Simulation of Carbon Diffusion in Steel Driven by a Temperature Gradient

Lars Höglund and John Ågren

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The basis of thermomigration in multicomponent alloys is summarized, and the general equations are given and implemented in the DICTRA software. Experimental information from Okafor et al. is analyzed with the new simulations and it is concluded that steady-state conditions was not established during their experiment. A heat of transport $Q_C^* = -44000$ J/mol, almost four times larger than the value given by Okafor et al., was found to give a satisfactory representation of the experimental information.

1. Introduction

A temperature gradient, imposed on a chemically homogeneous material, may cause diffusional transport of atoms, so-called thermomigration, see for example the text book by Philibert.[1] The phenomenon is technically important whenever a component is subjected to a temperature gradient during prolonged times, e.g., in superheaters, heat exchanger tubes, etc., made by steels or Ni-base alloys. The effect is more pronounced for the mobile interstitials than for the sluggish substitutional elements. However, it may also be important even during quite short times if the gradient is sufficiently strong, e.g., in solder joints.

Thermomigration stems from the cross effects described by the general phenomenological equations of irreversible thermodynamics, see for example Ref 2. These equations express the fluxes of various quantities as linear functions of gradients of the conjugated thermodynamic potentials. The basic equations become particularly simple if steady-state conditions have been established and it is then straight forward to evaluate a quantity called the *heat of transport* from a concentration profile once the temperature profile is known. This approach has been used by several authors, see for example Okafor et al.[3] and Mathuni et al.[4]

In the early 1990s, Andersson and Ågren[5] developed a general formalism to represent diffusion data for multicomponent systems in terms of intrinsic mobilities. Their method was implemented in the DICTRA software[6] and has now become widely used to analyze diffusion. However, it was not capable of taking temperature gradients into account. In the present report, a numerical solution of the full equations has been implemented in the DICTRA software, and the experimental information given by Okafor et al.[3] has been analyzed with DICTRA simulations.

2. Temperature Gradients and Diffusion

2.1 General Case and the Heat of Transport

The phenomenological equations for diffusional flux J_k of species k, in the presence of both a chemical potential and a temperature gradient of an n component system may be written,

$$J_k = -\sum_{i=1}^{n} \frac{L_{ki}}{T} \nabla \mu_k - \frac{L_{kT}}{T^2} \nabla T, \tag{Eq 1}$$

where μ_k is the chemical potential of species k evaluated at the temperature T. The L denotes the so-called phenomenological coefficients. A corresponding equation may be written for the heat flow but will not be given here as we are not concerned with the heat flow itself. The heat of transport Q_i^* for component i, is then introduced as

$$L_{kT} = \sum_{i=1}^{n} L_{ki} Q_i^*. \tag{Eq 2}$$

In a lattice-fixed frame of reference, the vacancy model for diffusion yields, see Ref 5

$$L_{kk} = \frac{u_k}{V_s} y_{Va} M_{kVa} \tag{Eq 3}$$

with all off-diagonal elements of the L matrix being zero. u_k is related to the ordinary mole fraction x_k by means of

$$u_k = \frac{x_k}{\sum_{i \in s} x_i}, \tag{Eq 4}$$

where the summation in the denominator is taken only over the substitutional elements. V_s is the molar volume per mole of substitutional atoms and M_{kVa} is the mobility. y_{Va} is the fraction of vacant lattice sites. Transformation to a

Lars Höglund and **John Ågren,** Division of Physical Metallurgy, Department of Materials Science and Engineering, Royal Institute of Technology, 100 44 Stockholm, Sweden. Contact e-mail: john@kth.se.

