1. Introduction

In solid-state transformations, interfaces play a key role from both thermodynamics and kinetics points of view (see e.g. the classic review [1]). It is very seldom, however, that a single interface is present, and the triple line where these interphases meet is also a key actor, although very often overlooked. The present contribution illustrates this fact in three situations of increasing complexity. In Section 2 the case of normal and abnormal grain growth is examined. In Section 3 the case of surface alloying is considered, and in Section 4 the role of the condition at the interface to lift the degeneracy of pattern selection in discontinuous precipitation is discussed.

2. Triple line and grain growth

Grain size is a key parameter controlling the efficiency of a microstructure. In many cases, grain size reduction is a goal, and ultrafine grain size materials have been the topic of numerous investigations in recent years. However, the presence of small grain sizes also challenges the stability of the materials: both the large capillary forces and the short diffusion distances contribute to destabilizing the structure. Controlling grain sizes and stabilizing them against grain growth is traditionally done either by pinning the grain boundaries with particles (Zener pinning) or by reducing grain boundary mobility via solute additions (Cahn's solute drag). For both effects, triple lines react differently from the grain boundaries themselves. In a simple "Zener-like" approach for pinning, meaning purely geometrical, the amount of the grain boundary surface that disappears when a particle is positioned on a triple line is larger than when it lies on a grain boundary: one expects the pinning effect to be larger on triple lines than on grain boundaries. On a similar line, triple lines are structurally more disordered than grain boundaries: the chemical interaction of impurities is likely to be of the same sign as for grain boundaries but slightly higher, and one therefore expects that solute drag will be more important and that mobility of the triple line will be reduced. When the grain size is reduced, the proportion of atoms involved in the triple line relative to the ones on the grain boundary increases. Therefore the pinning effect of particles and the viscous drag of the solute are expected to increase with this increasing role of triple lines. Two questions arise here. When does one expect the triple line effect to become relevant? Is it simply a matter of slowing down grain growth?

The reduced mobility of triple lines was observed experimentally in Zn tricrystals by Czubayko et al. [2].

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Using a vertex simulation for grain growth, which allows different mobilities to be attributed to the grain boundary and the triple line, Weygand et al. [3] were able to reproduce both the kinetics and the shapes in the tricrystal geometry. Implementing the same ingredient in a three-dimensional vertex simulation enabled the expected effect on grain growth to be investigated. The relevant dimensionless parameter which monitors the influence of triple-line mobility is $\Lambda'' = \frac{m_{TL}\cdot\langle r\rangle}{m_{GB}}$ where m are the mobilities, TL and GB refer to the triple line and the grain boundaries, respectively, and $\langle r\rangle$ is the average grain size. In standard grain growth, the theoretical kinetic are such that the average area $\langle A\rangle$ increases linearly with time, and the grain size distribution is scaling. When the triple-line mobility is reduced, the linear behaviour disappears and the grain size distribution is no longer scaling.

With the values obtained for Zn [2] one would expect to see a measurable effect for grain sizes below a few microns.

The situation is more dramatic where particle pinning is concerned. In the classical Zener approach, the pinning force per unit surface of grains is independent of grain size. This is no longer the case when preferential pinning of the triple junction occurs; indeed, it is expected that particles will sit preferentially at triple junctions and quadruple points. When the grain size decreases, a situation may occur where there are more triple junctions to be pinned than available particles. In this situation, when the grain size increases, the pinning efficiency per unit surface increases. Above a critical grain size, which is of the order of the interparticle distance, more and more particles will sit on the grain boundaries with a reduced efficiency: in this region, the pinning force per unit surface of grain boundary will decrease, and when the grain size is large enough, one recovers the standard Zener pinning situation. The shape of the pinning force per unit surface as a function of grain size has been calculated in detail in Ref. [4], together with the conditions for abnormal grain growth. The existence of a region with a pinning force as a decreasing function of the grain size will lead to non-quadratic kinetics and will trigger abnormal grain growth, as has been observed experimentally in ferritic steels with ultrafine grains [5]. It was shown in this special case that the variation of the Zener pinning force in the range of grain sizes considered is more that a factor 2 (see Fig. 1).

3. Triple line and surface alloying

A number of situations in microstructural evolution are associated with interface migration [6]. In situations where bulk diffusion is too slow, interface diffusion along a migrating interface may be an efficient short circuit toward equilibrium. Examples of this are discontinuous precipitation and diffusion-induced GB migration (DIGM). An interesting generalization of DIGM was found experimentally by Hillert and Purdy [7] in Fe–Zn. At the surface of an iron sample into a Zn vapour, the grain boundary inside the iron may migrate and create an alloying layer that is richer in zinc. The geometry of this situation is shown in Figure 2. Note that diffusion takes place here along a grain boundary which is moving.

The conditions necessary to obtain this situation were derived in Ref. [8] for the simple situation where the GB would be perpendicular to the free surface. A more sophisticated analytical approach allows the effect of the geometrical conditions at the triple junction and, more specifically, of the contact angle θ_0 to be evaluated. This quantity may depend on the various interfacial energies involved (especially in highly anisotropic materials), but also on possible reduced mobility of the triple line. Both the velocity V and the depth of penetration H can be computed analytically as functions of the contact angle and the normalized inverse of the driving force β:

$$\beta = \frac{m(\Omega\sigma)^2}{KD\delta\Delta G}$$

where ΔG is the driving force, D is the GB diffusion, δ is the GB width, m is the mobility, K is the segregation

Figure 2. Geometry of surface alloying.

