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A kinetic model for electromigration in face-centred cubic alloys

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Abstract. A detailed microscopic understanding of electromigration processes in alloys is still lacking. This study is intended to analyse the atomic fluxes in dilute substitutional alloys with electromigration driving forces. The five-frequency model, developed for the description of diffusion via the single-vacancy mechanism in dilute alloys, is applied here for the study of electromigration. The model is generalized to a case in which an alloying atom changes the electromigration driving force on surrounding host atoms. For some choices of parameters the atomic fluxes deviate from expressions found in the literature. Analysis and kinetic Monte Carlo simulation of some limiting cases confirm the new expressions. The properties of the flux equations are studied in detail for several interesting cases. In particular, it is shown that the addition of a few atomic per cent of alloying atoms can reverse the direction of the flux of host atoms under certain conditions. Such a mechanism can slow down electromigration mass transport and could therefore be of great technological importance for the development of electromigration-resistant alloys.

1. Introduction

Electromigration-induced damage has been a concern in the microelectronics industry for a long time [1]. Nevertheless even the underlying electromigration transport is not yet understood from a microscopical point of view. Electromigration transport is driven by the electromigration force, which is due to the momentum transfer of current-carrying electrons and drives atoms of a metal interconnect to the anode side. Doing so it induces the formation of voids on the cathode side. Such voids not only increase the resistivity but may even render the interconnect useless.

It was shown in the early 1970s [2] that the development of damage in aluminium (Al) conductor lines due to electromigration is slowed down effectively by the addition of a few atomic per cent of copper (Cu). This effect is attributed to a dramatic decrease of the diffusivity as a function of Cu concentration, for which Rosenberg [3] gave an expression, based on binding between Cu atoms and vacancies. Rosenberg assumed that these bound vacancies are immobile and do not contribute to transport. However, such a mechanism can only work if the vacancy concentration is independent of the Cu concentration. This is very unlikely if there is an attractive binding energy between Cu atoms and vacancies in a substitutional alloy.

Ho [4] later considered the alloying effect from the point of view of the kinetic theory of diffusion. Kinetic theory translates atomic jump frequencies into diffusion properties and atomic fluxes. The most prominent model for the description of diffusion in dilute FCC alloys, the five-frequency model, was formulated by Lidiard [5] and expressions for the fluxes were derived by Bocquet [6]. Allnatt [7] later showed that these expressions were exact apart from the numerical value of the so-called escape rate (for a review see reference [8]). Ho [4] combined

diffusion and electromigration data to obtain values for the atomic jump frequencies, but the data for Cu in bulk Al did not indicate any interesting behaviour. The conclusion was that the dramatic reduction of damage formation due to Cu has to do with the particular situation at grain boundaries.

The further development of theory and the increase of computing power has made it possible to take another approach today. Quantities determining single atomic jumps, such as barrier heights and energies for the interaction between defects can be calculated atomistically using empirical potentials [9,10] or *ab initio* methods (e.g. [11]). Furthermore, the development of *ab initio* Green's function methods permits one to calculate the electromigration driving forces in the bulk [12, 13] and at a surface [14, 15]. This means that theoretical values for all essential microscopic quantities determining the atomic jumps are now available. These quantities can be used directly to evaluate the kinetic expressions for the atomic fluxes in the alloy.

The usual kinetic theory for dilute alloys distinguishes five different frequencies which cover the differences in the most important jumps near the alloying atom. This model will be described in section 2.1. The fluxes resulting from this model have been described in reference [8]. In these models the electromigration forces on all host atoms are assumed to be equal. However, our *ab initio* calculations for Al-based alloys [16] show that the forces on host atoms within the first shell of an alloying atom are considerably changed. This inspired us to derive kinetic expressions, which are generalized to handle different forces on host atoms jumping within the first shell of an alloying atom.

Interestingly, the new expression for the flux of host atoms differs from the published expression. In particular, the Onsager coefficient l_{AA} deviates considerably. Because of this difference, the derivation of the expressions for the fluxes is described in detail in section 2. In section 3, the electromigration fluxes are studied in some special cases to argue that the new expressions are physically meaningful. In one case, in which the expressions show a large deviation, the new expression is confirmed using a kinetic Monte Carlo simulation. The new equations show very interesting behaviour, especially in the limit where the old expressions fail. It turns out that the direction of the host flux can be reversed by the addition of alloying atoms if they have particular properties. In section 4 the flux expressions are used to derive these conditions.

