ON SIZE AND SHAPE COARSENING OF NEEDLE-SHAPED PRECIPITATES

Freundlich P.[1], *Militzer M.*[2]

[1] *Department of Materials Engineering, Faculty of Metallurgy and Materials Engineering, VŠB-TU Ostrava, 17. listopadu 15, 70833 Ostrava-Poruba, Czech Republic*

[2] *Centre for Metallurgical Process Engineering, The University of British Columbia, 309-6350 Stores Road, Vancouver, BC, V6T 1Z4, Canada*

ROZMĚROVÉ A TVAROVÉ ZHRUBNUTÍ JEHLICOVITÝCH PRECIPITÁTŮ

Freundlich P.[1], *Militzer M.*[2]

[1] *Katedra Materiálového inženýrství, Fakulta metalurgie a materiálového inženýrství, VŠB-TU Ostrava, 17. listopadu 15, 70833 Ostrava-Poruba, Česká republika.*

[2] *Středisko pro inženýrink metalurgických procesů, Universita Britské Kolumbie, 309-6350 Stores Road, Vancouver, BC, V6T 1Z4, Kanada*

Abstrakt

Navrhuje se teorie zhrubnutí, která postihuje jak rozměrové, tak i tvarové změny částic s konstantní mezifázovou energií. Teorie popisuje časový vývoj středního objemu jehlicovitých precipitátů. Odchylky od zákona krychlového zhrubnutí klasické teorie LSW jsou predikovány s počátečními rychlostmi zhrubnutí, které jsou výrazně vyšší ve srovnání s rychlostmi pro sférické částice. Vzhledem k současnému zhrubnutí tvaru se původně jehlicovité precipitáty postupně přibližují sférickému (kulovitému) tvaru a tím i příslušným nižším rychlostem zhrubnutí. Teorie může být jednoduše rozšířena i na precipitáty ve tvaru disku.

Abstract

A coarsening theory is proposed which incorporates both size and shape changes for particles having a constant interfacial energy. The theory describes time evolution of the mean volume of needle-shaped precipitates. Deviations from the cubic coarsening law of the classical LSW theory are predicted with initial coarsening rates being significantly larger compared to those of spherical particles. Because of simultaneous shape coarsening the initially needle-like precipitates approach gradually the spherical shape and the associated lower coarsening rates. The theory can be simply extended to disc-shaped precipitates.

Introduction

In a two-phase precipitate-matrix system after a first-order phase transformation, a large amount of interfacial area can be present which increases the total free energy of the system. In order to lower the free energy, diffuse fluxes between the precipitates occur which result in a dissolution of small precipitates and the growth of large ones. As a result, the mean particle size increases while the number of particles decreases. This process, originally discovered at the beginning of this century by W. Ostwald, is called coarsening or Ostwald ripening. According to Gibbs-Thomson equation, the driving force for the coarsening process is related to the curvature of the interface. The higher the curvature of the precipitate-matrix interface, the higher the driving force for atoms to flow from regions of high curvature to regions of low curvature. Thus, the coarsening kinetics is generally controlled by volume diffusion through the matrix.

The first attempt to describe the Ostwald ripening quantitatively was proposed by Greenwood in 1956 [1]. A generally accepted coarsening theory was proposed in 1961 by Lifshitz and Slyozov [2] and Wagner [3], now simply known as LSW theory. Considering the limiting case of zero volume fraction of spherical precipitates with the mean radius and a particle size distribution (PSD) function obeying the equation of continuity, the LSW theory predicts a cubic coarsening law

. (1)

where is the initial mean particle radius before the coarsening process, *K* is the coarsening rate constant and *t* is time. The cubic coarsening law (1) is derived from the Gibbs-Thomson equation and the Fick's law by assuming a small degree of supersaturation and constant coarsening rate *K* [1]. The assumption of constant coarsening rate requires constant temperature and interfacial energy per unit surface during coarsening. Based on the above-mentioned assumptions, the LSW theory predicts the coarsening kinetics, i.e. the mean particle size and the PSD function. In spite that a cubic coarsening law is frequently observed in experimental studies, the details of the predictions by the LSW theory are usually in disagreement with experimental results.