number-fixed frame of reference with respect to the substitutional elements and expansion in interdiffusion coefficients, see Andersson and Ågren,[5] then yields

$$J'_k = -\sum_{i=1}^{n} D_{ki}^{n'}\frac{1}{V_s}\nabla u_i - \frac{L'_{kT}}{T^2}\nabla T, \qquad \text{(Eq 5)}$$

where $D_{ki}^{n'}$ is the matrix of interdiffusion coefficients and component n is arbitrarily taken as the dependent component. The primes denote the number-fixed frame of reference, i.e., $\sum_{k \in s} J'_k = 0$. The matrix L'_{kT} is given by

$$L'_{kT}/T^2 = \sum_{i=1}^{n}(\delta_{ki} - u_k a_i)\frac{u_i}{V_s}y_{Va}M_{iVa}Q_i^*\frac{1}{T}, \qquad \text{(Eq 6)}$$

where the Kronecker delta $\delta_{ki} = 1$ when $k = i$ and zero otherwise. $a_i = 1$ when i denotes a substitutional element and zero otherwise.

2.2 Application to Fe-M-C Alloys

For the case when M is a substitutional element, Eq 6 takes the form

$$L'_{FeT}/T^2 = \frac{1}{V_s}\big((1 - u_{Fe})u_{Fe}M_{Fe}Q_{Fe}^* - u_{Fe}u_M M_M Q_M^*\big)\frac{1}{T} \qquad \text{(Eq 7)}$$

$$L'_{MT}/T^2 = \frac{1}{V_s}\big(-u_M u_{Fe}M_{Fe}Q_{Fe}^* + (1 - u_M)u_M M_M Q_M^*\big)\frac{1}{T}$$
$$= -L'_{FeT}/T^2 \qquad \text{(Eq 8)}$$

$$L'_{CT}/T^2 = \frac{u_C}{V_s}\big(-u_{Fe}M_{Fe}Q_{Fe}^* - u_M M_M Q_M^* + y_{Va}M_{CVa}Q_C^*\big)\frac{1}{T}, \qquad \text{(Eq 9)}$$

where we have defined $M_k = y_{Va}M_{kVa}$ for the substitutional elements. The mobilities of the substitutional atoms are many orders of magnitude lower than these of the interstitials and we may approximate

$$L'_{CT}/T^2 \cong \frac{u_C}{V_s}y_{Va}M_{CVa}Q_C^*\frac{1}{T}. \qquad \text{(Eq 10)}$$

If there are no substitutional concentration gradients and we neglect sluggish substitutional diffusion, Eq 5 becomes

$$J'_C = -D_{CC}^{Fe'}\frac{1}{V_s}\nabla u_C - \frac{u_C}{V_s}y_{Va}M_{CVa}Q_C^*\frac{1}{T}\nabla T. \qquad \text{(Eq 11)}$$

Invoking the relation,[5] $D_{CC}^{Fe'} = u_C y_{Va}M_{CVa}d\mu_C/du_C$ Eq 11 may be further simplified

$$J'_C = -D_{CC}^{Fe'}\frac{1}{V_s}\left(\nabla u_C + Q_C^*\frac{1}{Td\mu_C/du_c}\nabla T\right). \qquad \text{(Eq 12)}$$

2.3 Stationary Diffusion

Under steady-state conditions and planar geometry, the flux is everywhere the same and in a closed system it must vanish. Under steady-state conditions and the condition $J_C = 0$, Eq 12 may be rewritten

$$Q_C^* = \frac{1}{T}\frac{d\mu_C}{du_c}\frac{du_C}{d(1/T)}. \qquad \text{(Eq 13)}$$

Previous authors have assumed the ideal solution behavior $d\mu_C/du_c = RT/u_C$ and Eq 13 yields $Q_C^* = Rd\ln u_C/d(1/T)$. If the logarithm of concentration is plotted as a function of inverse temperature, the data should fall on a straight line with the slope Q_C^*/R.

