Precipitation accelerated grain growth

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Abstract

Grain growth in a binary alloy is considered. In contrast to common conception it is shown that under certain conditions the precipitation of second-phase particles may accelerate grain boundary motion and, as a result, speed up grain growth in the system. The conditions under which this effect occurs are outlined. We present experimental data that support the predicted effect.
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1. Problem

It is textbook knowledge that second-phase particles slow down the process of grain growth [1,2]. In this study we rise the question whether the formation of a second-phase always slows down grain growth in polycrystals, in particular in nanocrystals. For this we consider grain boundary motion in an alloy with a miscibility gap. When the sample (polycrystal) is single phase, grain boundary motion or the rate of grain growth is described by the theories of impurity drag as elaborated by Lücke and Detert [3], Cahn [4] and Lücke and Stüwe [5]. However, if we lower the temperature by ΔT or change the concentration by Δc (Fig. 1) the systems changes to a two-phase field. This causes two changes, namely the formation of precipitates of a second-phase and a reduction of the matrix concentration. Hence, grain growth is impeded by the formed precipitates but concurrently, impurity drag becomes less strong. It depends on the magnitude of both effects whether grain growth slows down or is accelerated. If grain growth is accelerated, this manifests itself experimentally as a negative activation energy or in an increase of grain growth rate with rising concentration.

2. Theory

It is apparent that this effect is only feasible when certain conditions are met. In the following we will determine these conditions. Decreasing the temperature by ΔT will offset the system to the two-phase field and the ratio W_p of the precipitates with respect to the solid solution $W_{sol.sol.}$ will be according to the lever rule (Fig. 1)

$$\frac{W_p}{W_{sol.sol.}} = \frac{c_0 - c_A}{c_B - c_0} \tag{1}$$

In the two-phase field the equilibrium concentration of the solid solution $c_0' = c_A$ (Fig. 1). The general condition for acceleration of grain boundary migration reads

$$V(c_0' = c_A, \text{precipitates}) > V(c_0) \tag{2}$$

where V is the boundary migration rate.

We note that the boundary migration rate V corresponds to $V = \frac{1}{2}\frac{d\overline{R}}{dt}$ where $\overline{R}$ is the average grain size. For sake of simplicity we will denote V as the grain growth rate in the following.

Two situations have to be distinguished, namely, large immobile and small mobile precipitates. Let us first consider large immobile particles. In this case the grain growth rate can be represented as

$$V = m_b\left[P - P_{im}^{tp}(V) - P_p\right] > m_b\left[P - P_{im}^{SS}(V)\right] \tag{3}$$

where $P = \frac{\gamma}{\overline{R}}$ is the driving force for grain growth, γ is the grain boundary surface tension, P_{im}^{SS} and P_{im}^{tp} are dragging forces in the solid solution and the two phase

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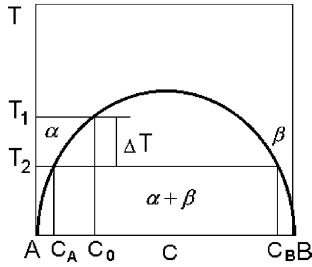*URL:* http://www.imm.rwth-aachen.de.

Fig. 1. Binary phase diagram with miscibility gap (see text for details).

regime, respectively. P_p is the dragging force by immobile particles and α is a geometrical parameter that correlates grain size and grain boundary curvature and will be taken to be $\alpha = 3$ in the following. To assess Eq. (3) we will use the Zener- and Lücke–Detert approximations for particle drag and impurity drag, respectively

$$P_p = \frac{3f\gamma}{2r} \tag{4}$$

$$P_{im} = \Gamma \frac{V}{D_{im}} kTm_b \tag{5}$$

f—the volume fraction of the particles, r—particle radius, Γ—adsorption at the grain boundary, D_{im}—bulk diffusion coefficient of the solute atoms.

For grain growth in a solid solution we arrive at

$$V = \frac{m_b P}{1 + \Gamma(c_0)\frac{kT}{D_{im}}m_b} \approx \frac{D_{im}P}{kT\Gamma(c_0)} \tag{6}$$

and for grain growth in a solid solution with second-phase particles we obtain

$$V = \frac{m_b\left[P - \frac{3f\gamma}{2r}\right]\frac{D_{im}}{kT}}{\Gamma(c_0' = c_A)} \tag{7}$$

For acceleration of grain growth caused by precipitation

$$\frac{P - \frac{3f\gamma}{2r}}{\Gamma(c_0' = c_A)} > \frac{P}{\Gamma(c_0)} \tag{8}$$

