

Non-Metal Diffusivity in Some Binary Transition Metal Nitrides and Carbides

D. Rafaja¹, W. Lengauer²

¹*Faculty of Mathematics and Physics, Charles University, 121 16 Praha 2, Ke Karlovu 5, Czech Republic*

²*Institute for Chemical Technology of Inorganic Materials, University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria*

Abstract

Two methods, which are used for calculation of diffusion coefficients in multiphase binary systems are outlined and compared – the investigation of the layer growth kinetics and the fitting of concentration profiles. The methods are discussed in view of their particular advantages and disadvantages and illustrated on the non-metal diffusion coefficients in the Nb-N, Nb- C, Cr-N, Cr-C, Ta-N and Ta-C systems. It is shown that the best way for determining the non-metal diffusivity in multiphase systems is the combined refinement of diffusion coefficients employing both the layer growth enhancement and the concentration profile fitting.

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1 Introduction

The transition metal *nitrides* and *carbides* are hard refractory materials, which are advantageously used as diffusion barriers, as construction materials for high-temperature applications, and in the production of cutting tools. In these compounds, diffusion processes occur both in production and use, and therefore the knowledge of diffusion kinetics is important. In addition, the diffusion couple experiments can offer an exceptional opportunity to obtain an insight into binary systems because the phase band structure arising during the diffusion

processes represents an isothermal cut in the phase diagram. Still, the diffusion coefficients, which characterise the diffusion kinetics, are lacking in the majority of the nitrides and carbides of transition metals.

The following systems were investigated

- nitrides
 - Nb-N
 - Cr-N
 - Ta-N
- carbides
 1. Nb-N
 2. Cr-N
 3. Ta-N

2 Model of the reactive diffusion

If samples of the pure metal are annealed in the nitrogen atmosphere or in the graphite powder, the reactive diffusion is described by the following model. At the beginning of the diffusion process all phases according to the phase diagram arise, starting from the non-metal-richest which is located at the sample surface and ending with the non-metal-poor one which fills the core. During the diffusion process the concentration of the in-diffusing non-metal increases that can be observed as weight gain, as growth of the individual phases (the layer growth or the phase boundary movement) or as the change in the concentration profile. The layer growth in multiphase diffusion couples is known from experiments to follow the parabolic rule [1, 2]

$$x_i = K_i \sqrt{t} \quad (1)$$

where x_i is the thickness of the phase (layer) i after the diffusion time t . K_i is the respective rate constant. One-dimensional continuity equation equation (1) was approved theoretically by Kidson [3] to be valid for infinite (very thick) diffusion couples. Kidson's analysis also explained the meaning of the rate constant K , as the movement of phase boundaries was described by the following system of transcendental equations:

$$x_n = \int_{\lambda}^{\infty} \frac{1}{\tau} \exp\left(\frac{\xi_n \tau}{D_{n+1}}\right) d\tau \quad (2)$$

3 Calculation of diffusion coefficients

3.1 Layer growth enhancement

Our procedure for calculating the non-metal diffusion coefficients from layer growth employs the layer growth enhancement and the successive disappearance of individual phases in wedge-shaped samples. Such a sample geometry is favourable because the wedge contains apparently more samples with different thicknesses, which are annealed in the same experimental run (with exactly the same experimental conditions). If the angle of the wedge is sufficiently small (10° - 15°), the wedge can still be regarded as a one-dimensional diffusion couple. This was verified experimentally by annealing wedge-shaped samples together with the planar diffusion couples having different thicknesses. The observed positions of phase boundaries were the same both in the wedges and in the parallel sheets.

