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Abstract

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Some Data on the Heterodiffusion Coefficients in Cu–Ni, Fe–Ni, and Fe–Cr Alloys with Distorted and Undistorted Crystal Lattices

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In the present study an X-ray determination of heterodiffusion coefficients was carried out by the method described in (^{1}). The specimens prepared were flat disks of one of the components, 7 mm in diameter, electrolytically coated with a film of the other metal of the required thickness. The composite specimen was placed in a cylindrical chamber for back-reflection X-ray photography, with a drum diameter of 72 mm, mounted on the cathode of a sharp-focus tube (Fig. 1). During the exposure the specimen was rotated about an axis perpendicular to its surface. The small instrumental breadth of the lines was ensured by obtaining a sharp focus located on the focusing circle on which the film and specimen were also placed. The linear dimensions of the focal spot usually did not exceed 70–80 μ. In studying different systems, radiation of different wavelengths from different anodes was used (Fe for the Cu–Ni system, V in the study of the Fe–Cr system, and Cr for obtaining X-ray photographs in the Fe–Ni system; the Fe anode was used with a Mn filter, while with the vanadium anode only the β_1 line was used). Owing to the low thermal conductivity of the material of the anodes employed, the current through the tube usually did not exceed 0.25–0.5 mA at a voltage of 30–40 kV. The tube was supplied from an ordinary high-voltage unit, in which the tube-filament heating circuit was stabilized. To compare the intensities of lines on different photographs, which was useful for control purposes, the photographs were taken with a standard prepared in the form of a superposed flat sector of a thin disk (0.2–0.3 mm) made of a substance giving interference lines in a favorable angular interval.

In studying the Cu–Ni, Fe–Ni, and Fe–Cr systems, specimens were used consisting of disks of each component coated with a layer of the other. Separate Ni, Cu, and Fe films detached from the substrate were also prepared; prior to diffusion annealing they were subjected to a separate heating in order to remove lattice "distortions" and bring the metal into a state close to equilibrium.

A preliminary X-ray study showed that, immediately after electrolysis, the films obtained exhibit broadening of the lines on the X-ray photographs. Calculation of the photometric curves of the broadened lines, performed by the methods of harmonic analysis (^{2}), made it possible to determine the magnitude of the

Fig. 1. Schematic for obtaining radiographs: 1—tube housing, 2—tube anode, 3—camera housing, 4—diaphragm, 5—specimen and standard holder, 6—specimen and standard, 7—motor shaft, 8—spring, 9—gasket, 10—mounting washer, 11—standard shape

Figure 1: Fig. 1. Schematic for obtaining radiographs: 1—tube housing, 2—tube anode, 3—camera housing, 4—diaphragm, 5—specimen and standard holder, 6—specimen and standard, 7—motor shaft, 8—spring, 9—gasket, 10—mounting washer, 11—standard shape

"microstrains" and the size of the mosaic regions in the films. After preliminary annealing, even at comparatively low temperatures (400-500°), the initial broadening of the lines was practically removed. Diffusion annealing was carried out for specimens: 1) of an electrolytic film deposited on a massive disk; 2) of two electrolytic films deposited successively; and 3) of an electrolytic film obtained in the free state and preliminarily annealed to a sufficiently high temperatures (Cu films—up to 1060°, Ni and Fe films—up to 1100°), after which it was pressed against a massive equilibrium disk of the second component in order to ensure reliable contact. Thus heterodiffusion was carried out: (a) in specimens in which both components were in a state close to equilibrium, (b) in specimens with both components initially nonequilibrium, and (c) in specimens with one equilibrium and one nonequilibrium component. Unfortunately, diffusion annealing of specimens with a pressed Cr film could not be performed satisfactorily, and therefore no diffusion data were obtained for the specimen with both components in the equilibrium state in the Fe—Cr system.

Fig. 1. Schematic for obtaining radiographs: 1—tube housing, 2—tube anode, 3—camera housing, 4—diaphragm, 5—specimen and standard holder, 6—specimen and standard, 7—motor shaft, 8—spring, 9—gasket, 10—mounting washer, 11—standard shape

Diffusion anneals of the specimens and preliminary anneals of the films were carried out either in a vacuum furnace (Fe—Cr) or in a furnace with an H_2 atmosphere. The optimum thicknesses of the electrolytic films were calculated from the thickness of the half-absorbing layer and verified experimentally (Ni film on Cu, 3 μ; Cu film on Ni, 3.5 μ; Fe film on Cr, 4.5 μ; Cr film on Fe, 2.5 μ; Ni film on Fe, 5.3 μ; Fe film on Ni, 1.3 μ. The figures given are valid for the X radiation indicated above).

