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DIFFUSION AND PRECIPITATION IN ALLOYS.* 1096

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SYNOPSIS.

A general review is given of recent work on diffusion and precipitation in alloys, with special emphasis on the theoretical mechanism of diffusion, and on the factors governing the shape and size of the precipitate. The effects of internal stresses on diffusion and precipitation, and of precipitation on the mechanical properties, are discussed.

I.—INTRODUCTION.

EXPERIMENTAL and theoretical work on diffusion is summarized in the books of Barrer,[1] Seith [2] and Jost.[3] There are detailed review articles by Mehl,[4, 5] the earlier of which contains a full bibliography. The practical aspects of diffusion in metals are discussed in an American Institute of Mining and Metallurgy symposium,[6] and precipitation and age-hardening are treated in an American Society for Metals symposium.[7] The present article is concerned largely with work published since these summaries, and especially with attempts to explain the observations in terms of atomic physics. The author's thanks are due to Professor N. F. Mott, F.R.S., Dr. F. C. Frank, and Mr. G. Wyllie for valuable discussions, and to Mrs. Frank for translation of papers from the Russian.

II.—THE MECHANISM OF DIFFUSION.

Consider a metal B containing an atomic concentration α of another metal A in solid solution. Suppose the concentration α at time t depends only on the cartesian co-ordinate x. Then it is found that the rate of change of α with time can be expressed by Fick's second law :

$$\frac{\partial \alpha}{\partial t} = -\frac{\partial}{\partial x}\left(D\frac{\partial \alpha}{\partial x}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here D, the coefficient of diffusion, may depend on α, but to a first approximation in dilute solutions this dependence may be neglected.

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The dependence of D on the absolute temperature T is usually of the form

$$D = D_0 e^{-Q/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Q is the activation energy for diffusion. Sometimes the law of temperature dependence departs widely from this form, and in such cases it has usually been possible to show that different mechanisms of diffusion are operating in different temperature ranges. The three broad types of mechanism are :

(a) migration of A over the surface of B. This process, which is characterized by a small value of Q in (2), is important when B is a hard metal of high melting point, so that penetration of A into the lattice of B is difficult;

(b) diffusion of A along the grain boundaries of B. The value of Q for this process is in general intermediate between the values in types (a) and (c);

(c) diffusion of A through the bulk of the grains of B. There is evidence in many cases that this is the effective mechanism of diffusion, especially at high temperatures. This is illustrated by examples in which the diffusion of A gives rise to chemical changes. The boundary of the changed region runs straight across the specimen, crossing the grain boundaries with no deviation. The value of Q is larger than for diffusion of types (a) and (b) and the value of D_0 is also larger. In the rest of this review we shall consider only this type of diffusion.

Several mechanisms have been suggested for the diffusion of A through the grains of B. One, due to Bernal,[8] involves large-scale shearing movements in the lattice, and seems unlikely in most cases. Another simple mechanism, the direct exchange of neighbouring atoms or ions in a substitutional solid solution, involves very large local distortions of the lattice, and the activation energy Q would probably be so large as to make such direct exchange a very rare process. Wagner [9] has considered a process in which ions of A which normally replace ions of B in a substitutional solid solution are able to diffuse through the crystal by moving into interstitial positions. In this model an ion of A in an interstitial position has a higher energy than an ion at a lattice point, so that only a small proportion of the A ions occupy such interstitial positions, but once an ion is in an interstitial position it can move to a neighbouring interstitial position by crossing a comparatively small energy barrier. That is to say, once the lattice has been sufficiently distorted to accommodate an ion of A in an interstitial position, the further distortion required to squeeze this ion through into a neigh-

bouring interstitial position is small. The other important mechanism of diffusion is by the migration of vacant sites or holes.[10] If a lattice site P is empty, thermal agitation will cause the atom at a neighbouring site Q to squeeze past its neighbours and fall into the hole. The site Q is now empty, and it is convenient to think of the process as a movement of the hole from P to Q. If the next atom R now falls into the hole, the hole has shifted to R, and so on. The displacement of atoms along the track of a moving hole gives rise to diffusion.