3.2 Survey on the non-metal diffusion coefficients

Results presented in this section were obtained by using the combined refinement of diffusion coefficients if the quality of measured concentration profiles was sufficient. This approach yielded the concentration-independent diffusion coefficients (calculated from the layer growth enhancement) and the concentration-dependent diffusion coefficients (calculated from concentration profiles). The investigation of the layer growth enhancement yielded diffusion coefficients in all phases which were present in the diffusion couple, whereas the concentration profiles were suitable only for calculation of diffusion coefficients in the non-metal rich phases. Whenever both methods could be applied, the diffusion coefficients were compared. Moreover, as these methods are independent, their combination offered a better insight into the diffusion kinetics because the concentration-dependent diffusion coefficients can be assigned to a certain non-metal concentration, whereas the concentration-independent diffusion coefficients correspond to the average non-metal concentration in the respective phase.

3.2.1 Nb-N system

The Nb-N system was investigated between 1400°C and 1800°C . In this temperature region three phases are stable: the solid solution of nitrogen in niobium, α -Nb(N), having the space group $Im\bar{3}m$ and two nitride phases, β -Nb₂N (P31m) and δ -NbN ($Fm\bar{3}m$). The homogeneity ranges measured using the electron probe microanalysis (EPMA/WDS) [11] are shown as a part of the phase diagram in Fig. 1.

As the position of the nitrogen-rich boundary in the phase diagram (the maximum concentration) for the α -NbN_{1-x} phase depends strongly on the nitrogen pressure, a different nitrogen pressure was applied at different temperatures to keep the nitrogen concentration at the sample surface constant. The diffusion

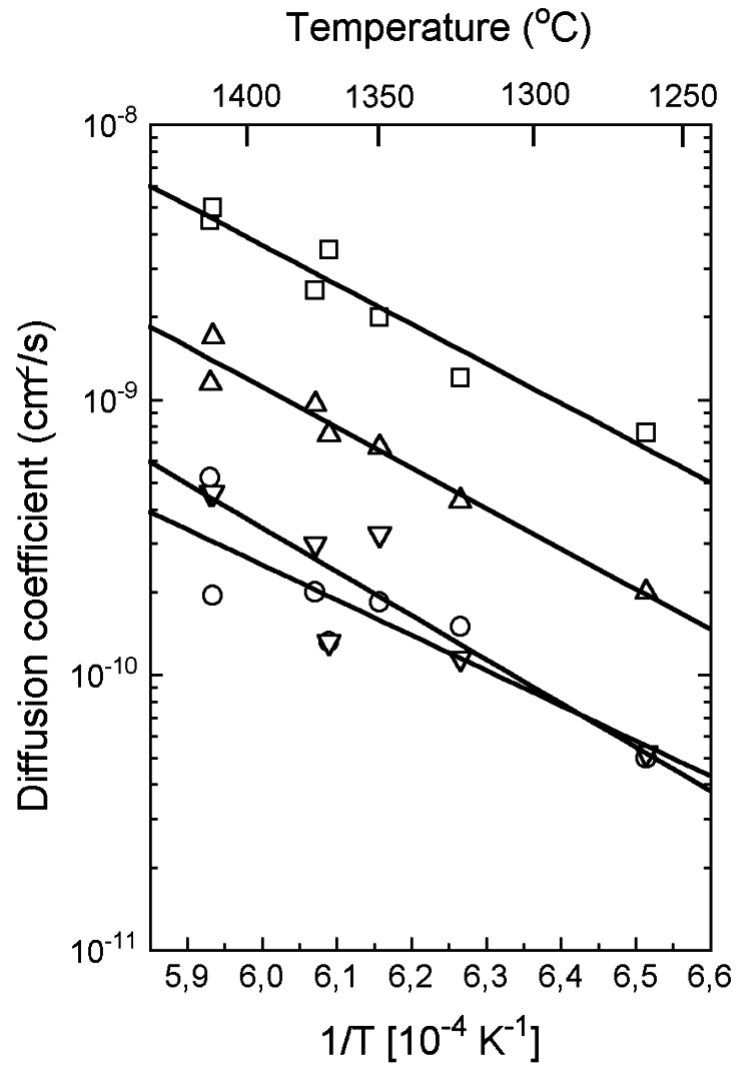


Figure 1: A part of the phase diagram for the Nb-N system. The circles indicate the limit concentrations used for calculation of diffusion coefficients from layer growth.

coefficients obtained from layer growth are summarised in Fig. 2 (open symbols) and compared with the diffusion coefficients calculated from the nitrogen concentration profiles. The Arrhenius dependence of the diffusion coefficients yielded the activation energies and pre-exponential factors, which are given in Tab. 1.

