Precipitation of Carbon and Nitrogen in Cold-Worked Alpha-Iron

S. HARPER
Institute for the Study of Metals, University of Chicago, Chicago, Illinois
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The strain-induced precipitation of carbon and nitrogen from supersaturated solution in alpha-iron is shown to be in agreement with a dislocation mechanism and estimates of the dislocation density required to produce the observed precipitation rates are in agreement with dislocation theory. The activation energies involved in the process are found to be 20,000 cal/mole for carbon and 17,200 for nitrogen, in agreement with published data for the activation energies of diffusion of the two solutes.

INTRODUCTION

PREVIOUS work by Griffis, Kenyon, and Burns, Davenport and Bain,[1] and Cottrell and Churchman[2] has shown that the precipitation of carbon and nitrogen from supersaturated solution in alpha-iron can be greatly accelerated by the presence of lattice distortions due to cold work, giving rise to the well-known strain aging phenomena. These experiments, however, have depended on the measurement of such factors as the change in hardness, electrical resistivity or the appearance of Luders bands on re-straining, factors which cannot be simply related to the rate of precipitation of the solute atoms.

By measuring the internal friction arising from the stress-induced interstitial diffusion of the solute atoms it is possible to measure the amount of dissolved solute at any time and thus conveniently and quantitatively study the precipitation process. This internal friction has been studied exhaustively by Snoek[3] and Dijkstra[4] and the technique well established for the study of normal precipitation from supersaturated solution by Wert.[5]

A recent analysis by Cottrell and Bilby[6] of the dislocation theory of "strain aging," deduces a quantitative estimate of the rate of precipitation in a strained material. The present paper describes a series of experiments which permit us to estimate the accuracy of such a dislocation mechanism.

EXPERIMENTAL PROCEDURE

Puron iron of purity 99.95 percent was used in these experiments. The iron was in the form of wires 0.03 in. in diameter and 12 in. in length. The carbon and nitrogen content of the iron was first reduced to less than 0.0005 wt percent by heating for a period of a few hours at 720°C in an atmosphere of wet hydrogen. Carbon or nitrogen was then introduced into the wire in controlled amounts. The carbon was dissolved by heating to 720°C, for a period of an hour or so, in an atmosphere of dry hydrogen and *n* heptane, the nitrogen by heating to 590°C in an atmosphere of dry hydrogen with a small amount of ammonia gas present. These alloys, on quenching to the aging temperatures used, showed no decrease in the amount of material in solution even after a period of some days. We are thus justified in assuming that the precipitation studied was due solely to the presence of cold work.

The wires were cold-worked by small extensions in a rigid frame apparatus and were then placed in the aging furnace. This furnace was required to control temperature in the range of room temperature. A forced air circulation furnace which could be water-cooled on the outside was used, the temperature being controlled by a de Khotinsky mercury regulator, the apparatus permitting control to 0.1°C within the range 15–60°C. The specimen attained the aging temperature within three minutes of straining, a negligible period with the rates of precipitation encountered.

The internal friction of the specimen was measured directly by means of a torsion pendulum, which was set oscillating and the friction measured by the decay of the free vibrations. The frequency corresponding to the internal friction peak at the temperature of aging was used in each case. This method has been already described in some detail by Kê.[7]

DISLOCATION MODEL OF STRAIN AGING

Cottrell and Bilby in considering this problem show that the aggregation of solute atoms, in *substitutional* solution, around a simple edge dislocation would lower the strain energy of the system. Thus the interaction energy between an atom and a positive edge dislocation is equal to

$$V=\frac{4}{3}G\epsilon r_a^3\lambda\frac{1+\nu}{1-\nu}\frac{\sin\alpha}{r}=A\frac{\sin\alpha}{r}, \tag{1}$$

where G is the rigidity modulus, ν Poisson's ratio, r_a and $r_a(1+\epsilon)$ are the atomic radii of solvent and solute. r and α are the polar coordinates of the position of the atom with the dislocation at the origin, and λ is the slip distance.

