Scripta METALLURGICA Vol. 3, pp. 313-316, 1969 Pergamon Press, Inc.
Printed in the United States

THE ROLE OF EXCESS VACANCIES IN PRECIPITATION

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(Received March 20, 1969)

Introduction

Excess vacancy concentrations are known to have a strong effect on rates of precipitation from solid solution. In quenched Al-4w/o Cu alloys, for example, precipitation rates are many orders of magnitude greater than predicted on the basis of extrapolated high temperature diffusivities (1). Similar effects have been observed in other alloy systems (1,2,3). This enhancement is usually attributed to the increased growth rate of precipitates due to the quenched-in vacancies. Diffusion in most metals is by the vacancy mechanism, so an n-fold increase in vacancy concentration gives an n-fold increase in diffusion rate.

Hart (4) suggested that in addition to increasing the growth rate, vacancies could also act as a chemical component in precipitation reactions. This note develops Hart's suggestion to show that the effect of excess vacancies on precipitate nucleation rates is two-fold. Excess vacancies always increase the pre-exponent in the nucleation rate equation, but in addition may also lower the nucleation barrier so as to make homogeneous incoherent precipitation possible.

Theory

The steady-state nucleation rate in condensed systems is given by Turnbull and Fisher (5) as

$$J = Z\beta_k C_k^\circ$$

where the Zeldovich non-equilibrium factor, Z, is a relatively unimportant factor of the order 10^{-2}, β_k is the rate solute atoms impinge on the critical nucleus, and C_k° is the metastable equilibrium concentration of critical nuclei, in nuclei/cm^3 for volume nucleation.

Let us consider volume (homogeneous) incoherent precipitation of nearly pure A from a dilute solution of A in B (α from β). We also assume surface tension and elastic isotropy and the same elastic properties for matrix and precipitate. In homogeneous precipitation β_k is limited by volume diffusion, regardless of the nature of the α-β interface (6). Critical nuclei in precipitation are probably quite small, so we may approximate

$$\beta_k \simeq c_v \Gamma_v \bar{c}/a^2$$

where c_v and $\bar{c}$ are atomic fractions of vacancies and A atoms, respectively, Γ_v is vacancy jump frequency, and a is lattice constant, all in the β phase. We see that β_k increases in proportion to any excess vacancy concentration.

The number of critical nuclei per unit volume is given by

$$C_k^\circ = N_o \exp(-\Delta G_k^\circ/kT)$$

where N_o is the number of lattice sites per unit volume and ΔG_k° is the free energy change on forming a critical nucleus from material in the supersaturated system.

Vacancies are neither created nor destroyed in coherent precipitation and in that case ΔG_k° would be relatively unaffected by a vancancy supersaturation. Vacancies may participate freely in incoherent precipitation and thereby relieve transformation strains. In addition, the tendency of excess vacancies to annihilate at incoherent boundaries may strain the critical nucleus in tension.* An undersaturation would induce a compressive stress.

ΔG_k° is obtained by finding the saddle point in the free energy of cluster formation expressed as a function of numbers of solute atoms and vacancies involved.

Let us write the reaction to form a cluster as

$$n\ A_1 + (n\ \varepsilon^T + x)\ A_o \rightarrow A_n$$

where A_1, A_o, and A_n represent solute atoms, vacancies, and clusters of n atoms, respectively. $\varepsilon^T = (V_\alpha - V_\beta)/V_\beta$, and x is the excess (or shortage) of vacancies compared to the number needed for a strain-free transformation.

The driving force, capillarity, and strain energy (7) terms may be summed to yield

$$\Delta G^\circ = n\Delta\mu_A + (n\varepsilon^T + x)\Delta\mu_v + (4\pi)^{1/3}(3V_\alpha)^{2/3}\sigma n^{2/3} + Ex^2V_\alpha/9n(1-\nu) \qquad (1)$$

E is Young's modulus, ν is Poisson's ratio, and σ is the nucleus-matrix surface tension.

$$\Delta\mu_A = -kT\ell n(\bar{c}/c_\beta)$$

where c_β is concentration of A in β at the solvus, and

$$\Delta\mu_v = -kT\ell n(c_v/c_v^e)$$

where c_v^e is the equilibrium concentration of vacancies in β. For quenches from the solvus temperature, T_o, we may also write

$$\Delta\mu_A = -\Delta\bar{H}\Delta T/T_o$$

and

$$\Delta\mu_v = -\Delta H_f\Delta T/T_o$$

$\Delta\bar{H}$ is the partial atomic enthalpy of mixing A in β, ΔH_f is the enthalpy of vacancy formation in β, and $\Delta T = T_o - T$.

Evaluation of ΔG° at the saddle point gives

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*Dr. John Cahn kindly pointed this out to me.

$$\frac{\Delta G_k^\circ}{kT} = \frac{16\pi\sigma^3 V_\alpha^2}{3kT(\Delta\mu_A + \varepsilon^T\Delta\mu_v - 9\Delta\mu_v^2\,(1-\nu)/4V_\alpha E)^2} \tag{2}$$

Similar expressions may be derived for ellipsoidal or faceted nuclei.

For $\Delta\mu_v = 0$, $\Delta\mu_A$ is the only driving force and Eq. 2 reduces to the usual expression for strain-free, incoherent nuclei. The term $\varepsilon^T\Delta\mu_v$ represents the driving force from the vacancies that relieve the transformation strain. This term may be positive or negative. The term quadratic in $\Delta\mu_v$ is from destruction of more or fewer vacancies than needed to relieve the transformation strains. This term always reduces ΔG_k°.

