

# Competition of $K$ and $F$ sinks during Void Formation<sup>1</sup>

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**Abstract**—The kinetics of void evolution in a binary alloy with two competing types of vacancy sinks is considered. In the course of interdiffusion, the competition of  $F$  and  $K$  sinks manifests itself in the competition of Frenkel voiding and the Kirkendall shift. The equations for the void-growth rate are obtained, depending on the dislocation-sink strengths. The maximal void sizes which can be reached during individual growth stage are found for two cases: (1) for a homogenous quenched alloy and (2) for a diffusion zone during interdiffusion process.

**Keywords:** interdiffusion, evolution of voids, Frenkel effect, Kirkendall effect

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## 1. INTRODUCTION

Control of voiding (pore formation) in alloys is an important practical problem of materials science. As a rule, the voiding should be suppressed since it usually deteriorates the mechanical properties of materials and their joints [1, 2]. For example, voiding in copper–tin solder contacts sooner or later leads to the formation of Frenkel voids at the interface and inside the  $\text{Cu}_3\text{Sn}_1$  phase. These voids ultimately lead to failure of microelectronic circuits. It is well known that irradiated materials usually demonstrate swelling, which means void formation under the effect of fluxes of high-energy particles with a consequent sharp deterioration of the mechanical properties of the reactor walls.

Voiding is a result of relaxation of pure material or alloy supersaturated with vacancies. At that, the relaxation of vacancy subsystem can proceed via at least two ways. The first way is voiding as a result of vacancy relaxation at the so-called  $F$  sinks (terminology of Ya. E. Geguzin [3]), which means just joining of vacancies into voids. The second way is vacancy relaxation without voiding, at the so-called  $K$  sinks, according to the same terminology of Ya. E. Geguzin (at dislocation kinks, at the surface of crystal grains). The competition of  $K$  and  $F$  sinks during interdiffusion was studied by Geguzin's group in experiments with diffusion couples at relatively low pressures [4]. In particular, the pressure of up to 100 atm was shown to almost completely suppress the void formation, although it almost did not change the frequencies of diffusion jumps. Thus, the Frenkel effect practically vanished during interdiffusion, whereas the Kirkendall effect (marker shift due to lattice shift) became stronger. Recently,

the teams of Alivisatos [5, 6], Gösele [7], Nakamura [8], Beke [9, 10], and some others realized the opposite case in nanosized spherical and cylindrical shells—the suppression of Kirkendall effect (lattice shift) and almost full consumption of nonequilibrium vacancies via the formation and growth of a centrosymmetric void, i.e., the production of hollow nanoshells. Such nanoshells can be used in medicine, for example, for drug delivery (a theoretical analysis of this effect can be found in [11–14]).

In this paper we present a theoretical analysis of the competition of  $F$  and  $K$  sinks irrespective of the reason of vacancy supersaturation (interdiffusion with different partial diffusivities, quenching, etc.). Here, we limit ourselves to the case of zero concentration of interstitials.

We will analyze this problem step by step, starting from the commonly known standard model and then gradually introducing complications.

## 2. VOIDS GROWTH IN A SUPERSATURATED SINGLE-COMPONENT MATERIAL WITHOUT $K$ SINKS (STANDARD QUASI-STEADY-STATE MODEL)

First, we consider the void growth in a supersaturated single-component material without  $K$  sinks. The equation for the vacancy flux to a spherical void is as follows:

$$\Omega j_V(r) = -D_V \frac{\partial c_V}{\partial r},$$

where  $\Omega$  is the atomic volume,  $D_V$  is the vacancy diffusion coefficient, and  $c_V$  is the mole fraction of the

<sup>1</sup> The article was translated by the authors.

vacant sites. The equation for the change in the vacancy concentration around the void in time is

$$\frac{\partial c_V}{\partial t} = -\text{div}(\Omega \mathbf{j}_V) + 0,$$

The zero in the right-hand side of the equation indicates that we ignore (in this first model) the possibility for a vacancy to go to the  $K$  sinks or annihilate with an interstitial defect.

In the quasi-stationary approximation commonly accepted for such problems, we can write:  $\frac{\partial c_V}{\partial t} \approx 0 \Rightarrow$

$$\text{div}(\Omega \mathbf{j}_V) \approx 0, \quad \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \Omega j_V) = 0. \text{ Hence, we immedi-}$$

ately obtain  $r^2 \Omega j_V = \text{const}$ ,  $\Omega j_V = \frac{a}{r^2}$ . Taking into account the equation for the vacancy flux, we obtain the following quasi-steady-state distribution of vacancies around the void:

$$-D_V \frac{\partial c_V}{\partial r} = \frac{a}{r^2} \Rightarrow c_V = \frac{a}{D_V r} + b.$$

The boundary condition at infinity is fixed by the given supersaturation  $\Delta$  ( $c_V|_{\infty} = c_V^{eq} + \Delta$ ) and gives  $b = \Delta$ .

The other constant,  $a$ , is obtained via the Gibbs–Thomson equation for the equilibria on curved surfaces, on the surface of the void ( $r = R$ ):

$$c_V(R) = c_V^{eq}(R) = c_V^{eq} e^{\frac{2\gamma\Omega}{RkT}} \approx c_V^{eq} \left( 1 + \frac{2\gamma\Omega}{kT} \frac{1}{R} \right) = c_V^{eq} + \frac{\alpha}{R},$$

$$\alpha = c_V^{eq} \frac{2\gamma\Omega}{kT};$$

So,

$$c_V^{eq} + \frac{\alpha}{R} = \frac{a}{D_V R} + c_V^{eq} + \Delta \Rightarrow a = D_V R \left( \frac{\alpha}{R} - \Delta \right).$$

Thus,

$$\Omega j_V(R) = \frac{a}{R^2} = -\frac{D_V}{R} \left( \Delta - \frac{\alpha}{R} \right) = -\frac{D_V \left( c_V - c_V^{eq} - \frac{\alpha}{R} \right)}{R}.$$

The condition of conservation for the total empty volume in the pure material without  $K$  sinks gives an equation for the description of the void growth:

$$\frac{dN}{dt} = -j_V(R) 4\pi R^2 = \frac{4\pi R}{\Omega} D_V \left( \Delta - \frac{\alpha}{R} \right), \text{ or}$$

$$\frac{dR}{dt} = \frac{D_V \left( \Delta - \frac{\alpha}{R} \right)}{R} \quad (1)$$

( $N$  is the number of vacancies united in the void; the void growth process is assumed to be additive).

