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DETERMINATION OF DIFFUSION COEFFICIENTS WITH A GENERAL TEMPERATURE PROGRAM USING DTA EQUIPMENT

P. KUBÍČEK, B. WOZNIAKOVÁ and J. LEŠKO

Institute of Metallurgical Process Theory, Czechoslovak Academy of Sciences, 703 00 Ostrava (Czechoslovakia)

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ABSTRACT

This paper deals with a method for the determination of diffusion coefficients in molten metals with a general temperature program and using DTA equipment. The method was tested by measuring the diffusion of ^{110}Ag into molten Zn, and was found to be effective, with an accuracy comparable with the commonly used method using the constant temperature of diffusion heating.

INTRODUCTION

In the present work attention is given to the study of diffusion in liquid metals applying the most frequently used capillary method (the thin layer method). A radionuclide of the element whose diffusion is to be investigated is placed above or below the sample in a capillary, and the specimens prepared in this way are submitted to a diffusion heating. The concentration distribution of the diffusing element along the specimen is determined either by the section or slot method [1–4].

During the diffusion heating there is a period of temperature rise from the melting point to the temperature of diffusion, the diffusion period and the period of decrease of temperature at the end of the experiment. The periods of temperature rise and decrease bring about a certain unexactness of experimental results. The mathematical correction of this negative effect is given in ref. 5. The aim of the present work is to show an advantageous possibility of using DTA equipment for the diffusion heating of specimens and the mathematical evaluation of experimental results for diffusion heating with a general temperature program. A programmed course of temperature can be used with these experiments. The method is applicable only if the common temperature dependence of diffusion coefficient, e.g., the Arrhenius relation, is known in advance.

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THEORETICAL

The equation of diffusion is expressed as

$$\frac{\partial c(x,t)}{\partial t} = D \cdot \frac{\partial^2 c(x,t)}{\partial x^2} \tag{1}$$

where $c(x,t)$ is the concentration of a diffusing component along the specimen, and D is the diffusion coefficient. If the thin layer method is used, the initial and boundary conditions are considered as

$$c(x,0) = \begin{array}{ll} c_0 & 0 \le x < h \\ 0 & h < x \le L \end{array} \tag{2}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = \left.\frac{\partial c}{\partial x}\right|_{x=L} = 0 \qquad t > 0$$

where h is the thickness of the layer and L is the length of the sample. With respect to ref. 5, the solution of this problem for a general temperature program $T(t)$, $D = \mathrm{f}[T(t)]$, can be written as

$$c(x,t) = c_0 \left\{ \frac{h}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \exp\left[- \left(\frac{\pi n}{L} \right)^2 D_{\mathrm{ef}} \cdot t \right] \cos \frac{\pi n x}{L} \sin \frac{\pi n h}{L} \right\} \tag{3}$$

where effective diffusion coefficient D_{ef} is defined by the relation

$$D_{\mathrm{ef}} \cdot t_{\mathrm{m}} = \int_0^{t_{\mathrm{m}}} D[T(t)] \mathrm{d}t \tag{4}$$

where t_{m} is the duration of diffusion heating.

Let the function $D[T(t)]$ be expressed by the Arrhenius equation

$$D[T(t)] = D_0 \cdot \mathrm{e}^{-E/RT(t)} \tag{5}$$

where E is the activation energy and D_0 is the frequency factor.

If the temperature course $T(t)$ is known from the experiment, then the effective diffusion coefficient D_{ef} may be determined by substituting eqn. (5) into eqn. (4), supposing that E and D_0 are known. The case met in practice is contrary to this, which means that the values of D_0 and E are unknown, while the effective diffusion coefficients for different temperature courses $T_i(t)$ are experimentally given. For this purpose, we consider D_{0i} as a formal function of variables E, D_{ef_i} and $T_i(t)$. On the basis of relations (5) and (4)

$$D_{0i}[E, D_{\mathrm{ef}_i}, T_i(t)] = \frac{D_{\mathrm{ef}_i} \cdot t_{\mathrm{m}_i}}{\int_0^{t_{\mathrm{m}_i}} \mathrm{e}^{-E/RT_i(t)} \mathrm{d}t} \tag{6}$$