2.4 Experimental Information

Okafor et al.[3] considered an Fe—32 mass% Ni—0.14 mass% C alloy and arranged a situation with a stationary temperature profile, roughly shaped as a Gaussian spanning from 1000 to a maximum of 1400 K. In that temperature range, the alloy should be fully austenitic. After 102 h, the carbon concentration profile was measured and the heat of transport was evaluated from a plot of the logarithm of concentration as a function of inverse temperature, $Q_C^* = Rd\ln u_C/d(1/T)$, i.e., the steady-state profile for ideal solution behavior. When the authors decided, the time that would be needed to achieve steady state they considered the average temperature, which is ca. 1200 K and they concluded that at this temperature ca. 100 h would be sufficient. However, it should be immediately clear from the carbon and temperature profiles that have been included in Fig. 1 as symbols and dashed line, that steady state could not have been reached in their experiment. Equation 13 shows that when there is no change in temperature there should be no change in composition which is obviously not the case in their figure. Consequently their exposure time of 102 h was not long enough to fully approach steady state.
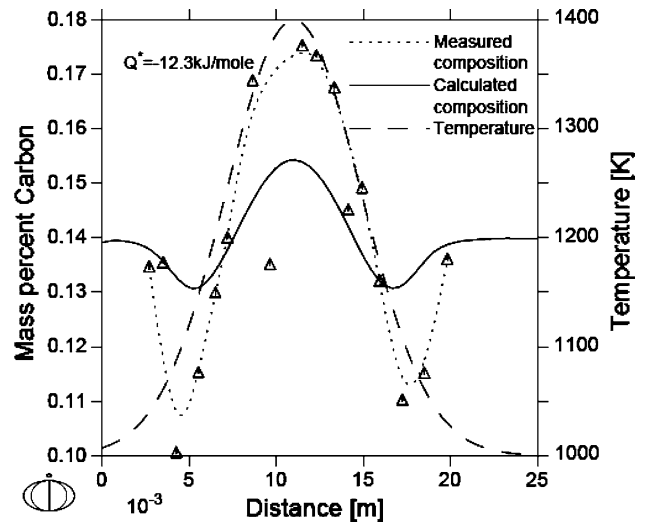

Fig. 1 Temperature (*dashed line*) and experimental carbon contents from [3] (*symbols*). Calculated carbon profile for 102 h with $Q^* = -12300$ J/mol from ref 3 (*solid line*)

Of course one also has to consider that the parts at the lowest temperatures have the time to approach steady state.

3. Implementation in DICTRA

The numerical solution of the diffusion equations, i.e., the conservation equations, in the DICTRA code is based on the Galerkin method.[7,8] The partial differential equations

$$\frac{1}{V_s}\frac{\partial u_k}{\partial t} = -\nabla \cdot J_k, \qquad (\text{Eq 14})$$

where Eq 5 is inserted for J_k, are discretized in space yielding a system of ordinary differential equations of the type

$$A\frac{1}{V_m}\frac{du_k}{dt} = -R_k + \sum B_{kj}u_j + B_{kT}T, \qquad (\text{Eq 15})$$

where A is the so-called mass matrix and u_k is a columnar vector containing the content of component k in each grid point. R_k is a columnar vector containing the boundary conditions. In a closed system, all its elements are null. B_{kj} is called the stiffness matrix and contains the diffusion coefficients. The term $B_{kT}T$ is the extra term arising from the effect of the temperature gradient and the matrix B_{kT} contains the L'_{kT}/T^2 coefficients and is similar to the stiffness matrix. T is the columnar vector containing the temperature in each grid point. The last term in Eq 15 is known as a function of time because we have assumed that the function $T(t, x)$ is given. In the simple geometries represented by only one distance variable r, the matrix elements of B_{kT} are given by

$$B_{kT}^{ij} = \int f\frac{\partial \varphi_i}{\partial r}\frac{\partial \varphi_j}{\partial r}dr, \qquad (\text{Eq 16})$$

where the φ_js are the so-called test functions of the finite element method and $f = g(r)L'_{kT}/T^2$ and $g(r)$ is a function determined by the geometry.

