Treatment of Diffusionprofiles with the Method of Nets

H. Helfmeier

Institut für Metallforschung, Technische Universität Berlin

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Diffusion measurements on the copper-nickel-system were made with two kinds of geometries. Thin Cu-films were evaporated on Ni-single crystals and single crystals of Ni and Cu were brought into contact as semi-infinite solids. Different methods of evaluating the concentration dependent diffusion coefficient were used and the results discussed.

Specimens with copper layers of a thickness of up to 10% of the penetration depth can be evaluated with the thin film solution. The accuracy is satisfactory as well with respect to the diffusion coefficient at the nickel boundary as to the layer thickness. Beyond 10% the erf-solution for the thick layer yields good values for the diffusion coefficient but not for the layer thickness. The method of nets, using the difference equation, is a powerful tool to treat nearly any initial condition and any concentration dependence of the diffusion coefficient.

1. Introduction

For diffusion profiles from experiments with layers of finite thickness on semi infinite specimens no analytical method for the determination of the diffusion coefficient (DC) is available if the DC is concentration dependent. This problem was treated by the method of nets[1] based on the difference equation. In the present work the applicability and accuracy of the method were tested including the limiting cases of a thin layer and of a pair of semi-infinite solids.

2. Experimental

The investigations were performed on the copper-nickel-system where the chemical DC covers about two orders of magnitude. Well degassed single crystals of Ni and Cu were obtained by zone melting metal rods of 99.999% purity several times vertically in an electron beam furnace. The diameter of the crystals was 5 mm, the length up to 70 mm. The limiting values of the purities given by the manufacturer are listed below.

nickel		*copper*	
Si	< 5 ppm	Ag	< 0.3 ppm
Fe	3 ppm	Pb	< 0.5 ppm
Mg	< 1 ppm	Fe	< 0.7 ppm
Al	< 1 ppm	Ni	< 0.5 ppm
Co	0.1 ppm	Sb	< 0.5 ppm
Ca, Cd, Cr, Cu, Pb	0.5 ppm	Se	< 0.5 ppm

The single crystals were cut into disks of 1.5 mm length. On both sides of the polished and annealed nickel specimens copper layers were evaporated with increasing thickness from specimen to specimen. Four crystals were prepared in that way. Another specimen was prepared by putting a nickel and a copper disk into a husk of pure copper which was closed by flanging to assure proper contact between the two disks representing the two semi-infinite solids. All specimens were separately sealed in quartz tubes, but brought to the diffusion run all together. The temperature was $900\,^\circ\mathrm{C} \pm 0.2\,^\circ\mathrm{C}$ over 100 hours. The concentration profiles were measured by an electronmicroprobe, the x-ray intensities being corrected by a program. For a concentration drop down to the e-th part the penetration depth was about 15 μm.

3. Results

Considering the dimensions of the specimens and the penetration depth, the restriction to one dimension in the analysis is justified. In order to make quite sure that former measurements[2, 3] were not affected by the method of evaluation, the layered specimens were first treated with the thin-film solution

$$c(x,t) = \frac{M}{\sqrt{\pi D \cdot t}} \exp\left(-\frac{x^2}{4 D \cdot t}\right).$$

A constant DC is assumed in this solution and it is possible to calculate $c(x,t)$ as well as the reverse, D and M, in a straight forward way. The results for the DC and the thickness a of the layer equivalent to the quantity M are listed under case 1 in Table 1.