2. Theory

2.1. Five-frequency model; basics

The five-frequency model [5, 17] is a well-known model for describing diffusion by the single-vacancy mechanism in a binary dilute alloy. It is the simplest model, which explicitly accounts for the most important jumps in the alloy. These are the unperturbed jump of the host atoms, the jump of an alloying atom and the jumps of a vacancy to, from and within the first shell of an alloying atom. The model can be used to describe the differences in diffusion behaviour between the pure host and the alloy directly in terms of the atomic jump frequencies.

This model is applied to calculate electromigration fluxes in the FCC lattice. Any fluxes due to gradients in the concentration, stress or temperature are neglected. Translated into experimental terms, the model describes electromigration in a single-crystalline FCC metal in which the concentrations of alloying atoms and vacancies are kept constant by perfect sinks and sources on both the anode and cathode ends.

2.2. Five-frequency model; definitions and procedure

The five inequivalent atomic jump frequencies distinguished in the five-frequency model [5, 17] are displayed in figure 1. The frequencies are normalized to the jump frequency in the pure host ω_{host} . The frequency for a jump of the vacancy away from an alloying atom is written as $\alpha\omega_{\text{host}}$, a jump towards an alloying atom is characterized by $\beta\omega_{\text{host}}$ and a jump within the first shell of an alloying atom is characterized by $\gamma\omega_{\text{host}}$. These jumps all contribute to the host flux. The fifth jump is the jump of an alloying atom characterized by a frequency $W\omega_{\text{host}}$.

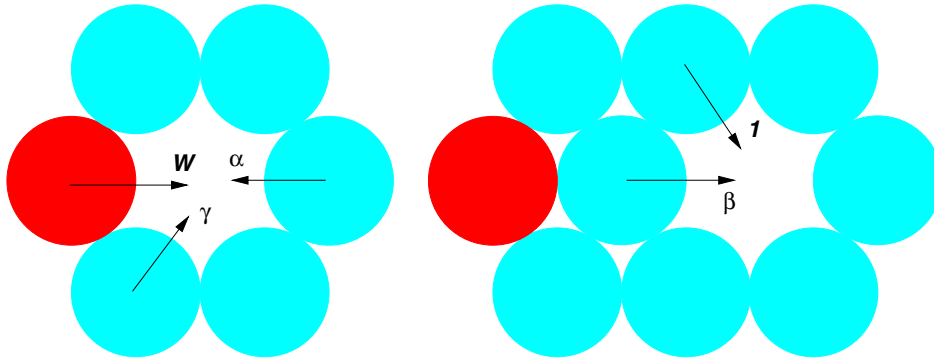


Figure 1. Atomic jump frequencies near an alloying atom normalized to the jump frequency in the pure host.

An electromigration flux arises because the work done by the electromigration driving force increases the probability for a jump in one direction and decreases it for a jump in the opposite direction. As an example, the probability for a jump in the direction of the force in the pure host is enhanced by a factor $1 + 2\epsilon$, with

$$2\epsilon = \frac{a}{2\sqrt{2}} F_{\text{host}}/kT \quad (1)$$

where a is the FCC lattice constant, F_{host} is the electromigration driving force on a host atom, T is the temperature and k is the Boltzmann constant. Under conditions which correspond to usual electromigration experiments, the work done during a jump is of the order of a μeV . This is at least four orders of magnitude smaller than kT .

Previous treatments only distinguished two driving forces, namely the forces on the host and the alloying atoms. The ratio of these driving forces is given by

$$\eta = \frac{F_{\text{alloy}}}{F_{\text{host}}}. \quad (2)$$

The model is extended here for a different driving force rF_{host} on a host atom jumping within the first shell of an alloying atom. This extension is motivated by the results of *ab initio* calculations of the electromigration driving forces in Al alloys [16], which show that the driving force differs particularly strongly for host atoms in direct contact with an alloying atom. The force factors η and r are shown in figure 2.

All ingredients of the model are defined with the specification of these forces and the jump frequencies. The next step is to calculate the atomic fluxes from these quantities. Of course, the flux of alloying atoms depends directly on the jump frequencies. However, it is also important to know how often an alloying atom has a vacancy on its anode and on its cathode side. To calculate these quantities one first labels the positions $\{i, j\}$ as shown in figure 3. Here, i labels the shell with respect to the nearest alloying atom and j labels its component in

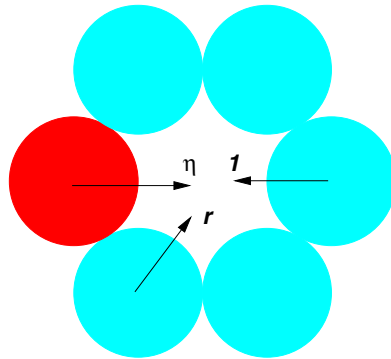


Figure 2. Forces near an alloying atom normalized to the force in the pure host.