The barrier for semi-coherent nucleation will also be affected if vacancies are created or destroyed in forming the critical nucleus. Such reactions are rather specific, and should be considered individually.

Discussion

Turnbull (8) has shown that the high surface tensions in incoherent precipitation prevent an appreciable nucleation rate except at very high supersaturations ($\bar{c}/c_\beta > 100$). Such supersaturations are hard to obtain, and if achieved, involve cooling to temperatures where diffusion is very difficult.

Let us consider a quench from T_0 (the solvus temperature) which retains the high-temperature concentrations of solute and vacancies. For $A\ell$ alloys, typically $\Delta H = .25$ ev and $\Delta H_f = .8$ ev. If $\varepsilon^T = +0.3$, ΔG_k° at any ΔT is only about 1/4 that in the case of vacancy equilibrium. One would also gain a factor of 10^6-10^{17} in the pre-exponent through an enhanced diffusivity. Copious nucleation would be observed at $\bar{c}/c_\beta \simeq 10$, rather than the $\bar{c}/c_\beta = 100$ just estimated in the case of vacancy equilibrium. Homogeneous incoherent nucleation of precipitate thus seems quite possible for the case considered. If instead, $\varepsilon^T = -0.3$, the quench from T_0 would quadruple ΔG_k°, as compared to the case of vacancy equilibrium, and homogeneous precipitation would probably be impossible. In the intermediate case, when ε^T is negative but small, excess vacancies would first increase, and then reduce ΔG_k°, with increasing ΔT.

These effects would be qualitatively the same in the general case of nucleation involving anisotropic crystals, partially coherent interfaces, and non-dilute solutions. Quantitative evaluation would of course be much more difficult.

The foregoing provides an explanation of some observations of "inoculation", including those by Rosenbaum and Turnbull (2,3) of incoherent Si precipitation from Al-1w/oSi. The maximum number of particles was nucleated when the samples were quenched, held briefly (inoculated) at about room temperature, and then aged in the range 200°-400°C. Silicon has a greater atomic volume than Al($\varepsilon^T = +0.2$), so vacancies will reduce the free energy barrier for homogeneous incoherent nucleation. $\Delta G_k^\circ/kT$ (Eq. 2) shows a minimum at about 300°K in the case of Al-;%Si. (The dependence of Γ_v on T shifts the maximum nucleation rate to a somewhat higher temperature). Growth is slow at 300°K, and nuclei would take a long time to grow to observable size. Holding at a higher temperature increases the vacancy mobility, and the particles already nucleated grow rapidly.

Rosenbaum and Turnbull considered the possibility of homogeneous precipitation of Si or of nucleation of dislocation loops followed by precipitation on the loops, and favored the latter hypothesis. Saulnier (9) later found Si precipitation to be independent of dislocation loop formation. The preceding theory indicates that direct incoherent nucleation of precipitate is probably the more favorable reaction; the supersaturations for solute and vacancies both drive the reaction, and the α-β surface created has a much lower energy than the β-vacuum surface created in nucleation of vacancy loops.

In Al-Cu, both the semi-coherent θ' and incoherent θ ($CuAl_2$) phases form with a reduction in volume (1) ($\varepsilon^T = -0.1$ for θ). The nucleation barriers for formation of these phases (given by expressions similar to Eq. (2)) would probably be somewhat increased by the presence of excess vacancies. This effect, noted qualitatively by Kelly and Nicholson (1), may be part of the reason neither phase forms immediately from supersaturated solutions obtained by quenching.

Precipitate-free bands 10^2-10^4 Å wide are frequently observed adjacent to grain boundaries in Al-Si and other alloy systems after aging has occurred. There are several possible reasons for this (1) and the preceding provides another if the precipitates are not fully coherent. Grain boundaries are known to be excellent vacancy sinks; the adjacent matrix is rapidly depleted of vacancies by diffusion to the sink. If vacancies are consumed in the precipitation reaction ($\varepsilon^T > 0$), the nucleation rate near the boundary will be sharply cut as vacancy loss occurs. This is generally more drastic than the decrease in nucleation and growth rates due to a diminished diffusivity in the precipitate-free zone.

We note finally that incoherent nucleation on grain boundaries and dislocation lines will not be affected by a vacancy supersaturation in the matrix, because the supersaturation does not exist in the vicinity of these sinks.

Acknowledgement

I want to thank Dr. Bill Giessen for acquainting me with this problem and acknowledge the support of the Advanced Research Projects Agency.

References

1. A. Kelly and R. B. Nicholson, Precipitation Hardening in Progr. Mat. Sci. 10 (1963).
2. H. S. Rosenbaum and D. Turnbull, Acta Met. 6, 653 (1958).
3. H. S. Rosenbaum and D. Turnbull, Acta Met. 7, 664 (1959).
4. E. W. Hart, Acta Met. 6, 553 (1958).
5. D. Turnbull and J. C. Fisher, J. Chem. Phys. 17, 71 (1949).
6. K. C. Russell, Acta Met. 16, 761 (1968).
7. J. D. Eshelby, Proc. Roy. Soc. A241, 376 (1957).
8. D. Turnbull, in Impurities and Imperfections (ASM, Cleveland, 1955).
9. A. Saulnier, Mem. Sci. Rev. Met. 57, 91 (1960).