

ДЕФЕКТЫ КРИСТАЛЛИЧЕСКОЙ РЕШЁТКИ

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Analytically Solvable Differential Diffusion Equations Describing the Intermediate Phase Growth

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Analytical method to solve differential diffusion equations describing the growth of the phase wedge during the intermetallic-compound formation with a narrow concentration range of homogeneity in bicrystals is proposed. A model describing the diffusion phase growth from point source inside the polycrystal grains is regarded. Analytical method to solve differential diffusion equations for such a model is suggested. Parabolic, cubic, and fourth power diffusion regimes for different scales from nanometers to micrometers and millimeters are analysed.

Key words: diffusion, reaction, phase-growth law, intermetallic compounds, grain boundaries.

Запропоновано аналітичну методу розв'язування диференційного рівняння, що описує кінетику утворення інтерметалевої фази вздовж межі між зернами з одночасним проникненням у самі зерна. Розглянуто модель, який описує кінетику утворення інтерметалевої фази з точкового джерела всередині полікристалічних зерен. Запропоновано відповідну аналітичну методу розв'язування диференційного рівняння такого моделю. Проаналізовано дифузійні режими (параболічний, кубічний, четвертого степеня) для різних масштабів — від нанометрового до мікрометрового та міліметрового.

Ключові слова: дифузія, реакції, закон зростання фази, інтерметалеві сполуки, міжфазні межі.

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Предлагается аналитический метод решения дифференциального уравнения, которое описывает кинетику образования интерметаллического соединения вдоль границы между зёрнами с одновременным проникновением в сами зёрна. Рассматривается модель, которая описывает кинетику образования интерметаллического соединения из точечного источника внутри поликристаллических зёрен. Предлагается соответствующий аналитический метод решения дифференциального уравнения такой модели. Анализируются диффузионные режимы (параболический, кубический, четвёртой степени) для разных масштабов — от нанометрового до микрометрового и миллиметрового.

Ключевые слова: диффузия, реакции, закон роста фазы, интерметаллические соединения, межфазные границы.

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1. INTRODUCTION

Analytical method of interdiffusion problems was presented in [1]. The researchers analysed concentration profile of Zn in the diffusion region of Zn–Cu alloy (α -brass, solid-state solution, concentration of Zn was less than 30%). This system has several intermediate phases too (β -brass, concentration of Zn is about 50%, γ -brass, concentration of Zn is about 68%, ε -brass, concentration of Zn is about 84%). These phases are formed between α -brass and Zn during diffusion. Approximation of constant diffusion flux along the diffusion direction within the width of each phase is used (so-called constant flux method) for describing the growth kinetics of the phases which was theoretically grounded in [2]. This technique necessitates no allowance for the concentration dependence of $D(C)$. Deviations from the parabolic law of phase growth in cylindrical and spherical samples were analysed in [3] using this method. This method was applied for describing the growth kinetics of thin γ -brass and ε -brass layers in a cylindrical sample at 400°C (Cu was in the centre of the cylindrical specimens). The γ -brass layer grew slower and the ε -brass layer grew more rapidly than in the planar sample [4]. Model of the growth of an intermediate phase between low-soluble components on diffusion at grain boundaries involving outflow was suggested in [5] and criteria for a transition from the Fisher regime $t^{1/4}$ to a parabolic one were established. It was proved in [6] that perpendicular grain boundaries do not influence phase growth kinetics in B-regime. This result allows us to use the well-known model of a polycrystal as a 3D array of grain boundaries to be perpendicular to the interface for describing the phase growth. There were no explanations in [5, 6] how one can solve differential diffusion equations because of a very complicated method. The formalism suggested was extended to the case of the growth of a solid-state solution with an expo-

nential concentration dependence of the diffusion coefficient. Analytical solution and Monte Carlo modelling of the Kirkendall effect were suggested in [7]. Grain boundary (GB) diffusion parameters determination using A-kinetics of intermetallic layer formation was proposed in [8]. Experimental data on Cu_5Zn_8 (γ -brass) diffusion growth kinetics were used for separate determination of the volume diffusion activation enthalpy and the GB activation enthalpy. Alternative models of competition of voiding and Kirkendall shift during compound growth in reactive diffusion were analysed in [9]. One can improve the methods to solve the diffusion equations for the growth of intermediate phase in bicrystals, polycrystals and inside grains.