If the process is diffusion-controlled, this equation is applicable for the single voids at the stages of both nucleation and growth, as well as coalescence.

### 3. VOID GROWTH IN A SUPERSATURATED BINARY ALLOY WITHOUT $K$ SINKS

Now, we consider a **binary** alloy supersaturated by vacancies, still neglecting  $K$  sinks. We perform considerations similar to those used in Section 2, but taking into account the cross effects. First, we write down the equation for the vacancy flux and the flux of the component  $B$  in the vicinity of the void [3, 13, 14]:

$$\begin{cases} \Omega j_V = -D_V \frac{\partial c_V}{\partial r} + (D_B - D_A) \frac{\partial c_B}{\partial r}; \\ \Omega j_B = -D_B \frac{\partial c_B}{\partial r} + \frac{c_B D_B^*}{c_V} \frac{\partial c_V}{\partial r}, \end{cases} \quad (2)$$

where  $D_A^*$  and  $D_B^*$  are the tracer diffusivities; and  $D_B = D_B^* \phi$  and  $D_A = D_A^* \phi$  are the partial diffusion coefficients, which are associated with the tracer diffusivities by the thermodynamic factor  $\phi$  [3].

The time variation of the vacancy concentration and concentration of atoms  $B$  is determined by the continuity equations for the vacancies and for the atoms  $B$ . In these equations, it is taken into account that the absence of  $K$  sinks means the absence of dislocation climb, which means the absence of the lattice motion:

$$\begin{cases} \frac{\partial c_V}{\partial t} = -\text{div}(\Omega \mathbf{j}_V) - \left( \frac{c_V - c_V^{eq}}{\tau_V} \right), \quad \frac{c_V - c_V^{eq}}{\tau_V} = 0, \\ \frac{\partial c_B}{\partial t} = -\text{div}(\Omega \mathbf{j}_B + c_B \mathbf{u}), \quad \mathbf{u} = 0. \end{cases} \quad (3)$$

Now, let us apply the quasi-steady-state approximation to both independent concentrations of the quasi-ternary system  $A$ – $B$ – $V$  ( $\frac{\partial c_V}{\partial t} \approx 0$ ,  $\frac{\partial c_B}{\partial t} \approx 0$ ):

$$\begin{cases} \frac{\partial}{\partial r} (r^2 \Omega j_V) = 0, \\ \frac{\partial}{\partial r} (r^2 \Omega j_B) = 0, \end{cases} \Rightarrow \begin{cases} r^2 \Omega j_V = a_V, \\ r^2 \Omega j_B = a_B, \end{cases} \quad (4)$$

where  $a_V$  and  $a_B$  are the so far unknown constants. Since we are interested in the qualitative characteristics of the process of void formation, we assume that all the diffusion parameters are approximately independent of concentration, which makes it possible to linearize the problem (see Discussion). Then, from the set of Eqs. (2) with allowance for Eqs. (4) we obtain

$$\begin{cases} -D_V \frac{\partial c_V}{\partial r} + (D_B - D_A) \frac{\partial c_B}{\partial r} = \frac{a_V}{r^2}; \\ -D_B \frac{\partial c_B}{\partial r} + \frac{c_B D_B^*}{c_V} \frac{\partial c_V}{\partial r} = \frac{a_B}{r^2}, \end{cases} \quad (5)$$

It follows (again, in the approximation of constant coefficients that appear before the gradients) that the

spatial distributions  $c_B$  and  $c_V$  should satisfy a hyperbolic law:

$$\begin{cases} c_V = k_V \frac{1}{r} + b_V, \\ c_B = k_B \frac{1}{r} + b_B, \end{cases} \quad (6)$$

where the constants  $b_B, b_V, k_B, k_V$  are determined from four boundary conditions:

$$\begin{cases} c_V(\infty) = c_V^{eq} + \Delta; \\ c_V(R) = c_V^{eq} + \frac{\alpha}{R}; \\ c_B(\infty) = \bar{c}_B; \\ \Omega j_B - c_B \frac{dR}{dt} = 0. \end{cases} \quad (7)$$

The first of equations (7) defines the vacancy supersaturation far from the growing void; the second determines the concentration near the surface of the void with allowance for the Gibbs–Thomson equation; the third equation defines the composition of the alloy far from the void; and the fourth equation of (7) means that the flux of atoms  $B$  through the moving surface of the void is zero, that is, the atoms do not evaporate into the void. Substituting the boundary conditions (7) into Eqs. (6), we obtain the unknown constants as  $b_V = c_V^{eq} + \Delta$ ,  $b_B = \bar{c}_B$ ,  $k_V = R \left( \frac{\alpha}{R} - \Delta \right)$ ,  $k_B =$

$R \left( \frac{\alpha}{R} - \Delta \right) \frac{c_B c_A (D_B^* - D_A^*)}{c_V \tilde{D}_D}$ . Hence, using Eqs. (5), we obtain:

$$a_V = D_V k_V - (D_B - D_A) k_B = R \left( \frac{\alpha}{R} - \Delta \right) D_V^{ef}; \quad (8V)$$

$$a_B = D_B k_B - \frac{c_B D_B^*}{c_V} k_V = c_B R \left( \Delta - \frac{\alpha}{R} \right) D_V^{ef}, \quad (8B)$$

Here, we call the quantity  $D_V^{ef} = \frac{D_B^* D_A^* \Phi}{c_V \tilde{D}_D} =$

$\frac{D_B^* D_A^*}{c_V (c_A D_B^* + c_B D_A^*)}$  the effective diffusion coefficient of vacancies, which means that it is less than the conventional vacancy diffusion coefficient (approximately equal to  $D_V = \frac{c_A D_B^* + c_B D_A^*}{c_V}$ ) and is determined by the slower component.

