Reports of the Academy of Sciences of the USSR

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Vol. 120, No. 4

PHYSICAL CHEMISTRY

Ya. E. Geguzin

ON THE ACTIVATION ENERGY OF THE PROCESS OF DIFFUSIONAL CREEP OF METALLIC DISORDERED SOLID SOLUTIONS OF SUBSTITUTION

(Presented by Academician G. V. Kurdyumov, 15 I 1958)

1. The experimental material accumulated in the study of irreversible deformation of metals, occurring at high temperatures and loads, when the rate of elongation is proportional to the load ($\dot{\varepsilon} \sim P$), is quite satisfactorily described within the framework of ideas about the diffusion mechanism of the phenomenon ($^{1-3}$). The idea underlying these concepts is as follows: the macroscopically observed creep is a consequence of a directed self-diffusion flux of vacancies, which occurs under the influence of a gradient of the vacancy concentration proportional to the externally applied load. The coefficient of proportionality between the elongation rate and the applied load—the so-called creep coefficient, $\chi = 1/\eta$, where η is the viscosity coefficient—turns out to be proportional to the product of the concentration of vacant sites (ξ) by the vacancy self-diffusion coefficient D_b^s at the temperature of the experiment:

$$\chi = \frac{1}{\eta} \sim \xi D_b^s. \tag{1}$$

Relation (1), generally speaking, should be equally applicable both to one-component objects and to objects consisting of atoms of several kinds, if these objects are disordered solid solutions of substitution (d.s.s.s.).

2. It is known (^{4}) that the following relation holds between the self-diffusion coefficients of vacancies and atoms (D_a^s):

$$\xi D_b^s = D_a^s. \tag{2}$$

In the case of two-component solutions an analogous relation may be written in the form:

$$\xi D_b^s = C D_A^s + (1-C) D_B^s \tag{3}$$

and, in the general case of an n-component solution:

$$\xi D_b^s = \sum_{i=1}^{n} C_i D_i^s. \tag{4}$$

In the relations written above, D_i^s is the self-diffusion coefficient of the i-th component in the solution, where its concentration is C_i. In (2)—(4) it is taken into account that the vacancy concentration is negligibly small in comparison with the total concentration of atoms,

$$\xi \ll \sum_{i=1}^{n} C_i = 1.$$

Relations (2)—(4) follow naturally from ideas about the vacancy mechanism of self-diffusion and are a statement of the following obvious

assertion: the probability of an elementary act of self-diffusive displacement of one of the atoms of the solid solution (irrespective of the kind of atom!) is equal to the probability of an elementary act of self-diffusive displacement of a vacancy.

Having in what follows two-component solid solutions in mind, and also taking into account (1), (3), and the circumstance that the viscosity coefficient of the solution varies with temperature according to an exponential law, one may write the following relation:

$$\frac{1}{\eta} \sim C D_A^s + (1-C) D_B^s \sim e^{-\theta(C)/RT}, \tag{5}$$

where $\theta(C)$ is the activation energy of the process of diffusional creep of the solution, depending on its concentration. From relation (5), naturally, there follows an expression determining the magnitude $\theta(C)$:

$$\theta(C) = R\,\frac{\Delta\left[\ln\left(C D_A^s + (1-C) D_B^s\right)\right]}{\Delta(1/T)}. \tag{6}$$

According to (6), the quantity $\theta(C)$ can be determined if the concentration and temperature dependences of the self-diffusion coefficients of the components of the solution are known. These dependences can be determined, for example, in experiments using radioactive isotopes.

3. The quantity $\theta(C)$ can be determined by a method different from that described above and based on knowledge of the constants characterizing the corresponding equilibrium diagram. It is known that the entropy jump upon melting (ΔS) is practically the same for all metals having one and the same type of crystal lattice. It is natural to assume*, that in the case of substitutional solid solutions on a given base ΔS will depend neither on the kind of dissolved atoms nor on their concentration, but will be determined by the type of crystal lattice of the base metal. Assuming ΔS to be independent of C, one may introduce the concept of the effective melting temperature of the alloy ($T_s(C)$), which is a substitutional disordered solid solution:

$$T_s(C) = T_s(O)\,\frac{Q_k(C)}{Q_k(O)} = \frac{Q_k(C)}{\Delta S}, \tag{7}$$

where $T_s(O)$ is the melting temperature of the base metal, $Q_k(C)$ is the "configurational" heat of melting of a solution with concentration C. Let us recall that the "configurational" heat of melting of an alloy is the heat expended on changing its phase state and is equal to the total experimentally measured heat of melting minus the heat expended on heating the alloy in the range of melting (7).

