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Heterogeneous nucleation theory revisited: Effect of triple junction line energy

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ABSTRACT

This paper will re-consider the basic aspects of solid state classical heterogeneous nucleation theory. In particular it will show how recent experimental work that has been able to estimate grain boundary triple junction line energy can be used to supplement the understanding of the energy balance operating during nucleation. This implies that the energy of the newly created interface needs to be recalculated, assuming that the additional line energy of the line surrounding the precipitate in the plane of the boundary is taken into account. Examples will be given of the application of this revised approach to GB precipitate nucleation of cap-shaped particles of chromium carbide in nickel based alloys. It will be shown that original assumed values of the precipitate-matrix interfacial energy for this transformation have to be revised downward for critical nucleus sizes of less than about 10 nm.

1. Introduction

Recent work [1–3] has shown that it possible to make experimental estimates of triple junction line energies in copper. This is because, for the first time, atomic force microscopy has enabled measurement of very small movements of grain boundaries, and, in particular, triple junction lines, in tri-crystals. This work has highlighted that there is an additional heterogeneous feature that has hitherto been neglected in the mechanistic understanding of heterogeneous nucleation.

Traditional heterogeneous nucleation theory [4] calculates an activation energy required for the formation of the critical nucleus based on the ratio of the energy consumed in forming the critical nucleus to the driving force for the transformation. The energy consumed is normally taken to be the difference between the energy of the surface or interface created and the energy of the heterogeneous interface destroyed.

It is the intention of this paper to demonstrate how this energy balance is changed by the need to include a new energy; that of the line connecting the interface to the precipitate. This new energy is now experimentally determinable by the Shvindlerman analysis [1–3] mentioned above. It will be shown that this substantially affects the overall energy required to form the critical nucleus, especially when this nucleus radius is below 10 nm.

2. Triple line energy estimations in copper

Triple junction line energies have received increasing attention in recent years with advent of new experimental techniques and computer modelling [1–10]. The most recent experimental and thermodynamically correct approach is put forward in [1,10]. The basic idea of the approach is as follows: the equilibrium of four line tensions is considered, i.e. grain boundary triple line and three triple lines at the bottom of the thermal grooves (Fig. 1) attached to the triple line. From the equilibrium of the four line tensions it follows for the triple line tension

$$\gamma_{tj}^{l} = \gamma_{1-2}^{IS} \sin\zeta_{1-2} + \gamma_{1-3}^{IS} \sin\zeta_{1-3} + \gamma_{2-3}^{IS} \sin\zeta_{2-3} \quad (1)$$

where γ_{tj} and γ_{i-j}^{IS} are the grain boundary triple junction line tension and the line tension of triple lines at the bottom of the thermal grooves, respectively, ζ_{i-j} are the angles at each groove root of the corresponding grain boundary

$$\sin\zeta_{i-j} = \sin\left(\arctan\frac{\partial u_{i-j}}{\partial r}\bigg|_{r=0}\right) = \frac{\frac{\partial u_{i-j}}{\partial r}}{\sqrt{1+\left(\frac{\partial u_{i-j}}{\partial r}\right)}}\bigg|_{r=0} \quad (2)$$

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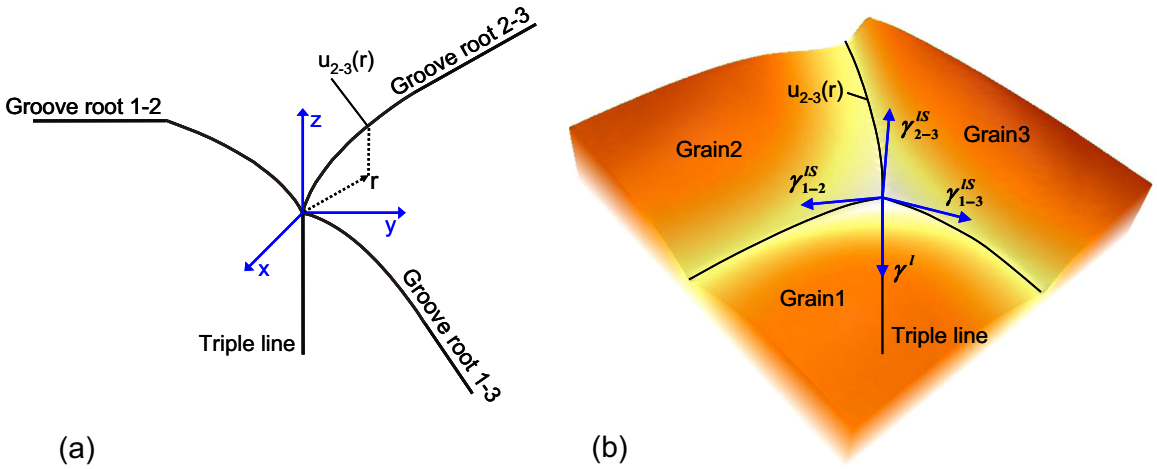

Fig. 1. (a) Schematic 3D-view of the line geometry at a triple junction. (b) AFM 3D-view of the line tension equilibrium at a triple junction [1].