[1] E. W. Davenport and E. C. Bain, Trans. Am. Soc. Metals 23, 1047 (1935).
[2] A. H. Cottrell and A. T. Churchman, J. Iron Steel Inst. (July, 1949).
[3] J. L. Snoek, Physica 8, 711 (1941).
[4] L. J. Dijkstra, Philips Research Repts. 2, 357 (1947).
[5] C. Wert, Am. Soc. Metals Symposium on Thermodynamics in Physical Metallurgy, Cleveland (1949).
[6] A. H. Cottrell and B. Bilby, Proc. Phys. Soc. (London) Series A, 62, 49 (1949).
[7] T. S. Kê, Phys. Rev. 71, 533 (1947).

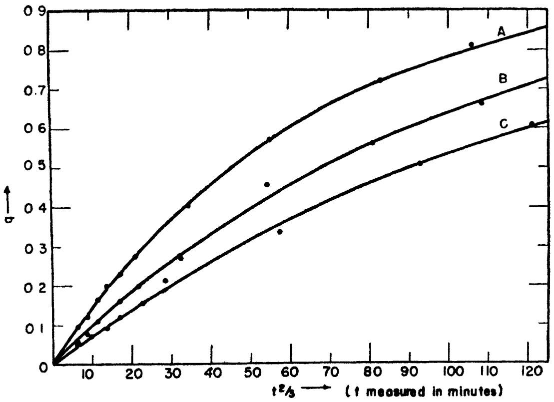

FIG. 1. Variation of strain aging with the degree of cold work (carbon in alpha-iron).

From this basis they estimate the rate at which solute atoms should migrate towards such a dislocation, and obtain:

$$N_t = 2n_0 L(\tfrac{1}{2}\pi)^{\frac{1}{3}}(ADt/kT)^{\frac{2}{3}} \qquad (2)$$

where N_t is the number of atoms precipitated, per unit volume of material in time t, L is the total length of edge dislocation per unit volume, n_0 is number of solute atoms per unit volume, and D is the diffusion coefficient at the absolute temperature T. Or we have

$$q = 2L(\tfrac{1}{2}\pi)^{\frac{1}{3}}(ADt/kT)^{\frac{2}{3}} \qquad (3)$$

where q is the fraction of the original amount of solute material which has precipitated during the time t. This law will only be applicable during the early stages of

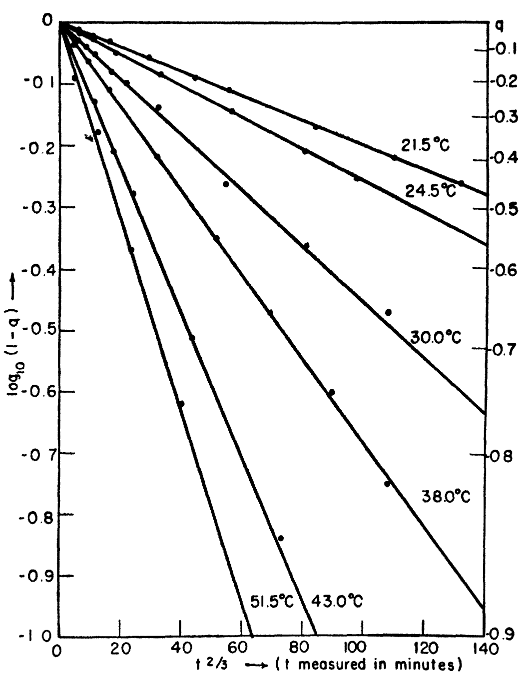

FIG. 2. The effect of temperature on the rate of strain aging (carbon in alpha-iron).

the precipitation, as the rate of precipitation will decrease more rapidly with time than Eq. (3) would indicate because of the mutual interference of the growing precipitates, continually reducing the value of n_0. It seems reasonable to assume that the decrease in the precipitation rate will be proportional to the fraction already precipitated (Johnson and Mehl[8]). The equation governing the precipitation will then be

$$\partial q/\partial t = (1-q)f(t). \qquad (4)$$

Solving this with the boundary condition $t \doteq 0$ defined by Eq. (3) we have

$$q = 1 - \exp[-2L(\tfrac{1}{2}\pi)^{\frac{1}{3}}(ADt/kT)^{\frac{2}{3}}]. \qquad (5)$$

PRECIPITATION OF CARBON

The magnitude of the internal friction peak is linearly proportional to the amount of material in solution.