The equation for the balance of fluxes at the void boundary,  $\frac{dR}{dt} = -\Omega j_V(R) = \frac{a_V}{R^2}$ , together with Eq. (8), gives the final equation for the void-growth kinetics:

$$\frac{dR}{dt} = \frac{D_V^{ef}}{R} \left( \Delta - \frac{\alpha}{R} \right). \quad (9)$$

Since, as was mentioned above,  $D_V^{ef}$  is controlled by the slow component, the void-growth rate in the absence of  $K$  sinks also is controlled by the slower component of the alloy. The void cannot grow further until the slowest atoms come.

Using (8) and the value of the constant  $b_B$  from the set of equations (6), we can obtain the value of the concentration of atoms  $B$  on the surface of the void:

$$c_B = k_B \frac{1}{r} + b_B = \left( \frac{\alpha}{R} - \Delta \right) \frac{c_A c_B (D_B^* - D_A^*)}{c_V \tilde{D}_D} + \bar{c}_B. \quad (10)$$

As we see from Eq. (10), the difference between this concentration and the average concentration in the alloy (i.e., the magnitude of segregation) is proportional to the difference in the diffusion coefficients of the components. This segregation is kinetic rather than thermodynamic; it is caused not by energy-related advantage (or disadvantage) for  $B$ -type atoms to be located at the surface, but is due to different frequencies of vacancies' exchanges with atoms of different species, and it only occurs while there is a directional vacancy flux. This phenomenon is called the inverse Kirkendall effect; it was discovered and explained for the behavior of alloys under irradiation [17, 18].

The control of the void growth by the diffusion of the slow component also is one of the manifestations of the inverse Kirkendall effect; the segregation of one of the components to the surface means the emergence of a concentration gradient of the component, which enters as a cross member into the equations for flux of vacancies (see the first equation of the set (2)). This cross member reduces the vacancies flux, which is a manifestation of the general Le Chatelier principle (principle of the buffer—a generalization of the Lenz rule known in electrodynamics onto the general case of homeostasis of various systems).

#### 4. VOID GROWTH IN A SUPERSATURATED PURE MATERIAL WITH A GIVEN STRENGTH OF $K$ SINKS

Now we consider the void growth in a real single-component material which contains a sufficient number of dislocations and, thus, a finite but limited strength of  $K$  sinks. We characterize the strength of sinks by the relaxation time  $\tau_V$  or by the mean free path of vacancies  $L_V = \sqrt{D_V \tau_V}$ . The parameter  $L_V$  seems to be more convenient, since it is directly related to the density of dislocations and only slightly depends on the temperature (in contrast to the relaxation time), and, thus, it is a characteristic of defect structure. Now, we may write down the change in the vacancy concentration with time on the coarsened spatial scale [16]:

$$\frac{\partial c_V}{\partial t} = -\text{div}(\Omega j_V) - \frac{c_V - c_V^{eq}}{\tau_V}. \quad (11)$$

Vacancy concentration can be represented as the sum of the homogeneous and inhomogeneous (in the vicinity of the void) parts:  $c_V = c_V^{inh} + c_V^{hom}$ .

For the homogeneous part, we write the usual relaxation equation

$$\frac{\partial c_V^{hom}}{\partial t} = -\frac{c_V^{hom} - c_V^{eq}}{\tau_V} \Rightarrow c_V^{hom} = (c_V^0 - c_V^{eq})e^{-t/\tau_V} + c_V^{eq}.$$

The solution to the relaxation equation is written here for the case of the initial uniform distribution of vacancies with an initial concentration  $c_V^0$ .

Then, the equation for the inhomogeneous part has the following form:

$$\frac{\partial c_V^{inh}}{\partial t} = -\text{div}(-D_V \nabla c_V^{inh}) - \frac{c_V^{inh}}{\tau_V}, \quad (12)$$

and the inhomogeneous part tends to zero far from the void.

As in previous cases, we consider the quasi-steady-state regime of void growth, but the steady-state approximation will be used now for the inhomogeneous part. Then Eq. (11) is reduced to a screening-type equation

$$\left( \nabla^2 - \frac{1}{L_V^2} \right) c_V^{inh} = 0. \quad (13)$$

A centrally symmetric solution to Eq. (13) has the form

$$c_V^{inh} = \frac{A}{r} e^{\frac{r-R}{L_V}} + \frac{B}{r} e^{-\frac{r-R}{L_V}}, \quad (14)$$

where  $A$  and  $B$  are the constants, which can be found from the boundary conditions (15):

$$\begin{cases} c_V^{inh}(r \rightarrow \infty) = 0, \\ c_V^{inh}(r = R) = c_V(R) - c_V^{hom}(t) \\ = c_V^{eq} + \frac{\alpha_V}{R} - c_V^{hom}(t) = \frac{\alpha_V}{R} - (c_V^0 - c_V^{eq})e^{-t/\tau_V}. \end{cases} \quad (15)$$

Thus,  $A = 0$  and  $B = \left( \frac{\alpha_V}{R} - (c_V^0 - c_V^{eq})e^{-t/\tau_V} \right) R$ .

