A PROCEDURE TO DETERMINE THE SEGREGATION PARAMETERS IN TERNARY SYSTEMS FROM EXPERIMENTAL DATA OF A LINEAR TEMPERATURE RUN.

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Profiles of surface concentrations as a function of temperature, where the temperature is increased at a constant rate, contain the necessary information to extract segregation parameters. A model using rate equations can be used to simulate these profiles. Even on a high-speed computer, solving these equations can take hours. For ternary and higher component alloys the fit parameters are at least nine and finding the best fit manually can extend the search to days. Theoretical segregation and diffusion models show two temperature regions of interest. In the low-temperature region, representing the kinetics of segregation, the diffusion coefficients of the species dominate the flux of atoms to the surface, and in the high-temperature region the surface concentrations are independent of the diffusion coefficients. In the high-temperature equilibrium region the surface concentrations are determined only by the segregation energies and interaction coefficients. A procedure is presented that can find a good set of segregation parameters within seconds. The sensitivity of selecting the kinetics, as well as the equilibrium temperature regions will be demonstrated. The procedure is used to extract the segregation parameters for a Cu(111) 0.13 at% Sn 0.18 at% Sb system.

Keywords: Segregation profile; temperature run; segregation kinetics; interaction coefficient; segregation parameters.

1. Introduction

Measuring the surface concentration of a segregating species as a function of temperature, where the temperature is increased linearly with time at a constant rate, gives segregation profiles with more than enough information to extract segregation parameters. This experimental method is also known as linear temperature ramping (LTR).

The modified Darken model describing both the kinetics and equilibrium concentrations has proved

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to be a very useful model.[1-3] The model is discussed by du Plessis[1] and it describes the rate of segregation in the layers for an m-component alloy. The number of coupled differential rate equations are $(m-1)(N+1)$ for $N+1$ layers and m species. The solution gives the profile for a certain set of segregation parameters and takes much computational time, even if one increases the integration steps and uses "smart" mathematical routines to reduce the number of equations. A typical profile can take up to 24 h to generate. The problem gets more time-consuming when this model is used to simulate a measured segregation profile with the purpose of extracting segregation parameters from the best mathematical fit. In ternary systems, the number of fit parameters are nine (two frequency factors, two activation energies, two segregation energies, and three interaction parameters) and to start with a good initial set of segregation parameters is essential.

A two-step procedure is presented which can find a good set of starting parameters within seconds. The first step uses Fick's semi-infinite diffusion description, describing the kinetics of segregation,[2] to find the diffusion coefficients. The second step generates the segregation energies and interaction coefficients from Guttmann's equilibrium equations of segregation.

2. The Fit Procedure

2.1. Step 1

From theory,[1] the low-temperature region of the segregation profile is not sensitive to the segregation and interaction energies. This temperature region can thus be simulated using Fick's semi-infinite dif-

interaction between the segregating atoms and the rate of transfer of atoms from the near surface layer

surface concentration of the segregated atoms.

$$X^{\varphi} = X^{B}\left(1 + \frac{2\,Dt}{d\,\pi}\right)^{1/2}. \qquad (1)$$

Viljoen et al.[2] introduce an enrichment factor $\beta(T) = \frac{X^{\varphi}(T) - X^{B}}{X^{B}}$, the diffusion equation $D = D_0 e^{-E/RT}$, as well as the relation between temperature and time

in the linear temperature run $T = T_0 + \alpha t$, and used Eq. (1) to derive

$$\frac{1}{2}\beta^2 = \frac{2\,D_0}{\pi\,\alpha d^2}\int_{T_0}^{T_E} e^{-E/RT}\,dT. \qquad (2)$$

The integration can be solved numerically and Eq. (2) yields two of the segregation parameters namely the activation energy E and pre-exponential factor D_0.

It is clear that this approach ignores the segregation energies as well as the interaction energies and the question is in which temperature range (T_0 to T_E) this approximation will be valid? For a system where these parameters have low values the temperature range will be wide and vice versa.