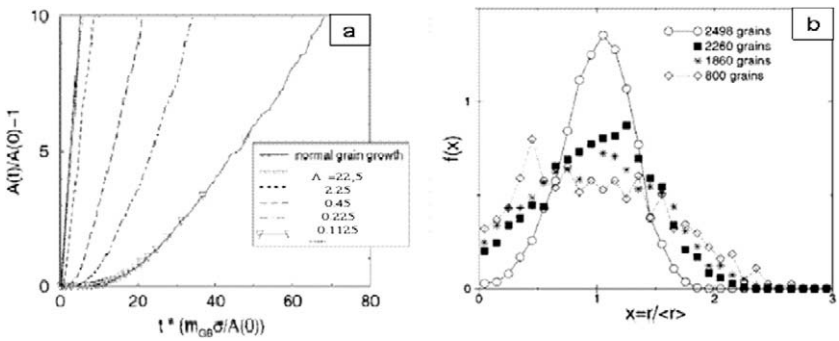

Figure 1. Effect of a reduced triple-line mobility (a) on grain growth kinetics for different values of the Λ'' parameter and (b) on normalized grain size distribution for different times (corresponding to different numbers of remaining grains). (After Ref. [3].)

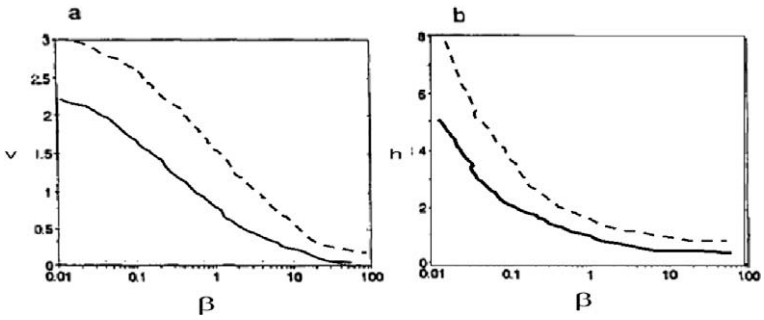

Figure 3. Normalized velocities (a) and penetration depth (b) as functions of the normalized driving force, for different values of the contact angle at the triple line (dashed line $\pi/3$, full line $\pi/2$).

coefficient, Ω is the atomic volume and σ is the surface energy.

The influence of the contact angle at the triple line is shown in Figure 3a and b.

It can be seen that, for the same driving force, changing the contact angle from $\pi/2$ to $\pi/3$ might change the velocity and the depth of the alloyed layer by a factor 2. This suggests that coupling surface alloying experiments, local chemical analysis and EBSD observations may lead to interesting results.

4. Triple line and discontinuous precipitation

Pattern selection is a classic unsolved problem in many cases in physical metallurgy. Lamellar structures offer a simple geometry to address this question, since the selection issue consist in defining the lamellar spacing corresponding to a given driving force ΔG and a given value of the transport coefficient D (see Fig. 4). This geometry occurs in a variety of situations, in solidification (lamellar eutectic) as well as in solid-state transformations (eutectoids, discontinuous precipitation) [9], and in most cases the problem is degenerate, i.e. one can derive a relation between the front velocity and the spacing, and a minimum spacing for which all the available free energy is consumed as interfacial energy, but the value of the velocity or the front remains unset. Discontinuous precipitation is, in a sense, simpler than eutectid or eutectoid reactions: the mother phase is identical to one of the two daughter phases, and the second daughter phase is, in general, a stoichiometric compound (which leaves no freedom for composition gradients). In addition, the diffusion process occurs along the boundary [9].

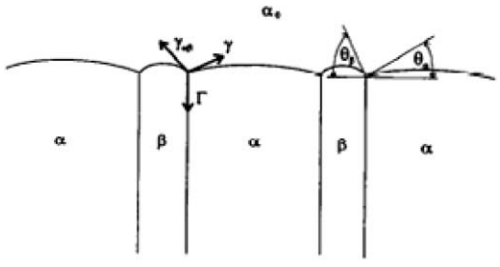

Figure 4. Lamellar geometry for discontinuous precipitation: decomposition of a solid solution α_0 into a lamellar structure of a less saturated solid solution α and a stoichiometric phase β.

The problem to be solved is then (i) solving the transport equation along the grain boundary between the two solid solutions: the driving force is the gradient in solute concentration; (ii) solving the transport equation along the boundary separating the solid solution and the stoichiometric compound, where the driving force is the gradient in curvature; and (iii) making sure that both velocities are equal. The mathematical tools to deal with these issues were developed by Cahn [10] and Hillert [11] for (i) and Mullins [12] for (ii). The boundary conditions ensuring the continuity between the two solutions are defined at the triple junction. The details of the full analytical solution are to be found in Ref. [13]. The condition set at the triple junctions are equilibrium conditions for the composition in the vicinity of the triple point, which imposes both the local curvature of the stoichiometric phase and the local concentration at the GB between the two solid solutions. The key result of this approach is that this boundary condition at the triple line removes the degeneracy of the problem only when the transport equations are different between the two interphases, and a flux conservation equation is imposed at this very point. The triple line appears clearly here as the point where the two migrations are coupled.

5. Conclusions

The triple line appears to be a key actor in microstructure evolution, since it is the unavoidable locus where two interfaces meet. As such, it can be preferentially pinned or polluted by impurities, and thus controls the overall kinetics. It is also the place where coupling between two different modes of growth occurs, and plays a key role in pattern selection.

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