By substituting these constants into Eq. (13), we obtain

$$c_V^{inh} = \frac{R}{r} e^{\frac{R-r}{L_V}} \left( \frac{\alpha_V}{R} - (c_V^0 - c_V^{eq})e^{-t/\tau_V} \right), \quad r > R, \quad (16)$$

so that

$$\begin{aligned} \nabla c_V^{inh} &= R \left( (c_V^0 - c_V^{eq})e^{-t/\tau_V} - \frac{\alpha_V}{R} \right) \\ &\times e^{\frac{R-r}{L_V}} \frac{r+L_V}{r^2 L_V} = \nabla c_V. \end{aligned} \quad (17)$$

The void-growth rate is determined, as before, by the equation of the balance of fluxes on the moving boundary:

$$\frac{dR}{dt} = -\Omega j_V|_{r=R} = D_V \nabla c_V|_{r=R}. \quad (18)$$

Substituting Eq. (17) into Eq. (18) at  $r = R$ , we obtain the final equation for the void-growth kinetics in the material with a limited strength of  $K$  sinks:

$$\frac{dR}{dt} = \left( \Delta c_V - \frac{\alpha_V}{R} \right) \left( \frac{1}{L_V} + \frac{1}{R} \right) D_V, \quad (19)$$

where  $\Delta c_V$  is a uniform (on the coarsened spatial scale) vacancy supersaturation decreasing with time. In the case of a uniform initial supersaturation, we have  $\Delta c_V = (c_V^0 - c_V^{eq})e^{-t/\tau_V}$ . When the mean free path of vacancies  $L_V$  tends to infinity (i.e., when there are no  $K$  sinks), Eq. (19) is reduced to Eq. (1), as expected.

## 5. VOID GROWTH IN A SUPERSATURATED BINARY ALLOY WITH A GIVEN STRENGTH OF $K$ SINKS

This case is a combination of the two previous cases, that is, the void growth in the binary alloy without  $K$  sinks and the void growth in a pure material with  $K$  sinks. As in Section 4, the change in the vacancy concentration and in the concentration of  $B$  atoms is determined by Eq. (11). As in the previous cases, we consider the quasi-steady-state regime; therefore,

$$\begin{cases} \frac{\partial c_V}{\partial t} = -\text{div}(\Omega \mathbf{j}_V) - \frac{c_V - c_V^{eq}}{\tau_V}, \\ \frac{\partial c_B}{\partial t} = -\text{div}(\Omega \mathbf{j}_B + c_B \mathbf{u}) \approx 0, \\ \frac{\partial c_A}{\partial t} = -\text{div}(\Omega \mathbf{j}_A + c_A \mathbf{u}) \approx 0. \end{cases} \quad (20)$$

In Eqs. (20) it is taken into account that the effect of the  $K$  sinks is inextricably linked to the dislocations climb, and thus with the shift of lattice with some velocity  $\mathbf{u}$ . Therefore, under the sign of the divergence in Eqs. (20) we already have the total flux of both atoms  $A$  and  $B$  in the laboratory reference frame, with taking into account the displacement of the lattice. For the vacancies, the convective term  $c_V \mathbf{u}$  is small, since the vacancy concentration is small. Therefore, in the first equation of set (20) we have neglected this term at once.

Adding of equations (20), given that  $c_A + c_B + c_V = 1$  and  $\mathbf{j}_V + \mathbf{j}_B + \mathbf{j}_A = 0$ , yields

$$\begin{aligned} 0 &= -\frac{c_V - c_V^{eq}}{\tau_V} - \text{div}(\Omega \mathbf{j}_V + \Omega \mathbf{j}_B + \Omega \mathbf{j}_A + \mathbf{u}) \\ &= -\frac{c_V - c_V^{eq}}{\tau_V} - \text{div}(\mathbf{u}) \Rightarrow \text{div} \mathbf{u} = -\frac{c_V - c_V^{eq}}{\tau_V}. \end{aligned}$$

It is convenient to express both the left-hand and the right-hand sides of this equation as the sums of two terms:

$$\operatorname{div} \mathbf{u}^{global} + \operatorname{div} \mathbf{u}^{local} = -\frac{c_V^{hom} - c_V^{eq}}{\tau_V} - \frac{c_V^{inh}}{\tau_V},$$

where

$$\operatorname{div} \mathbf{u}^{global} = -\frac{c_V^{hom} - c_V^{eq}}{\tau_V}, \quad \operatorname{div} \mathbf{u}^{local} = -\frac{c_V^{inh}}{\tau_V}.$$

Here  $\mathbf{u}^{local}$  is the velocity of the material movement around the void relative to its center (for a spherically symmetric void, it can be expected that all such displacements are directed radially);  $\mathbf{u}^{global}$  is the velocity of movement of the void center due to whole material densification under the effect of  $K$  sinks. In this section, we are interested in the fluxes and velocities only with respect to the void center. Thus, the equation for the vacancies (the first one in the set (20)) can also be split into two equations:

$$\begin{aligned} \frac{\partial c_V^{hom}}{\partial t} &= -\frac{c_V^{hom} - c_V^{eq}}{\tau_V} = \boxed{\text{hom}} \\ &= c_V^{eq} + (c_{V0} - c_V^{eq}) \exp(-t/\tau_V), \\ \frac{\partial c_V^{inh}}{\partial t} &= -\operatorname{div}(\Omega \mathbf{j}_V) - \frac{c_V^{inh}}{\tau_V}. \end{aligned}$$

By applying the quasi-steady-state approximation for the inhomogeneous distribution of vacancies to the last equation, we obtain:

$$\operatorname{div} \Omega \mathbf{j}_V = -\frac{c_V^{inh}}{\tau_V}. \quad (21)$$

Thus,

$$\operatorname{div} \mathbf{u}^{local} = \operatorname{div} \Omega \mathbf{j}_V.$$

From the equality of divergences in the case of radial symmetry, it is implied that for the radial projections of the velocity and flux we have

$$u = \Omega j_V + \frac{p}{r^2}, \quad (22)$$

where  $p$  is a constant, which is unknown yet.