Consequently, numerous attempts have been made to propose improved theories by considering finite volume fractions of the second phase [4-12] or elastic stress interactions either between precipitates or on the precipitate-matrix interface [13-18]. Although these modifications usually result in the change of the PSD shape, the coarsening kinetics of the precipitates obeys in most cases the cubic law; deviations from the cubic law are predicted when elastic stress interactions occur between particles [15].

Surprisingly small attention was paid to the effect of non-spherical shape of precipitates. Due to the anisotropy of surface energy in many systems, the precipitates grow in a shape with lower symmetry than spherical [19-21]. When the coarsening starts at the end of the growth process, precipitates have still non-spherical morphology and thus the basic assumption of the LSW theory is not valid. Since the curvature along the surface of a non-spherical particle vary, volume diffusion to and from the surface will vary too. For growing particle, according to the Gibbs-Thomson equation, the volume diffusion of atoms will be lower to the regions of high curvature and higher to the regions of low curvature. In addition, new diffuse fluxes occur along the particle surface and this interface diffusion will exist together with the volume diffusion. The volume diffusion, therefore, changes both the shape and the size of a non-spherical particle while interface diffusion changes only the particle shape.

A few theories of shape coarsening of an isolated plate-shaped precipitate have been developed [22-25]. Shiflet *et al.* [22] considered only volume diffusion and, in addition, a special case of precipitate growth by the ledge mechanism, which require coherent or semi-coherent precipitates. Merle and Doherty [23] developed an alternative model for interface controlled diffusion, in which the volume diffusion is neglected, and thus, the model describes only shape coarsening or, strictly speaking, only the shape changes. Zwillinger [24] analysed the coarsening of a collection of non-spherical particles of general shape. He introduced a shape function, which described the shape of each particle but in the same time, the shape function was assumed to be time independent, i.e. each particle was constrained to remain in its original shape during coarsening. By this restriction, the model describes only size coarsening and, as one could expect, the coarsening kinetics obeys the cubic law. Recently, Marsh and Glicksman [25] proposed a more general approach to size coarsening in non-spherical morphologies by describing time evolution of small convex interfacial patches. The patches were, again, constrained to have a fixed shape in time, and the model did not take into account diffuse fluxes along surface of the patches. However, due to the general approach, the model is applicable to arbitrarily curved surfaces. Thus, its results are used as starting point in the present work.

As experiments show, size and shape coarsening processes occur simultaneously and the diffuse fluxes associated with shape coarsening are often comparable in magnitude to the interparticle fluxes [26]. Therefore, an attempt is presented in the following to develop a simple coarsening theory for incoherent needle-shaped precipitates by incorporating both size and shape changes.

Size coarsening

The needle-shaped precipitate can be mathematically modelled by a prolate symmetrical ellipsoid with two independent variables describing its shape, i.e. two principal axes or one of them and the aspect ratio. If a is the major and b the minor axis, the eccentricity ε of the prolate symmetrical ellipsoid is defined as

. (2)

For each point on the ellipsoid surface, two orthogonal principal radii of curvature R_1 and R_2 can be defined (Fig.1).

Fig.1 Small interfacial patch on a precipitate surface, the normal vector

and the two orthogonal principal radii of curvature R_1 and R_2 [25]

The normal vector, perpendicular to the ellipsoid surface at the given point, is orthogonal to both radii. By introducing the angular variable θ (see Fig.2), the reciprocal of the local principal radii, i.e. the local principal curvatures and can be written as [27]

, (3)

where

(4)

is the interfocal distance.