It is possible for an ion on a lattice site to jump into a neighbouring interstitial position, so producing simultaneously a hole and an interstitial ion.[11] If, however, the energy required to produce one of these types of defect is large, the other type alone is formed. Such a process can occur only at a grain boundary or some other imperfection of the crystal. Holes formed at a surface may diffuse through the grain, displacing ions of A or of B. Interstitial ions may wander among the interstitial sites, but they may also change places with ions on lattice sites, forcing these into interstitial positions without great expenditure of energy. The various possible processes have been discussed in detail by many authors (cf. Mott and Gurney,[12] Seitz [13, 14]). For the self-diffusion of copper, Huntington and Seitz [15, 16] have calculated that less activation energy is required for diffusion by the migration of holes than for any other process. It seems likely that this result will hold for self-diffusion and mutual diffusion in all metals and substitutional solid solutions having close-packed structures with hard ions in contact. In other cases the mechanism is still uncertain. Small ions such as carbon and nitrogen which form interstitial solid solutions diffuse readily among the interstitial sites (cf. Snoek [17] and Polder [18]).

By the use of radioactive isotopes it is possible to measure the coefficients of self-diffusion of metals. The outstanding general result [19] is that the activation energy for self-diffusion in a metal B is larger than that for the diffusion of dilute solutions of most other metals A in B. R. P. Johnson [20] has suggested that this contradicts the simple hole theory of diffusion, which is otherwise well substantiated. The migration of atoms of A results from their falling into holes which have diffused to them through the lattice of B. Even if no activation energy is required for A to fall into the hole, the diffusion of A in B is limited by the rate of diffusion of holes through the lattice of B, and cannot be greater than the self-diffusion of B. Johnson points out that this argument is incorrect. The hole and the substituent atom of A are both imperfections in the lattice of B, and it is likely that in many cases there will be an attraction between the two. As a result, a fairly stable "hole-A molecule" is formed, and it is easy to see that such a "molecule" can wander freely through the lattice. Ultimately the "molecule" dissociates, and the A atom is again anchored to its lattice site until another hole reaches it. The chance that at any given time a given atom of A has a hole as a nearest neighbour, and is therefore mobile, may greatly exceed the chance that a given atom of B (or of its radioactive isotope) has a hole as a nearest neighbour. Thus D_0 in (2) is increased, while Q is reduced by the binding energy of the "molecule". A more detailed discussion of this process has been given by Wyllie.[21]

The "hole" mechanism of diffusion, like other mechanisms, leads in a perfect crystal to a simple one-for-one exchange of atoms, and the theory of precipitation given in this review depends on the assumption that this simple exchange always occurs. If, however, the continuity of the lattice is destroyed, either by grain boundaries or imperfections already existing, or by recrystallization or formation of a particle of precipitate with a lattice which has broken away from that of the matrix, it is possible for the holes which travel with the diffusing atoms to be generated or to disappear within the body of the specimen. In this way it may be possible to explain the anomalous volume changes during diffusion observed by Kirkendall,[22, 23] and also the well known fact that in age-hardening systems the hardness diminishes after the particles of precipitate have "broken away", even though the precipitate continues to grow. (But cf. discussion by C. S. Smith [24] of the paper by Smigelskas and Kirkendall.)

III.—Diffusion in Precipitating Systems.

The coefficient of diffusion D in (1) has long been known to depend on the concentration α. It is reasonable to expect that when α is not small the rate of diffusion should be proportional, not to the gradient of concentration, but to the gradient of chemical activity, since the activity and not the concentration is the governing factor in problems of thermodynamic equilibrium. Birchenall and Mehl [25] have recently shown, in the cases of copper–zinc and iron–carbon, where the activities are known from vapour pressure measurements, that the coefficient D_{12} which expresses the rate of diffusion in terms of the gradient of activity varies only by a factor of two over a range of concentrations in which D varies by a factor of 20, and so confirm this expectation. We shall see below that a residual variation of D_{12} is to be expected. Birchenall and Mehl deduce from their results that the mechanism of diffusion must be one of simple place-change, but remark that a "hole" mechanism, which effectively results in simple one-for-one place-change, is not excluded.