The expression under the sign of divergence in the second equation of the set (20) can be written as

$$\begin{aligned} \Omega \mathbf{J}_B &= \Omega \mathbf{j}_B + c_B \mathbf{u}^{local} = \Omega \mathbf{j}_B + c_B \left( -\Omega \mathbf{j}_A - \Omega \bar{\mathbf{j}}_B + \frac{p}{r^2} \frac{\mathbf{r}}{r} \right) \\ &= -(c_A D_B + c_B D_A) \nabla c_B + \frac{c_A c_B}{c_V} (D_B^* - D_A^*) \nabla c_V + c_B \frac{p}{r^2} \frac{\mathbf{r}}{r}. \end{aligned}$$

Then, the quasi-steady-state condition with respect to the component  $B$  ( $\operatorname{div}(\Omega \mathbf{j}_B) \approx 0$ ) has the following form (in the approximation of constant coefficients appear-

ing before the gradients and taking into account that  $\operatorname{div} \frac{\mathbf{r}}{r^3} = 0$  for  $r \neq 0$ ):

$$-(c_A D_B + c_B D_A) \nabla^2 c_B + \frac{c_A c_B}{c_V} (D_B^* - D_A^*) \nabla^2 c_V \approx 0,$$

that is,

$$\nabla^2 c_B = \frac{c_A c_B}{c_V} \frac{(D_B^* - D_A^*)}{(c_A D_B + c_B D_A)} \nabla^2 c_V. \quad (23)$$

For the concentration gradients, under the same approximation of constant coefficients, analogous relation is valid up to the term with the zero divergence:

$$\nabla c_B = \frac{c_A c_B}{c_V} \frac{(D_B^* - D_A^*)}{(c_A D_B + c_B D_A)} \nabla c_V^{inh} + \frac{q}{r^2} \frac{\mathbf{r}}{r}. \quad (23')$$

Substituting into equation (21) the equation for the vacancies flux from Eq. (2), we obtain (again, in the approximation of constant coefficients)

$$-D_V \nabla^2 c_V^{inh} + (D_B - D_A) \nabla^2 c_B = -\frac{c_V^{inh}}{\tau_V}. \quad (24)$$

Substituting Eq. (23) into Eq. (24), we obtain

$$\begin{aligned} -(D_B - D_A) \frac{c_A c_B}{c_V} \frac{(D_B^* - D_A^*)}{(c_A D_B + c_B D_A)} \nabla^2 c_V^{inh} \\ + D_V \nabla^2 c_V^{inh} = \frac{c_V^{inh}}{\tau_V}, \end{aligned}$$

from which we have

$$D_V^{ef} \nabla^2 c_V^{inh} = \frac{c_V^{inh}}{\tau_V}, \quad D_V^{ef} = \frac{D_B^* D_A^*}{c_V (c_A D_B^* + c_B D_A^*)}.$$

Thus, we again obtain a screening-type equation (as in Section 4):

$$\left( \nabla^2 - \frac{1}{(L_V^{ef})^2} \right) c_V^{inh} = 0, \quad \text{where } L_V^{ef} = \sqrt{D_V^{ef} \tau_V}. \quad (25)$$

The solution to Eq. (25) is an equation similar to (14):

$$c_V^{inh} = \frac{A}{r} e^{\frac{r-R}{L_V^{ef}}} + \frac{B}{r} e^{-\frac{r-R}{L_V^{ef}}}. \quad (26)$$

We find the constants in Eq. (26) in the same way as in Section 4. The final equation for the vacancies concentration is

$$c_V^{inh}(r) = \left( \frac{\alpha_V}{R} - (c_V^0 - c_V^{eq}) e^{-t/\tau_V} \right) \frac{R}{r} e^{-\frac{r-R}{L_V^{ef}}},$$

from which we have

$$\nabla c_V|_{r=R} = \left( (c_V^0 - c_V^{eq}) e^{-t/\tau_V} - \frac{\alpha_V}{R} \right) \left( \frac{1}{R} + \frac{1}{L_V^{ef}} \right). \quad (27)$$

In this case, the equation for the void-growth kinetics, in contrast to Section 4, contains the diffusion coefficients of  $A$  and  $B$  atoms, and it has the form

$$\begin{aligned} \frac{dR}{dt} &= -\Omega j_V|_{r=R} \\ &= -(D_B - D_A) \nabla c_B|_{r=R} + D_V \nabla c_V^{inh}|_{r=R}. \end{aligned} \quad (28)$$

The gradient of vacancy concentration is already known (Eq. (27)). The expression for the gradient of concentration of atoms  $B$  can be obtained by combining Eqs. (23') and (27):

$$\begin{aligned} \nabla c_B|_{r=R} &= \frac{c_A c_B}{c_V \tilde{D}_D} (D_B^* - D_A^*) \\ &\times \left( (c_V^0 - c_V^{eq}) e^{-t/\tau_V} - \frac{\alpha_V}{R} \right) \left( \frac{1}{L_V^{ef}} + \frac{1}{R} \right) + \frac{q}{R^2}. \end{aligned} \quad (29)$$

Now, we must find the unknown constants  $q$  and  $p$ . To this end, we use the boundary conditions for zero fluxes of the components  $A$  and  $B$  with respect to the moving boundary of the pore:

$$\Omega j_A(R) + c_A u^{local}(R) - c_A \frac{dR}{dt} = 0; \quad (30a)$$

$$\Omega j_B(R) + c_B u^{local}(R) - c_B \frac{dR}{dt} = 0. \quad (30b)$$

The sum of equations (30A) and (30B) with allowance for the balance of the fluxes,  $\mathbf{j}_V + \mathbf{j}_A + \mathbf{j}_B = 0$ , gives

$$-\Omega j_V(R) + u^{local}(R) - \frac{dR}{dt} = 0.$$

Taking into account that  $\frac{dR}{dt} = -\Omega j_V(R)$ , we obtain

$$u^{local}(R) = 0. \quad (31)$$

The substitution of the condition (31) into (22) gives us an expression for the constant  $p$ :

$$p = -R^2 \Omega j_V(R).$$

So

$$u^{local}(r) = \Omega j_V(r) - \frac{R^2}{r^2} \Omega j_V(R). \quad (32)$$

The substitution of Eq. (31) into (30B) gives

$$\begin{aligned} \Omega j_B(R) + c_B \Omega j_V(R) &= -(c_A D_B + c_B D_A) \nabla c_B \\ &+ \frac{c_A c_B}{c_V} (D_B^* - D_A^*) \nabla c_V = 0. \end{aligned}$$

