

THERMAL DIFFUSION IN SOLIDS - AN OVERVIEW

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ABSTRACT

Thermal diffusion in liquids and gases has been the focus of a number of studies and is considered, at present, a reasonably wellknown topic. In solids though, the phenomena is far less understood namely in what regards the effects of thermal gradients upon the integrity and characteristics of materials. Furthermore it is not clear whether or not thermal diffusion can be used as a purification method for solids. Yet, many current techniques such as the laser, used in metalworking and other solids, induce strong thermal gradients being, therefore, potential cause for the occurrence of thermal diffusion. In this work, a survey and discussion of theoretical and experimental studies of thermal diffusion in solids is undertaken.

INTRODUCTION

Under a temperature gradient a demixing of solid solutions occurs: in the initially homogeneous multicomponent solid material a flow of atoms appears and a concentration gradient is created.

This is known by thermal diffusion, thermal transport, thermomigration effect or Soret effect.

The magnitude and sign of this effect can be expressed in terms of the heat of transport (Q^*) of the components, since the thermal gradient produces a difference in the heats of transport of solute and solvent that is possible to measure.

Some questions can be asked about the Soret effect in solids:

- are the direct and indirect effects of migration

induced by the temperature gradient perceptible enough in a solid body?

- how can the temperature gradients in solid bodies be used to increase the purity of materials such those used in some technologies, like electronics, nuclear technology, etc.?

THERMAL GRADIENTS IN MATERIALS

One of the first purifications of materials under the influence of thermal gradients was studied by BUDA (1) in monocrystalline silicone samples previously saturated by prolonged diffusional doping with radioactive N_i^{63} by using electrical measurements of resistivity layer, radioisotope analysis and analysis on a mass spectrometer. BUDA observed that:

- a) the temperature gradient causes intensive migration of the nickel in a direction conformable to the direction of the temperature gradient, and a concentration gradient of the nickel appears;
- b) the concentration gradient grows with time;
- c) the concentration gradient also grows with the temperature gradient;

d) the nickel always concentrates in the high temperature side independently of the temperature gradient value.

ODA, SON and MIYAKE (2) studied the thermomigration of carbon in niobium by a steady-state method using radioactive tracer. They observed that under a thermal gradient the interstitial carbon atoms in niobium are subjected to a driving force towards the hotter region.

Nuclear power reactor components and cemented carbide cutting tools are two examples of materials in which the problem of thermodiffusion is encountered. Niobium metal and its alloys are alternative structural materials for fast reactors and they can probably be used as first wall for fusion reactors, where large temperature gradients exist (3). This is the reason why studies of thermal diffusion with niobium are very important, particularly in the cases where tritium and carbon mobilities in it are concerned.

In Japan, SUGISAK et al. (4) studied the motion of tritium in niobium produced by the driving force due to the thermal gradient for temperatures between 100-300°C. They concluded that the ratio between the partial pressure of tritium in the higher temperature side and that in the lower temperature side, is modified by one order of magnitude by the effect of thermal diffusion.

That means that thermal diffusion has an appreciable influence on tritium permeation in the niobium and that physico-chemical behaviour of tritium in a first wall is considerably more complex under a thermal gradient than in isothermal conditions.

The thermodiffusion behaviour of carbon in niobium was investigated in one-phase and two-phase con-

ditions, using radioactive tracer techniques by CARLSON et al. (5). The results of their experiments show rather conclusively that carbon is thermotransported to the hotter region of niobium in both one-phase and two-phase conditions. The heat of transport has the rather large value of $-13 \pm 1 \text{ K cal mol}^{-1}$ for either condition. The first paper with quantitative results in thermodiffusion on glasses appeared in 1980 (6). Two lithium silicate glasses were prepared, subjected to a constant temperature gradient and lithium concentration was measured. It was observed that under a temperature gradient the lithium ion migrates to the higher temperature region through the rigid silicate network. Heats of transport in glasses were measured and compared with thermotransport experiments in metals. It was noticed that glasses' heats of transport are of the same order of magnitude of metal's. It means that thermodiffusion occurs not only in crystalline solids but also in amorphous ones and so that thermotransport is not due to the existence of free electrons in the solid. One can conclude that:

- using temperature gradient to force and to guide the stream of one or several elements is effective and can be utilized as a procedure to remove impurities in solid state;
- factors limiting migration of impurities (purification) were not found;
- the sublimation of impurities from the surface of samples under a perpendicular temperature gradient is more intensive than under isothermal conditions.

PHYSICAL INTERPRETATIONS AND MATHEMATICAL MODELS

The simplest physical interpretation of the phenomena is the interstitial diffusion of impurity atoms in a heavy host lattice atoms under the influence of a temperature gradient. As the mobility of the solute atoms is sufficiently higher than that of host lattice atoms, one can safely assume that only the migration of interstitial solute atoms is significant for the redistribution and that, as the host lattice atoms can be considered a rigid one, it provides a convenient frame of reference for the flux. This fact permits a much simpler analysis of the phenomena than if the mobilities of both components should be considered and no one could be taken as a reference to the movement of the other.

Nature of driving forces in thermaldiffusion has been discussed by several authors (7, 8, 9, 10).

The so-called intrinsic contribution and the scattering effects of heat, carriers, such as phonons and electrons, are, in general, considered as the main contributions to the driving forces in thermaldiffusion and it has generally been concluded that electron scattering is dominant (10, 9, 2).