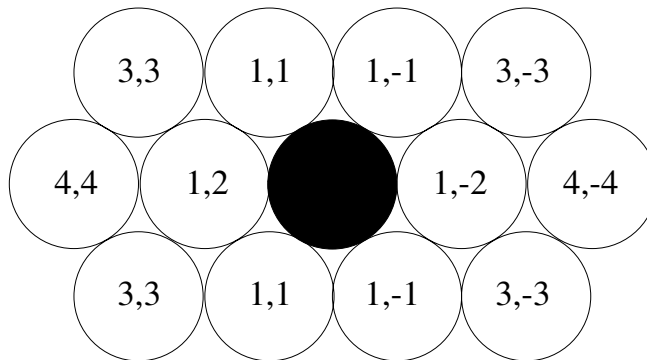


Figure 3. Atomic positions with labels $\{i, j\}$ in a (111) plane of the FCC structure near an alloying atom. The alloying atom is indicated by the filled circle. The positions are labelled by the shell i and the component in the direction of the driving force j .

the direction of the driving force. The calculation of the flux requires knowledge of the density of vacancies at position $\{i, j\}$, which is given by the concentration of alloying atoms c and the probability $p_{i,j}$ normalized by the atomic volume V_{at} .

In the absence of a driving force, the probability for finding a vacancy at position $\{i, j\}$, $p_{i,j}$, only depends on the shell index i . Under these conditions, the probability $p_{1,j}$ is increased by a factor β/α with respect to the vacancy concentration p_0 in the pure host. The ratio β/α therefore represents an effective attraction or repulsion of vacancies by alloying atoms. The probability for finding a vacancy remains unchanged for the other shells ($i > 1$).

The addition of the electromigration driving force changes these probabilities. The calculation of these changed probabilities will be sketched by considering the vacancies at positions $\{1, 2\}$. The jump of a vacancy from such a position against the direction of the wind force moves it away from the alloying atom. The work done by the driving force is $+2kT\epsilon$, so the jump frequency for this jump can be written as $\omega = \omega_{\text{host}}\alpha(1 + 2\epsilon)$ and the vacancy ends up in position $\{4, 4\}$. Because the component of the path in the direction of the driving force is $a/\sqrt{2}$, the contribution of all these jumps to the flux is

$$(c/V_{\text{at}})p_{1,2}\omega_{\text{host}}\alpha(1 + 2\epsilon)a/\sqrt{2}.$$

Analogously, the frequency of a jump of the vacancy towards a position $\{3, 3\}$ is $\omega_{\text{host}}\alpha(1 + \epsilon)$. There are four such jumps for each position $\{1, 2\}$ only two of which lie in this (111) plane.

Because the component of this jump in the direction of the force is only $a/2\sqrt{2}$, the contribution of these jumps to the flux of host atoms is

$$(c/V_{\text{at}})p_{1,2}4\omega_{\text{host}}\alpha(1+\epsilon)a/2\sqrt{2}.$$

The vacancy can also jump towards two positions labelled $\{2, 2\}$, which are not in the plane shown in figure 3. These jumps with frequency $\omega_{\text{host}}\alpha$ do not contribute to the flux in the direction of the driving force. If the vacancy jumps to position $\{1, 1\}$ it stays within the first shell of the alloying atom. The driving force is changed by a factor r , which is the generalization with respect to the usual five-frequency model. The jump frequency is $\omega_{\text{host}}\gamma(1-r\epsilon)$. The last jump to be considered is the jump of the alloying atom. This atom experiences a force, which differs by a factor η from the force felt by a pure host atom, so the jump frequency is $\omega_{\text{host}}W(1-2\eta\epsilon)$. Counting all the jumps of vacancies away from $\{1, 2\}$ and analogously the jumps to this position, it follows that

$$\begin{aligned} \frac{1}{\omega_{\text{host}}}\frac{dp_{1,2}}{dt} = & -p_{1,2}(W(1-2\eta\epsilon) + \gamma(4-4r\epsilon) + \alpha(7+6\epsilon)) \\ & + p_{1,-2}W(1+2\eta\epsilon) + p_{1,1}\gamma(4+4r\epsilon) + 2p_{2,2}\beta \\ & + 4p_{3,3}\beta(1-\epsilon) + p_{4,4}\beta(1-2\epsilon). \end{aligned} \quad (3)$$