By characterizing the melting of a substitutional disordered solid solution by a certain temperature, we thereby compare it with some pure metal having the same lattice as the solution and a heat of melting equal to $Q_k(C)$. Taking into account the expression, known from (7), which determines $Q_k(C)$, and applying to the case of a substitutional disordered solid solution the relation previously established by V. Z. Bugakov (8) between the activation energy of the process of self-diffusion (and also of viscous flow—see above) and the melting temperature of the metal ($\theta = 20RT_s$), one may write:

$$\theta(C) = \frac{20R}{\Delta S}\left[Q_A(1-C) + Q_{BC} + NC(1-C)\left(u_0^{\mathrm{I}} - u_0^{\mathrm{II}}\right)\right]. \tag{8}$$

Here Q_A and Q_B are the heats of melting of the components calculated per 1 mole, u_0^{I} and u_0^{II} are, respectively, the mixing energies in the liquid and solid phases calculated per particle, and N is Avogadro' s number. Formula (8) makes it possible

---

* The assumption that the entropy jump upon melting of a substitutional disordered solid solution is independent of the concentration of the solution was made earlier by B. Ya. Pines (5,6) and used by him in carrying out calculations of the simplest equilibrium diagrams of binary alloys and of certain physical characteristics of solid solutions.

Fig. 1

Figure 1: Fig. 1

calculate $Q(C)$, if the heats of fusion of the components and the difference of mixing energies in the liquid and solid phases are known. The latter can be determined from the contours of the corresponding equilibrium diagram (^{5,6,9}).

4. Thus, three independent methods can be indicated for finding the activation energy of the process of diffusional creep of an unordered substitutional solid solution:

a) From data on the temperature dependence of the self-diffusion coefficients of the components of the solution in a solution of specified concentration (see formula (6)).

b) From data on the heats of fusion of the components of the solution and on the value $\Delta u_0 = u_0^{\mathrm{I}} - u_0^{\mathrm{II}}$, determined from the equilibrium diagram (see formula (8)).

c) Experimentally—from data on the temperature dependence of the diffusional-creep rate of an unordered substitutional solid solution of specified concentration.

All three of these methods can be checked using the Au—Ni system as an example. To implement the first method, we shall use the data of works (^{10,11}), in which, by means of the radioactive-isotope method, the temperature and concentration dependences of the self-diffusion coefficients of gold and nickel atoms were studied over the entire concentration range of their solutions. The results of our calculation of the dependence $\theta(C)$ using formula (6) are given in Fig. 1.

Fig. 1. $1, 2$—dependence $\theta(C)$: 1—under the assumption of the law of additivity ($\Delta u = 0$, see formula (8)); 2—according to formula (6); $3, 4$—deviation of $\theta(C)$ from additivity: 3—found by formula (8), 4—found by subtracting curve 1 from curve 2.

For calculating $\theta(C)$ by the second of the indicated methods, we determined the value Δu_0 from the position of the point of equal concentrations, using the formulas contained in (^{9}), which proved to be $\Delta u_0 = -1.2 \cdot 10^{-13}$ erg/particle $=$ -1.75 kcal/mol, and it was assumed that $\Delta S = 2.3$ cal/g • deg. To compare the results of calculating $\theta(C)$ by formulas (6) and (8), it is convenient to compare the deviations of the curves $\theta(C)$ from the straight line connecting the values of the activation energies of the diffusional creep of the components of the solution*. In the case of formula (8), this quantity is determined by the relation:

$$L(C) = \frac{2\theta}{\Delta S} NC(1-C)\Delta u_0,$$

shown in Fig. 1 by the dashed line. As follows from Fig. 1, both methods used lead to concordant results.