Fig.2 Definition of the major half-axis *a* and minor half-axis *b* of a symmetrical ellipsoid and the angle θ between the z axis and the normal vector perpendicular to the ellipsoid surface at point *P*

It is common to describe the local geometry by its aspect ratio, i.e. the ratio of the principal radii or curvatures

. (5)

By using (3) and (4), the aspect ratio of an arbitrary point on the ellipsoid surface can be rewritten as

. (6)

Marsh and Glicksman [25], who studied coarsening of small interfacial patches, redefined the shape factor as

, (7)

in order to avoid divergences, since for convex surfaces while . They considered an isolated interfacial patch sufficiently small to ensure that the shape factor remains constant over the patch. According to their results, the coarsening kinetics of this isolated patch obeys the cubic law

, (8)

where V is the volume of the curved wedge bounded by the patch (see Fig.1). The coarsening constant K in equation (8) is

, (9)

where K_S is the coarsening constant for a patch of a sphere ($s = 0$). It is obvious that the coarsening rate increases as the shape of the patch varies from spherical ($s = 0$) to cylindrical $s = 1$.

By using equation (7), the coarsening constant (9) can be expressed as a function of the aspect ratio

. (10)

Assuming, that the overall coarsening constant of the ellipsoid K_E is the mean value of the coarsening constants over the surface, we can write

. (11)

The local coarsening constant K_S depends on the interfacial energy and thus on the local degree of coherency. In the case of an interfacial energy, which is constant along the entire surface of the particle, equation (11) can be rewritten as

. (12)

The assumption of a constant interfacial energy restricts this approach to particles with a constant degree of coherency along its surface, e.g. fully incoherent particles, whereas coherency changes during coarsening cannot be described in the above way. In case of needle-like precipitates, this would be consistent with the assumption that they experienced their transition from initially coherent or semi-coherent particles to incoherent particles during growth before the coarsening stage.

According to equation (6), the mean aspect ratio over the surface of the ellipsoid is

, (13)

since . By using equation (2) and (13), equation (12) can be rewritten as

(14)

Since , needle-shaped particles coarsen always faster then particles of spherical shape.

By introducing the mean aspect ratio (13) and the mean coarsening constant (14), we have neglected the differences in local curvature that are responsible both for diffuse fluxes along the particle interface and for different local coarsening rates. These phenomena will lead to shape changes of particles, which are described in the following section.

Shape coarsening

Let us consider a fully incoherent needle-shaped precipitate, which is in equilibrium with the matrix. In general, differences in curvature along particle surface result in diffuse fluxes of atoms along the surface. Thus, to calculate the shape change quantitatively, a proper description of interfacial diffusion is needed, which requires solving a two-dimensional diffusion problem.

For simplicity, shape coarsening is considered from a phenomenological point of view. The shape change of the particle is driven by the difference between the surface energy of the needle-shaped particle and the surface energy of a spherical particle of the same volume. If S_E is the surface area of the needle-shaped precipitate represented by an ellipsoid, and S_S the surface area of a sphere of the same volume as the ellipsoid, the driving force for shape change is , where γ is the interfacial energy of the unit surface. The decrease in the surface area of the particle in time is proportional to ΔE, which leads to a simple differential equation

, (15)

The unit of the constant C is $m^2\ J^{-1}s^{-1}$ and thus C can be interpreted as a mobility, , where D is the diffusion coefficient of interfacial diffusion at temperature T and k is the Boltzman constant. The solution of the differential equation (15) in dimensionless variables is given by

, (16)

where

, ,

and S_{E0} is the initial surface area of the precipitate. According to [28], the surface of a prolate ellipsoid S_E is

and by normalising to

(17)

is obtained. An equation describing the shape coarsening of a needle-shaped precipitate can be derived from equation (16) and (17) such as

. (18)

where the dimensionless time , is introduced. Equation (18) can be solved numerically for . The time evolution of eccentricity is shown on Fig.3 for four different values of initial . It is evident that a needle-shaped precipitate approaches spherical symmetry asymptotically and the time required to attain the spherical shape, ε=0, increases with initial eccentricity.

