ON THE TIME REQUIRED FOR ESTABLISHING THE EQUILIBRIUM CONCENTRATION OF VACANCIES

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ON THE TIME REQUIRED FOR ESTABLISHING THE EQUILIBRIUM CONCENTRATION OF VACANCIES

The magnitude of the time required for establishing the equilibrium concentration of vacancies—the relaxation time τ_v—in a system in which a supersaturation of the lattice with vacancies has been created in one way or another is of great importance for processes occurring at high temperatures in which diffusion plays the determining role.

From experiments on annealing excess vacancies after quenching (^{1}), when the supersaturation of the lattice with vacancies (i.e., the deviation of the vacancy concentration from equilibrium) reaches several orders of magnitude, it follows that the principal sinks of vacancies are dislocations and, consequently, τ_v is determined by the mobility of vacancies D_v and the dislocation density ρ:

$$\tau_v \approx L^2/D_v,$$

where D_v is the vacancy diffusion coefficient; L is the vacancy path length to a sink, $L \sim \rho^{-1/2}$. However, there are no experimental data on the magnitude of τ_v under conditions of small deviations of the system from equilibrium (quasi-equilibrium conditions).

To study the process of vacancy relaxation under quasi-equilibrium conditions, a pulse method for measuring the high-temperature heat capacity c was developed (^{2}). In this method a massive metallic specimen is heated by several degrees ($\Delta T = 1 \div 13^\circ$) by a current pulse; the mean heat capacity is obtained by dividing the heat used to heat the specimen by ΔT.

The principal new element of the procedure was the measurement of the heat capacity as a function of the pulse duration Δt. With a sufficiently long pulse ($\Delta t \gg \tau_v$), the equilibrium vacancy concentration n_v^p has time to become established in the crystal, and c is equal to the sum of the heat capacities of the lattice (c_{latt}) and of the vacancies c_v; with a short pulse ($\Delta t \ll \tau_v$), vacancies do not have time to form and $c = c_{\text{latt}}$.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

The method can be used at sufficiently high temperatures, when the contribution of vacancies to the heat capacity c_v reaches several percent. We note that the possibility of experimentally determining c_{latt} is of independent interest.

Measurements were carried out of the high-temperature heat capacity of Al (purity 99.99%; 600–640°) and Pb (purity 99.9%; 280–310°); $\Delta t = 0.1 \div 15$ sec.; $\Delta T = 1 \div 13^\circ$. The thickness of the specimens was 0.3–0.6 mm. The results $\{c = f(T)\}$ are given in Fig. 1, and the kinetic curves for Al, straightened in the coordinates

$$\lg \frac{c_v^p - c_v}{c_v^p} \; - \; \Delta t$$

are given in Fig. 2 (c_v^p is the equilibrium value of the vacancy heat capacity; $c_v = c_v^p$ at $\Delta t \to \infty$). As is seen from Fig. 1, with a pulse of 0.1 sec. the points lie on a straight line—this is the heat capacity of the lattice without vacancies (c_{latt}). At $\Delta t > 1$ sec. the points deviate upward: the deviation characterizes the contribution of vacancies to the heat capacity c_v. In the investigated interval of values of ΔT, the heat capacity of vacancies did not depend on ΔT, i.e., on the magnitude of the supersaturation of the lattice with vacancies.

The data obtained made it possible to estimate the concentration n_v^p, the formation energy Q_{fv}, and the relaxation time of vacancies τ_v. While the first two quantities agree well with the results of quenching experiments, the value of τ_v (1.0 ± 0.3 sec for Al and 1.2 ± 0.3 sec for Pb, thickness 0.3 mm; 4.0 ± 0.3 sec for Al, thickness 0.53 mm; near T_{m}) proved to be 2-3 orders of magnitude larger. This is possible if vacancies arise at the surface of the specimen (or at grain boundaries; the grain size in our experiments was greater than the specimen thickness), i.e., dislocations are not effective sources of vacancies.

Fig. 1. Dependence of the heat capacity of Al and Pb (specimen thickness about 0.3 mm) on temperature for different pulse durations: *a*—more than 1 sec; *b*—about 0.4 sec; *c*—about 0.1 sec.

Fig. 2. Plot for determining τ_v in Al under quasi-equilibrium conditions. $\tau_{v1} = 4.3$ sec, $\tau_{v2} = 3.6$ sec. Specimen thickness 0.53 mm.

The result obtained contradicts theoretical estimates ([3]), according to which a segment of a dislocation line (of length $1\,\mu$) absorbs vacancies already when the lattice is supersaturated with vacancies by about 1%. In our experiments the supersaturation reached approximately 15% (at $\Delta T \approx 13^\circ$).

In studying vacancy relaxation in the alloy $\text{Al} + 1.7$ at.% Cu, τ_v (Fig. 3) was, at 550°, 10 sec for a specimen of thickness 0.1 mm and 120 sec for a specimen of

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

thickness 0.33 mm, which again corresponds to the generation of vacancies at the specimen surface. For the same specimen thickness and the same homologous temperature (T/T_m), τ_v in the alloy is almost two orders of magnitude larger than in pure Al, which is apparently explained by a decrease in the mobility of vacancies interacting with impurity Cu atoms.

We note that both our results and the results of other authors, obtained under substantially nonequilibrium conditions with large supersaturations of the lattice by vacancies (quenching, deformation), fall on one and the same straight line in the coordinates $\lg \tau_v$–$\lg L$ (Fig. 4), except that, under quasi-equilibrium conditions, L coincides with one half of the specimen thickness, whereas under nonequilibrium conditions L is estimated from the known dislocation density.

Thus, the time for establishment of the equilibrium high-temperature vacancy concentration at sufficiently large supersaturations of the lattice with vacancies (up to 15%) proved to be two to three orders of magnitude greater than follows from quenching experiments. This effect may play a substantial role in many diffusion processes. The change in the value of τ_v is apparently associated with the peculiarities of the dislocation structure and, in particular, with the blocking action of impurity atoms around dis-

location. Simple estimates, analogous in meaning to (3), show that if the interaction energy of an impurity atom with a dislocation is taken to be about 0.1 of the vacancy-formation energy, then at an impurity concentration of 10^{-4} even a supersaturation of the lattice with vacancies of about 30% may be insufficient for effective operation of dislocations as sources (or sinks) of vacancies. In this case the system is forced to use the surface for the formation or annihilation of vacancies, and the relaxation time turns out to be large.

Fig. 3. Graph for finding τ_v in an alloy Al + 1.7 at.% Cu under quasiequilibrium conditions.
1—550°; 2—537°; 3—526°; 4—515°; 5—552°. Lines $1, 2, 3, 4$—for a specimen 0.1 mm thick; line 5—0.33 mm.
$\tau_{v1} = 10.1$ sec.; $\tau_{v2} = 11.3$ sec.; $\tau_{v3} = 13.9$ sec.; $\tau_{v4} = 15.7$ sec.; $\tau_v = 120$ sec.

Fig. 4. Dependence of the vacancy relaxation time in metals (I) and alloys (II) at T_pl on the vacancy path to a sink. Logarithmic scale. Quasiequilibrium conditions: 1—Al; 2—Pb; 3—Al (4); $4, 5$—alloy Al + 1.7 at.% Cu; 6—Pb-based alloys (5). Nonequilibrium conditions: 7—Al (6); 8—Cu (6); 9—Au (7); 10—Al (6).

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