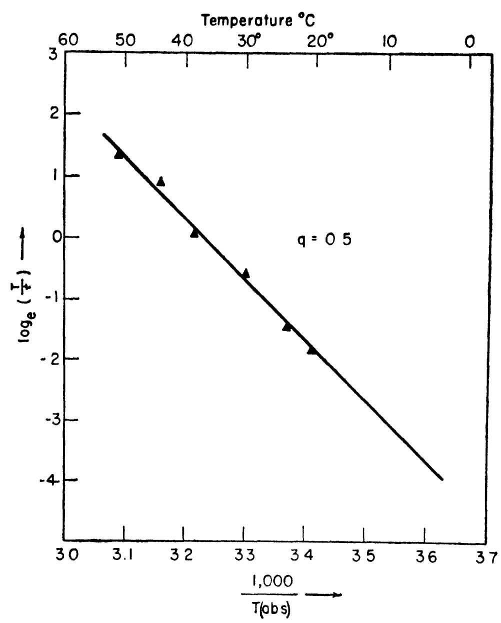

FIG. 3. The activation energy for strain aging (carbon in alpha-iron).

We can thus measure the quantity

$$1 - q = Q_t^{-1}/Q_0^{-1}, \qquad (6)$$

where Q_0^{-1} and Q_t^{-1} are the values of the maximum of the internal friction peak at the beginning of aging and after aging has proceeded for a period of time t, respectively. Three specimens were taken with carbon contents of 0.015, 0.009, and 0.013 wt percent and were strained by approximately 5, 10, and 15 percent extensions, respectively, and aged at 30°C. Figure 1 shows the parameter (q) plotted against $t^{\frac{2}{3}}$, the full lines being equations of the type of Eq. (5). The parameter A has been estimated, for this case of

[8] W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Mining Engrs. **135**, 416 (1939).

interstitial solution, from the volume change produced when a carbon atom enters a unit cell of the iron lattice, this data being taken from the x-ray work of Lipson and Parker[9] on martensite. The value of D at the temperature in question was taken from the work of Wert and Zener.[10] These three specimens gave values of L as follows:

A. 15 percent extension	$L=3.72\times10^{11}$ lines cm^{-2}
B. 10 percent extension	2.46×10^{11} lines cm^{-2}
C. 5 percent extension	1.86×10^{11} lines cm^{-2}.

These values of dislocation density are compatible with previous estimates.[11]

Because of some uncertainty in estimating the constants in Eq. (5), the absolute values of L obtained are subject to some error and are only valuable as an order of magnitude estimate. Much greater reliance can be placed, however, on their relative values.

ACTIVATION ENERGY FOR STRAIN PRECIPITATION

We should expect the activation energy for this process to be identical with that for the diffusion of carbon in alpha-iron. Indeed, Nabarro[12] has analyzed data published by Davenport and Bain and shown that the activation energy involved is of this magnitude. To obtain further confirmation of this, 6 specimens were loaded with carbon and each strained as nearly as possible by the same amount (about 10 percent extension). They were then stored in liquid nitrogen until required and were then aged at the following temperatures: 21.5°, 24.5°, 30°, 38°, 43°, and 51.5° C. Figure 2 shows the aging curves for these specimens, while Fig. 3 shows the plot of $\log_e(T/t)$ against the inverse of the absolute temperature for the case of 50 percent precipitation ($q=0.5$). The slope of this line gives an energy of 20,000 cal/mole in good agreement with the published values of Snoek[13] and Polder[14] (18,000 cal/mole) and Wert and Zener[10] (19,800 cal/mole).

PRECIPITATION OF NITROGEN

Nitrogen behaves in an exactly similar manner as carbon in this matter, giving the same shaped aging curve. Figure 4 shows the results obtained from four specimens given identical strains and aged at 19.5°, 26°, 31.5°, and 34.5°C, respectively. Values taken from these curves at $q=0.5$ are plotted in Fig. 5, giving an activation energy of 17,200 cal/mole, again in agreement with published values for the diffusion of nitrogen in α-Fe (Snoek[13] (16,400 cal/mole) and Wert[10] (17,700 cal/mole)).