2. MODELS AND METHODS

Model 1. The model of the phase layer growth during the intermetallic compound formation with a narrow concentration range of homogeneity, ΔC_1 , in bicrystals is based on the following assumptions [5, 6]:

1. An intermediate phase forms at first on the base of the grain boundary; the latter, transforming from the boundary $A-A$ to the boundary $I-I$, remains, due to easy influx with a diffusion coefficient D_b and having a thickness of $\delta \approx 1$ nm (*i.e.*, the GB is not overgrown with a new phase and does not bifurcate).

2. Formed phase I broadens normally to the GB due to volume diffusion with a diffusion coefficient $D \ll D_b$.

3. At all the points of the formed $I-A$ phase boundary between the broadening phase I and the matrix A the concentration of the component B is C_1 on the side of phase I and is zero on the side of phase A (solubility of B in A is ignored).

4. Outflow from the GB is the same at all GB points:

$$\frac{\partial C}{\partial x} = \frac{\Delta C(x)}{x(t, y)} = \frac{\Delta C_1}{x(t, 0)}, \quad x(t, 0) = \sqrt{\frac{2D\Delta C_1}{C_1} t}. \quad (1)$$

5. A flow in the volume of a phase wedge normal to the GB is constant along x (a corresponding property is proved in [2]) in a reference system associated with the moving nose of the wedge, $y(t)$.

The equation for $y(t)$ has such a form [5, 6]:

$$\frac{dy(t)}{dt} = \frac{A}{y(t)} - B \frac{y(t)}{\sqrt{t}}, \quad (2)$$

where $A = D_b \Delta C_1 / C_1$, $B = (1 / \delta) \sqrt{2D\Delta C_1 / C_1}$.

There were no explanations in [5, 6] how equation (2) can be solved as a very complicated method was used. A simpler method can be pointed out.

Method 1. One can simplify equation (2) by the following way

$$\frac{dz(t)}{dt} = 2A - \frac{2B}{\sqrt{t}} z(t), \quad (3)$$

where $z(t) = u(t)v(t) = y_0^2(t)$.

One can transform equation (3) into

$$\frac{du(t)}{dt} v(t) + u(t) \left(\frac{dv(t)}{dt} + \frac{2B}{\sqrt{t}} v(t) \right) = 2A. \quad (4)$$

Assumption

$$\frac{dv(t)}{dt} + \frac{2B}{\sqrt{t}} v(t) = 0$$

leads to $v(t) = \exp(-4B\sqrt{t})$.

Next step gives:

$$u(t) = 2A \int e^{4B\sqrt{t}} dt = \frac{A}{B} \sqrt{t} e^{4B\sqrt{t}} - \frac{A}{4B^2} e^{4B\sqrt{t}} + \frac{A}{B} C_0. \quad (5)$$

General solution of Eq. (3) is as follows:

$$z(t) = \frac{A}{B} \sqrt{t} - \frac{A}{4B^2} + \frac{A}{B} C_0 e^{-4B\sqrt{t}}. \quad (6)$$

Using initial conditions $z(t=0) = 0$ one can obtain finally:

$$z(t) = \frac{A}{B} \sqrt{t} - \frac{A}{4B^2} (1 - \exp(-4B\sqrt{t})) \quad (7)$$

or

$$y(t) = \sqrt{\frac{A}{B} \sqrt{t} - \frac{A}{4B^2} (1 - \exp(-4B\sqrt{t}))}. \quad (8)$$

Equation (8) shows the Fisher diffusion regime:

$$y(t) = \sqrt[4]{\frac{D_b^2 \delta^2 \Delta C_1}{2DC_1} t} \quad (9)$$

for

$$\sqrt{\frac{D_b}{2D}} \delta < y(t) < \frac{D_b}{2D} \delta.$$

Model 2. A model of the phase layer growth during the intermetallic

compound formation with a narrow concentration range of homogeneity inside grains is based on the following assumptions:

1. An intermediate phase *I* forms inside grains from a point source of substance *A* that is surrounded by substance *B*. The point source has a diameter of $\delta \approx 1$ nm. The dislocations steps can be the point sources in nanometers scale.