In Fig. 1 the modified Darken model was used to generate segregation profiles in binary systems. The following diffusion parameters were used: $D_0 = 1 \times 10^{-4}\,\mathrm{m^2 s^{-1}}$ and $E = 220\,\mathrm{kJ\,mol^{-1}}$ and to demonstrate the influence of the interaction coefficients, high attractive and repulsive energies were used: $\Omega = 30\,\mathrm{kJ\,mol^{-1}}$ in profile A, and $\Omega = -30\,\mathrm{kJ\,mol^{-1}}$ in profile B. The Fick approximation (broken line) clearly shows the effect of the segregation energies and interaction parameters on the kinetic profiles at an early (low temperature) stage. The procedure performs poorly when interaction energies are involved. A good fit is still possible if the high
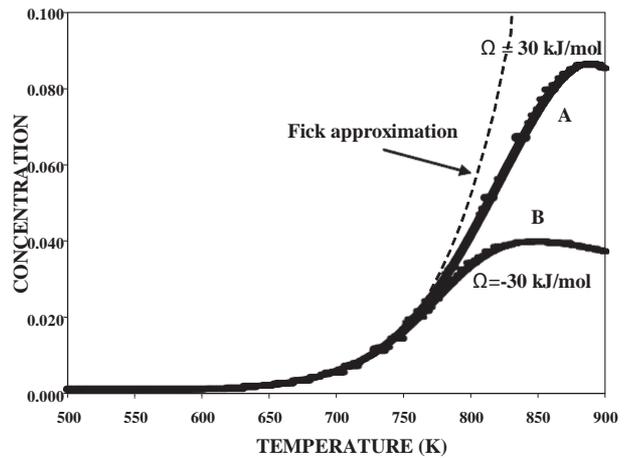

Fig. 1. The profiles are simulations of binary systems with $D_0 = 1 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$ and activation energy $E = 220\,\mathrm{kJ\,mol^{-1}}$. The segregation energy $\Delta G = 60\,\mathrm{kJ\,mol^{-1}}$ and interaction energies as indicated. The broken line is a Fick approximation (Eq. (2)).

temperature limit (T_E) is selected at a temperature where the coverage is less than 10% of the maximum coverage. Viljoen et al.[2] also argued that this method is only valid if the activation energy $E > 100\,\mathrm{kJ\,mol^{-1}}$.

Simulations also indicate that segregation parameters, generated from the fits, are not sensitive to the lower temperature limit T_0, and that the higher the segregation energy the lower the upper limit of the temperature region (T_E) for which the procedure generates D_0 and E within a 10% accuracy.

2.2. *Step 2*

It was shown[1] that the segregation equations of a ternary system in equilibrium, reduce to the Guttman equilibrium equations given by:

$$X_n 1 = X_1^B \exp(\Delta G_1 / RT) / (1 - X_1^B$$
$$+ X_1^B \exp(\Delta G_1 / RT) \qquad (3)$$
$$- X_2^B + X_2^B \exp(\Delta G_2 / RT)),$$

$$X_n 2 = X_2^B \exp(\Delta G_2 / RT) / (1 - X_1^B$$
$$+ X_1^B \exp(\Delta G_1 / RT) \qquad (4)$$
$$- X_2^B + X_2^B \exp(\Delta G_2 / RT)),$$

where

$$\Delta G_1 = \Delta G_1^0 + 2\Omega_{13}(X_1^B - X1)$$
$$+ \Omega^!(X2 - X_2^B), \qquad (5)$$

$$\Delta G_2 = \Delta G_2^0 + 2\Omega_{23}(X_2^B - X2)$$
$$+ \Omega^!(X1 - X_1^B), \qquad (6)$$

and

$$\Omega^! = \Omega_{12} - \Omega_{13} - \Omega_{23}. \qquad (7)$$

In the temperature region where equilibrium has already set in, the surface concentrations of the segregating species are independent of the bulk diffusion coefficients. The concentrations only depend on the segregation energies and interaction coefficients (see Eqs. (3) and (4)). Heating the sample at a constant temperature, the time to reach surface equilibrium depends on the temperature. The higher the temperature the sooner equilibrium is reached. It is thus obvious that in a LTR run at high enough temperatures, the segregation profile will resemble equilibrium surface coverage very closely. Once this region has been identified in the experimental data, the Guttmann equations can be used in a suitable

mathematical minimizing fit routine to extract the segregation parameters. The experimental equilibrium region can also be extended by cooling the sample at a low rate.[4] Most of the time the cooling down is necessary, because a typical equilibrium profile shows a "stiff" change in concentration as a function of temperature. The result is that one cannot find a unique set of parameters which fit this small equilibrium temperature region. Extending the equilibrium temperature region (T_b to T_e) can move closer toward a unique set of equilibrium parameters.