By comparing this equation with Eq. (23'), we obtain the other constant as well:  $q = 0$ . Substituting Eqs. (27) and (29) into Eq. (28) at  $q = 0$ , we obtain the final

equation for the void-growth kinetics in the binary alloy with two competing types of sinks:

$$\frac{dR}{dt} = \left( (c_V^{hom} - c_V^{eq}) - \frac{\alpha_V}{R} \right) \left( \frac{1}{L_V^{ef}} + \frac{1}{R} \right) D_V^{ef}. \quad (33)$$

Recall that in this equation the vacancy diffusion coefficient obtained in Section 4 is replaced by the effective coefficient of the same order, which, however, is controlled by the slow component.

## 6. VOID GROWTH IN THE DIFFUSION ZONE OF A DIFFUSION COUPLE

In the cases described above, the initial vacancy supersaturation was uniform and determined by the conditions of quenching. Now, we consider the problem where the supersaturation arises as a result of interdiffusion. The rate of change in the number of nonequilibrium vacancies in a given site of the diffusion zone is defined by the differential equation [3, 13, 14]

$$\begin{aligned} \frac{\partial \Delta c_V(x,t)}{\partial t} &= -\frac{\partial}{\partial x} (\Omega j_V) - \frac{\Delta c_V}{\tau_V} \\ &= \frac{\partial}{\partial x} \left( D_V \frac{\partial c_V}{\partial x} - (D_B - D_A) \frac{\partial c_B}{\partial x} \right) - \frac{\Delta c_V}{\tau_V}. \end{aligned} \quad (34)$$

Equation (34) is written for a coarsened spatial scale, on which the characteristic length scale is greater than the free path of vacancies.

The principal approximation employed when deriving Eq. (34) is that on a coarsened scale it is only  $K$  sinks that are taken into account. In other words, we describe the effect of supersaturation on the void formation, but do not take into account (in this paper) the effect of void formation on the global distribution of vacancy supersaturation in the diffusion zone. The allowance for such a feedback (unfortunately, only numerical rather than analytical) will be done in a separate paper. Without taking this effect into account, the below analysis is applicable only to the initial stage of void formation. In particular, it can be applied to analyze the possibility of suppressing Frenkel effect.

The process of diffusion homogenization and the related occurrence of vacancy supersaturation can be divided into three stages [3, 16]: the first corresponds to the time  $0 < t < \tau_V$ ; the second, to the time  $\tau_V < t < \tau_V/c_V$ ; and the third one, to the time  $t > \tau_V/c_V$ . Starting from the second stage, the quasi-steady-state condition for vacancies is fulfilled, but the condition for the quasi-steady state for the main component in the diffusion couple is not achieved. Therefore, the basic equations for the diffusion couple are written (in the approximation of constant coefficients) as follows:

—the quasi-steady-state equation for the vacancies (on a coarsened spatial scale):

$$\left( \frac{\partial^2}{\partial x^2} - \frac{1}{D_V \tau_V} \right) \Delta c_V(t, x) = \frac{D_B - D_A}{D_V} \frac{\partial^2 c_B}{\partial x^2}; \quad (35)$$



—the time-dependent equation for the  $B$  component in the laboratory frame (with allowance for the Kirkendall effect):

$$\frac{\partial c_B(x,t)}{\partial t} = (c_A D_B^* + c_B D_A^*) \varphi \frac{\partial^2 c_B}{\partial x^2} - \frac{c_A c_B}{c_V} (D_B^* - D_A^*) \frac{\partial^2 \Delta c_V}{\partial x^2}. \quad (36)$$

In the derivation of Eq.(36), the usual Darken's scheme for transition to the new reference frame was employed, but with allowance for the contributions of nonequilibrium vacancies into the fluxes of both the main component and vacancies (see, for example, [19, Eqs. (6) and (7)]).

The solution to Eq. (35) is of a nonlocal (integral) type with a range of nonlocality equal to the mean vacancy free path:

$$\Delta c_V(t, x) = -L_V^2 \frac{D_B - D_A}{D_V} \int_{-\infty}^{\infty} \frac{1}{2L_V} \exp\left(-\frac{|x-x'|}{L_V}\right) \frac{\partial^2 c_B}{\partial x'^2} dx'. \quad (37)$$

In the third stage (which is most often studied experimentally), nonlocality can be neglected when the width of the diffusion zone is greater than the vacancy mean free path. Then, formally one can take  $L_V \rightarrow 0$ . In this case, the kernel of the integral transformation in Eq. (37) becomes a Dirac delta function:

$$\frac{1}{2L_V} \exp\left(-\frac{|x-x'|}{L_V}\right) \rightarrow \delta(x-x').$$

Then, the nonlocal Eq. (37) is transformed into

$$\Delta c_V(t, x) = -L_V^2 \frac{D_B - D_A}{D_V} \frac{\partial^2 c_B}{\partial x^2}. \quad (38)$$

In this case, the last term in Eq. (36) becomes negligibly small:

$$\frac{c_A c_B}{c_V} (D_B^* - D_A^*) \frac{\partial^2 \Delta c_V}{\partial x^2} \approx -L_V^2 c_A c_B \frac{(D_B - D_A)^2}{c_A D_A + c_B D_B} \frac{\partial^4 c_B}{\partial x^4} \xrightarrow{L_V \rightarrow 0} 0.$$

Then, Eq. (36) in the approximation of constant coefficients transforms into the usual parabolic equation:

$$\frac{\partial c_B(x,t)}{\partial t} \approx D_D \frac{\partial^2 c_B}{\partial x^2}, \quad D_D = (c_A D_B^* + c_B D_A^*) \varphi. \quad (39)$$