The contribution of the vacancies at position $\{1, 2\}$ to the flux of host atoms can be written as

$$(c/V_{\text{at}})p_{1,2}\left(\alpha(1+2\epsilon)\omega_{\text{host}}\frac{a}{\sqrt{2}} + 4\alpha(1+\epsilon)\omega_{\text{host}}\frac{a}{2\sqrt{2}} + 4\gamma(1-r\epsilon)\omega_{\text{host}}\frac{-a}{2\sqrt{2}}\right). \quad (4)$$

The construction of these equations for all possible vacancy positions is straightforward but tedious. Under the assumption of a steady state, $dp_{i,j}/dt = 0$, a matrix equation is derived for all of the $p_{i,j}$. Because the contribution of each vacancy position to the fluxes is known and an equation is available for the probability of each vacancy position, the fluxes can then be calculated.

2.3. Details of the vacancy probabilities

Only five shells are explicitly taken into account here, which means that $p_{i,j} = p_0$ for shells $i > 5$. It has been shown [7] that this approximation does not affect the functional form of the resulting flux equations; it only changes the numerical value of the so-called escape rate F , which will be introduced later. The procedure leads to a set of 28 equations similar to equation (3), four of which are trivial and do not contain the electromigration driving force. In the remaining equations each probability $p_{i,j}$ can be written as a sum of the probability in equilibrium ($\epsilon = 0$) and a perturbation proportional to ϵ :

$$p_{i,j} = p_0\left(1 + \left(\frac{\beta}{\alpha} - 1\right)\delta_{i1} + \epsilon q_{i,j}\right) \quad (5)$$

where $\delta_{i,j}$ is the Kronecker delta. It can be easily shown that the deviations for $\{i, j\}$ and $\{i, -j\}$ are antisymmetric, $q_{i,j} = -q_{i,-j}$. With this symmetry operation, the number of equations is reduced to 12 and they can be solved by commercial mathematical computer programs like *Mathematica* [18].

Actually, the number of equations is further reduced to 7, because it is found, by inspection of the equations, that $q_{1,2} = 2q_{1,1}$, $q_{3,3} = q_{3,1} + q_{3,2}$, $q_{4,4} = 2q_{4,2}$, $q_{5,3} = q_{5,1} + q_{5,2}$ and

$q_{5,4} = 2q_{5,1} + q_{5,2}$. The resulting matrix equation is

$$\underline{\underline{A}} \begin{bmatrix} q_{1,1} \\ q_{2,2} \\ q_{3,1} \\ q_{3,2} \\ q_{4,2} \\ q_{5,1} \\ q_{5,2} \end{bmatrix} = \begin{bmatrix} (\beta/\alpha)(2W\eta + 4\gamma r) - 6\beta \\ 4(\beta - 1) \\ 2(\beta - 1) \\ 4(\beta - 1) \\ 2(\beta - 1) \\ 0 \\ 0 \end{bmatrix} \quad (6)$$

where $\underline{\underline{A}}$ is given by

$$\underline{\underline{A}} = \begin{bmatrix} 2W + 2\gamma + 7\alpha & -\beta & -2\beta & -2\beta & -\beta & 0 & 0 \\ -2\alpha & 2\beta + 4 & -2 & -1 & 0 & -2 & -2 \\ -\alpha & -1 & 2\beta + 11 & 0 & -1 & -1 & -2 \\ -2\alpha & 0 & -2 & 2\beta + 8 & -2 & -2 & 0 \\ -\alpha & 0 & -2 & -2 & \beta + 11 & -2 & -1 \\ 0 & 0 & 0 & -1 & -1 & 12 & 0 \\ 0 & -1 & -2 & 0 & 0 & -2 & 10 \end{bmatrix}. \quad (7)$$

Solving this equation, it is possible to write down the deviations $q_{i,j}$. For example, $q_{1,1}$ can be written as

$$q_{1,1} = \frac{1}{\Omega} \left(\frac{\beta}{\alpha} (2W\eta + 4\gamma r - 6\alpha) + 14(\beta - 1)(1 - F) \right) \quad (8)$$

where $\Omega = 2W + 2\gamma + 7F\alpha$. The function F appears as the ratio of two polynomials of β in the inverse of the matrix $\underline{\underline{A}}$ and corresponds to the escape rate mentioned above. Taking into account only four shells in our calculation, we exactly reproduce the expression for F given by Bocquet [6]. Adding shells explicitly only changes the values of the coefficients in the polynomials. Koiwa and Ishioka [19] derived an exact expression for this quantity in the dilute limit. This function decreases monotonically from $F(0) = 1$ to $F(\infty) = \frac{2}{7}$.

