ATOMIC MOBILITIES AND VACANCY WIND
EFFECTS IN MULTICOMPONENT ALLOYS

by

M. A. Dayananda

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY JH Kahn/lamb
DATE 10/9/70

For diffusion by vacancy mechanism in an n-component alloy, kinetic expressions for intrinsic fluxes of the diffusing species may be written to include additional contributions arising from the vacancy wind effect⁽¹⁾. Thus, the intrinsic flux of component i referred to the local lattice plane can be expressed⁽²⁾ by

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} + J_{iv} \quad (i = 1, 2 \dots n) \quad [1]$$

where C_i is the concentration (number per unit volume), β_i is the atomic mobility and $\partial \mu_i / \partial x$ is the gradient of chemical potential of the component i. J_{iv} is the additional flux term due to the vacancy wind effect. Although flux terms involving chemical potential gradients of components other than i do not explicitly appear in Eq. [1], it has been shown by Manning⁽²⁾ that Eq. [1] is equivalent to the general thermodynamic diffusion equation given by

$$J_i = - \sum_{j=1}^n L_{ij} \frac{\partial \mu_j}{\partial x} \quad (i = 1, 2 \dots n) \quad [2]$$

where the cross-coefficients, L_{ij} ($i \neq j$), are nonzero quantities and arise entirely from the vacancy wind effect. Manning has also derived expressions for all L_{ij} coefficients, both diagonal and nondiagonal, in terms of tracer diffusion coefficients, D_i^* ($i = 1, 2 \dots n$), which can be determined by n independent measurements.

M. A. Dayananda, Member AIME, is Associate Professor, School of Materials Science and Metallurgical Engineering, Purdue University, Lafayette, Indiana, 47907.

July 16, 1970

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

P6944 *fy*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

An alternative approach based on marker motion studies in diffusion couples is presented in this paper for the determination of atomic mobilities and vacancy wind terms for all components in a multicomponent alloy. It is shown that a pair of independent diffusion couples with their marker planes identified by the same composition will suffice, for the determination of all kinetic data at that common composition regardless of the number of diffusing species.

For a random alloy model Manning⁽³⁾ has shown that the vacancy wind effect is directly proportional to the vacancy flux, J_v . Hence, one can write that

$$J_{iv} = -\alpha N_i \beta_i J_v \quad [3]$$

where N_i is the atom fraction of component i and the constant of proportionality, α , is a function of composition and crystal structure; α is designated as the vacancy wind parameter in this paper. Substitution of Eq. [3] in Eq. [1] yields:

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} - \alpha N_i \beta_i J_v \quad [4]$$

But, J_v is given in terms of intrinsic fluxes by

$$J_v = -\sum_{j=1}^n J_j \quad [5]$$

Hence, Eq. [4] becomes

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} + \alpha N_i \beta_i \sum_{j=1}^n J_j \quad [6]$$

Dividing Eq. [6] by β_i and summing on i , one gets

$$\sum_{i=1}^n \frac{J_i}{\beta_i} = -\sum_{i=1}^n C_i \frac{\partial \mu_i}{\partial x} + \alpha \sum_{i=1}^n N_i \sum_{j=1}^n J_j \quad [7]$$

If local thermodynamic equilibrium is assumed,

$$\sum_{i=1}^n c_i \frac{\partial \mu_i}{\partial x} = 0$$

Hence,

$$\alpha = \frac{\sum_{i=1}^n J_i / \beta_i}{\sum_{i=1}^n J_i}$$

LEGAL NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

[8]

[9]

Substitution of Eq. [9] in Eq. [6] yields:

$$J_i = -c_i \beta_i \frac{\partial \mu_i}{\partial x} + N_i \beta_i \sum_{j=1}^n \frac{J_j}{\beta_j} \quad (i = 1, 2 \dots n) \quad [10]$$

Eq. [10] may be considered as a general expression for intrinsic fluxes in terms of atomic mobilities.

The interrelationship among mobilities, fluxes and the vacancy wind parameter is obtained from a rearrangement of Eq. [9]; thus,

$$\sum_{i=1}^n \frac{J_i}{\beta_i} - \alpha \sum_{i=1}^n J_i = 0$$

or

$$\sum_{i=1}^n J_i \left(\frac{1}{\beta_i} - \alpha \right) = 0 \quad [11]$$

During isothermal annealing of an infinite or semi-infinite diffusion couple, inert markers initially placed at the plane of discontinuity in concentration move⁽⁴⁾ parabolically with time at a constant composition.