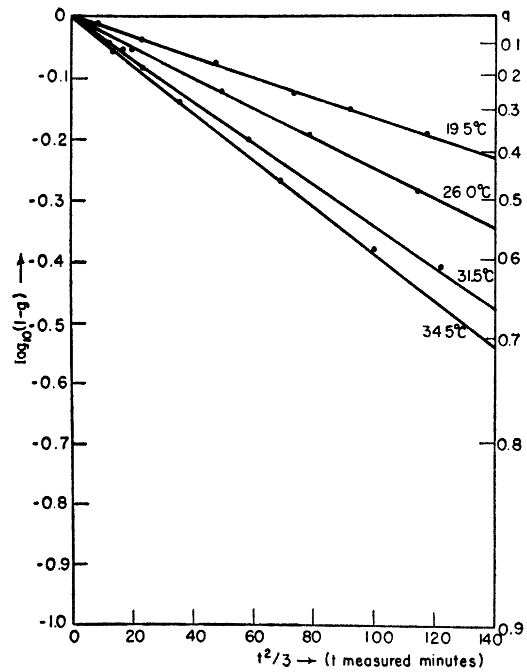

FIG. 4. The effect of temperature on the rate of strain aging (nitrogen in alpha-iron).

CONCLUSIONS

The experimental results obtained are in agreement with the dislocation model of the process. Equation (3) was closely obeyed up to about 25 percent of the total precipitation, whereas Eq. (5) was applicable as far as

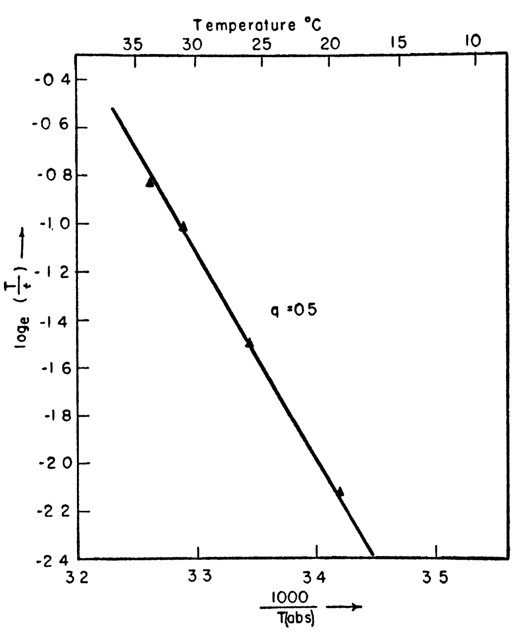

FIG. 5. The activation energy for strain aging (nitrogen in alpha-iron).

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[9] H. Lipson and A. M. B. Parker, J. Iron Steel Inst. **149**, 123 (1944).

[10] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[11] J. S. Koehler, Phys. Rev. **60**, 397 (1941). F. Seitz and T. A. Read, J. Appl. Phys. **12** (1941). W. L. Bragg, Trans. North East Coast Inst. Eng. & Shipbuilders **62**, 25 (1945). G. I. Taylor and H. Quinney, Proc. Roy. Soc. (London), Series A, **143**, 307 (1934); **163**, 157 (1937). W. F. Brown, Phys. Rev. **60**, 139 (1941).

[12] F. R. N. Nabarro, Report of Bristol Conference, Phys. Soc. (London) **38** (1948).

[13] J. Snoek, Physica **6**, 591 (1939).

[14] D. Polder, Philips Research Repts. **1**, 1 (1945).

the experiments were carried out (to about 90 percent of the total precipitation).

An interesting outcome is that the work affords a simple experimental method of measuring dislocation densities, although in a limited range and only in body-centered cubic alloys exhibiting this type of internal friction. It must be realized also that the theory leading to this estimated value is only approximate, as the solute atoms are treated as substitutional and hence only the relief of hydrostatic stress around the dislocation is considered. With the nonsymmetrical distortion produced by interstitial atoms, relaxation of shear stresses can also occur (Nabarro[12]), and thus there will be a tendency for such atoms to migrate to the Burgers type component of the dislocations.

Nevertheless the method may be of use in studying problems involving the amount of internal strain in a material.

Finally, by studying the case of carbon and nitrogen separately it has been possible to show that the temperature dependence of the process is identical with that of the diffusion of the elements in the mother metal.