2. Dislocation pipe is easy path for *A*-atoms to go from substance *A* to the dislocations steps with a diffusion coefficient $D_d \approx D_b$ and a diameter of $\delta \approx 1$ nm.

3. Formed spherical phases *I* broadens in 3*D* space from the dislocations steps due to diffusion with a diffusion coefficient D_1 ($D < D_1 < D_d$).

Method 2. One can use constant flux method [3] to get differential equation for intermetallic compound growing inside polycrystals grains from a point source and forming small spherical particles (which form the polycrystals [10] and 3-dimensional integrated circuits [11]):

$$J_{\text{sph}} = \frac{4\pi\delta R(t)D_1\Delta C_1}{2R(t) - \delta} = 4\pi R^2(t)C_1 \frac{dR(t)}{dt}, R(t) \gg \frac{\delta}{2} \quad (10)$$

or

$$\frac{dR(t)}{dt} R^2(t) = \frac{D_1\Delta C_1}{2C_1} \delta, \quad (11)$$

and the solution

$$R(t) = \sqrt[3]{\frac{3D_1\Delta C_1\delta}{2C_1} t}. \quad (12)$$

3. ANALYSIS

It was proved in [6] that perpendicular grain boundaries do not influence phase growth kinetics in B-regime. This result allows us to use the well-known model of a polycrystal as a 3*D* array of grain boundaries to be perpendicular to the interface for describing the phase growth. The growth phase layer law in polycrystals for diffusion time

$$t_{\frac{1}{4} \rightarrow \frac{1}{2}} > \frac{D_b^2 C_1 \delta^2}{8D^3 \Delta C_1} \quad (13)$$

is parabolic because volume diffusion is more pronounced than GB diffusion.

Parabolic diffusion regime is valid (in micrometers and millimetres

scales [4]) for $y(t) > (D_b\delta)/2D$ [5, 6]:

$$y(t) = \sqrt{\frac{2D\Delta C_1}{C_1} t}. \quad (14)$$

Parabolic diffusion regime is valid in nanometres scale and the growth phase layer law is as follows:

$$y(t) = \sqrt{\frac{2D_b\Delta C_1}{C_1} t}. \quad (15)$$

A comparison of Eqs. (12) and (15) show that

$$t_{\frac{1}{2} \rightarrow \frac{1}{3}} \approx \frac{C_1\delta^2}{\Delta C_1} \sqrt{\frac{D_b^3}{2D^5}}. \quad (16)$$

One can find:

$$t_{\frac{1}{3} \rightarrow \frac{1}{4}} \approx \frac{D_b^2 C_1 \delta^2}{6D_1^3 \Delta C_1}$$

and

$$y\left(t_{\frac{1}{3} \rightarrow \frac{1}{4}}\right) \approx \left(\frac{D_b}{2D_1}\right)^{2/3} \delta. \quad (17)$$

4. SUMMARY

The growth law of the phase layer during the intermetallic compound formation with a narrow concentration range of homogeneity is parabolic for diffusion time

$$t < \frac{C_1\delta^2}{\Delta C_1} \sqrt{\frac{D_b^3}{2D^5}}.$$

The growth phase layer law inside polycrystals grains is proportional to $\sqrt[3]{t}$ in about 100 nanometres scale for diffusion time

$$\frac{C_1\delta^2}{\Delta C_1} \sqrt{\frac{D_b^3}{2D^5}} < t < \frac{D_b^2 C_1 \delta^2}{6D_1^3 \Delta C_1}.$$

The growth phase layer law in bicrystals in B-regime is the same as the Fisher solution: the phase wedge is proportional to $\sqrt[4]{t}$ for diffusion time:

$$\frac{D_b^2 C_1 \delta^2}{6D_1^3 \Delta C_1} < t < \frac{D_b^2 C_1 \delta^2}{8D^3 \Delta C_1}.$$

The phase wedges and roughness are smoothed during phase growth [4, 6]. Smoothing rate is the more pronounced, the smaller the roughness radius [3]. The growth phase layer law in polycrystals in micrometers and millimetres scales for diffusion time

$$t > \frac{D_b^2 C_1 \delta^2}{8D^3 \Delta C_1}$$

is parabolic because volume diffusion is more pronounced than GB diffusion.

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