When Eq 15 is solved with the required degree of implicity, we use an average value of $T(t, x)$ during each time step.

In order to test the implementation, simulations where performed until a steady condition was obtained. The value of Q_C^* was then evaluated along the calculated concentration profile using Eq 13 and was found to be consistent with the prescribed value.

4. Simulations

The fixed temperature profile reported by Okafor et al.[3] was represented by a Gaussian that was given as a global condition in DICTRA. The heat of transport is assumed to be independent of temperature and composition and in the simulations, the effects on Fe and Ni are neglected simply setting the corresponding heat of transport coefficients to zero. The simulation was then run with the Q_C^* value reported by Okafor et al.[3] until steady-state conditions were established which required about 3000 h. A series of simulations were then run with different values of Q_C^* until the value that gave the best agreement with the reported concentration profile after 102 h was found.

5. Results and Discussion

From a more qualitative point of view, the shape of the carbon profile should roughly follow the temperature profile which is not the case in Fig. 1 where the temperature profile (dashed curve) and the experimental carbon content (symbols) from Okafor et al.[3] have been plotted. The dotted line has been plotted to guide the eye. It is thus obvious that the value of Q_C^* presented by Okafor et al. cannot have been evaluated under steady-state conditions. Thus, it can only be considered as a lower limit. As can be seen from Fig. 1, the simulations confirm this conclusion because the calculated curve for 102 h (solid line) falls much below the experimental points.

The value that gave the best agreement between simulated composition profile and the experimentally observed one after 102 h was $Q_C^* = -44000$ J/mol which is almost four times larger than the value given in the original report. The results with $Q^* = -44000$ are shown in Fig. 2. A better agreement could possibly be obtained by allowing Q_C^* to vary with temperature or composition, but that was not pursued further in the present work. The long-term steady-state profile is also included in the figure and shows that the maximum carbon content at steady state will reach 0.27 mass% compared to 0.18 mass% after 102 h.

It is easy to understand why the time used by Okafor et al. was too short. They argued that ca. 100 h would be
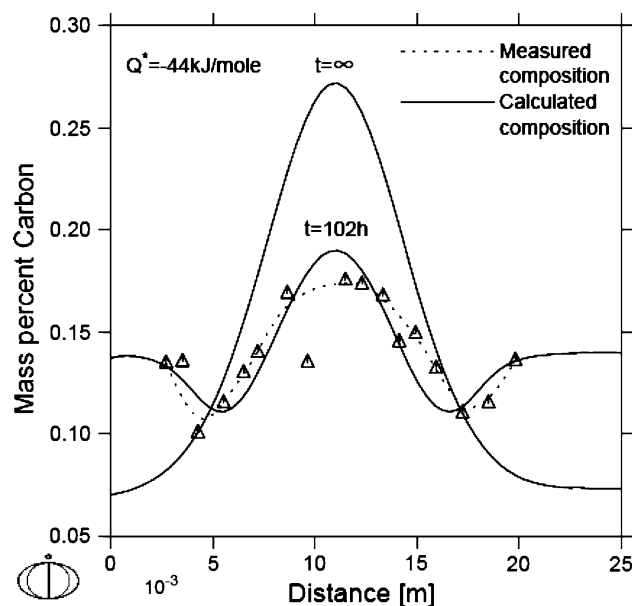

Fig. 2 Calculated carbon profile with $Q^* = -44000$ J/mol fitted to experimental data from ref 3 after 102 h

enough to establish steady-state conditions if the system had been kept isothermally at the average temperature. However, in order to approach steady-state conditions it is necessary that carbon diffuses from the coldest regions toward the hotter and that requires much longer time. In fact, at the lowest temperature 1000 K the carbon diffusivity is roughly 20 times smaller than at the average temperature of 1200 K. Instead of 100 h, one would thus need 2000 h.

Acknowledgment

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