A constant DC is also assumed in the solution for a thick layer

$$c(x,t) = \frac{c_0}{2}\left[\operatorname{erf}\frac{x+a}{2\sqrt{D \cdot t}} - \operatorname{erf}\frac{x-a}{2\sqrt{D \cdot t}}\right].$$

Reprint requests to Dr. H. Helfmeier, Institut für Metallforschung, Technische Universität Berlin, Straße des 17. Juni 135, *D-1000 Berlin 12.*

Table 1. Comparison of the results of different solutions of the diffusion equation for different layerthicknesses $D[10^{-12}\,\mathrm{cm}^2\,\mathrm{s}^{-1}]$, $a[\mu\mathrm{m}]$.

specimen	case 1 exp-approx. D_{exp}	a_{exp}	case 2 erf-approx. D_{erf}	a_{erf}	case num-solution D_{num}	a_{num}
I	1.367	0.3022	1.367	0.3022	1.36	0.300
II	1.378	0.5624	1.377	0.5624	1.36	0.545
III	1.394	1.9533	1.376	1.9533	1.32	1.875
IV	1.586	9.2900	1.287	8.7287	1.25	6.021

In this case D and a cannot be extracted in a straight forward way. Therefore an iterative approximation was used as simplification of the method of the steepest descent. The values are listed under case 2 in Table 1. The respective least squares fitted curves in Fig. 1 for both cases show considerable deviations from the measured values for the specimen with the thickest layer in the concentration range above 10%. The fitting was done by successively eliminating the values with deviations of more than 5% from the least squares curve.

The method of nets, based on the difference equation, is illustrated in Figure 2. The dimensions of space and time are divided into equidistant parts and any starting concentration distribution is at-