The theory of diffusion in concentrated and supersaturated solutions has been developed by Becker,[26] Dehlinger, [27, 28] and Ilkevich.[29] The following treatment is based on that of Becker. In the solid solution of concentration α, let

$$F = U - TS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

be the free energy of the whole solution, divided by the total number of atoms in the solution. In an ideal solution, the binding energies $-V_{AA}$, $-V_{AB}$, $-V_{BB}$ between two A atoms, an A and a B, and two B's, are all equal, and U is independent of the concentration α. The entropy of mixing is zero for pure A or pure B, and reaches a maximum for $\alpha = \frac{1}{2}$. The free energy F correspondingly has a minimum at $\alpha = \frac{1}{2}$, and the graph of F as a function of α is everywhere concave upwards. This means that the free energy of a mixture of two phases of concentrations α_1 and α_2, which is represented by a point on the chord joining their representative points, is always greater than that of a single-phase solid solution of the mean composition, represented by a point on the F–α curve. This means that if the two phases are brought into contact, diffusion will occur to lower the free energy by building a single phase of intermediate composition. The condition for normal "downhill" diffusion is thus

$$\frac{\partial^2 F}{\partial \alpha^2} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The theory of eutectoid transformation, in which a single phase breaks up into two other phases, has been worked out by Zener [30] in the particular case of the decomposition of austenite. The precipitate of pearlite in this case consists of alternate sheets of ferrite and cementite. The carbon content of austenite in contact with ferrite is higher than that of austenite in contact with cementite, and carbon diffuses through the austenite from the edges of the ferrite plates to the edges of the cementite plates. In this way both components of the precipitate grow.

The theory of segregation and nucleation in a single phase is more complicated. Following Becker, we consider the ordering energy

$$2V = 2V_{AB} - (V_{AA} + V_{BB}) \quad . \quad . \quad . \quad . \quad (5)$$

If V is negative, like atoms tend to keep apart, and at low temperatures an ordered structure is formed with the greatest possible number of A–B bonds. This minimizes the term U in (3). At high temperatures the term $-TS$ in (3) is more important, and a disordered solution with large S is formed. If V is positive, like atoms tend to segregate. At high temperatures the state of lowest free energy is still the single-phase

solid solution, but at low temperatures the stable state contains two phases of different compositions. The graph of F as a function of α has two minima separated by a maximum, and the stable phases are represented by the points of contact of the common tangent to the two minima. For concentrations near the minima, where condition (4) is satisfied, diffusion is normal, and evens out any local variations of concentration. For concentrations near the maximum of free energy,

$$\frac{\partial^2 F}{\partial \alpha^2} < 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and the free energy is reduced by any increase in local variations of concentration. This is "uphill" diffusion. Becker shows that if osmotic pressure (which is essentially the same quantity as chemical potential) is taken to be the "driving force" of diffusion, the diffusion coefficient is given by

$$D = \alpha(1 - \alpha)\, M \frac{\partial^2 F}{\partial \alpha^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where M is the mobility of ions of A in the lattice. This mobility M is always positive, so that D has always the sign of $\partial^2 F/\partial \alpha^2$, but its value will in general depend both on temperature T and on α. We expect that if increase in α raises the melting point of the alloy, M will be a decreasing function of α, and *vice versa*, but this can only be regarded as a semi-empirical working rule.

If the single-phase alloy is prepared in the region where (6) is satisfied, segregation occurs spontaneously at a rate limited only by the speed of diffusion. Daniel [31] has recently carried out an X-ray study of the kinetics of this process in the alloy Cu_4FeNi_3. If, however, the single-phase alloy, though unstable, lies so near to one of the equilibrium concentrations that $\partial^2 F/\partial \alpha^2$ is still positive, diffusion is still normal, and tends to remove local fluctuations of concentration. The growth of a nucleus of material of an equilibrium concentration in such cases has been studied by Borelius.[32, 33] If a nucleus of N atoms is formed, and gradually increases in concentration, while the concentration of the matrix decreases infinitesimally, the free energy of the system increases by a quantity $N\Delta F$ above that of the supersaturated solid solution and then decreases again. This energy $N\Delta F$ is of the nature of an activation energy which must be provided by thermal agitation before the nucleus can attain its equilibrium concentration and increase in size, and the time required for precipitation is increased by a factor

$$\exp.\,(N\Delta F/kT) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Borelius determines this factor experimentally, estimates ΔF from the

phase diagram of the system, and so forms an estimate of N, which turns out to be about 100 atoms.