The unknown values of E and D_0 can be determined from relation (6) if the value of D_{ef_i} and the corresponding temperature course $T(t)$ are known for each experiment. In practice it is sufficient to find the points of intersection of functions $\log D_{0i}(E)$. In this way the activation energy and frequency factor D_0 characterizing diffusion can be determined simply and quickly if equipment for thermal analysis is used for diffusion heating. At the same time the beginning and the end of the experiment, i.e. the time interval t_{mi} between melting and solidification of the sample, are determined by the DTA method. Obviously parameters D_0 and E can be found from the series of at least two measurements of different samples or, if the slot method is applied [3,4], from two measurements of the same sample after two diffusion heatings. If several measurements on different samples are realized, we can judge whether the used analytical expression of $D(T)$ dependence is valuable. In a counter case the values of D_0 and E from different couples of measurements are considerably different.

The problem mentioned above was solved in a similar way to that presented in ref. 6 for the determination of kinetic parameters of chemical reactions.

EXPERIMENTAL

The method was proved when heterodiffusion of ^{110}Ag into molten Zn in the temperature range 420–830°C was investigated. The MOM derivatograph (Hungary) was used for diffusion heating. Fragments of Ag weighing 2–3 mg and containing the radioactive isotope ^{110}Ag, whose specific activity was 250 MBq, were placed on the bottom of Al_2O_3 capillaries of 0.3 cm inner diameter; Zn cylinders of 2–3 cm height and 0.3 cm diameter were inserted above them. A series of capillaries with the samples (see Fig. 1) was placed in the derivatograph. The holder of the capillaries was made from a commonly used multiplate crucible. Examples of diffusion heating courses are shown in Fig. 2. The mean temperature $\bar{T}_i$ for the ith experiment is

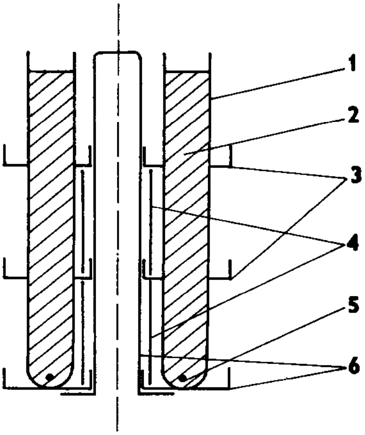

Fig. 1. Scheme of the holder with samples. 1, Capillary; 2, molten metal; 3, plates with holes; 4, Pt ring; 5, radionuclide; 6, multiplate crucible.

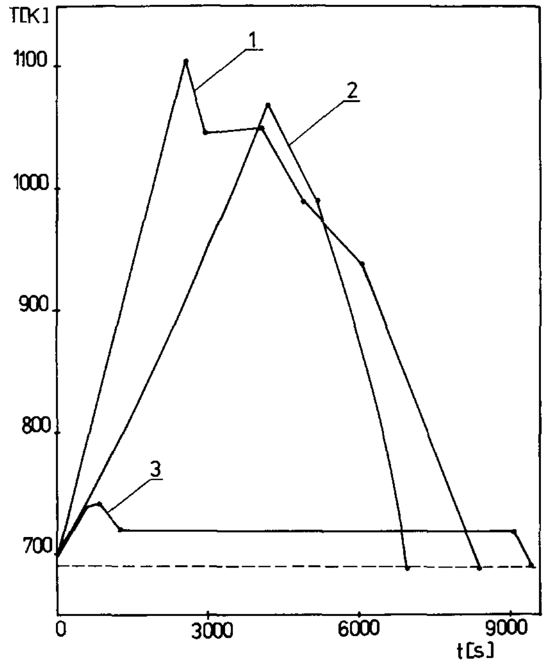

Fig. 2. Diffusion heating courses. 1, $\bar{T} = 723$ K; 2, $\bar{T} = 899$ K; 3, $\bar{T} = 927$ K.

defined by the relation

$$\bar{T}_i = \frac{1}{t_{\mathrm{m}i}} \int_0^{t_{\mathrm{m}i}} T(t)\,\mathrm{d}t \tag{7}$$

where the time interval $t_{\mathrm{m}i}$ represents the time from melting down the sample to solidification of sample that is determined from DTA. The values of $t_{\mathrm{m}i}$ ranged from 6×10^3 to 10^4 s. After the termination of diffusion heating the concentration profile of ^{110}Ag was evaluated by the slot method [3] and the section method [7,8]. The values of effective diffusion coefficients D_{ef} were obtained from least-squares fits to the theoretical regression function (3) by means of a computer.