Relation (8) is valid under the assumption that the impurity diffusion coefficient is independent of concentration. With the driving force for grain growth $P = 3 \cdot \frac{\gamma}{\bar{R}}$, and the Henry adsorption isotherm $\Gamma(c) = Bc$, relation (8) reads

$$\frac{\frac{1}{\bar{R}} - \frac{f}{2r}}{c_A} > \frac{1}{\bar{R}c_0} \tag{9}$$

The volume fraction of the particles is $f = \frac{W_p\Omega_p}{W_p\Omega_p + W_{sol.sol.}\Omega_{sol.sol.}}$, where Ω_p and $\Omega_{sol.sol.}$ are the molar volumes of precipitates and the solid solution, respectively. For sake of simplicity we will assume $\Omega_p \simeq \Omega_{sol.sol.}$. It is pointed out that, strictly speaking, in the vicinity of the boundaries the isotherms should be used which take into consideration the interaction between species [6,7]. We use the Henry isotherm for a rough estimate, to establish

the essential physical link between the parameters of the problem.

From Eqs. (1), (2), and (9) we obtain

$$\frac{1 - \frac{c_0 - c_A}{c_B - c_A} \cdot \frac{\bar{R}}{r}}{c_A} > \frac{1}{c_0} \tag{10}$$

or, using evident relationships between c_A, c_0, c_B, we arrive at

$$\frac{\bar{R}}{r} < \frac{c_B}{c_0} \tag{10a}$$

The relations (10) and (10a) determine the conditions under which precipitation accelerates grain growth (PAGG) in the alloy. As mentioned, the relations (10) and (10a) are derived under the assumption that the second-phase particles are immobile. Apparently, the larger r (particle radius) and the smaller $\bar{R}$ (mean grain size) the better the approach. For $c_B \sim 1$, $c_0 \sim 10^{-3}$, $c_A \sim 10^{-4}$ the relation (10a) yields $\frac{\bar{R}}{r} < 10^3$.

However, the phenomenon discussed holds as well for the particles moving together with the grain boundary, in other words, for small, mobile particles. The theory of grain boundary motion dragged by mobile particles was considered in [6,8].

The physical reason for particle drag is an attractive force between grain boundary and particle (so-called Zener force and its variants [6,9]). As shown in [8] the velocity of joint motion of a grain boundary and the particles reads:

$$V = \frac{Pm_b}{1 + \sum_i n_i \frac{m_b}{m_p(r_i)}} \tag{11}$$

where n_i and $m_p(r_i)$ are the number of particles with radius r_i per unit area and the mobility of particles with radius r_i, respectively.

For a continuous size distribution of particles $\bar{n}(r)$ we obtain

$$V = \frac{Pm_b}{1 + \int_0^\infty \frac{\bar{n}(r)m_b}{m_p(r)}\,dr} \tag{12}$$

where $m_p(r)$ is the mobility of a particle of size r. The total number of particles per unit area n

$$n = \int_0^\infty \bar{n}(r)\,dr \tag{13}$$

The border between free grain boundary motion and the joint motion of the grain boundary with the particles is established by dimensionless criterion ρ:

$$\rho = \int_0^\infty \frac{\bar{n}(r)m_b}{m_p(r)}\,dr \tag{14}$$

If $\rho \ll 1$ then $V \cong m_b P$, and the grain boundary velocity is determined by the mobility of the boundary. If $\rho \gg 1$ grain boundary motion is determined by the mobility of the particles and their distribution function

$$V \cong \frac{P}{\int_0^\infty \frac{\bar{n}(r)}{m_p(r)} \, dr} \tag{15}$$

or in the simple case of a uniform size distribution $r = r_0$

$$\bar{n}(r) = n_0 \delta(r - r_0)$$

$$V = \frac{P m_p(r_0)}{n_0} \tag{16}$$

$$\rho = \frac{n_0 m_b}{m_p(r_0)}$$

where $n(r_0)$ is the number of particles of size r_0 per unit area.

The particle mobility is determined by its size and the mass transport mechanism. If mass transport is conducted through the bulk of a particle, $m_p(r) \sim \frac{1}{r^3}$, if it operates by interfacial diffusion, $m_p(r) \sim \frac{1}{r^4}$ [6].

For instance, when the particles move by interfacial diffusion (D_S), their mobility can be derived as [6]

$$m_p(r) = \frac{\Omega_a D_S \lambda}{kT r^4} \tag{17}$$

where Ω_a, D_S, λ are the atomic volume, interfacial diffusion coefficient and thickness of the interfacial layer in which the diffusion occurs, respectively.