IV.—Size and Shape of the Particles of Precipitates.

Becker [34] has extended to metallic solid solutions the analysis by Volmer [35] of the factors determining the size of a nucleus of condensation in a supersaturated vapour. The treatment of free energy in this discussion has till now considered only the free energy of phases in bulk. For a small nucleus of a new phase or of a region of different concentration there is also a surface energy. Suppose, for example, that A precipitates from B because the bond between two A atoms is strong. If atoms in the lattice have Z nearest neighbours, the free energy of A corresponds to a crystal in which each A atom has Z A–A bonds. The atoms on the surface of a nucleus have an average only $\frac{1}{2}Z$ A–A bonds and $\frac{1}{2}Z$ weaker A–B bonds, and therefore have a higher free energy than atoms in a bulk precipitate.

Let the decrease of free energy for each atom that is transferred from the supersaturated solid solution to the bulk precipitate be f, and let the energy of an atom on the surface of the precipitate be higher than that of an atom in the body of the precipitate by σa^2, where a is the linear dimension of an atom. The quantity σ thus has the dimensions of a surface tension. If N atoms form a cubical nucleus, the surface area of the nucleus is $6N^{\frac{2}{3}}a^2$, and its free energy exceeds that of the supersaturated solid solution by

$$\delta F = 6N^{\frac{2}{3}}\sigma a^2 - Nf \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If N is small, δF is positive, and increases with N, and the nucleus is unstable. The nucleus becomes stable, and grows spontaneously, when N is so large that $d(\delta F)/dN$ is zero. This occurs when

$$N = 64\sigma^3 a^6/f^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

corresponding to

$$\delta F_{\max.} = 32\sigma^3 a^6/f^2 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This energy $\delta F_{\max.}$ is an energy of activation, which must be supplied by thermal agitation before the nucleus is large enough to grow spontaneously. The time taken to form a precipitate therefore includes a factor

$$\exp.\,(\delta F_{\max.}/kT) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The time taken to form a precipitate can now be represented as a product of three factors. The first varies inversely as the rate of diffusion, and so from (2) is of the form

$$\exp.\,(Q/kT) \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The second factor, corresponding to the surface energy of the smallest stable nucleus, is given by (12) and (11). If the concentration of the matrix is not one which lies in a region of uphill diffusion, there is a further factor given by (8), where N, the number of atoms, is determined by (10).

If the original solution is but slightly supersaturated, the drop in free energy f on precipitating one atom is small, and may be taken proportional to $(T_{\text{eq.}} - T)$, where $T_{\text{eq.}}$ is the temperature at which the original solution is just saturated. We see from (10) that when f is small N is large, and from (11) $\delta F_{\max.}$ is also large. It follows from (8) and (13) that the time taken to precipitate increases very rapidly as T approaches $T_{\text{eq.}}$, while from (13) it follows that precipitation also becomes slow at low temperatures where diffusion is slow.

It is known from X-ray studies [36, 37] that the initial nuclei in many cases form as flat plates, whereas consideration of surface energy would lead to the formation of spherical or equi-axed polyhedral nuclei. The controlling factor here appears to be elastic strain energy.[38] For example, a spherical precipitate of silver ($a = 4{\cdot}0778$ Å) in a hole in a matrix of copper ($a = 3{\cdot}6080$ Å) which had originally contained as many copper atoms as it now contains silver atoms, would have a strain energy of about 75 cal./g. This is larger than the drop in free energy produced by the separation of a supersaturated solid solution into strain-free copper and strain-free silver. But if, as actually occurs, the silver forms thin sheets on (100) planes of copper, the thickening of the sheet requires little elastic energy, and the only energy is that required to compress the silver sheet in its own plane, which is about 25 cal./g.