2.4. Atomic fluxes

Using the procedure described above, the electromigration fluxes can be written in Onsager form:

$$J_{\text{host}}(c) = J_{\text{host}}(0)(1 + c[l_{AA} + l'_{AA}(r - 1) + l_{AB}\eta]) \quad (9)$$

$$J_{\text{alloy}}(c) = J_{\text{host}}(0)c[l_{AB} + l'_{AB}(r - 1) + l_{BB}\eta] \quad (10)$$

where c is the concentration of alloying atoms and the coefficients l_{ij} are given by

$$l_{AA} = 1 + 4l_{BB} + 2G\beta \frac{2\gamma + 2\alpha}{\Omega} - G \frac{2W + 2\gamma + 7\alpha}{\Omega} \quad (11)$$

$$l'_{AA} = 4l'_{BB} + G\beta \frac{2\gamma}{\Omega} \quad (12)$$

$$l_{AB} = -2l_{BB} + G\beta \frac{W}{\Omega} \quad (13)$$

$$l'_{AB} = -2l'_{BB} \quad (14)$$

$$l_{BB} = \frac{1}{2} \frac{\beta}{\alpha} \frac{2W(2\gamma + 7F\alpha)}{\Omega} \quad (15)$$

$$l'_{BB} = \frac{\beta}{\alpha} \frac{2W\gamma}{\Omega}. \quad (16)$$

The function G is related to the escape rate F by

$$G = 14 \frac{(1 - F)}{\beta} + 4(7F - 2). \quad (17)$$

All terms and functions on the right-hand sides of the equations for the coefficients l_{ij} are positive definite. The flux of host atoms (equation (9)) can therefore only be reduced by negative force ratios r or η , or by the negative terms in the coefficients. These are the fourth term of l_{AA} in equation (11) and the first term of l_{AB} in equation (13).

It is interesting to note here that the expressions for the coefficients l_{ij} , equations (11)–(16), are independent of the number of shells around an alloying atom, which are explicitly taken into account.

3. Case studies and analysis of the flux equations

By considering some special cases it is shown in this section that the expressions derived above are physically sensible.

3.1. Case I: the pure host

A trivial case is encountered if the host atoms and the alloying atoms have exactly the same properties. In this case $W = \alpha = \beta = \gamma = \eta = r = 1$ and the flux of alloying atoms is proportional to the concentration c , so $J_{\text{alloy}}(c) = cJ_{\text{host}}(0)$. This flux must be subtracted from the pure-host flux to obtain the flux of host atoms in the alloy.

3.2. Case II: $\beta = 0$: vacancies avoid alloying atoms

Another particularly simple case occurs when the vacancies avoid the first shell of the alloying atoms. This means that $\beta = 0$, and that the flux of alloying atoms is zero. The flux of host atoms is then reduced due to two effects. First, the host atoms in the first shell are unable to exchange positions with a vacancy and are therefore taken out of the electromigration process. Second, the complex of the alloying atom with its first shell acts as an obstacle to the motion of the other host atoms. Together, the two effects reduce the flux of host atoms by a factor of $1 - 25.2c$.

3.3. Case III: $W = 0$: no jumps of alloying atoms

The analysis of this case is relatively simple, because there is no coupling between the motion of the host and alloying atoms. The host flux can be written as

$$\frac{J_{\text{host}}(c)}{J_{\text{host}}(0)} = 1 + c \left(1 + G \frac{2\beta(2\gamma + 2\alpha) - (2\gamma + 7\alpha)}{2\gamma + 7F\alpha} \right) \quad (18)$$

still considering $r = 1$ for simplicity.

In the limit of large β , equation (18) is dominated by $1 + c(1 + 2G\beta)$. A different expression for the host flux is obtained for the limit of large β from the literature. The flux given on page 397 of the book by Allnatt and Lidiard [8] is dominated by

$$\frac{J_{\text{host}}^{\text{AL}}(c)}{J_{\text{host}}(0)} \approx 1 + 40c\beta \frac{2\gamma - 3\alpha}{2\alpha + 2\gamma} \quad (19)$$

which is a decreasing function of β , when $2\gamma < 3\alpha$.