One can then integrate Eq. [10] with respect to time t employing a procedure^(5,6) adopted in the analysis of diffusion couples with negligible vacancy wind effects for the determination of diffusion coefficients and mobilities. Thus, for fluxes at the marker plane

$$A_i = \int_0^t J_i dt = - \int_0^t C_i \beta_i \frac{\partial \mu_i}{\partial x} dt + \int_0^t N_i \beta_i \sum_{j=1}^n \frac{J_j}{\beta_j} dt$$

or

$$A_i = - 2t C_i \beta_i \frac{\partial \mu_i}{\partial x} + N_i \beta_i \left[\sum_{j=1}^n \frac{A_j}{\beta_j} \right]_{\text{marker plane}}$$

or

$$\left[(1-N_i) \frac{A_i}{\beta_i} - N_i \sum_{k=1}^{n-1} \frac{A_k}{\beta_k} \right]_{\text{marker plane}} = - 2t C_i \frac{\partial \mu_i}{\partial x} \quad (i = 1, 2 \dots n) \quad [12]$$

where k refers to components other than i . A_i refers to the cumulative intrinsic flux of component i across the marker plane during time t . From the known location of this plane after diffusion, all A_i 's can be determined^(4,6,7) in terms of appropriate areas under the concentration profiles. Hence, Eq. [12] yields $(n-1)$ independent relations involving n mobilities for a single couple. Hence, if one of the n mobilities is known, the other $(n-1)$ mobilities can be evaluated at the marker plane of the couple.

An expression for α in terms of A_i 's and β_i 's can be derived by integrating Eq. [6] with respect to time to get

$$A_i = - 2t c_i \beta_i \frac{\partial \mu_i}{\partial x} + \alpha N_i \beta_i \left[\sum_{j=1}^n A_j \right] \quad (i = 1, 2 \dots n) \quad [13]$$

marker
plane

Dividing Eq. [13] by β_i , summing on i , and substituting Eq. [8], one gets

$$\alpha = \frac{\sum_{i=1}^n \frac{A_i}{\beta_i}}{\sum_{i=1}^n A_i} \quad [14]$$

A pair of independent diffusion couples, infinite or semi-infinite, with their marker planes identified by the same composition may be employed for the experimental determination of β_i and α in a multicomponent system. From such a complementary pair of couples, a pair of relations can be set up for a given i from Eq. [13] and can be simultaneously solved for β_i and α . The consistency of the evaluations can be checked, as α can be determined separately from each pair of equations set up for each of the components.

The kinetic coefficients, L_{ij} , in Eq. [2] can be expressed in terms of β_i 's and α . Summing on i in Eq. [6] and rearranging, one gets

$$\sum_{i=1}^n J_i = - \sum_{i=1}^n c_i \beta_i \frac{\partial \mu_i}{\partial x} / \left(1 - \alpha \sum_{i=1}^n N_i \beta_i \right) \quad [15]$$

Substitution of Eq. [15] in Eq. [6] yields on rearrangement:

$$J_i = - \sum_{j=1}^n c_j \beta_j [\delta_{ij} + \eta N_i \beta_i] \frac{\partial \mu_j}{\partial x} \quad (i = 1, 2 \dots n) \quad [16]$$

where

$$\eta = \frac{\alpha}{1 - \alpha \sum_{i=1}^n N_i \beta_i} \quad [17]$$

and δ_{ij} is the Kronecker delta function. A comparison of Eq. [16] with

Eq. [2] shows that

$$L_{ii} = C_i \beta_i (1 + \eta N_i \beta_i) \quad [18]$$

$$\text{and } L_{ij} = C_j \beta_j (\eta N_i \beta_i) \quad [19]$$

where $i \neq j$. Hence, from the evaluated β_i 's and α at the marker plane, both the diagonal and nondiagonal thermodynamic coefficients of the general flux equations can be determined from Eqs. [18] and [19].

In conclusion, from a pair of multicomponent diffusion couples with marker planes of identical composition, one can evaluate all kinetic parameters, including atomic mobilities of all diffusing species, the vacancy wind parameter and the thermodynamic kinetic coefficients at the common marker composition.

This work was supported by Contract AT(11-1)-1436 with the United States Atomic Energy Commission.

References

1. J. R. Manning: Diffusion Kinetics for Atoms in Crystals, p. 139, Van Nostrand Co., London, 1968.
2. J. R. Manning: Met. Trans., 1970, Vol. 1, pp. 499-505.
3. J. R. Manning: Acta Met., 1967, Vol. 15, pp. 817-26.
4. M. A. Dayananda and R. E. Grace: Trans. TMS-AIME, 1965, Vol. 233, pp. 1287-93.
5. A. G. Guy and J. Philibert: Z. Metallk., 1965, Vol. 12, pp. 841-45.
6. M. A. Dayananda: Trans. TMS-AIME, 1968, Vol. 242, pp. 1369-72.
7. A. G. Guy and V. Leroy: The Electron Microprobe, pp. 543-61, John Wiley and Sons, New York, 1966.