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The Contribution of the Pauli Moment to π-Meson Production by Photons*

M. F. KAPLON
University of Rochester, Rochester, New York
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The photon-nucleon production of π-mesons has been calculated incorporating in the interaction a Pauli-type term representing the interaction of the photon with the anomalous magnetic moments of the nucleons. The effect of the added interaction for the scalar theory is to increase somewhat the charged meson production while leaving the neutral production virtually unchanged. For the pseudoscalar theory the charged meson production is relatively unaffected while the neutral meson production is greatly enhanced. Comparison with the neutral meson experiments in hydrogen therefore favors the pseudoscalar theory.

I. INTRODUCTION

Weak coupling calculations of the production of neutral π-mesons by photons[1] yield cross sections which are much smaller than the charged π-meson production cross sections for both the scalar and pseudoscalar theories.[2] That is, it can be shown that if the anomalous magnetic moments of the nucleons are neglected,

$$d\sigma(\pi^0)/d\sigma(\pi^+)=(\boldsymbol{q}\cdot\boldsymbol{K}_0/\boldsymbol{P}\cdot\boldsymbol{K}_0)^2,$$

where ($K_{0\mu}$, q_μ, and P_μ are the four-momenta for the photon, meson, and recoil nucleon respectively) which, for instance, decreases from $\sim 1/5$ at 180° to $\sim 1/500$ in the forward direction at a photon energy of 250 Mev. This small ratio contradicts recent experimental results in hydrogen[3] which indicate that the neutral and charged cross sections are comparable.

One may ask the question whether it is possible within the context of weak coupling theory to eliminate the disagreement between theory and experiment by including a Pauli-type term in the hamiltonian to represent the interaction of the electromagnetic field with the anomalous magnetic moments of the nucleons. It turns out that such a phenomenological approach markedly improves the agreement for the pseudoscalar theory, whereas it actually increases the discrepancy for the scalar theory. At the same time it must be shown that the good qualitative agreement between the pseudoscalar theory[4] and experiment for charged π-meson production is not affected by taking into account the anomalous magnetic moments. We here report the results of calculations on the effect of the anomalous magnetic moments on meson production by photons, treating them in the Pauli fashion and assuming that the static values can be used at photon energies of several hundred Mev.

The calculations have been performed with the Feynman[5] techniques. The notation is that of Feynman with the exception $(\gamma^5)^2=-1$. The interaction of the electromagnetic field with the anomalous magnetic moment[6] of the nucleon $(1/2)F_{\mu\nu}\gamma^\mu\gamma^\nu$, when transformed to momentum space, is $(\mu/2M)(\mathfrak{K}_0\mathfrak{A})$, where[7] $\mathfrak{A}=\epsilon_\mu\gamma^\mu$ (ϵ_μ is the 4-polarization of the photon), $\mathfrak{K}_0=K_{0\mu}\gamma^\mu$ ($K_{0\mu}$

* Assisted by the AEC.

[1] G. Araki, Prog. Theor. Phys. **5**, 507 (1951). K. Brueckner, Phys. Rev. **79**, 641 (1950).

[2] The neutral π-meson is known to possess spin 0 and we shall assume that the charged π-meson also possesses spin 0 although this must still be demonstrated.

[3] W. Panofsky, private communication; preliminary results are $(d\sigma_{\pi 0}/d\Omega)(90°)\approx 3\times 10^{-30}$ cm²/sterad compared to $(d\sigma_{\pi^+}/d\Omega)(90°)\approx 8\times 10^{-30}$ cm²/sterad. Panofsky also finds $d\sigma_{\pi 0}(45°)\approx 2d\sigma_{\pi 0}(90°)$.

[4] Bishop, Steinberger, and Cook, Phys. Rev. **80**, 291 (1950); see Brueckner, reference 1.

[5] R. P. Feynman, Phys. Rev. **76**, 749, 769 (1949).

[6] W. Pauli, Handbuch d. Physik **24**, I (233).

[7] We use $\mathfrak{A}=A_\mu\gamma^\mu$; $\boldsymbol{A}\cdot\boldsymbol{B}=A_4B_4-\mathbf{A}\cdot\mathbf{B}$; and A is the length of the three vector $\mathbf{A}$; thus $\mathfrak{A}$ is a 4-vector associated with a 4-matrix.