Because $G\beta$ is bound in the limit of large β , the flux of host atoms according to our solution equation (18) is bound and independent of γ (and α). In contrast, equation (19) depends on

γ and α and is unbound. That the latter is unreasonable can be understood by considering the process sketched in figure 4. The arrow indicates the path of a vacancy jumping between the first shell of an alloying atom and its surrounding shells. The alloying atom is indicated by the filled circle. The vacancy enters the second shell at point 1. It then jumps between the first and second shell and it leaves the second shell again at point 2. If β is large, a vacancy jumps easily towards an alloying atom and therefore jumps many times between the first shell and the second shell. This means that the average distance between point 1 and 2 increases with increasing β . This process increases the diffusivity, and because there is no coupling between the flux of host and alloying atoms this increases the flux directly. From a certain value of β there is no correlation between point 1 and point 2. Then, raising the value of β does not increase the flux any more. In this limit it is not important whether the vacancy also jumps within the first shell. Consequently, the flux must also be independent of γ .

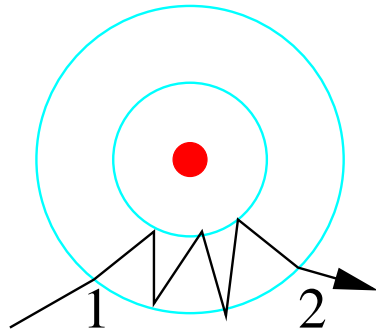


Figure 4. An example of the path of a vacancy, which is jumping between the first- and the second-neighbour shells of the alloying atom, assuming $W = 0$ and $\beta = \alpha \gg 1$.

The different expressions are tested directly using kinetic Monte Carlo simulations of the motion of a single vacancy in a FCC lattice with periodic boundary conditions and one single alloying atom under the additional assumptions that $\gamma = 1$ and $\beta = \alpha$. The latter assumption means that the vacancy concentration is independent of the concentration of alloying atoms. Figure 5, which displays the fluxes according to equation (18) and from the simulations, clearly confirms the new expression. It invalidates the Onsager coefficients given in reference [8] and equation (19), which would not even fit on the plot.

3.4. Case IV: large β , $W \neq 0$

A particularly interesting situation occurs when β is large and the alloying atoms are also allowed to move. If the frequencies for jumps of alloying atoms W and of vacancies within the first shell γ are of the same order of magnitude, and if the frequency α of vacancies jumping away from the first shell is not much larger, the fluxes are dominated by

$$\frac{J_{\text{host}}(c)}{J_{\text{host}}(0)} = 1 - 2 \frac{J_{\text{alloy}}(c)}{J_{\text{host}}(0)} \quad (20)$$

$$\frac{J_{\text{alloy}}(c)}{J_{\text{host}}(0)} = \frac{cW}{\Omega} \left(2 \frac{\beta}{\alpha} \gamma (\eta - 2r) + 2\beta(\eta - 2) \right). \quad (21)$$

For $\eta > 2r$ or for $\eta > 2$, the flux of alloying atoms can become large enough to change the sign of the flux of host atoms. This occurs when a vacancy and an alloying atom effectively move as a pair. The displacement of such a pair requires the displacement of two host atoms

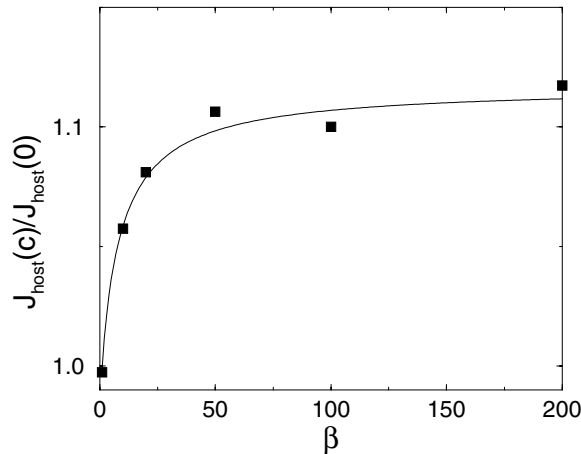


Figure 5. Normalized flux as a function of β with the parameters $W = 0$, $\gamma = 1$ and $\beta = \alpha$. The solid line is calculated using equation (18) and F from Koiwa and Ishioka [19]. The points are values obtained from kinetic Monte Carlo simulations.

in the opposite direction. The preferential direction of the pair is determined by the balance between the driving force on the alloying atom, indicated by η , and the force on the two host atoms moved in the opposite direction.