ATOMIC MOBILITIES AND VACANCY WIND EFFECTS IN MULTICOMPONENT ALLOYS

by

M. A. Dayananda

For diffusion by vacancy mechanism in an n-component alloy, kinetic expressions for intrinsic fluxes of the diffusing species may be written to include additional contributions arising from the vacancy wind effect⁽¹⁾. Thus, the intrinsic flux of component i referred to the local lattice plane can be expressed⁽²⁾ by

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} + J_{iv} \quad (i = 1, 2, \dots, n) \quad [1]$$

where C_i is the concentration (number per unit volume), β_i is the atomic mobility and $\partial \mu_i / \partial x$ is the gradient of chemical potential of the component i. J_{iv} is the additional flux term due to the vacancy wind effect.

Although flux terms involving chemical potential gradients of components other than i do not explicitly appear in Eq. [1], it has been shown by Manning⁽²⁾ that Eq. [1] is equivalent to the general thermodynamic diffusion equation given by

$$J_i = - \sum_{j=1}^n L_{ij} \frac{\partial \mu_j}{\partial x} \quad (i = 1, 2, \dots, n) \quad [2]$$

where the cross-coefficients, L_{ij} ($i \neq j$), are nonzero quantities and arise entirely from the vacancy wind effect. Manning has also derived expressions for all L_{ij} coefficients, both diagonal and nondiagonal, in terms of tracer diffusion coefficients, D_i^* ($i = 1, 2, \dots, n$), which can be determined by n independent measurements.

M. A. Dayananda, Member AIME, is Associate Professor, School of Materials Science and Metallurgical Engineering, Purdue University, Lafayette, Indiana, 47907.

JULY 16, 1970

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

An alternative approach based on marker motion studies in diffusion couples is presented in this paper for the determination of atomic mobilities and vacancy wind terms for all components in a multicomponent alloy. It is shown that a pair of independent diffusion couples with their marker planes identified by the same composition will suffice, for the determination of all kinetic data at that common composition regardless of the number of diffusing species.

For a random alloy model Manning⁽³⁾ has shown that the vacancy wind effect is directly proportional to the vacancy flux, J_v . Hence, one can write that

$$J_{iv} = -\alpha N_i \beta_i J_v \quad [3]$$

where N_i is the atom fraction of component i and the constant of proportionality, α , is a function of composition and crystal structure; α is designated as the vacancy wind parameter in this paper. Substitution of Eq. [3] in Eq. [1] yields:

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} - \alpha N_i \beta_i J_v \quad [4]$$

But, J_v is given in terms of intrinsic fluxes by

$$J_v = - \sum_{j=1}^n J_j \quad [5]$$

Hence, Eq. [4] becomes

$$J_i = -C_i \beta_i \frac{\partial \mu_i}{\partial x} + \alpha N_i \beta_i \sum_{j=1}^n J_j \quad [6]$$

Dividing Eq. [6] by β_i and summing on i , one gets

$$\sum_{i=1}^n \frac{J_i}{\beta_i} = - \sum_{i=1}^n C_i \frac{\partial \mu_i}{\partial x} + \alpha \sum_{i=1}^n N_i \sum_{j=1}^n J_j \quad [7]$$

If local thermodynamic equilibrium is assumed,

$$\sum_{i=1}^n c_i \frac{\partial \mu_i}{\partial x} = 0 \quad [8]$$

Hence,

$$\alpha = \frac{\sum_{i=1}^n J_i / \beta_i}{\sum_{i=1}^n J_i} \quad [9]$$

LEGAL NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Substitution of Eq. [9] in Eq. [6] yields:

$$J_i = -c_i \beta_i \frac{\partial \mu_i}{\partial x} + N_i \beta_i \sum_{j=1}^n \frac{J_j}{\beta_j} \quad (i = 1, 2, \dots, n) \quad [10]$$

Eq. [10] may be considered as a general expression for intrinsic fluxes in terms of atomic mobilities.

The interrelationship among mobilities, fluxes and the vacancy wind parameter is obtained from a rearrangement of Eq. [9]; thus,

$$\sum_{i=1}^n \frac{J_i}{\beta_i} - \alpha \sum_{i=1}^n J_i = 0$$

or

$$\sum_{i=1}^n J_i \left(\frac{1}{\beta_i} - \alpha \right) = 0 \quad [11]$$

During isothermal annealing of an infinite or semi-infinite diffusion couple, inert markers initially placed at the plane of discontinuity in concentration move⁽⁴⁾ parabolically with time at a constant composition.