RESULTS AND DISCUSSION

Experimental values of effective diffusion coefficients D_{ef} and the corresponding mean temperatures of diffusion heating are listed in Table 1. The graphs of functions log $D_{0i}(E)$ for values of $D_{\mathrm{ef}i}$ from Table 1 are shown in Fig. 3, the corresponding courses of $T_i(t)$ temperatures are given in Fig. 2. Furthermore, these functions were calculated for $\bar{D}_{\mathrm{ef}i} \pm \Delta\bar{D}_{\mathrm{ef}i}$, which characterize the effect of the dispersion of experimental values on the values of

TABLE 1

Experimental values of diffusion coefficients of $^{110}Ag \rightarrow Zn$ with a general temperature program

Mean temperature of diffusion heating $\bar{T}$ (°C)	Duration of diffusion heating t_m (s)	$D_{ef} \times 10^5$ ($cm^2\ s^{-1}$)	$(\bar{D}_{ef} \pm \Delta \bar{D}_{ef}) \times 10^5$ ($cm^2\ s^{-1}$)
450	9420	2.12	
		2.17	
		1.82	2.04 ± 0.14
		1.91	
		2.18	
626	11220	3.62	
		3.83	
		4.02	3.82 ± 0.14
		3.68	
		3.96	
654	8400	3.91	
		4.69	
		3.50	4.04 ± 0.35
		4.14	
		3.96	

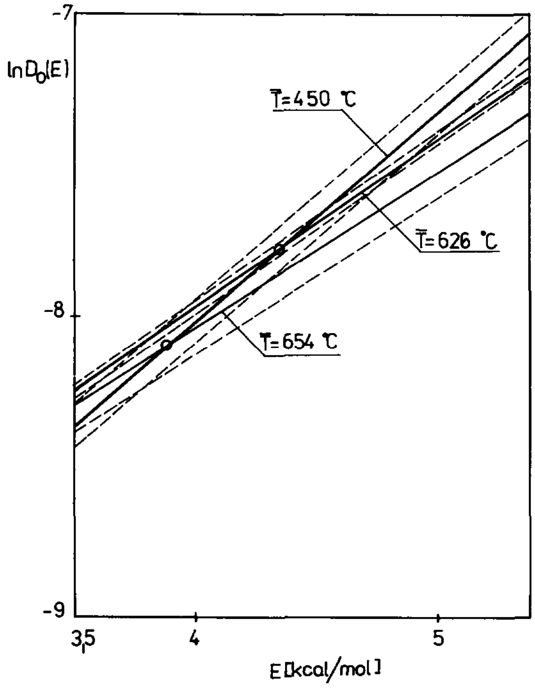

Fig. 3. Graphs of functions $\ln D_0(E)$ for different temperatures $\bar{T}$.

D_0 and E to be determined. We have to stress that this method is applicable only if the mean temperatures of diffusion heatings are widely different. In our case it means that the points of intersection of function $D_{0_i}(E)$ were determined for pairs of temperatures $\bar{T} = 450°\mathrm{C}$, $\bar{T} = 626°\mathrm{C}$ and $\bar{T} = 450°\mathrm{C}$, $\bar{T} = 654°\mathrm{C}$. These points of intersection are marked by circles in Fig. 3 and the mean values of D_0 and E are

$$\bar{D}_0 \pm \Delta \bar{D}_0 = (3.6 \pm 0.6) \times 10^{-4}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$$

$$\bar{E} \pm \Delta \bar{E} = 4100 \pm 200\ \mathrm{cal\ mole}^{-1}$$

Let us analyze the error of the method, i.e. calculate the maximum possible error of D_0 and E determined for one point of intersection. The magnitude of error is first of all influenced by the dispersion of D_{ef} values, then by the difference of mean temperatures $\bar{T}_i$ of individual experiments and by the magnitude of activation energy, E.