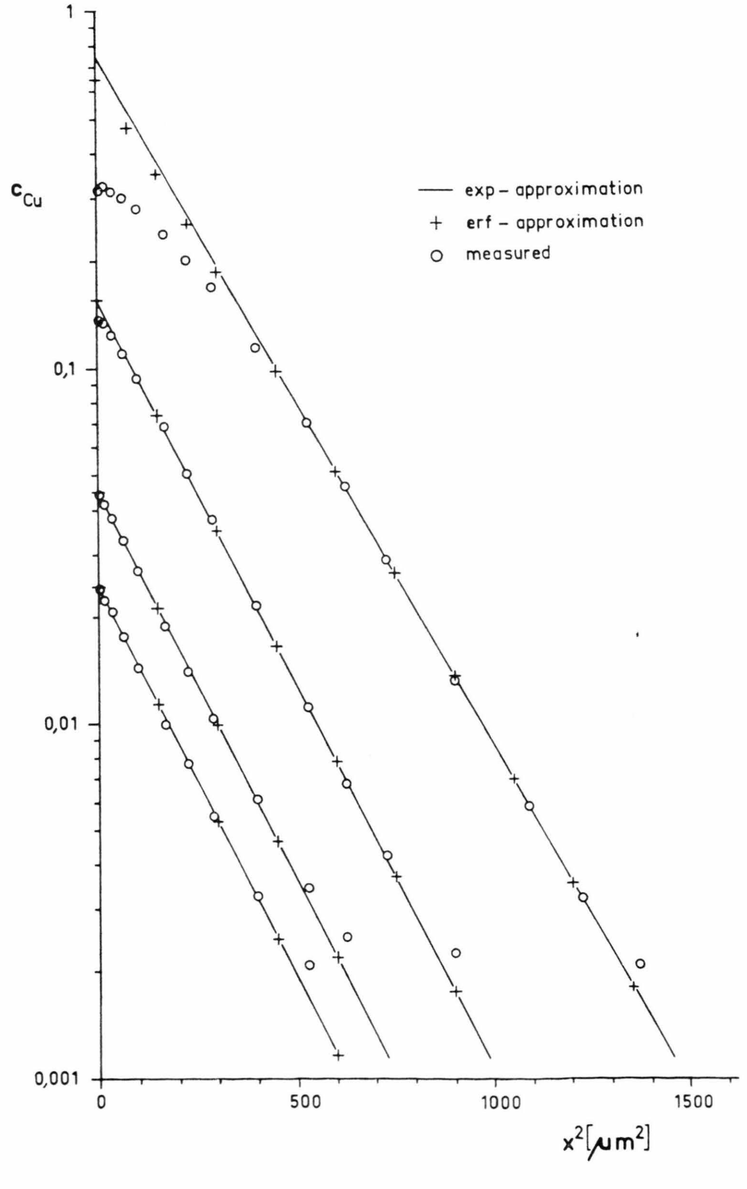

Fig. 1

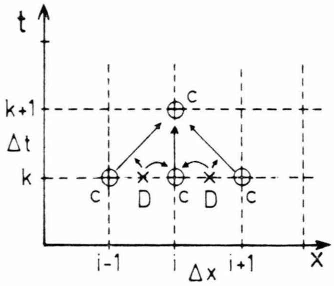

Fig. 2

tributed to the discrete points at time $k = 0$ by interpolating a given table or function. The concentration profile for time $k+1$ is calculated step by step by the following difference equation:

$$c_i^{k+1} = c_i^k + \frac{\Delta t}{(\Delta x)^2} [D_{i+1/2} (c_{i+1}^k - c_i^k) - D_{i-1/2} (c_i^k - c_{i-1}^k)] \, .$$

After rearranging, this equation can easily be recognized as the first approximation of the relevant differential equation. Concentration dependent values of the DC are similarly taken from a stored table or formula and assigned to the mean concentrations of the intervals. This equation is stable and convergent under the condition of Rjabenki and Filippov [4]

$$2 \cdot \mathrm{Max}(D) \frac{\Delta t}{(\Delta x)^2} \leqq 1 \, .$$

For a given maximum of the DC, the minimum number of points and with it the computer time is a reciprocal function of the local stepwidth to the third power.

The concentration dependence of D is obtained by a systematic variation of a hypothetical $D(c)$-curve until a satisfactory coincidence with the experimental values is achieved. Thus the specimen of two semi-infinite solids yielded the $D(c)$-curve V of Figure 3. Applied to the layered specimens the method of nets yielded curves which coincided with the solution for the thick layer when a constant DC was taken. The fitting to the experimental values was done by varying $D(c)$ in the concentration range measured. Above that range, the slope was smoothly connected to the curve for two semi-infinite solids. This procedure is justified by the variation of sensitivity of the calculated concentration profile on changes in the $D(c)$-curve. Therefore the curves I – IV in Fig. 3 are drawn as solid lines in the measured concentration range and else with broken lines. The accuracy of the method in the solid line region is 3 – 5%. The four curves are in good agreement within this range. The values of the DC on the nickel side and the thickness of the layers are listed under case 3 in Table 1.

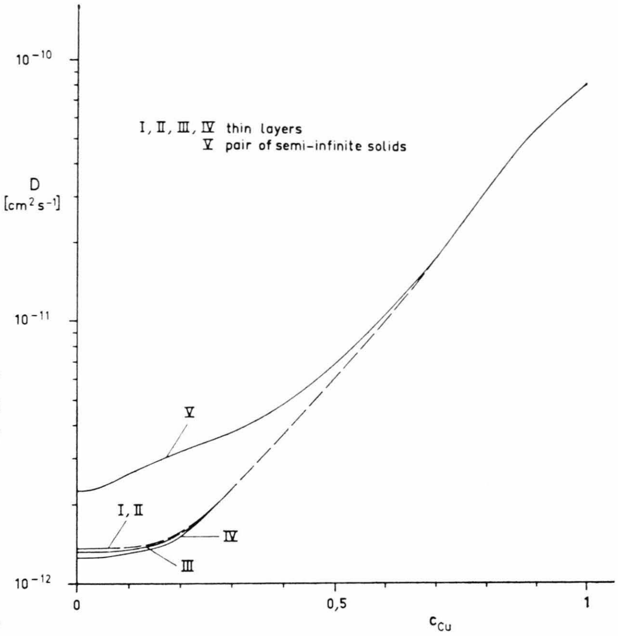

Fig. 3

4. Discussion

Comparing the results of the layered specimens in Table 1, specimen IV shows an error in the DC of + 15% applying the exponential approximation (case 1). The DC is decreased by 6% in both the error function approximation and the numerical solution, although the deviation was expected not to exceed 3%. The true thickness of the layer is determined only by the numerical solution. For the diffusion of copper in nickel the exponential or thin-film solution can be applied as long as the layer thickness does not exceed 10% of the penetration depth.