In the case of a stepwise initial profile with a jump in the Matano plane  $x_M = 0$ , the solution to this equation has the form of an error function

$$c_B(t, x) = \frac{c_{BR} + c_{BL}}{2} + \frac{c_{BR} - c_{BL}}{2} \operatorname{erf}\left(\frac{x}{\sqrt{4D_D t}}\right),$$

with the second derivative

$$\frac{\partial^2 c_B}{\partial x^2} = -\frac{c_{BR} - c_{BL}}{4\sqrt{\pi}} \frac{x}{(D_D t)^{3/2}} \exp\left(-\frac{x^2}{4D_D t}\right). \quad (40)$$

Substituting Eq.(40) into Eq.(38) gives

$$\Delta c_V(t, x) = \frac{L_V^2}{D_V} (D_B - D_A) \frac{c_{BR} - c_{BL}}{4\sqrt{\pi}} \frac{x}{(D_D t)^{3/2}} \exp\left(-\frac{x^2}{4D_D t}\right). \quad (41)$$

(Note that in [3] a similar formula ((3.20)) is given, but it contains several technical mistakes.)

The arguments completely analogous to those used in Section 5 with the substitution of  $c_V^{hom} - c_V^{eq}$  for  $\Delta c_V(t, x)$  yields the following expression for the rate of void growth:

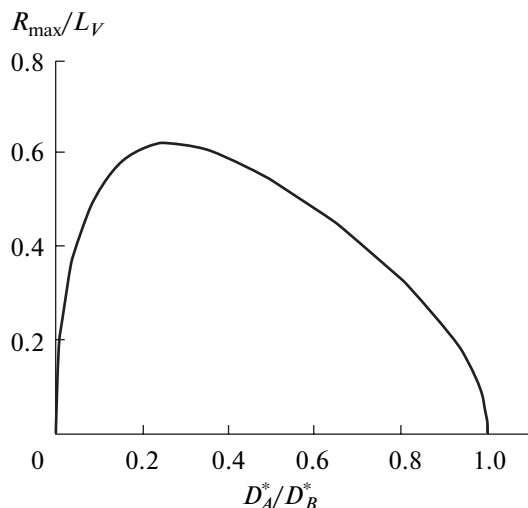
$$\frac{\partial R(t, x)}{\partial t} = \left(\Delta c_V(t, x) - \frac{\alpha_V}{R}\right) \left(\frac{1}{L_V^{ef}} + \frac{1}{R(t, x)}\right) D_V^{ef}. \quad (42)$$

## 7. MAXIMUM VOID SIZE AT THE INDEPENDENT-GROWTH STAGE

Let the initial supersaturation for vacancies, diffusion parameters of the alloy, and the relaxation time of vacancies on the  $K$  sinks be fixed. Physically, it is clear that even in the absence of a void the vacancies would go to  $K$  sinks and the supersaturation would decrease at least to a level at which the void formation becomes impossible. This means that the void in the alloy with a given initial supersaturation and a limited strength of sinks cannot grow infinitely. The question is what is the maximum void size which is achieved when all of the specified parameters are known. In the future, this result can be used to obtain the criterion for the Frenkel effect: if the maximum void radius is less than the critical value, for example, for a given initial supersaturation, the void formation will not even start.

The peculiar properties of pore nucleation will be explored in a separate paper. Here, we assume that heterogeneous nuclei are always can exist in the system and the only question is whether they will grow and to what size. Therefore, we neglect the term  $\alpha_V/R$  below (taking into account that the typical value of  $\alpha_V$  is on the order of a nanometer).

Integration of Eqs. (19) and (33) makes it possible to find a simple dependence of the maximum void radius on the diffusion parameters and on the mean free path for vacancies. Logically, this problem is divided into two particular cases: (1) globally uniform quenched alloy; and (2) the diffusion zone upon the interdiffusion in a diffusion couple.



Dependence of the maximum void size (in the vacancy-mean-free-path units) on the ratio of the partial diffusion coefficients at the stage of individual growth in the Frenkel effect.

### 7.1. Dependence of the Maximum Void Radius on Diffusion Parameters in a Pure Material with a Given Strength of $K$ Sinks

Let us, referring to the problem that is described in Section 4, integrate Eq.(19), taking into account that at  $t \rightarrow \infty$ ,  $R$  tends to  $R_{\max}$ . Then,

$$\frac{R_{\max}}{L_V} - \ln\left(\frac{R_{\max}}{L_V} + 1\right) = (c_V^0 - c_V^{eq}). \quad (43)$$

If  $R_{\max} \ll L_V$ , then after expanding Eq.(43) in  $R_{\max}/L_V$  (as in a small parameter) to the second order of smallness, we obtain

$$R_{\max} = \sqrt{2(c_V^0 - c_V^{eq})} \cdot L_V. \quad (44)$$

The opposite case is never realized. Indeed, if we assume that  $R_{\max} \gg L_V$ , then  $\ln(1 + R_{\max}/L_V) \approx \ln(R_{\max}/L_V)$ . Since at large arguments  $\ln \ln(R_{\max}/L_V) \ll R_{\max}/L_V$  is much less than  $R_{\max}/L_V = (c_V^0 - c_V^{eq})$ , we obtain that  $R_{\max} \gg L_V$  from Eq. (43). The right-hand side of this equation is much less than 1, and the left-hand side is much greater than 1. Thus, the assumption leads to a contradiction. Therefore, we can state for sure that  $R_{\max} \ll L_V$  always.

A similar result for a binary homogeneous quenched alloy, with the replacement of the vacancy diffusion coefficient by an effective vacancy diffusion coefficient and, correspondingly, with the replacement of  $L_V$  by  $L_V^{ef}$  :

$$R_{\max} = \sqrt{2(c_V^0 - c_V^{eq})} L_V^{ef}. \quad (45)$$

If we take a typical value of 1  $\mu\text{m}$  for the vacancy mean free path and  $\Delta c_V = 2 \times 10^{-4}$  for the initial super-

saturation (a typical vacancy concentration near the melting point), then the maximum void radius proves to be equal to 20 nm.