The electronic contribution is the inelastic scattering of electrons by solute atoms, resulting from the electric field present in metallic conductors under a temperature gradient. This is the well-known thermoelectric effect.

KIRCHHEIM and FROMM (11) derived an expression relating the heat of transport to the analogous electrotransport parameter Z^*

$$Q = U_e Z^* \quad (1)$$

the quantity U_e being defined as the energy of

transport of electrons. If the electron scattering contribution is dominant and as electrons move from a higher energy level to a lower energy level U_e will always be negative, i.e. Q^* and Z^* should have opposite signs. This sign correlation has been noted by other authors and the experimental study of different metal interstitial solute systems shows a very little number of exceptions.

According to the model proposed by BHAT and SWALIN (12) for the particular case of liquid metals, Q^* can be decomposed in 2 parcels: one resulting from the interaction of the conduction electrons with solute ions and the other resulting from the interaction of the difusing ion with the other ones. The latter can be calculated by assuming that the liquid metal is a dense gas and applying the thermotransport theory in binary gas mixtures. The sign of this part is determined primarily by the difference of the masses of the two ions, the heavier impurity migrating to the colder end. According to SORBELLO'S (10) analysis, if phonon scattering is the dominant factor and if the interstitial solute atoms are lighter than the matrix atoms, the solute atoms migrate against the phonon wind, i.e., towards the cold region.

The flux of solute atoms (J) is calculated from irreversible thermodynamics (13, 14) and is generally written as

$$J = -D [\text{grad } N + (Q^* N/RT^2) \text{ grad } T] \quad (2)$$

The steady-state $J=0$ and equ. 1 can be written as

$$Q^* = - \frac{RT^2}{N} \cdot \frac{\text{grad } N}{\text{grad } T} = -RT \frac{\nabla(\text{Ln } N)}{\nabla(\text{Ln } T)}$$

$$\text{since } \frac{1}{T} \nabla(\text{Ln } T) = -\nabla\left(\frac{1}{T}\right)$$

$$Q^* = R \frac{\nabla' \ln N}{\nabla' \left(\frac{1}{T}\right)}$$

For the one dimensional case

$$Q^* = R \frac{d \ln N}{d \left(\frac{1}{T}\right)} \quad (3)$$

From equ. (3) it is obvious Q^* can be obtained from the slope of a plot $\ln N$ versus $\frac{1}{T}$ for the steady-state condition.

For the particular case of the thermodiffusion of carbon in niobium the plot of $\ln N$ versus $\frac{1}{T}$ is shown in figure 1.

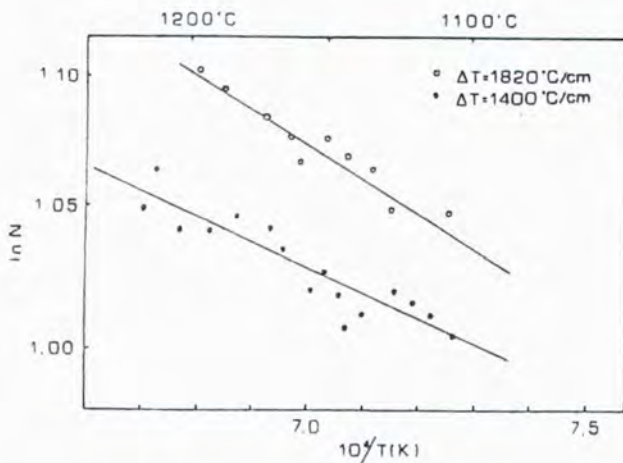


FIGURE 1 - \ln specific carbon activity vs. reciprocal temperature

Relative carbon concentration along the axial direction of the specimen is plotted as a function of the reciprocal temperature, assuming the temperature distribution along the axial direction of the specimen is linear.

The graph shows that carbon in niobium becomes richer in the higher temperature region and that the heat of transport has a negative value.

Another example can be the thermodiffusion of lithium in silicate glasses.

The logarithm of the lithium concentration referred to the initial concentration is plotted versus the reciprocal temperature.

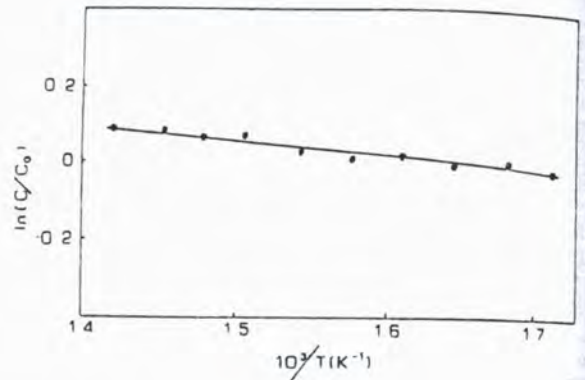


FIGURE 2 - Steady-state concentration of lithium vs. reciprocal temperature

Once again the graph shows the lithium ion migrates to higher temperatures.

The so-called Soret coefficient is defined as

$$S_T = \frac{D'}{D} \quad (4)$$

and it can be shown that it relates with the temperature (T) and the heat of transport (Q^*) by the following expression

$$S_T = \frac{Q^*}{RT^2} \quad (5)$$

Usually S_T is very small and therefore thermal diffusion may be neglected as compared to ordinary diffusion.

From (2) and (5) the impurity flux is