Each specimen was subjected to diffusion anneals of 1 h duration at successively increasing temperatures, beginning at 400°, in 100° increments. After each diffusion hold, the change in the concentration distribution was recorded in comparison with that obtained after annealing at the preceding, lower temperature. This excluded the possibility of treating the results by the widely known Matano method (3), but instead provided the advantage of greater reliability in determining the temperature dependence of D, since all values of D

at different temperatures were established from the results of experiments with one specimen. The method for calculating the magnitude of D as a function of concentration is described in communication (^{1}).

Figs. 2 and 3 show radiographs of specimens of the Fe—Ni and Fe—Cr systems after diffusion anneals at different temperatures. The specimen in the Fe—Cr system consisted of an electrolytic Fe film deposited on nonequilibrium Cr, and in the Fe—Ni system—of a Ni film on nonequilibrium Fe.

Fig. 4 shows the experimentally found concentration distributions in the same specimens after anneals at different temperatures. The curves in the Fe—Ni system exhibit a plateau at 600° in the region where the Fe—Ni_3 phase forms. From the curves of Fig. 4 and other similar curves pertaining to the remaining specimens, values of D as a function of concentration and temperature were calculated (Table 1). From the dependence of $\lg D$ on

$$\frac{1}{T}$$

the activation energies Q were determined, the values of which are also given in Table 1.

As follows from the data obtained, the heterodiffusion coefficients for "nonequilibrium" and for preliminarily annealed specimens differ very markedly (for example, in the Cu—Ni system by a factor of 20). This circum-

Table 1

A. Cu—Ni system. $D \cdot 10^{11}$ cm^2/sec.

t,° C	Both components nonequilibrium Cu 17 at.%	Both components nonequilibrium Cu 33 at.%	Both components nonequilibrium Cu 50 at.%	Both components nonequilibrium Cu 72 at.%	Both components nonequilibrium Cu 90 at.%	Cu equilibrium, Ni nonequilibrium Cu 17 at.%	Cu equilibrium, Ni nonequilibrium Cu 33 at.%	Cu equilibrium, Ni nonequilibrium Cu 50 at.%	Cu equilibrium, Ni nonequilibrium Cu 72 at.%	Cu equilibrium, Ni nonequilibrium Cu 90 at.%	Both components equilibrium Cu 17 at.%	Both components equilibrium Cu 33 at.%	Both components equilibrium Cu 50 at.%	Both components equilibrium Cu 72 at.%	Both components equilibrium: Cu 90 at.%
600	2,0	–	–	–	6,3	0,5	–	–	–	0,6	–	–	–	–	–
700	4,6	5,0	5,5	6,7	10	1,5	1,6	1,6	1,7	2,0	–	–	–	–	0,1
800	–	9,6	10,2	11,0	20,1	4,4	4,5	4,6	4,8	5,5	0,4	–	–	0,6	1,0
900	–	–	–	–	–	–	10,2	10,3	11,0	12,2	3,2	3,4	3,6	4,0	–
1000	–	–	–	–	–	–	–	–	–	–	19,0	21,2	23	–	–

t, °C	Both components nonequilibrium: Cu 17 at.%	Both components nonequilibrium: Cu 33 at.%	Both components nonequilibrium: Cu 50 at.%	Both components nonequilibrium: Cu 72 at.%	Both components nonequilibrium: Cu 90 at.%	Cu equilibrium, Ni nonequilibrium: Cu 17 at.%	Cu equilibrium, Ni nonequilibrium: Cu 33 at.%	Cu equilibrium, Ni nonequilibrium: Cu 50 at.%	Cu equilibrium, Ni nonequilibrium: Cu 72 at.%	Cu equilibrium, Ni nonequilibrium: Cu 90 at.%	Both components equilibrium: Cu 17 at.%	Both components equilibrium: Cu 33 at.%	Both components equilibrium: Cu 50 at.%	Both components equilibrium: Cu 72 at.%	Both components equilibrium: Cu 90 at.%
Q, $\frac{\text{kcal}}{\text{g-at}}$		13	–	–	11	–	21	–	–	20	53,6	–	–	48,4	–