2.2.1. *The minimizing procedure*

Because the LTR involves a number of temperatures, the minimizing method consists of two minimizing loops nested into each other. The first loop is used with Eqs. (3) and (4), to determine the surface concentration for a given set of segregation parameters at a given temperature. Once all surface concentrations in the specified temperature range (T_b to T_e) are calculated the second loop attempts to minimize a function R, which is the difference between the calculated and measured surface concentrations, using $\Delta G_i^0 s$ and $\Omega_i s$ as variables. This function is given by:

$$R = \sum_{i=T_b} (X1(i) - X_m 1(i))^2 + (X2(i)$$
$$- X_m 2(i))^2. \qquad (8)$$

In Eq. (8), $X1(i)$ is the calculated surface coverage of species 1 using the Guttman equations, and $X_m 1(i)$ is the measured surface coverage at temperature i. Minimizing R means to find values for the Ωs and ΔGs to best fit the measured surface concentrations in the temperature range T_b–T_e. This procedure can only be used for equilibrium coverage and is therefore applied on the high-temperature side of a LTR profile.

Figure 2 shows the flowchart that is used to get the best fit from the experimental data. In this specific example, the minimizing function attempts to return a set of $\Delta G_i^0 s$ and $\Omega_i s$ which is a local minimizer of the function R (see Eq. (8)) near the starting vector.

To illustrate the sensitivity of the fit procedure as a function of the change in the parameters, equilibrium segregation profiles for a ternary
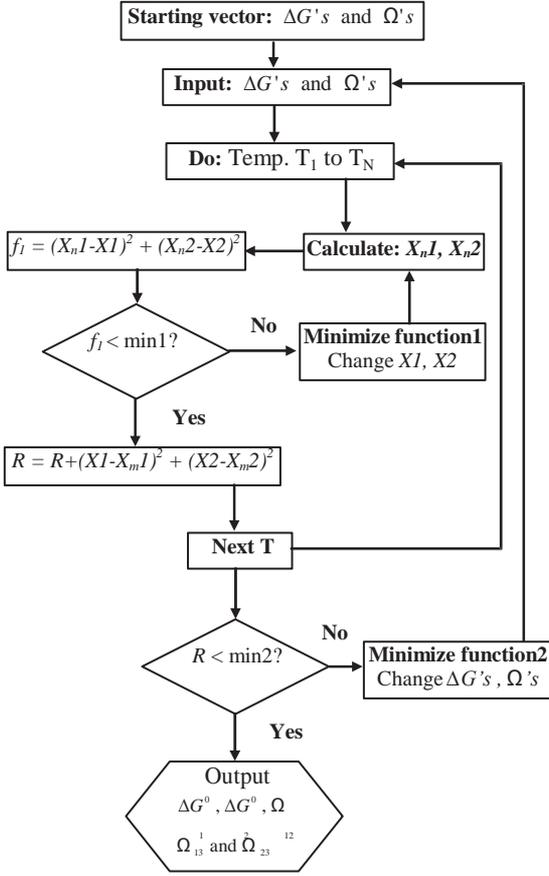
Flowchart to solve Guttman's segregation equations

Starting vector: $\Delta G's$ and $\Omega's$

Input: $\Delta G's$ and $\Omega's$

Do: Temp. T_1 to T_N

Calculate: X_n1, X_n2

$f_1 = (X_n1-X1)^2 + (X_n2-X2)^2$

$f_1 < min1$? No → Minimize function1 Change $X1, X2$

Yes

$R = R+(X1-X_m1)^2 + (X2-X_m2)^2$

Next T

$R < min2$? No → Minimize function2 Change $\Delta G's$, $\Omega's$

Yes

Output
$\Delta G^0_1, \Delta G^0_2, \Omega$
$\overset{1}{\Omega}_{13}$ and $\overset{2}{\Omega}_{23}$

Fig. 2. Flowchart indicating the two nested minimizing functions to solve Eqs. (3) and (4).
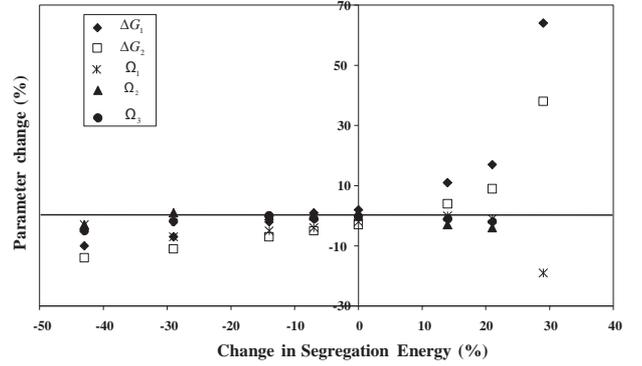
Fig. 3. Percentage change in the segregation parameters vs percentage change in segregation energy of species 1. The data were calculated using the minimizing routines as proposed by the flowchart in Fig. 2.