With the formation of precipitates the solute concentration of the solid solution is reduced, causing also grain boundary mobility and grain boundary surface tension to increase. The surface tension increases in such a process only very moderately. So, the condition for grain growth acceleration can be written (in case of a uniform size distribution $r = r_0$) as

$$V = \frac{P m_p(r_0)}{n_0} > V(c_0) \tag{18}$$

The volume fraction f of the particles is given by the expression:

$$f = \frac{W_p \Omega_p}{W_p \Omega_p + W_{sol.sol.} \Omega_{sol.sol.}} = \frac{c_0 - c_A}{c_B - c_A} \tag{19}$$

On the other hand, $f = \frac{4}{3} \pi r_0^3 N$, where N is the number of particles per unit volume

$$N = \frac{3}{4 \pi r_0^3} \cdot \frac{c_0 - c_A}{c_B - c_A} \tag{20}$$

It follows that

$$n_0 = 2 r_0 N = \frac{3}{2 \pi r_0^2} \cdot \frac{c_0 - c_A}{c_B - c_A} \tag{21}$$

From (17)–(21) we arrive at the condition for grain growth acceleration by precipitation of mobile second-phase particles:

$$r_0^2 < \Omega_a \lambda \Gamma(c_0) \frac{D_S}{D_{im}} \cdot \frac{c_B - c_A}{c_0 - c_A} \tag{22}$$

We remind that the concentration dependence of grain growth rate was estimated in the Lücke–Detert

approximation. For $D_S \approx 10^{-10}$ m^2 s^{-1}, $D_{im} \approx 10^{-14}$ m^2 s^{-1}, $\Omega_a \approx 10^{-5}$ m^3 mol^{-1}, $\Gamma(c_0) \approx 105$ mol m^{-2}, $\lambda \approx 10^{-9}$ m, $c_B = 1$, $c_A \approx 10^{-4}$, $c_0 \cong 10^{-3}$, we obtain $r_0 < 10^{-6}$ m.

Grain boundary motion together with the particles is bound to have a point of detachment. As mentioned above the limiting velocity of grain boundary motion together with the particles is described by Eq. (12) while the detachment condition can be represented as

$$f(r_0) m_p(r_0) < V(c_A) \tag{23}$$

or, using for $f(r)$ the relation derived in [6]: $f(r_0) = \frac{3}{2} \pi \gamma_b r_0$ and for $m_p(r_0)$ the expression (17), we arrive at

$$\frac{r_0^3}{R} > \lambda \Omega_a \Gamma(c_A) \frac{D_S}{D_{im}} \tag{24}$$

For the values of the parameters given above Eq. (24) is obeyed for $\frac{r_0^3}{R} > 10^{-15}$ m^2, for instance, by $r_0 > 10^{-7}$ m and $\overline{R} < 10^{-6}$ m.

Consequently, the predicted effect can actually occur in systems with mobile and immobile particles. From Eqs. (10) and (10a) follows that the effect in samples with immobile particles is more pronounced in systems with low solute solubility (c_A and c_0 are small) and rather small mean grain size $\overline{R}$. In contrast, for mobile particles the only constraint is the size of the particles: they must be sufficiently small.

The authors are not aware of any experimental report on this effect. Industrial annealing practices frequently make use of specific processing windows to optimize recrystallization kinetics, which may be related to the discussed effect.

The only experimental data known to the authors which can be connected with the effect discussed is the recrystallization of Al–Mn alloys [10] (Fig. 2).
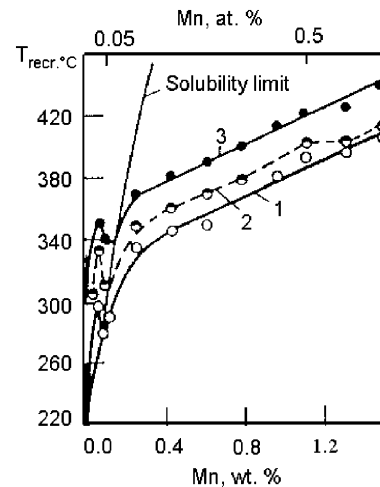

Fig. 2. Concentration dependence of recrystallization temperature $T_{recr.}$ of Al–Mn alloys with different Mn content: (1) beginning of recrystallization; (2) 50% recrystallized volume; (3) terminal recrystallization.

Fig. 2 shows the concentration dependence of recrystallization in Al–Mn alloys for the temperature of different stages of recrystallization—the early stage $(1 - t_r^e)$, 50% recrystallized $(2 - t_r^{0.5})$ and the final stage of recrystallization $(3 - t_r^f)$ [10] (Fig. 2). It is seen that in the close vicinity of the solubility limit a sharp minimum can be observed for all t_r, indicating an acceleration of the process. It is stressed that the mentioned minimum is also evident for temperatures at the end of recrystallization, when the major contribution to the microstructure change is associated with grain growth, as assumed in the theoretical frame work given above. From the analysis given above it is obvious that the necessary conditions for the effect of PAGG are not so tough, and certainly ought to be observed in nanocrystalline materials.

3. Conclusions

It is shown that the decrease of solute drag during precipitation can lead to an acceleration of grain growth. This effect is expected to be most likely for very fine grained or nanocrystalline material and occurs irrespective whether the precipitated particles are mobile or not. Circumstantial experimental evidence for PAGG is provided for Al–Mn alloys.

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