B. Fe–Ni system. $D \cdot 10^{12}$ cm^2/sec.

C. Fe–Cr system. $D \cdot 10^{11}$ cm^2/sec.

°C	Fe – Ni, both components nonequilibrium: Ni 31 at.%	Fe – Ni, both components nonequilibrium: Ni 46 at.%	Fe – Ni, both components nonequilibrium: Ni 62 at.%	Fe – Ni, both components nonequilibrium: Ni 77 at.%	Fe – Ni, both components nonequilibrium: Ni 92 at.%	Fe – Ni, both components equilibrium: Ni 31 at.%	Fe – Ni, both components equilibrium: Ni 41 at.%	Fe – Ni, both components equilibrium: Ni 62 at.%	Fe – Ni, both components equilibrium: Ni 77 at.%	Fe – Ni, both components equilibrium: Ni 92 at.%	°C	Fe – Cr, both components nonequilibrium: Cr 44 at.%	Fe – Cr, both components nonequilibrium: Cr 62 at.%	Fe – Cr, both components nonequilibrium: Cr 81 at.%	Fe – Cr, both components nonequilibrium: Cr 94 at.%
600	1,7	–	–	2,5	2,6	–	–	–	–	–	800	1,0	1,1	1,4	2,1
700	6,6	8,0	9,5	11,6	–	1,3	–	–	–	2,6	900	2,0	2,3	2,9	6,3
800	–	28,1	–	–	–	11,1	–	–	21	20	1000	–	3,3	4,0	9,3
900	–	–	–	–	–	70,0	92	122	–	–					
Q, $\frac{\text{kcal}}{\text{g-at}}$	25	25	–	–	–	–	46	–	46	–	Q, $\frac{\text{kcal}}{\text{g-at}}$		13,5	13,5	–

This circumstance sometimes escapes observation when diffusion coefficients are determined by certain methods using radioactive isotopes, where the required duration of diffusion anneals is tens of hours and the initial differences in the behavior of the specimens have time to level out.

In this connection it should be noted that the X-ray method for determining D is designed to record the diffusion process over a length

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$x \approx 5 \cdot 10^{-4} \text{ cm},$$

which, for times from 10 to 10^4 sec, makes it possible to determine diffusion coefficients in the range $\sim 10^{-8}$–10^{-12} cm^2/sec. The possibility of using short holding times makes it possible, in an X-ray investigation, to establish differences in the diffusion coefficients of specimens with an equilibrium and a distorted lattice (^{4}), which play a definite role in various crystallization processes associated with diffusion over short distances (of the order of microns).

The error described above in determining the values of heterodiffusion coefficients by the X-ray method is composed of the relative errors of the values of the concentration gradient $\dfrac{dc}{dx}$ and of the area

$$\int_{x_1}^{x_2} \Delta c \cdot dx$$

(1). Taking into account the error caused by the assumptions adopted in determining···

Fig. 2. X-ray diffraction patterns of a diffusion specimen of the Fe–Ni system. Both components are nonequilibrium, Ni on top. K_α radiation of Cr.

Fig. 3. X-ray diffraction patterns of a diffusion specimen of the Fe–Cr system. Both components are nonequilibrium, Fe on top. K_β radiation of V.

in the calculation, the total error in determining D amounts to from 40 to 60% when the full width of the interference line (doublet) is equal to 0.1 of the full concentration interval. If the width of the interference line constitutes a large part of the full concentration interval, the computational error increases and, when the line width is 1/3 of the full concentration interval, reaches 200% of the measured value.

Fig. 4. Examples of concentration-distribution curves; the construction was carried out by the method described in (1), using the data of the X-ray diffraction patterns of Figs. 2, 3.

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REFERENCES

1. B. Ya. Pines, E. F. Chaikovskii, *DAN*, **111**, No. 6 (1956).
2. B. Ya. Pines, *Defocused X-ray Tubes and Applied X-ray Structural Analysis*, 1955.
3. V. Z. Bugakov, *Diffusion in Metals and Alloys*, 1949.
4. S. T. Konobeevskii, *Izv. AN SSSR, Ser. Khim.*, No. 5 (1937).

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