Fig.3 Time evolution of eccentricity from its initial value in dimensionless variable t^*

Size and shape coarsening

Since size and shape coarsening occur simultaneously, rather complicated combination of volume and interfacial diffuse fluxes arise around a needle-shaped precipitate. By using the above-mentioned mathematically simple approaches, the simultaneous size and shape coarsening can be described at least qualitatively. The cubic coarsening law (8) can be rewritten for a needle-shaped precipitate by using equation (14) as

. (19)

The constants C and γ have been included in the coarsening constant K_S. The mean volume of the precipitates as a function of time, , is given by

. (20)

Results of numerical integration are shown in Fig.4 for four different values of initial eccentricity . On this figure, the normalised volume change is plotted as a function of normalised time where represents the mean precipitate volume at the beginning of coarsening. According to the cubic law (8), coarsening of a spherical precipitate () would be represented by a straight line with a slope equal to coarsening constant K_S. Since non-spherical precipitates change shape during coarsening, K_E is not constant in time and the graph of the function is curved. For sufficiently high initial eccentricity, rapid initial coarsening is being predicted before the eccentricity decreases with time and the coarsening rate approaches that of spherical particles.

Fig.4 The mean volume change during coarsening of a needle-shaped precipitate in dimensionless variables

Conclusions

A coarsening theory has been developed which describes coarsening of needle-shaped precipitates. The theory incorporates two phenomena, size coarsening and shape coarsening, and thus consists of two parts. The first one is based on the size coarsening theory of a small interfacial patch developed by Marsh and Glicksman. A needle-like precipitate is geometrically represented by a symmetrical ellipsoid and the coarsening constant is expressed as a function of eccentricity.

In the second part, a simple theory of shape coarsening has been developed which attempts to describe shape changes of precipitates. Instead of complicated analysis of concentration gradients and diffuse fluxes along the particle-matrix interface, the proposed shape coarsening theory is based on the assumption that precipitates tend to minimise the surface energy by 'spheroidisation'. The shape change is expressed by the time evolution of eccentricity.

In coarsening of needle-shaped particles, the coarsening rate is a function of precipitate eccentricity and the eccentricity varies in time. Thus, the cubic coarsening law is not valid and has to be reformulated. Numerical calculation shows that coarsening rates of needle-shaped particles are significantly larger compared to those of spherical particles and decrease in time as the particle shape approaches a sphere. This theory can be extended to disc-shaped particles simply by reformulating equation (2) and (3) and repeating the process of derivation.

Acknowledgements

The authors are grateful to Prof. Ludmila Hyspecká from the Department of Materials Engineering, VŠB-Technical University of Ostrava, Czech Republic, for many useful and stimulating discussions.

Literature

[1] Greenwood, G.W.: The Growth of Dispersed Precipitates in Solutions, Acta metall. vol. 4, 1956, pp. 243-248.

[2] Lifshitz, I.M. and Slyozov, V.V.: The Kinetics of Precipitation From Supersaturated Solid Solutions , J. Phys. Chem. Solids vol.19, 1961, No. 1, pp. 35-50.

[3] Wagner, C.: Theorie der Alterung von Niederschlagen durch Umlosen, Z. Elektrochemie vol 65, 1961, pp. 581-591.

[4] Ardel, A.J.: The Effect of Volume Fraction on Particle Coarsening: Theoretical Considerations, Acta metall. vol. 20, 1972, pp. 61-71.

[5] Brailsford, A.D. and Wynblatt, P.: The Dependence of Ostwald Ripening Kinetics on Particle Volume Fraction, Acta metall. vol. 27, 1979, pp.489-497.

[6] Marqusee, J.A. and Ross, J.: Theory of Ostwald ripening: Competitive growth and its dependence on volume fraction, J. Chem. Phys. vol. 80, 1984, No. 1, pp.536-543.

[7] Voorhees, P.W. and Glicksman, M.E.: Solution to the Muti-Particle Diffusion Problem with Applications to Ostwald Ripening - I. Theory, Acta metall. vol 32, 1984, No. 11, pp. 2001-2011.

[8] Voorhees, P.W. and Glicksman, M.E.: Solution to the Muti-Particle Diffusion Problem with Applications to Ostwald Ripening - II. Computer Simulations, Acta metall. vol. 32, 1984, No. 11, pp. 2013-2030.

[9] Enomoto, Y., Tokuyama, M. and Kawasaki, K.: Finite Volume Fraction Effect on Ostwald Ripening, Acta metall. vol. 34, 1986, No. 11, pp. 2119-2128.