Usually the misfit is much smaller than in the case just considered, and is further reduced by the precipitate forming on such habit planes and with such an orientation of its lattice that the lattices of the matrix and of the precipitate fit along the plane of contact with only very small strains. Sometimes the strain is still further reduced by the precipitate forming in a transitional lattice which, though not the most stable at the temperature of precipitation, fits into the lattice of the matrix with little strain energy. This occurs in both the examples discussed below.

The process of nucleation is thermodynamically reversible, and if an alloy which has formed nuclei at room temperature is heated for a short time the nuclei redissolve (except for the largest, which begin to grow rapidly owing to the increased rate of diffusion and the increased concentration of solute in the matrix), and the alloy reverts to the "as-quenched" state of a solid solution. This effect, discovered by Gayler,[39] was studied by various workers (e.g. Hartnagel [40]). The theory has been developed by Konobeevsky [41] on the simplifying

assumption that all nuclei in a given specimen have the same dimensions. Like Becker, he finds that small nuclei are unstable, but nuclei above a critical radius r' grow spontaneously. As these nuclei grow, the matrix becomes impoverished, and the nuclei again reach a stable equilibrium (subject to the condition that they all remain the same size) at a larger size r''. By combining these considerations with a formula of the type (12) he provides a satisfactory analysis of the experimental results of Petrov. (Unpublished work by Guinier shows that more complicated effects may occur.)

The strain energy in a plate of precipitate is smaller than that in a particle of precipitate of another shape, but it still cannot be reduced below a limiting value E for unit volume of precipitate so long as the lattices of the matrix and of the precipitate remain coherent. Consider a plate of radius R, and small thickness t. If it remains coherent with the matrix, its elastic energy is $\pi R^2 tE$, and its surface energy is $2\pi R^2\sigma$, where σ is the Becker surface energy of unit area. If the plate breaks away from the matrix and is free to recrystallize, its strain energy is reduced almost to zero,[42] while its surface energy is increased from σ to a much larger value Σ corresponding to a surface of misfit between the lattices. The condition that breaking away should reduce the energy is thus

$$\pi R^2 tE > 2\pi R^2(\Sigma - \sigma)$$

or

$$t > 2(\Sigma - \sigma)/E \quad . \quad . \quad . \quad . \quad . \quad (14)$$

For copper precipitating from silver this gives a critical thickness of about two atoms, while for Ag_2Al precipitating from aluminium the thickness is about 300 atoms. Both of these estimates are in general agreement with experiment.

V.—Comparison with Experiment.

The general principles discussed above are well confirmed by the work of Guinier,[43] Gayler,[44] and Mehl and Jetter [7] on the system aluminium–copper, in which the difference of atomic radii is large, and by the work of Guinier [43] and Geisler, Barrett, and Mehl [45] on the system aluminium–silver, where the difference of atomic radii is small. We shall discuss these systems briefly. Unpublished work by Guinier has revealed unexplained anomalies in the system aluminium–zinc.

In the first stage of precipitation in the aluminium–copper system, copper atoms segregate on (100) planes of the lattice, and the sheets of aluminium atoms on either side of these sheets of small copper atoms move closer together. This stage is reached at room temperature, and corresponds to the first rise in hardness.

In the second stage, which is reached after days at 100° C. or hours at 150° C., the hardness remains constant for some time, and then rises to the second maximum. Gayler's " light phenomenon " appears in the microstructure. The streaks in the Laue photographs caused by the plates of copper atoms contract into rows of spots at distances corresponding to a spacing of four (100) lattice planes. The structure consists of microscopic regions enriched in copper roughly to the composition $CuAl_2$. There is no long-range order within the microscopic regions, but a short-range order in which every fourth (100) plane is almost pure copper, while the planes adjoining these are also enriched.