Activation energies and pre-exponential factors calculated from the temperature dependence of the nitrogen diffusivity in niobium and niobium nitrides, which was obtained by using concentration profile fitting and the forward finite difference simulation.

Table 1: Concentration profile fitting

Phase	α -NbN (high c)	δ -NbN (low c)
E [eV]	3.19	3.20
D[cm ² /s]	0.68	1.10

The diffusion coefficients of nitrogen in -NbN_{1-x} were found to be nearly independent of the nitrogen concentration, the first indicator of which was a good agreement between the measured concentration profiles and the concentration profiles simulated using the FFD method with concentration-independent diffusion coefficients (Fig. 1). Note that upon the calculation of diffusion coefficients from layer growth only the measured and the simulated positions of phase boundaries are compared, not the concentration profiles.

3.2.2 Cr-C system

The Cr-C system was investigated between 1260 °CC and 1410 °CC [4]. The homogeneity ranges measured using EPMA/WDS are shown as a part of the phase diagram. However, because of the narrow homogeneity ranges the measured concentration profiles were not suitable for calculation of diffusion coefficients, and therefore the comparison of two independent sets of diffusion coefficients cannot be given here.

The diffusion coefficients obtained from layer growth are summarised in Fig.3. Their temperature dependence yielded the activation energies and pre-exponential factors. As the measured concentration profiles could not be evaluated by the profile fitting, the concentration dependence of the diffusion coefficient could not be examined. Nevertheless, regarding the narrow homogeneity ranges the diffusion coefficients can be assumed to be independent of the carbon concentration. The relatively high scattering in the carbon diffusion coefficients is caused partly by different porosity of the sample surface arising during the reactive diffusion, partly by lower precision of diffusion coefficients calculated in phases with a narrow homogeneity range. The sample surface porosity influences especially the diffusion coefficients in the carbon-rich phases, Cr₃C₂ and Cr₇C₃, where the largest fluctuations of the diffusion coefficients were observed. The narrow homogeneity ranges imply a low concentration gradient inside individual