3.5. General comments

These special cases and the simulations show that the flux equations (9) and (10) are reasonable. Furthermore, the latter example shows that the addition of a small quantity of alloying atoms may reverse the flux of host atoms in particular cases. More general conditions for this interesting behaviour are derived in section 4.

Although the solution which is derived here does not agree with results published previously [8], it is interesting to note that the flux equations (9) and (10) together with the coefficients of equations (11)–(16) agree with the equations given in reference [8] for the special case of $\beta = 1$ and in the limit $\beta \rightarrow 0$, which corresponds to an escape rate of $F = 1$.

The last subject of this section concerns the extension of the five-frequency model with a different electromigration force on host atoms jumping within the first shell of an alloying atom. The flux equations can be written in the usual form of non-equilibrium statistical mechanics using the phenomenological constants. However, the Onsager relation $l_{AB} = l_{BA}$ seems to be violated if $r \neq 1$. This seemingly paradoxical situation can be resolved if one considers that the Onsager relation relates fluxes between species which feel different forces. The Onsager relations are recovered if we consider the alloy as a ternary system, consisting of the alloying atoms, the host atoms in the first shell of the alloying atoms and the other host atoms.

4. Results and discussion

The entire range of the solutions of equations (9) and (10) is very rich and books have been written about the subject [8, 20]. However, one set of solutions, which is of great importance for the interpretation of electromigration data, has not been analysed thoroughly enough. Namely, solutions where the flux of host atoms is reduced or even reversed due to the addition of alloying atoms. In this section all the ways to reduce the flux of host atoms within the

dilute alloy are investigated systematically. These can be separated into three classes. The first is connected to a repulsive interaction between alloying atoms and vacancies. The second describes cases in which the alloying atoms reverse the force on the surrounding host atoms. In the third class, the motion of alloying atoms induces a reverse motion of host atoms. Case IV, described in section 3.4, is an example of the latter class.

4.1. Repulsion between alloying atoms and vacancies

If alloying atoms repel vacancies, the fourth term of equation (11) becomes important. The extreme case is the limit for $\beta \rightarrow 0$. This case has already been considered in section 3.2. This mechanism leads to a maximal reduction of the flux of host atoms by a factor $(1 - 25.2c)$. For small concentrations of alloying atoms this mechanism is therefore not very important.

4.2. Reversal of the driving force on host atoms

A reduction of the flux of host atoms is also expected if the electromigration force on host atoms jumping within the first shell of an alloying atom is opposite to the force on the other host atoms. Such a reversal of the force is indicated by a negative value of r . This effect can be important if $l_{AA}^r|r|$ is large and dominates $l_{AA} - l_{AA}^r$. In general, this does not appear to be a common case, but it can happen if l_{BB}^r and therefore also l_{BB} are large and if at the same time $2\gamma|r| > 7F\alpha$. This is fulfilled, for example, for very small α . A second contribution to a reduction of the flux comes from a large negative term $l_{AB}\eta$. However, the class of large l_{AB} will be considered below.

Another range of parameters for which a reduction of the flux of host atoms is found corresponds to a large negative r ($r < -1$) and large $G\beta$. However, this case is not expected to be very important, because a reversed force of the same magnitude as the force on a host atom due to the presence of one single alloying atom is never found in calculations of electromigration driving forces [16].

4.3. Coupling to the flux of alloying atoms

The third way to reverse the flux of host atoms is through the coupling with the flux of alloying atoms via the coefficient l_{AB} . This coupling can even change the sign of the host flux which occurs if the alloying atom effectively moves together with the vacancy. This can generally happen if the electromigration driving force on the alloying atom is significantly larger than that on a host atom, i.e. if $\eta > 2$ or $\eta > 2r$, and if the transport of the alloying atoms is significant, i.e. if l_{BB} or l_{BB}^r is large.

The important term is $2l_{BB}^r(2r - \eta)$, which corresponds to the motion of a pair consisting of an alloying atom and a vacancy. The motion of such a pair is only possible if two host atoms move in the opposite direction at the same time. The flux of such pairs can be written as the product of a pre-exponential factor and an exponent which contains the effective binding energy of the pair and its migration energy. The binding energy is contained in the ratio β/α and the migration energy is determined by the slowest of the jumps involved, i.e. the minimum of W and γ .

