Phase competition in ternary Ti–Ni–Al system

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HIGHLIGHTS

- Ti–Ni–Al Wagner integral diffusion coefficients.
- Experimental results of Ti–Ni–Al diffusion at 1173 K.
- Diffusion couple technique in studying the phase relations.
- Entropy production hypothesis of choosing the diffusion path.

ARTICLE INFO

ABSTRACT

In this paper the reactive diffusion in Ti–Ni–Al system is discussed at 1173 K. The calculation method based on the binary approach is presented. The key kinetic parameter is Wagner integral diffusion coefficient. The experimental and simulation results of reactive diffusion between pure Ti and β-NiAl are compared at 1173 K after 100 h.

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1. Introduction

The phase competition in ternary system is much more complex than in binary one. In binary all phases sooner or later appear during the diffusion process. In ternary system the number of possible regimes is greater and not all phases will grow [1]. According to the phase diagram some phases should appear at the diffusion zone, however they are absent. On the other hand some metastable phases absent at the phase diagram sometimes are formed instead of the stable phases [2–8].

The processes of new phase formation and growth in the diffusion zone of the binary and multicomponent systems are controlled by additional factors determining the evolution [9]:

1. the thermodynamic or kinetic suppression of some phases at nucleation stage,
2. the finite rate of mass transport through the interphase zone or, in the other words, the deviations from local equilibrium at the moving phase boundaries,
3. the effect of the fast diffusion paths,
4. the extreme principle methods, i.e., the use of semiempirical principle of maximum release rate of Gibbs free energy,
5. The micro-mechanical state at the interface.

The most known model describing the influence of interface kinetic was presented by Gosele and Tu already in 1982 [10]. The method predicts the well known linear-parabolic growth law for the single phase growth.

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The problem of regimes choice must be solved. In this paper this problem will be discussed. The idea is that the diffusion will cross the regimes with the highest entropy production value. Thus the entropy production will be calculated for each phase boundary and the most probable ones will be chosen.

2. Diffusion in ternary systems with low nonstoichiometry

The analysis is based on the generalized Darken method (mass conservation law) for each phase [1,11,12]. The component diffusion flux, $J_i^d \equiv c_i v_i^d$, should be expressed by the proper constitutive formula. In this work we implement the Nernst–Planck flux equation [13,14]:

$$J_i^d = -c_i B_i \frac{\partial \mu_i}{\partial x},\tag{1}$$

where μ_i is the diffusion potential; B_i denote the mobility ($B_i = D_i/kT$).

The chemical potential should be expressed by known thermo-dynamical functions. Thus, the target is to obtain the relation of the chemical potential on composition. In the multicomponent system at constant temperature and when stresses are negligible the integral form of the Gibbs relation becomes [15]:

$$G(n_1, \ldots, n_r) = n_1 \mu_1 + n_2 \mu_2 + \cdots + n_r \mu_r \tag{2}$$

where n_i denote the number of moles of component i.

Furthermore, by considering the Gibbs free energy per mole we obtain:

$$g = \frac{G}{n} = N_1 \mu_1 + N_2 \mu_2 + \cdots + N_r \mu_r \tag{3}$$

where n denotes the total number of moles and N_i the ith component molar fraction. Assuming, that the molar fractions are related by the relation:

$$N_1 + N_2 + \cdots + N_r = 1 \tag{4}$$

the free Gibbs energy, Eq. (3) can be rewritten in the following form:

$$g = N_1 \mu_1 + N_2 \mu_2 + \cdots + N_{r-1} \mu_{r-1} + (1 - N_1 - N_2 - \cdots - N_{r-1}) \mu_r \tag{5}$$

where g is the free Gibbs energy, μ_i denote the chemical potential. The differentiation of Eq. (5) by the molar fractions results in:

$$\frac{\partial g}{\partial N_1} = \mu_1 - \mu_r,$$
$$\frac{\partial g}{\partial N_2} = \mu_2 - \mu_r,$$
$$\ldots$$
$$\frac{\partial g}{\partial N_{r-1}} = \mu_{r-1} - \mu_r \tag{6}$$

which in the concise form can be written as:

$$\mu_i = \frac{\partial g}{\partial N_i} + \mu_r \quad \text{for } i = 1, \ldots, r - 1. \tag{7}$$

All the quantities in Eqs. (3)–(7) depend on time and position.

Eq. (7) allows to calculate the dependence of the chemical potential on the molar ratio:

$$\frac{\partial \mu_i}{\partial N_j} = \frac{\partial^2 g}{\partial N_i \partial N_j} + \frac{\partial \mu_r}{\partial N_j} \quad \text{for } i, j = 1, \ldots, r - 1. \tag{8}$$

Differentiation of the Gibbs relation ($0 = N_1 d\mu_1 + N_2 d\mu_2 + \cdots + N_r d\mu_r$) over N_1, follows:

$$0 = N_1 \frac{\partial \mu_1}{\partial N_1} + N_2 \frac{\partial \mu_2}{\partial N_1} + \cdots + N_r \frac{\partial \mu_r}{\partial N_1} \tag{9}$$

thus, equations defining the chemical potentials, Eq. (8) can be introduced instead of $N_2 \frac{\partial \mu_2}{\partial N_1}, \ldots, N_{r-1} \frac{\partial \mu_{r-1}}{\partial N_1}$, result in:

$$0 = N_1 \frac{\partial \mu_1}{\partial N_1} + N_2 \left(\frac{\partial^2 g}{\partial N_2 \partial N_1} + \frac{\partial \mu_r}{\partial N_1} \right) + \cdots + N_{r-1} \left(\frac{\partial^2 g}{\partial N_{r-1} \partial N_1} + \frac{\partial \mu_r}{\partial N_1} \right) + N_r \frac{\partial \mu_r}{\partial N_1} \tag{10}$$