[10] Enomoto, Y., Kawasaki, K. and Tokuyama, M.: Computer Modelling of Ostwald Ripening, Acta metall. vol. 35, 1987, No. 4, pp. 907-913.

[11] Enomoto, Y., Kawasaki, K. and Tokuyama, M.: The Time Dependent Behavior of the Ostwald Ripening for the Finite Volume Fraction, Acta metall. vol. 35, 1987, No.4, pp. 915-922.

[12] Enomoto, Y.: Finite Volume Fraction Effect on Coarsening - II. Interface-Limited Growth, Acta metall. mater. vol. 39, 1991, No. 8, 2013-2016.

[13] Johnson, W.C., Berkenpas, M.B. and Laughlin, D.E.: Precipitate Shape Transitions During Coarsening under Uniaxial Stress, Acta metall. vol. 36, 1988, No. 12, pp. 3149-3162.

[14] Johnson, W.C., Voorhees, P.W. and Zupon, D.E.: The Effect of Elastic Stress on the Kinetics of Ostwald Ripening: The Two-Particle Problem, Metall. Trans. vol. 20A, 1989, pp. 1175-1189.

[15] Enomoto, Y. and Kawasaki, K.: Computer Simulation of Ostwald Ripening with Elastic Field Interactions, Acta metall. vol. 37, 1989, No. 5, pp. 1399-1406.

[16] Leo, P.H., Mullins, W.W., Sekerka, R.F. and Vinals, J.: Effect of Elasticity on Late Stage Coarsening, Acta metall. mater. vol. 38, 1990, No. 8, pp. 1573-1580.

[17] Paris, O., Langmayr, F., Vogl, G. and Fratzl, P.: A Possible Criterion for Slowing Down of Precipitate Coarsening due to Elastic Misfit Interactions, Z. Metallkd. vol. 86, 1995, pp. 860-863.

[18] Fratzl, P. and Penrose, O.: Ising Model for Phase Separation in Alloys with Anisotropic Elastic Interaction - I.Theory, Acta metall. mater. vol. 43, 1995, No. 8, pp. 2921-2930.

[19] Ferrante, M. and Doherty, R.D.: On the Precipitate Growth Kinetics in Aluminium-Silver Alloys, Scripta met. vol. 10, 1976, pp. 1059-1064.

[20] Lee, J.K., Barnett, D.M. and Aaronson, H.I.: The Elastic Strain Energy of Coherent Ellipsoidal Precipitates in Anisotropic Crystalline Solids, Metall. Trans. vol. 8A, 1977, pp. 963-970.

[21] Backhaus-Ricoult, M.: Growth and Equilibrium Morphology of Metal Precipitates Formed Inside an Oxide Matrix, Interface Sci. vol. 4, 1997, pp.285-302.

[22] Shiflet, G.J., Aaronson, H.I. and Courtney, T.H.: Kinetics of the Approach to Equilibrium Shape of a Disc-Shaped Precipitate, Sripta met. vol. 11, 1977, pp. 677-680.

[23] Merle, P. and Doherty, R.D.: Evolution Towards Equilibrium Shape of θ Precipitates by Interface Diffusion, Scripta met. vol. 16, 1982, pp. 357-360.

[24] Zwillinger, D.: Coarsening of Non-Spherical Particles, J. Cryst. Growth vol. 94, 1989, pp. 159-165.

[25] Marsh, S.P., Glicksman, M.E.: Ostwald Ripening in Non-Spherical Morphologies, Mat. Sci. Eng. vol. A238, 1997, pp. 140-147.

[26] Aikin, R.M. and Plichta, M.R.: Concurrent Size and Shape Coarsening of γ' in Al-Ag, Acta metall. mater. vol. 38, 1990, No. 1, pp. 77-93.

[27] Mou, Y. and Howe, J.M.: Diffusion Fields Associated with Prolate Spheroids in Size and Shape Coarsening, Acta mater. vol. 45, 1997, No. 2, pp. 823-835.

[28] Isihara, A.: Determination of Molecular Shape by Osmotic Measurement, J. Chem. Phys. vol. 18, 1950, No. 11, pp.1446-1449.