In order to determine experimentally the value $\theta(C)$, we carried out creep tests with specimens of an Au–Ni alloy (50–50 at. %) at temperatures of 800, 860, and 920°. Measurements were made in the previously described (^{13}) quartz apparatus. To ensure a reliable value of θ, not distorted by possible differences in grain sizes (^{15}) in different specimens, the series of measurements at different temperatures was carried out on the same specimen. The value obtained in these experiments, $\theta_{C=1/2}$, proved to be equal to $45 \pm 2 \cdot 10^3$ cal/mol. In Fig. 1 this value is shown by the black point and agrees quite satisfactorily with the values following from (6) and (8).

5. We also undertook experiments with alloys of the Cu–Ni and Pb–Sn systems. In the case of these systems, there is no information on the values of D_i^s, and therefore $\theta(C)$ was determined by formula (8) and experimentally. The values Δu_0 for these systems were determined earlier (^{9,12}); they cor-

---

* The value θ_{Ni} was taken from work (^{14}).

Table 1

Alloy	Type of equilibrium diagram	Δu_0, erg/particle	θ kcal/mol, by (6)	θ kcal/mol, by (8)	θ kcal/mol, exp.
Cu	“Cigara”	0	–	53.4	54 ± 1.6
Cu–Ni (75%–25%)	“Cigara”	0	–	57.0	56.9 ± 1.6
Cu–Ni (50%–50%)	“Cigara”	0	–	58.9	59 ± 1.6
Pb	Eutectic with limited solubility	$-3 \cdot 10^{-14}$	–	24.0	25.2 ± 1.8
Pb–Sn (85%–15%)	Eutectic with limited solubility	$-3 \cdot 10^{-14}$	–	21.7	21.1 ± 1.8

Alloy	Type of equilibrium diagram	Δu_0, erg/particle	θ kcal/mol, by (6)	θ kcal/mol, by (8)	θ kcal/mol, exp.
Pb–Sn (75%–25%)	Eutectic with limited solubility	$-3 \cdot 10^{-14}$	–	19.9	21.2 ± 1.8
Au–Ni (50%–50%)	Point of equal concentrations at the minimum	$-1.2 \cdot 10^{-13}$	44.5	46.0	45 ± 2

respectively equal to: $\Delta u_0^{\text{Cu–Ni}} = 0$; $\Delta u_0^{\text{Pb–Sn}} = -3 \cdot 10^{-14}$ erg/particle (the α-solution of tin in lead is meant). The measurement of the rate of diffusional creep was carried out on pure metals and on alloys of two different concentrations. The results obtained in calculating the value θ and in its experimental determination are summarized in Table 1.

Kharkov State University
named after A. M. Gorky

Received
10 I 1958

REFERENCES

1. C. Herring, J. Appl. Phys., **21**, No. 5 (1950).
2. Ya. E. Geguzin, L. O. Maron, B. Ya. Pines, DAN, **87**, No. 4 (1952).
3. B. Ya. Pines, Usp. fiz. nauk, **52**, issue 4 (1954).
4. Ya. I. Frenkel, *Introduction to the Theory of Metals*, Moscow, 1948.
5. B. Ya. Pines, Izv. Sekt. fiz.-khim. anal., **16**, issue 1 (1943).
6. B. Ya. Pines, ZhETF, **13**, issues 11–12 (1943).
7. Ya. E. Geguzin, B. Ya. Pines, DAN, **85**, No. 3 (1950).

8. B. Z. Bugakov, *Diffusion in Metals and Alloys*, Moscow—Leningrad, 1948.
9. Ya. E. Geguzin, B. Ya. Pines, DAN, **85**, No. 4 (1950).
10. A. D. Kurtz, B. L. Averbach, M. Cohen, Acta Metall., **3**, 442 (1955).
11. J. E. Reinolds, B. L. Averbach, M. Cohen, Acta Metall., **5**, 29 (1957).
12. Ya. E. Geguzin, B. Ya. Pines, ZhFKh, **25**, issue 10 (1951).
13. Ya. E. Geguzin, V. I. Kudrik, Fiz. met. i metalloved., **7**, 19 (1958).
14. J. Weertman, P. Shahinian, J. Metals, **10**, 1223 (1956).
15. Ya. E. Geguzin, V. Z. Bengus, Fiz. met. i metalloved., **1**, issue 2 (1955).

Note: Figure translations are in progress. See original paper for figures.