One can then integrate Eq. [10] with respect to time t employing a procedure^(5,6) adopted in the analysis of diffusion couples with negligible vacancy wind effects for the determination of diffusion coefficients and mobilities. Thus, for fluxes at the marker plane

$$A_i = \int_0^t J_i dt = - \int_0^t C_i \beta_i \frac{\partial \mu_i}{\partial x} dt + \int_0^t N_i \beta_i \sum_{j=1}^n \frac{J_j}{\beta_j} dt$$

or

$$A_i = - 2t C_i \beta_i \frac{\partial \mu_i}{\partial x} + N_i \beta_i \left[\sum_{j=1}^n \frac{A_j}{\beta_j} \right]_{\text{marker plane}}$$

or

$$[1-N_i] \frac{A_i}{\beta_i} - N_i \sum_{k=1}^{n-1} \frac{A_k}{\beta_k} = - 2t C_i \frac{\partial \mu_i}{\partial x} \quad (i = 1, 2, \dots, n) \quad [12]$$

marker plane

where k refers to components other than i . A_i refers to the cumulative intrinsic flux of component i across the marker plane during time t .

From the known location of this plane after diffusion, all A_i 's can be determined^(4,6,7) in terms of appropriate areas under the concentration profiles. Hence, Eq. [12] yields $(n-1)$ independent relations involving n mobilities for a single couple. Hence, if one of the n mobilities is known, the other $(n-1)$ mobilities can be evaluated at the marker plane of the couple.

An expression for α in terms of A_i 's and β_i 's can be derived by integrating Eq. [6] with respect to time to get

$$A_i = -2c_i \beta_i \frac{\partial \mu_i}{\partial x} + \alpha N_i \beta_i \left[\sum_{j=1}^n A_j \right] \quad (i = 1, 2, \dots, n) \quad [13]$$

marker
plane

Dividing Eq. [13] by β_i , summing on i , and substituting Eq. [8], one gets

$$\alpha = \frac{\sum_{i=1}^n \frac{A_i}{\beta_i}}{\sum_{i=1}^n A_i} \quad [14]$$

A pair of independent diffusion couples, infinite or semi-infinite, with their marker planes identified by the same composition may be employed for the experimental determination of β_i and α in a multicomponent system. From such a complementary pair of couples, a pair of relations can be set up for a given i from Eq. [13] and can be simultaneously solved for β_i and α . The consistency of the evaluations can be checked, as α can be determined separately from each pair of equations set up for each of the components.

The kinetic coefficients, L_{ij} , in Eq. [2] can be expressed in terms of β_i 's and α . Summing on i in Eq. [6] and rearranging, one gets

$$\sum_{i=1}^n J_i = - \sum_{i=1}^n c_i \beta_i \frac{\partial \mu_i}{\partial x} \left(1 - \alpha \sum_{i=1}^n N_i \beta_i \right) \quad [15]$$

Substitution of Eq. [15] in Eq. [6] yields on rearrangement:

$$J_i = - \sum_{j=1}^n c_j \beta_j [\delta_{ij} + \eta N_i \beta_i] \frac{\partial \mu_j}{\partial x} \quad (i = 1, 2, \dots, n) \quad [16]$$

where

$$\eta = \frac{\alpha}{1 - \alpha \sum_{i=1}^n N_i \beta_i} \quad [17]$$

and δ_{ij} is the Kronecker delta function. A comparison of Eq. [16] with

Eq. [2] shows that

$$L_{ii} = C_i \beta_i (1 + \eta N_i \beta_i) \quad [18]$$

$$\text{and } L_{ij} = C_j \beta_j (\eta N_i \beta_i) \quad [19]$$

where $i \neq j$. Hence, from the evaluated β_i 's and α at the marker plane, both the diagonal and nondiagonal thermodynamic coefficients of the general flux equations can be determined from Eqs. [18] and [19].

In conclusion, from a pair of multicomponent diffusion couples with marker planes of identical composition, one can evaluate all kinetic parameters, including atomic mobilities of all diffusing species, the vacancy wind parameter and the thermodynamic kinetic coefficients at the common marker composition.

This work was supported by Contract AT(11-1)-1436 with the United States Atomic Energy Commission.

References

1. J. R. Manning: Diffusion Kinetics for Atoms in Crystals, p. 139, Van Nostrand Co., London, 1968.
2. J. R. Manning: Met. Trans., 1970, Vol. 1, pp. 499-505.
3. J. R. Manning: Acta Met., 1967, Vol. 15, pp. 817-26.
4. M. A. Dayananda and R. E. Grace: Trans. TMS-AIME, 1965, Vol. 233, pp. 1287-93.
5. A. G. Guy and J. Philibert: Z. Metallk., 1965, Vol. 12, pp. 841-45.
6. M. A. Dayananda: Trans. TMS-AIME, 1968, Vol. 242, pp. 1369-72.
7. A. G. Guy and V. Leroy: The Electron Microprobe, pp. 543-61, John Wiley and Sons, New York, 1966.