The line tension of the triple lines γ_{i-j}^{IS} can be determined by comparing the angle at the root of a grain boundary groove formed at a straight grain boundary and at a curved grain boundary, in particular at the crater of a grain boundary triple junction. In the case that the grain boundary remains flat but curved at the root of the groove one has to take into account an additional term which is akin to the Laplace pressure for 3D curved grain boundary surfaces. Therefore,

$$\gamma_B - \gamma^{IS}\frac{\frac{\partial^2 u}{\partial r^2}}{\left[1+\left(\frac{\partial u}{\partial r}\right)^2\right]^{3/2}} = 2\gamma_S \cos\frac{\xi}{2} \tag{3}$$

Eqs. (1)–(3) constitute the theoretical basis of the presented approach and can be used to calculate the triple line energy from the geometry of the merging boundaries at the triple junction.

From the AFM measurements all necessary parameters can be derived to extract the triple line tension, such as the grain boundary groove angles, the groove root angles at the curved part of the grain boundary, and the curvature of the groove roots. The measurements were performed with high-aspect-ratio tips (OLYMPUS AC11160BN-A2) in an atomic force microscope in non-contact mode [1–4].

With the determined grain boundary-free surface line tension, the grain boundary triple line tension can be derived based on the equilibrium of four line tensions at their point of intersection, Fig. 1.

The measured random high angle grain boundary value of the grain boundary triple line tension in copper, $\gamma_{TP}^{l} = (6.0 \pm 3.0)\cdot 10^{-9}$ J/m is the value chosen for use in the rest of this paper.

3. Heterogeneous nucleation

In solid state heterogeneous nucleation, a typical situation might be a cap-shaped nucleus, of effective radius R, forming on a grain boundary (see Fig. 2). In this case the rate of nucleation, J, is given by

$$J = Z\beta\, exp\left(\frac{-\Delta G}{RT}\right) \tag{4}$$

where Z is the Zeldovitch factor, β is a diffusion-related supply term, R is the gas constant, T is the absolute temperature, and ΔG is the activation energy for nucleation. Classically this activation energy is given by

$$\Delta G = \frac{16\pi}{3}\frac{\gamma net^3}{\Delta G_v^2} \tag{5}$$

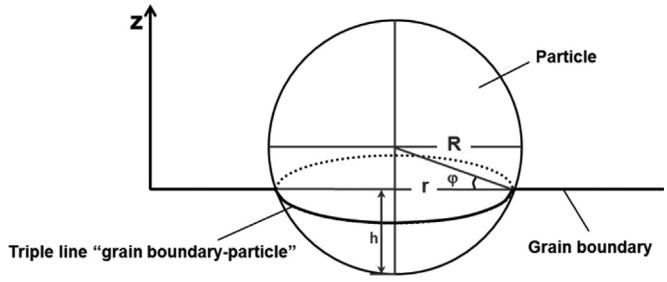

Fig. 2. Schematic illustration of the cap shaped particle of radius R nucleating on a grain boundary. The triple junction line is clearly shown.

where ΔG_v is the thermodynamic driving force for the transformation, and γnet is the net energy required to form the nucleus being considered. This value of γ is usually given by

$$\gamma net = 2\gamma_{pm} - \gamma_{GB} \tag{6}$$

where γ_{pm} is the particle-matrix interfacial energy and γ_{GB} is the grain boundary energy, in J m^{-2}. The particle-matrix interfacial energy, in the case of a cap-shaped nucleus, (see Fig. 2), is the energy of a hemispherical surface of radius R, plus the energy of a circular area equal to the area of grain boundary destroyed during the nucleation event. The grain boundary energy is the energy of a circular plane of radius R sin ϕ, where ϕ is the contact angle, which is the energy of the GB destroyed during nucleation (see Fig. 2).

This paper seeks to show that the above equation is imprecise: an additional term needs to be inserted; that of the line energy, γ_l, defining the line which is the perimeter of the circle of radius R sin ϕ

$$\gamma net = 2\gamma_{pm} - \gamma_{GB} + \frac{\gamma_l}{d} \tag{7}$$

where d is an effective width of the triple line. This equation can be expanded to precisely define the total energy required to form the cap-shaped nucleus as follows

$$\gamma_{tot} = \gamma_{pm} S - \gamma_{GB} A_{GB} + \gamma_l L \tag{8}$$

where

$$S = 2\pi R^2(1-\cos\varphi) + \pi(R\sin\varphi)^2$$

$$A_{GB} = \pi(R\sin\varphi)^2$$