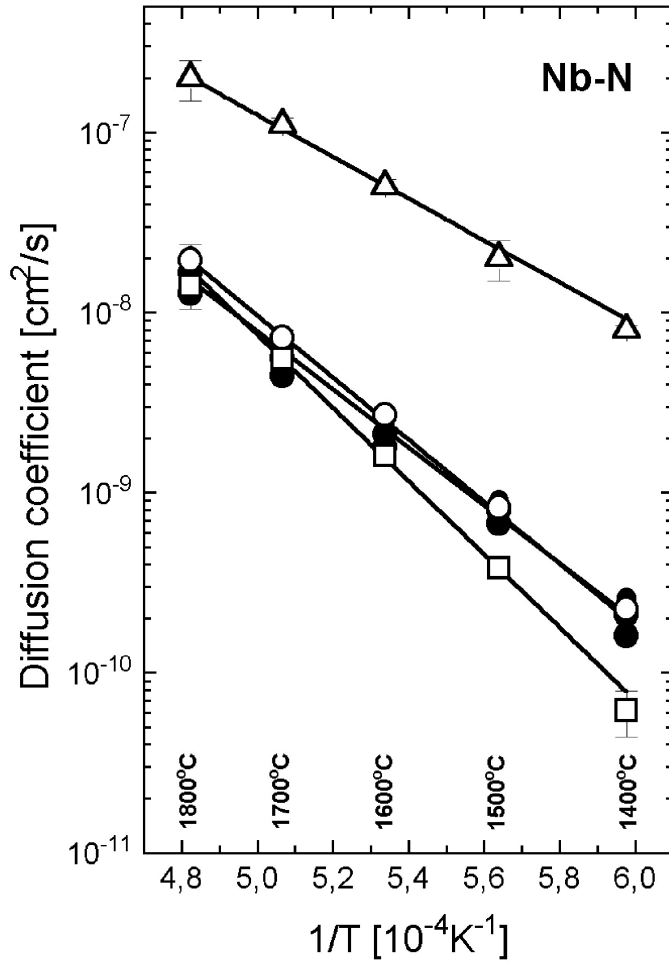


Figure 2: A part of the phase diagram for the Nb-N system. The circles indicate the limit concentrations used for calculation of diffusion coefficients from layer growth.

phases, which implies a low diffusion flow again. In such a case, the calculated positions of phase boundaries are less sensitive to the changes of the diffusion coefficients. Thus a good match in the calculated and observed phase boundary positions was obtained upon a lower precision in the diffusion coefficients. The consequence is a higher fluctuation of the diffusion coefficients calculated from layer growth.

4 Discussion

The diffusion kinetics was studied in relatively narrow temperature ranges. The choice of the appropriate temperature range was a compromise – the diffusion is a temperature-activated process, thus the non-metal diffusivity decreases exponentially with decreasing temperature, and the low temperatures imply very long diffusion times. Besides, the grain boundary diffusion, which can be neglected at high temperatures, becomes comparable with the bulk diffusion at low temperatures. The overlap of the grain boundary diffusion and the bulk diffusion would complicate the interpretation of results. On the other hand, the choice of the highest annealing temperature is mainly restrained by the melting point of the pure metal as the nitrides and carbides of the transition metals presented in this contribution are peritectic compounds. To avoid the melting of the core of the diffusion couple either moderate temperatures or a gradual heating up must be applied. The latter guarantees a successive increase of the non-metal concentration in the core and consequently a continuous transformation of the pure metal to the refractory material. However, the course of the diffusion process is more complex in such a case, and therefore it can cause a misinterpretation of diffusion coefficients.

Specific problems arising during the calculation of diffusion coefficients have been discussed above for individual materials. Besides, there are two common sources of errors in diffusion coefficients – inaccuracy in the concentration measurement and, investigating the layer growth, particularly the inaccuracy in reading the phase boundary positions. The inaccuracy in the concentration measurement affects both diffusion coefficients calculated from layer growth and concentration profiles, but differently. Whereas large scatter in the measured concentrations or some artefacts in the concentration profiles due to the polishing effects are the principal difficulties upon the concentration profile fitting, the diffusion coefficients obtained from layer growth are mainly affected by the inaccurate maximum and minimum non-metal concentrations within individual phases (see δ -TaN, for example). Problems in reading the phase boundary positions arise if a phase decomposes upon cooling or if the phase band is very narrow. The very narrow layer thickness does also the concentration profile fitting impossible because of the limited lateral resolution of EPMA.

5 Conclusions

Two methods for calculation of the non-metal diffusion coefficients were presented and illustrated on the Nb-N, Nb-C, Cr-N, Cr-C, Ta-N and Ta-C systems. The first method employed the layer growth enhancement in wedge-shaped diffusion couples; the second one calculated the diffusion coefficients in individual phases directly from the shape of the concentration profiles. Whereas the layer growth could be applied in all systems with known phase diagrams, the concentration profile fitting was applicable only for non-metal-rich phases with a sufficiently broad homogeneity range, which excluded the solid solution of the respective non-metal in the host metal as well as the line compounds definitely.

On the contrary, the investigation of the layer growth enhancement yielded the concentration-independent diffusion coefficients, whereas the information on the concentration dependence of the diffusion coefficients could only be obtained by the concentration profile fitting. Therefore, the best way how to achieve the maximum information on diffusion coefficients was to compare the concentration-independent diffusion coefficients calculated from the layer growth with the concentration-dependent diffusion coefficients calculated from concentration profiles.

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