The third stage appears only after softening has started, and corresponds to the formation of the tetragonal θ'-phase of Wassermann and Weerts. This phase forms in thin sheets on (100) planes in the matrix, and the lattices of matrix and precipitate fit exactly in the plane of contact. The lattice spacings normal to the plane of contact are 1·45 Å in the precipitate and 2·02 Å in the matrix, and there is evidence that the matrix and precipitate pull each other into register along the edges of a sheet at intervals of 10·1 Å, corresponding to the fact that 10·1 Å represents almost exactly 5 lattice spacings in the matrix and 7 lattice spacings in the precipitate.

In the fourth stage the transitional lattice of θ' decomposes into stable $CuAl_2$. There is no coherence between the lattices of the matrix and the precipitate, and the precipitate lattice has a large number of possible orientations in the matrix, which are determined by the mechanism of its formation from θ'.

Corresponding to the small difference in atomic radii in the aluminium–silver system (Al, $a = 4{\cdot}0414$ Å; Ag, $a = 4{\cdot}0778$ Å), the initial nuclei in this system are equi-axed, and may be thought of as periodic fluctuations in the concentration of silver with a wave-length of about 70 Å initially, increasing to about 140 Å after an hour's annealing at 150° C. In these initial nuclei two out of every three (100) planes are enriched in silver. There is no variation of concentration from one (111) plane to the next, although (111) is the habit plane of the new phase formed in the second stage.

The second stage begins when the composition Ag_2Al is attained in the nuclei, and consists of a sliding of (111) layers over one another to convert the close-packed cubic lattice into the hexagonal lattice of the transitional γ'-phase. The strain which keeps this new phase coherent with the lattice causes the alloy to be hard and give blurred X-ray lines.

The final stage in this system is the breaking-away of the hexagonal lattice to form the stable γ-phase, with very small changes of lattice

spacing (a goes from 2·858 to 2·879 Å, c from 4·607 to 4·573 Å). The aluminium and silver atoms are disordered on both γ' and γ lattices.

VI.—Relation of Strain, Diffusion, and Precipitation.

Radavich and Smoluchowski [46] find that hydrostatic pressure has little effect on the rate of diffusion, a pressure of 7000 kg./cm.^{2} reducing D by only 30%. Gertsriken and Golubenko [47] find that stress (? within the elastic limit) has no effect on the rate of diffusion, but that plastic strain may increase D by a factor of 2–5. There are indications that diffusion may be very rapid while plastic deformation is actually in progress, and is also faster in a metal which has been deformed than in one which has been annealed, but these two effects do not seem to have been clearly separated.

The effect of a pressure gradient on diffusion has been discussed by Konobeevsky.[48, 49] Large atoms tend to diffuse into regions of elastic dilatation and small atoms into regions of elastic compression. In this way the stress is released, but the strain (regarded as a measure of the deformation of the lattice from its original form in which lattice planes are truly flat) is not removed. The strains are stabilized by this process, and the initial effect of annealing a cold-worked unsaturated solid solution may be an increase in the hardness. The release of stress reduces the tendency to recrystallization.[50] The process is analogous to the reduction of external stress by diffusion which has been discussed as a mechanism of internal friction in metals by Gorski,[51] Snoek,[17] Polder,[18] and Zener.[52]

The theory is based on a balancing of the release of strain energy caused by the diffusion of solute atoms, which is large if the change of lattice parameter with change of concentration $da/d\alpha$ is large, against the increase of free energy caused by the non-uniform distribution of solute atoms, which we have already seen to be proportional to $\partial^2F/\partial\alpha^2$. If $\partial^2F/\partial\alpha^2$ is small, it is possible for internal stresses to set up fluctuations of concentration of 2–4% in a solid solution of mean concentration 10–15%.

Konobeevsky has pointed out that the internal stresses surrounding a nucleus of precipitate always act in such a way as to increase the rate of diffusion towards the nucleus, and that this effect may increase the rate of diffusion as much as ten-fold. The misfit of the nucleus in the lattice sets up stresses in the matrix, but, at least for a spherical nucleus,[53] these are pure shears without dilatation, and may be neglected. The concentration gradient surrounding the nucleus causes hydrostatic stresses which can only be relieved by a smoothing out of the concentration gradient. The energy of these hydrostatic stresses is an additional contribution to the "driving force" of diffusion.