Let us consider relation (6), and the effective temperature of experiment T_{ef_i} is defined as

$$e^{-E/RT_{\mathrm{ef}_i}} = \frac{1}{t_{\mathrm{m}_i}} \int_0^{t_{\mathrm{m}_i}} e^{-E/RT_i(t)}\, \mathrm{d}t \tag{8}$$

Substituting eqn. (8) into eqn. (6) gives

$$\log D_{0_i}(E) = \log D_{\mathrm{ef}_i} + \frac{E}{RT_{\mathrm{ef}_i}} \tag{9}$$

Relation (9) represents the equation of a straight line in logarithmic coordinates with respect to variable E. Let us consider the dispersion of experimentally measured effective coefficients $D_{\mathrm{ef}_i} \pm \Delta D_{\mathrm{ef}_i}$. A system of straight lines is obtained for each experiment and their points of intersection characterize the error of the determined values of E and D_0 (see Fig. 3). A simple calculation from eqns. (9) and (8) results in an approximate relation

$$\frac{\Delta E}{E} \lesssim \pm \frac{\dfrac{\Delta D_{\mathrm{ef}1}}{D_{\mathrm{ef}1}} + \dfrac{\Delta D_{\mathrm{ef}2}}{D_{\mathrm{ef}2}}}{\log D_{\mathrm{ef}1} - \log D_{\mathrm{ef}2}} \tag{10}$$

which expresses the maximum inaccuracy in the determination of activation energy and frequency factor on the basis of inaccuracies in determining the D_{ef_i} and mean temperature differences for two different experiments. If the value of ΔE is calculated from eqn. (10) supposing the value $E \pm \Delta E$ is known, then the value of $D_0 \pm \Delta D_0$ can be determined from eqn. (9).

In practice, the process is as follows. The value of $\Delta E/E$ is determined from relation (10) on the basis of experimental data; from the results of at least two experiments the activation energy E, is determined using the procedure mentioned above, and effective temperatures of individual experiments T_{ef_i} can be calculated from relation (8). In most practical cases the effective temperatures are supposed to approach the mean temperatures T_i defined by relation (7) (see ref. 5).

Applying the results from Fig. 3 and the values from Table 1, the maximum error $\Delta E/E = 21\%$ can be calculated from relation (10) for the point of intersection of functions $D_{0_i}(E)$ corresponding to the couple $\bar{T} = 654°\mathrm{C}$ and $\bar{T} = 450°\mathrm{C}$ and $\Delta E/E = 17\%$ for the couple $\bar{T} = 450°\mathrm{C}$ and $\bar{T} = 626°\mathrm{C}$.

Substituting eqn. (5) into eqn. (10) gives

$$\frac{\Delta E}{E} \leq \frac{T_{\mathrm{ef1}} \cdot T_{\mathrm{ef2}}}{T_{\mathrm{ef2}} - T_{\mathrm{ef1}}} \left(\frac{\Delta D_{\mathrm{ef1}}}{D_{\mathrm{ef1}}} + \frac{\Delta D_{\mathrm{ef2}}}{D_{\mathrm{ef2}}} \right) \cdot \frac{R}{E} \tag{11}$$

Equation (11) expresses the influence of the difference between effective temperatures, the inaccuracy in the determination of D_{ef}, and the magnitude E, on the relative error $\Delta E/E$. It is obvious that the greater the difference of effective temperatures and the magnitude of activation energy, E, the greater is the exactness of its experimental determination.

When comparing the results of the present work with those obtained by the same capillary method with constant temperature of diffusion heating [9], i.e. $D_0 = 2.5 \times 10^{-4}$ cm^2 s^{-1}, and $E = 3500 \pm 100$ cal mole^{-1}, we can say that their accordance is acceptable considering that the activation energy of the studied system is very small. Its value for most molten metals ranges from 10^4 to 2×10^4 cal mole^{-1}, which means that the precision in determining E can be 2.5–5 times greater if a similar ratio of effective temperatures of experiments is retained.

CONCLUSIONS

The theoretical analysis of diffusion coefficient determination in molten metals applying a capillary method with a general temperature program, and using DTA equipment has been presented in this work. The accuracy of this method increases with the magnitude of the activation energy E, the difference of mean temperatures $\bar{T}_i$, effective temperatures T_{ef_i}, and the exactness of the effective diffusion coefficient D_{ef_i} for the temperature course $T_i(t)$. The method has been tested by measurement of the diffusion of ^{110}Ag into molten Zn in the temperature range in which the Arrhenius equation holds. The results are in good accordance with the values presented in ref. 9 where the classical process with constant temperature of diffusion heating was applied. The method is effective and its accuracy is comparable with the commonly used method with constant temperature of diffusion heating, especially for systems with higher activation energies.

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