

fifty ($=\rho$) to give the points in Fig. 1, whereas for run 7 the time at T_2 was divided by fifty for the points plotted. The lines in Fig. 1 were drawn from a numerical integration of the equation

$$\int_0^z \frac{z \, dz}{a(1-W)} = Kt \quad (3)$$

in which a is a dimensionless parameter, t is the time, and K is a constant for any particular run that depends upon the temperature and the number density and shape of the precipitate particles. The relation between W and z is:

$$aW = 2z + z^2 + (4z^3/3\pi^2).$$

Equation (3) was derived for the diffusion-controlled growth of asymmetric particles,⁽⁴⁾ but it will be used here strictly as an empirical relation. The equation

$$-\ln(1-W) = Kt^n \quad (4)$$

with n a constant, is frequently compared to precipitation data, but equation (3) fitted the present results better than this equation.

DISCUSSION

There are several assumptions involved in using this method to find the activation energy for precipitation. One assumption is that the number of precipitate particles is constant throughout the precipitation process and at both temperatures. In all of the runs reported here the curves plotted with the ratios ρ given in Table I, such as those shown in Fig. 1, could be superimposed on the curves that resulted when a sample was aged at a temperature of T_1 throughout the entire precipitation process. For example, the curve for run 7 in Fig. 1 superimposes exactly on the curve in Fig. 1, ref. 2 for a unstrained wire aged at 120°C. These correspondences are good evidence that the number of particles is indeed constant, because a change in the number of particles by dissolution or formation at T_2 would result in different kinetic behavior at T_2 . Furthermore these results argue against any nucleation during the measured precipitation period, because the rate of such nucleation would almost certainly have a different temperature dependence than the growth rate of the particles. Thus the model proposed by Wepner⁽⁵⁾ cannot apply to this system, because this model requires continued nucleation throughout the precipitation process.

The average value of Q from Table I is 17.1 kcal/mole with a variation of ± 0.5 kcal/mole. In an earlier study Wert⁽⁶⁾ reported a value of 17.5 ± 1.7 kcal/mole from similar experiments on precipitation rates of

carbon in α -iron in the range 100°–150°C. The points in Fig. 4 of ref. 1 that were determined by the precipitation method seem to fall slightly below the curve for equation (1) although the graph is too small to make an accurate estimate. In any event the activation energy for precipitation seems to be appreciably lower than the activation energy for diffusion that is calculated from the relaxation experiments. The temperature of maximum internal friction at a given frequency did not vary with degree of precipitation for the runs reported in Table I; this same result has been found by other workers.^(7,8) Thus the relaxation process is not affected by the presence of precipitate particles, and the rate at which carbon atoms jump from one interstitial site to another is constant throughout the precipitation process.

The activation energy for precipitation will equal that for diffusion only if the precipitation process is entirely controlled by solute diffusion through the matrix. If a reaction at the particle surface is slow enough it may also influence the kinetics of precipitation. When a surface reaction entirely controls precipitation, W is proportional to t^3 for spherical particles in the early stages of precipitation; for mixed reaction and diffusion controlled processes the proportionality is between $t^{3/2}$ and t^3 for spherical particles.⁽⁹⁾ For aging temperatures above about 60°C the exponent of initial time-dependence of W is always less than 3/2 for the precipitation of carbon in α -iron, so a reaction at the particle interface is probably not influential in this process, although one cannot eliminate it completely from the experimental evidence available. In the remainder of this discussion we will assume that interface reactions are unimportant in the precipitation of carbon from α -iron.

The results in Table I show that the activation energy for precipitation of carbon in α -iron is constant within experimental error from 0° to 170°C at least. Neither changes in carbon concentration nor cold-working seem to affect this activation energy. The kinetics of carbide precipitation below about 60°C are different from those at higher temperatures. This phenomenon will be discussed more completely in a separate report, but it is interesting to note here that the activation energy for particle growth is not affected by this change. Presumably the different kinetics are caused by different nucleation mechanisms and consequent variations in the number density of particles, rather than any change in growth mechanism.

The lower activation energy for long-range diffusion of carbon atoms to precipitate particles may be caused