



Full length article

Generalized Gibbs-Thomson equation for nanoparticles at grain boundaries

M. Lin ^{a, c}, G. Gottstein ^{a, *, 1}, L.S. Shvindlerman ^{a, b}^a Institut für Metallkunde und Metallphysik, RWTH Aachen University, Kopernikusstr. 14, Aachen, Germany^b Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow Distr., Russia^c Institut für Eisenhüttenkunde, RWTH Aachen University, Intzestr. 1, Aachen, Germany

ARTICLE INFO

Article history:

Received 20 January 2017

Received in revised form

4 March 2017

Accepted 4 March 2017

Available online 19 March 2017

Keywords:

Gibbs-Thomson relation

Triple junction

Grain boundary

Precipitation

ABSTRACT

A general Gibbs-Thomson equation is derived from the complete free energy description of precipitates at grain boundaries, taking into account the excess free energy of the grain boundary – phase boundary junction. In this model, the equilibrium shape of particles shows a strong dependency on the particle size, which gives rise to a deviation from the classical theory of precipitation. The influence of the line tension of triple junctions on the nucleation energy barrier is discussed.

© 2017 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Precipitation is a common form of phase transformation in nature: from water droplets in clouds to second-phase particles in metals. The new phase is dispersed in the form of small particles in the mother phase and its total volume fraction is so small that the coalescence of different particles can be neglected. In a classical model of precipitation, a second-phase particle is treated as a sphere separated from the matrix by a phase boundary, whose excess energy gives rise to a nucleation barrier. In heterogeneous systems, nuclei are formed preferentially at certain locations with a low energy barrier. An important kind of nucleation site in a polycrystalline material is a grain boundary. It is commonly observed that the grain interior in the vicinity of a grain boundary is free of precipitates. One can expect that the precipitate-free-zone (PFZ) can cover the whole grain interior when the grain size falls below a certain value. In this case the precipitation at grain boundaries becomes dominant.

Second-phase particles formed at grain boundaries are

accompanied by a special line defect, the triple junction (TJ) where the phase boundary and the grain boundary meet. At the junction the atoms should rearrange to accommodate the lattice- and orientation differences of the three adjoining crystals and, consequently, may increase or decrease the total free energy. The line tension of a TJ, which is defined as the excess free energy with respect to the length of the TJ line, was first introduced by Gibbs [1] and recently accurately measured [2,3]. Also, molecular dynamics (MD) simulations were carried out to estimate the excess energy of a three-grain-boundary junction [4–7].

An analogon to a TJ in a liquid system is a three phase contact line (TPCL) at the bottom of a droplet on a solid substrate. The dependency of the contact angle at the TPCL on its curvature has been studied extensively in sessile droplet experiments. The Young equation, which describes the relation between contact angle θ and surface energy γ , was modified to take this phenomenon into account. A new parameter, the “line tension” τ , whose concept was first introduced by Gibbs [1], has been introduced to represent a curvature-dependent “force” on the TPCL. The modified Young equation for a droplet on a flat horizontal substrate [8–10] reads

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl} - \tau/r}{\gamma_{lg}} \quad (1)$$

where γ_{ij} are the surface tensions of the solid-gas (sg), solid-liquid

* Corresponding author.

E-mail address: gottstein@imm.rwth-aachen.de (G. Gottstein).

¹ This author was an Editor of the journal during the review period of the article. To avoid a conflict of interest, Christopher A. Schuh acted as Editor for this manuscript.

(sl) and liquid-gas (lg) interfaces, respectively; r is the radius of curvature of the TPCL, and τ is the line tension.

Both positive and negative values of TPCL tension were reported. In some sessile droplet experiments [11,12], smaller droplets showed stronger wetting (smaller contact angle) than predicted by the Young equation, which implies a negative line tension. In the MD simulations of symmetric-tilt-grain-boundary junctions by Srinivasan et al. [5] and Eich et al. [4], the TJ excess energy was found to be potentially negative.

Both the magnitude and the sign of the line tension are under controversy [13–15]. Deviation from the modified Young equation for submicrometer sessile droplets has been shown by accurate measurements on the contact angle [11,12,14]. Nevertheless, it is certain that the contact angle can change in both directions with the triple-junction curvature whose dependency can be semi-quantitatively described by the modified Young equation. Complete wetting or dewetting can be expected when the size of a droplet or particle approaches zero.

The quantity corresponding to τ in a solid material is the “triple-junction energy”. In this text, we use the terms “line tension” and “triple junction energy” interchangeably. The experimental results on pure copper and copper alloys yielded a positive triple junction energy. However, there is no proof that the triple junction energy in other solids cannot be negative. This excess energy is an extra driving force for microstructural restoration processes, such as grain growth or precipitation, which has not been considered in conventional theories.