4.4. General considerations

The cases described in sections 4.2 and 4.3 are more important than the one described in section 4.1, because the coefficients l_{ij} are generally unbound and can for example reach large values at low temperatures.

A reversal of the flux of host atoms similar to the reversal described in section 4.3 was also observed in recent kinetic Monte Carlo simulations of the electromigration process in a two-dimensional triangular lattice [21]. Using electromigration forces from *ab initio* calculations for the Al–Cu alloy ($\eta = 2.5$, $r = 0.6$), it was observed that at 300 K and for a Cu concentration of 2 at.% the Al flux is reversed when the binding energy between Cu atoms and vacancies is larger than 0.1 eV. This result of the numerical simulations can now be analysed with the analytical expressions for the fluxes, equations (9) and (10). It is found that the trends are similar and the same parameters are important. Not only does this apply to the two-dimensional triangular lattice and the FCC lattice, but also a flux reversal must be possible for other 2D and 3D lattices. Only in the 1D case and in strongly anisotropic two-dimensional lattices does such an effect not occur.

One important conclusion of the analysis is that a reversal of the direction of the flux of host atoms can only occur if the transport of alloying atoms is comparatively fast (see equation (20)). In a normal dilute alloy one would then expect that the alloying atoms are quickly transported away from the interesting region and may be ‘washed out’ of the alloy. This means that the alloying effect might disappear quickly, because the drift velocity of the alloying atoms should be a factor of about $1/2c$ larger than the drift velocity of the pure host. However, this is not necessarily the case. For example, if alloying atoms can be supplied from precipitates, like in the Al–Cu alloy, or from other sources, this alloying effect may be very efficient in reducing mass transport for a long time.

In this context of electromigration in alloys, a few comments should be made about a popular model for the alloying effects due to Rosenberg [3]. This model explains the alloying effect in Al–Cu alloys by a drop in the diffusivity due to the binding of vacancies and alloying atoms. Binding is assumed to immobilize the vacancies. The diffusion coefficient is then written as a function of concentration as

$$D(c) = \frac{1}{1 + cz(\beta/\alpha - 1)} D(0) \quad (22)$$

where z is the coordination number. The reduction of the diffusion coefficient is based on the assumption that the binding acts on the transport, but does not affect the vacancy concentration. However, for substitutional alloys the binding also lowers the formation energy and therefore the probability of finding a vacancy next to an alloying atom is increased by a factor of β/α (at constant pressure). Taking this into account cancels the reduction in equation (22) and $D(c) \approx D(0)$. Therefore, unless the formation of vacancies is somehow prohibited in the alloy, the model appears to be oversimplified and should not be used.

Macroscopic simulations of electromigration mass transport in real device geometries [22] should therefore be based on equations (9) and (10) instead of the simple Rosenberg model or other empirical descriptions. Such simulations are of crucial importance if the implications of the microscopic mechanistic model on macroscopic device properties are to be understood. For example, the flux reversal described above has the potential to considerably reduce damage accumulation. However, whether this potential can be used depends on many other effects, like the efficiency of sources and sinks for alloying atoms and stress effects, which can only be estimated from macroscopic models.

5. Conclusions and outlook

The electromigration fluxes in a dilute substitutional alloy of FCC lattice structure are calculated and analytically expressed in terms of the five atomic jump frequencies, which cover the most important jumps in the dilute alloy. Such five-frequency models have been considered

before [8, 17], but have apparently not been correct, since the older solutions give unphysical results for some limiting cases. The new solutions behave reasonably and are confirmed by kinetic Monte Carlo simulations in one limit. The usual five-frequency model is further extended to include a difference between the force on a host atom in the first shell of an alloying atom and that on the host atoms further away. This generalization was inspired by *ab initio* calculations of the electromigration driving force in Al alloys [16]. The derivation described here can easily be generalized further to account for more than five frequencies or a larger number of different forces.

An interesting alloying effect which has not attracted much attention so far occurs if vacancies effectively move together with alloying atoms. This can happen if an effective binding of alloying atoms and vacancies is combined with a large enough driving force on the alloying atoms. The flux of alloying atoms then moves the vacancies in the opposite direction to the one in which they would move in the pure host metal. The flux of host atoms is then reversed. Such a reversal could slow down the process of damage accumulation under electromigration conditions and could therefore be technologically important for the development of new electromigration-resistant alloys. To simulate such a process, however, the microscopic parameters have to be incorporated into more macroscopic modelling.

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