The capability of the method of nets was proved with the specimen of two semi-infinite solids. This problem can be solved exactly by the Boltzmann-Matano method. Reducing the stepwidth in the numerical solution it has to be considered that the used formula is merely the first approximation of the differential equation and moreover the errors of rounding are summed in the computation. From this point of view, for the method of nets not only the speed but also the accuracy of a computer calculation is of interest. An approximation method of Grube and Jedele [5], and another of Nyilas et al. [6], applied to this concentration profile, showed deviations of more than 100% in the concentration dependence of the DC, see Figure 4. A formerly discussed increase of the DC [7] towards the nickel side was excluded by investigations of Hehenkamp [8]. On the contrary, supported by other investigations [9, 10], a constant increase of the DC by about 40% in the region from 0 to 20% Cu at 1000 °C was found. The same value is found with specimen V of two semi-infinite solids in Figure 3. An increase of only 10% over the same range was calculated by Hehenkamp from selfdiffusion data at high temperature using Darkens formula, taking into account the thermodynamic factor and estimating the vacancy flow effect. His result is in good agreement with the measurements of the layered specimens in the unbroken part of the lines in Figure 3.

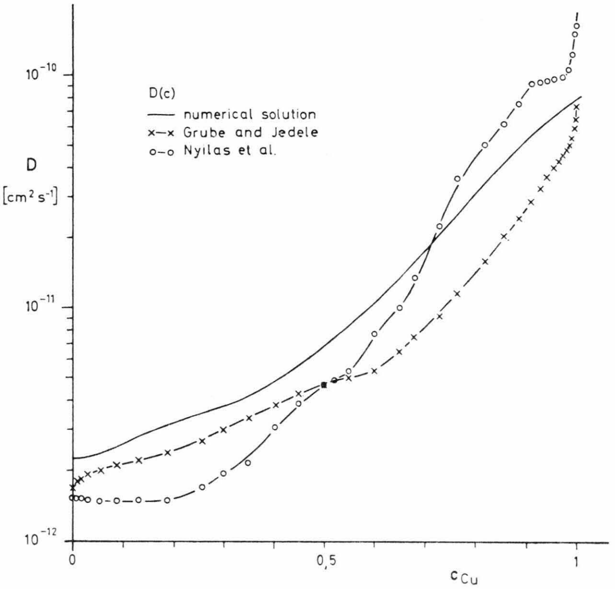

Fig. 4

The considerations are restricted to the nickel side because there are no corresponding measurements with layered specimens on the copper side done until now in our laboratory:

1. The DC found with the specimen of two semi-infinite solids exceeds that found with the layered specimens by about 70%. The higher value is in accordance with values from the literature [8–11] where welded semi-infinite solids or polycrystalline layered specimens were used. The reason is to be seen in enhanced diffusion due to grainboundaries and dislocations, existing in the specimen from its origin or caused by the welding and compression. A minor influence is expected to arise from impurities introduced by the contacting the parts of the semi-infinite specimens in the open air. The layered specimens, however, were prepared by evaporating Cu in a vacuum of 10^{-8} Torr. Thus any deformation of the nickel single crystals was omitted and there were fewer impurities in any case. Therefore the DC measured with the layered specimens is more trust worthy.

2. The increase of the DC with the concentration on the nickel side in Fig. 3 is steeper for the semi-infinite solids than for the layered specimens, as stated before. This must be regarded as a non constant increase of the DC over the measured range of the specimen of semi-infinite solids. The enhancement is related to the density of dislocations and impurities, the maximum of both remaining in the former plane of contact. Therefore the DC is increased more towards the middle of the concentration range than at the nickel boundary. This maximum of dislocation and impurity density in the case of semi-infinite solids is caused either by surface roughness of the specimens or by local heating during welding, or both. The dislocation and impurity density is not comparably increased in the layered specimens.

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