A triple line cannot exist independently of grain- or phase boundaries. It is therefore natural to express the triple line tension in relation to the excess interfacial free energy. A dimensional analysis yields that the ratio of the line tension τ to the surface energy γ_s has the dimension of a length. We introduce the quantity

$$r^* = \frac{\tau}{\gamma_s} \tag{2}$$

as a measure for the line tension of triple junctions and refer to it as “characteristic length”. By applying this quantity to the modified Young equation, the curvature-dependent term $\tau/\gamma r$ can be simplified to r^*/r , which will vanish for $r \gg r^*$. Thus, the characteristic length r^* is the length scale on which the triple junction energy is not negligible. Zhao et al. [2,3] measured the curvature dependency of the dihedral angle at thermal grooves using atomic force microscopy and determined the line tension of the GB-surface triple junction, i.e. the groove root to be $(2.5 \pm 1.1) \times 10^{-8} \text{ J/m}$. According to this measurement the characteristic length of the TJ tension is of the order of nanometers. In the following we shall investigate the effect of triple-junctions on precipitation at grain boundaries.

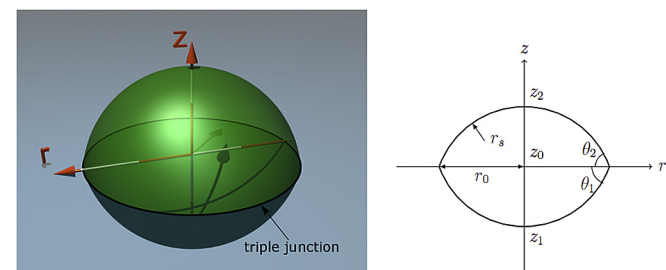


Fig. 1. Shape of a precipitate situated on grain boundary; the blue plane represents the grain boundary and the green surfaces represent the phase boundary.

2. Equilibrium shape of a particle at a grain boundary

Let us consider a second phase particle located at a grain boundary as shown in Fig. 1. Part of the grain boundary is replaced by the particle and a circular triple line is formed. Assuming that the grain boundary and TJ properties are isotropic, the particle should have rotation symmetry. Taking into account the contribution of the TJ excess energy τ , we can formulate the total free energy of the particle as

$$G = 2\pi \int_{x_1}^{x_2} \left(\gamma_s r \sqrt{1+r^2} - \Delta p \frac{r^2}{2} \right) dx + 2\pi \tau r_0 - \gamma_b \pi r_0^2 \tag{3}$$

where γ_s and γ_b are the phase boundary energy and grain boundary energy, respectively. Δp represents the general volumetric (bulk) driving force. If we only consider the chemical contribution, $\Delta p = (g_{\text{matrix}} - g_{\text{precipitate}})/V_{\text{precipitate}}^m$, where g denotes the effective molar free energy and $V_{\text{precipitate}}^m$ is the molar volume. For the precipitation of vacancies, the numerator in the expression should be replaced by the chemical potential of vacancies μ_v , that is $\Delta p = \mu_v/V_v^m$.

We derive the Euler equation and the transversality equations from the first-order variation of G .

$$\frac{1}{2\pi} \delta G = \int_{x_1}^{x_2} \left(F_r - \frac{d}{dx} F_r \right) \delta r dx + \left[F_r \Big|_{x_0-0}^{x_0+0} + (\tau - \gamma_b r_0) \right] dr_0 + (F - r' F_r) \Big|_{x_0+0}^{x_0-0} dx_0 \tag{4}$$

where $F(r, r') = \gamma_s r \sqrt{1+r^2} - \frac{\Delta p}{2} r^2$. The variation δG must be zero for an arbitrary variation δr , dr_0 and dx_0 , hence

$$\frac{\Delta p}{\gamma_s} = \frac{r''}{(1+r^2)^{3/2}} + \frac{1}{r\sqrt{1+r^2}} \tag{5}$$

$$0 = \gamma_s \frac{r'}{\sqrt{1+r^2}} \Big|_{x_0+0}^{x_0-0} + \frac{\tau}{r_0} - \gamma_b \tag{6}$$

$$0 = \frac{\gamma_s}{\sqrt{1+r^2}} \Big|_{x_0+0}^{x_0-0} \tag{7}$$

The first equation is the Euler equation. The second and third equation are the transversality conditions. Note that the right hand side of Eq. (5) is equal to two times of the mean curvature of the surface obtained by rotating the curve $r(x)$. Supposed that surface energy and driving force are constant for the upper and lower cap, these two caps should be Constant-Mean-Curvature (CMC) surfaces. The CMC surfaces with circular symmetry are known as Delaunay surfaces in geometry [16], such as plane, sphere, cylinder and catenoid.

Integrating $r(x)$ with the initial condition $r(x_1) = 0$ and $r'(x_1) = \infty$ yields a circle.

$$r = \sqrt{r_s^2 - (r_s + x_1 - x)^2} \tag{8}$$

The radius r_s is defined as the radius of curvature of the particle surface. We can derive from Eq. (5) that $r_s = \frac{2\gamma_s}{\Delta p}$.

Substituting the derivatives r' by trigonometric functions of the contact angles, the equations of the transversality conditions can be transformed to

Download English Version:

<https://daneshyari.com/en/article/5436232>

Download Persian Version:

<https://daneshyari.com/article/5436232>

[Daneshyari.com](https://daneshyari.com)