### 7.2. Dependence of the Maximum Pore Radius on the Diffusion Parameters in the Diffusion Zone of a Binary Diffusion Couple with Allowance for $K$ Sinks

Our description of the void formation during interdiffusion simultaneously uses two spatial scales—coarsened scale coordinates  $x$  along the diffusion zone and a fine scale  $r$  in the vicinity of each void. Therefore, assuming that in the vicinity of the void the alloy is locally homogeneous, we substitute Eq.(41) into Eq.(42) and integrate the result over time, assuming that if  $t \rightarrow \infty$ , then  $R$  is tending to  $R_{\max}$ :

$$\frac{R_{\max}}{L_V^{ef}} - \ln\left(\frac{R_{\max}}{L_V^{ef}} + 1\right) = \pm \frac{c_{BR} - c_{BL}}{2} \frac{1}{D_D} (D_B - D_A). \quad (46)$$

If  $R_{\max} \ll L$ , then from Eq.(46) we obtain

$$R_{\max} = \sqrt{(c_{BR} - c_{BL}) \frac{(D_B^* - D_A^*)}{(c_A D_A^* + c_B D_B^*)}} L_V^{ef}. \quad (47)$$

In both cases  $R_{\max}$  is proportional to  $L_V^{ef}$ .

## 8. FRENKEL-EFFECT CRITERIA IN INTERDIFFUSION

Let us try to formulate the dependence of the maximum void radius on the ratio of the tracer diffusivities. Using Eq. (47), and the equation for  $L_V^{ef}$ , we obtain

$$R_{\max} = \sqrt{(c_{BR} - c_{BL}) \frac{\frac{D_A^*}{D_B^*} \left(1 - \frac{D_A^*}{D_B^*}\right)}{\left(c_A \frac{D_A^*}{D_B^*} + c_B\right) \left(c_A + c_B \frac{D_A^*}{D_B^*}\right)}} L_V.$$

To estimate the order of magnitude of the effect we can take  $c_A = c_B = (c_{BR} + c_{BL})/2$ . In the case of a symmetric pair (for example, pure  $A$ —pure  $B$ , that is,  $c_{BR} = 1$ ,  $c_{BL} = 0$ ), we obtain 1/2. Then,

$$R_{\max} = 2L_V \sqrt{\frac{x(1-x)}{(1+x)(x+1)}}.$$

The dependence of the ratio  $R_{\max}/L_V$  on the ratio  $D_A^*/D_B^*$  is shown in Fig. 1.

## 9. DISCUSSION OF RESULTS

The dependence of the maximum void radius in the diffusion zone (before the start of the coalescence stage) on the ratio of the mobilities of the components appeared to be nonmonotonic. There is such a ratio



$D_A^*/D_B^*$  at which we can expect a maximum of void formation ( $D_A^*/D_B^* \approx 0.27$ ). At this value the maximum void radius reaches a value of about  $0.6L_V$ . Naturally, all above estimates are very rough, since we everywhere used the approximation of constant diffusion coefficients. This approximation had been analyzed by G.V. Scherbedinskii, P.N. Zakharov, A.P. Mokrov, and others [20, 21]. It holds well only for the incremental couples with small initial difference of concentrations (for example, 48–52%).

However, the void formation in the diffusion zone is much stronger than in quenching (at the same value of the vacancy free path). This is understandable, since after the quenching the excess vacancies go to sinks and will not be renewed. Upon the interdiffusion, the reserves of excess vacancies on the side of the faster component of the diffusion couple are replenished all the time (while the diffusion process continues), though with a decreasing velocity.

For a more complete analysis of the competition between two types of sinks (competition of Frenkel and Kirkendall effects) we must find the velocity of void nucleation and the evolution of the void-size distribution evolution with time under the heterogeneous conditions of the diffusion zone. This will be the subject of a separate paper.

It would also be desirable to experimentally study the influence of the radius of the cylindrical or spherical diffusion “couple” of nucleus–shell type on the degree of manifestation of the Frenkel effect. We can expect interesting effects when the radii are on the order of a micron (i.e., on the order of the vacancy free path in real alloys).

### 10. CONCLUSIONS

(1) The rate of the void growth in a vacancy-supersaturated binary alloy with dislocation sinks is determined

by the equation  $\frac{dR}{dt} = \left( (c_V^{hom} - c_V^{eq}) - \frac{\alpha_V}{R} \right) \left( \frac{1}{L_V^{ef}} + \frac{1}{R} \right) D_V^{ef}$ ,

where  $D_V^{ef} = \frac{D_B^* D_A^*}{c_V (c_A D_B^* + c_B D_A^*)}$  is the effective vacancy

diffusion coefficient, which is controlled by the slower

component, and  $L_V^{ef} = \sqrt{\frac{D_V^{ef}}{D_V}} L_V \approx$

$\sqrt{\frac{D_A^* D_B^*}{(c_A D_B^* + c_B D_A^*)(c_A D_A^* + c_B D_B^*)}} L_V$ ,  $L_V$  is the vacancy

mean free path.

(2) A similar equation holds for the void growth in the diffusion zone, with the replacement of  $c_V^{hom} - c_V^{eq}$  by the distribution of the vacancy supersaturation  $\Delta c_V(t, x)$  along the zone.

(3) The maximum void radius at the stage of individual growth can be estimated as

$$R_{max} = \sqrt{(c_{BR} - c_{BL}) \frac{(D_B^* - D_A^*)}{(c_A D_A^* + c_B D_B^*)}} L_V^{ef}.$$

(4) The dependence of the maximum radius on the ratio of the component mobilities is expected to be nonmonotonic, with a maximum.

(5) The theory proposed above also must be generalized onto the case of void nucleation with the inclusion of the inverse effect of void distribution on the vacancy-concentration distribution.

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