The effect of plastic strain immediately after quenching on the process of age-hardening has been studied by Gayler.[54] It is well known that after slight deformation the nuclei of precipitation are formed preferentially in the slip bands. This is consistent with the theory, because the elastic and surface energies associated with the formation of a nucleus in a perfect crystal may be greatly reduced if the nucleus forms in a region already heavily deformed. We thus expect ageing in a cold-worked metal to be quicker than in a metal annealed and quenched for four reasons:

(*a*) Easier formation of nuclei in strained regions;
(*b*) Accelerated diffusion due to internal stress gradients;
(*c*) Reduction in the distance atoms diffuse before reaching the nearest nucleus, owing to the increased number of nuclei;
(*d*) Accelerated diffusion due to general "loosening of the lattice".

The first effect is clearly established. The last is excluded by Gayler's work. For "loosening of the lattice" would result in a reduction of the activation energy for diffusion, while experimentally the temperature dependence d (log rate)$/d(1/T)$ is unaltered by cold work. Gayler's results indicate that the later stages of ageing are accelerated by cold work by a factor which is independent of the temperature of ageing, and that the effect is a genuine acceleration of the whole process and not simply the suppression of an incubation period. This suggests that (*c*) is the most important factor in the later stages.

The effect of precipitation on the mechanical properties has been discussed in terms of the theory of dislocations. According to this theory, plastic deformation of metals occurs principally by the motion of linear imperfections of the lattice across the glide planes of the crystal. When a dislocation moves completely across a glide plane from one side to the other, the material on one side of the glide plane is displaced relative to the material on the other side by a distance a. If the crystal is subjected to an external shear stress S, it is easily shown [55] that there is an effective force Sa on unit length of the dislocation, causing it to move in the direction which will relieve the external stress. The dislocation is not straight and rigid, but although it is flexible it has an energy per unit length of the order of μa^2, where μ is the rigidity of the material, and consequently, like a soap film, it can only bend into a curve of small radius under the influence of a large force. A stress $p\mu$ will bend a dislocation into a curve with a radius of order a/p. In

considering the effect of internal stresses we must distinguish between those stresses which are constant over large distances, and those which have opposite directions in regions separated by only a few atoms.

In the first case,[53] which is that of a precipitation-hardened alloy, the dislocation is effectively flexible, and forces acting on one part of its length cannot influence the movement of other parts. The dislocation as a whole can only move if the external stress S is large enough to overcome the internal stress S_0 (or rather the corresponding internal strain) over the whole length of the dislocation. The elastic limit of the crystal is thus of order S_0.

In a solid solution of concentration α the distance between neighbouring solute atoms is of order $\alpha^{-\frac{1}{3}}a$, and the internal stress on the dislocation changes direction in successive elements of its length separated by this distance. The dislocation cannot bend into a curve of this small radius under the influence of the existing internal stresses, and may be thought of as effectively rigid over a length L. In a preliminary study [56] L was taken to be $1000a$; a more detailed analysis is in progress. The force produced by the internal stresses on this length L changes sign $\alpha^{\frac{1}{3}}L/a$ times, and the contributions of opposite sign mostly cancel each other. The expected statistical residue is $(\alpha^{\frac{1}{3}}L/a)^{\frac{1}{2}}$ times the force acting on any one region of constant sign, and the total force acting on the length L is that which would be produced by an internal stress $(\alpha^{\frac{1}{3}}L/a)^{-\frac{1}{2}}S_0$. The solid solution flows plastically when the external stress is equal to this.

The value of S_0 should be much the same for the solid solution and for the precipitated alloy in its state of maximum hardness. The factor $(\alpha^{\frac{1}{3}}L/a)^{\frac{1}{2}}$, which is of order 25 in practical cases, represents the greater effectiveness of precipitation hardening in comparison with solution hardening.

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