3. Simulating Profiles in Cu(111)

Both Fick's approximation and the minimizing procedures were used to extract the segregation parameters of a Cu(111) 0.13 at% Sn 0.18 at% Sb system. The crystal was doped by a diffusion process and the profiles were measured with Auger electron spectroscopy. A temperature ramp of $0.075\,\mathrm{K\,s^{-1}}$ was used. The results are shown in Fig. 4. The solid lines are modified Darken fits which make use of segregation parameters extracted as described in this paper.
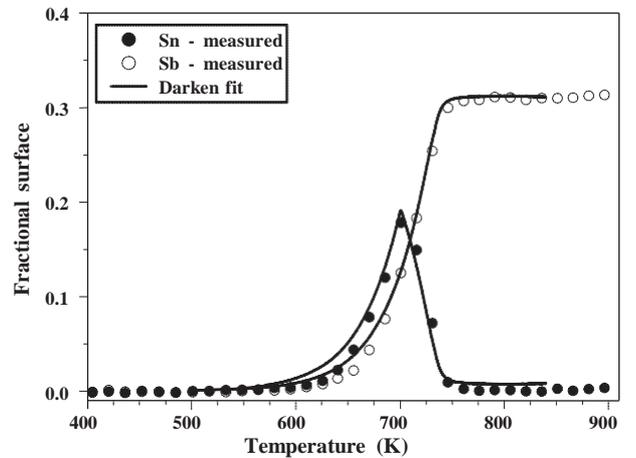

Fig. 4. Measured Sn and Sb segregation profiles in Cu(111). The solid lines are Darken fits with segregation parameters: $D_{o(Sn)} = 9 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$, $D_{o(Sb)} = 3 \times 10^{-3}\,\mathrm{m^2\,s^{-1}}$, $E_{Sn} = 196\,\mathrm{kJ\,mol^{-1}}$, $E_{Sb} = 206\,\mathrm{kJ\,mol^{-1}}$, $\Delta G_{Sn} = 68\,\mathrm{kJ\,mol^{-1}}$, $\Delta G_{Sb} = 86\,\mathrm{kJ\,mol^{-1}}$, $\Omega_{CuSn} = 4\,\mathrm{kJ\,mol^{-1}}$, $\Omega_{CuSb} = 16\,\mathrm{kJ\,mol^{-1}}$, and $\Omega_{SnSb} = -5\,\mathrm{kJ\,mol^{-1}}$.

system were simulated using the Guttman equations, Eqs. (4)–(7). Parameters typical of a copper system[4] were used in the simulations, with $\Delta G_1 = 70\,\mathrm{kJ\,mol^{-1}}$, $\Delta G_2 = 80\,\mathrm{kJ\,mol^{-1}}$, $\Omega_{1,2} = 10\,\mathrm{kJ\,mol^{-1}}$, $\Omega_{1,3} = 5\,\mathrm{kJ\,mol^{-1}}$, and $\Omega_{2,3} = -5\,\mathrm{kJ\,mol^{-1}}$. In the starting vector to the fit procedure, ΔG_1 was changed and all other parameters were kept fixed. Figure 3 is a plot of the change in segregation parameters as a function of the change in ΔG_1. It is clear that the fit procedure generates parameters within $\pm10\%$ of the simulated values even if the change in ΔG_1 is $\pm20\%$.

The mathematical method does not make provision for reconstruction of the surface or for complicated thermodynamic behavior such as discontinuous changes in surface concentrations due to a miscibility gap or compound formation.

It is clear that the segregation parameters resulted in profiles that simulate the kinetics and equilibrium segregation behavior of the system well. The difference between the measured and the fitted profiles is that the Fick approximation does not take the dumping of atoms by the segregation energies and interactions into account. Surface diffusion and experimental factors like sputtering can also contribute to the error. Although there are many factors that can influence the accuracy of the segregation parameters, the values, specified in the figure caption, corresponds well with the previous results.[5]

4. Conclusion

The fit procedure has shown that careful selection of the temperature ranges, where the Fick integral and the minimizing approximations are used is critical. Although the Fick approximation is strictly speaking only valid for binary systems it can be used successfully in ternary systems where the interaction energies are small. The success of the second step in the procedure depends on the starting vector and one can make use of other empirical formulas to fix some of the segregation parameters.

It has been shown that the two-step fit procedure presented here can quickly extract good segregation parameters for a ternary system. These parameters can act as starting parameters for models describing both the kinetics and equilibrium of segregation.

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