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The strains produced by precipitation in alloys

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If the process of diffusion in metals results simply in the interchange of pairs of atoms large strains must be set up when a new phase precipitates in an alloy. The strain energy involved is calculated for particles of precipitate of various shapes, and is found to be least if the precipitate forms thin plates. The shape of the particle actually formed is influenced by this energy, by the degree of supersaturation of the solid solution, and by surface effects; the calculated shape is shown to agree reasonably well with that observed experimentally.

1. Introduction

A preliminary account of some calculations of the strains produced by precipitation in alloys has already been given. (Mott and Nabarro (1940) referred to as I in the present paper, and Nabarro (1940) referred to as II.) In this paper the relation there assumed for the dependence of the strain energy of a particle on its shape is developed, and the relation of the theory to the experimental results is more fully discussed. It is found that the strain energy is large, and if the lattice of the precipitate remains continuous with that of the matrix the energy can only be reduced by a factor of the order of five by changes in the shape of the precipitated particles. If the lattice of the precipitate breaks away from that of the matrix, so that the stress in the inclusion is a simple hydrostatic pressure, the strain energy tends to zero if the particles of precipitate take the form of thin sheets. The dynamics of the precipitation, on the other hand, encourages the formation of spherical particles, as does the surface energy of the precipitate, and from a consideration of these factors a formula is deduced which represents the shape of the particles at any stage of their growth. The calculations of strain energy are contained in § 2, and the results obtained are applied in § 3.

2. Calculation of strain energies

The application of the theory of elasticity to a study of internal strains is subject to three limitations. The elastic equations are usually intractable unless the medium is isotropic, and even in the case of metals whose lattice

has cubic symmetry the condition of isotropy is usually not even approximately fulfilled. Then the scale of the internal strains is often small, so that the strain is only constant over a region of a few atoms, and the elastic equations of a continuous medium cannot properly be applied. Lastly, the strains themselves are large, perhaps as great as 10%, so that Hooke's law must break down and it seems likely that in consequence the elastic energies actually involved will be smaller than those calculated. These large strains are larger than the technical breakdown strain, but there is ample evidence that mechanical breakdown is a structure-sensitive property dependent for its initiation on a few sensitive spots, and it seems plausible that internal strains should be limited only by the theoretical breakdown strain, which is much greater than that observed experimentally. Quinney and Taylor (1937) have shown that an energy of 0·5–1 cal./g. can be stored in a metal by cold work, and this is greater than the energy of the metal stretched homogeneously to its breaking point, so that there is direct evidence that very large internal strains can exist in a metal. For example, the tensile strength of copper is certainly less than 30 kg./mm.^{2} and its Young's modulus is 10,400 kg./mm.^{2}, so that it cannot acquire an energy of more than 0·01 cal./g. by homogeneous extension without breaking, while Quinney and Taylor have observed the release of 0·5 cal./g. on annealing a twisted copper wire.

Strains may be produced in a metal by cold work, by such agencies as thermal expansion and magnetostriction, and by precipitation in alloys. The nature of the strains in a cold-worked metal is not easy to determine, although experimental evidence has been collected by Wood (1935), Brindley (1940) and others, and certain possible types of strain have been discussed theoretically by J. M. Burgers (1940). An alternative model of these strains has recently been put forward by W. L. Bragg (1940), but they seem to be of so complicated a nature that their influence on the properties of the metal is difficult to discuss in detail. The same is true of thermal and magnetostrictive strains, although Kersten (1935) and Dillinger and Bozorth (1935) have shown how magnetostrictive strains fix an upper limit to the initial permeability of the metal. It is the strains due to the precipitation of a new phase in an alloy which seem most likely to lend themselves to detailed analysis, because if the new phase is present only in small quantities the strained region round each particle of precipitate is separated from its neighbours by a region of the lattice which is almost free from strain. Each particle can be considered separately as a nucleus of strain in an infinite unstrained medium, and the type of strain produced can be visualized much more readily than the random interacting strains due to cold work.

According to the dislocation theory of slip in metals developed by G. I. Taylor and others, the strength of a precipitation-hardened alloy is proportional to some mean value of the shear produced in the lattice of the matrix by the presence of particles of inclusion. This shear can only be calculated when the shape of the particles of precipitate is known, and the particles must have a tendency to precipitate in such forms that the energy of the shear is as small as possible. The energy of a flat sheet of precipitate which has not broken away has been calculated in II. The discussion of § 3·1 shows that a particle which has broken away produces the same external strain as it would do if it were fluid, and in §§ 2·1–2·4 the strain energy due to an inclusion of compressed fluid is calculated for inclusions of certain specially simple shapes. These results are exhibited graphically and a smooth curve through them (figure 2) is taken to represent the dependence of the strain energy on the shape of the particle in the case of precipitates which have broken away.

2·1. The simplest type of inclusion which gives rise to internal strains is a sphere of unstrained radius $(1+\delta)\,r_0$ inserted in a spherical hole of radius r_0 in the matrix. The nature of the strain in this case has been discussed in I: the total elastic energy of a sphere of volume $V = \frac{4}{3}\pi r_0^3$ and bulk modulus K in a matrix of rigidity μ is

$$6\mu V\delta^2 \Big/ \left(1+\frac{4\mu}{3K}\right). \tag{1}$$

2·2. The case of a cylindrical inclusion may be treated similarly. The displacement at distance r from the axis must be of the form $\alpha r + \beta r_0^2 r^{-1}$. When the inclusion is incompressible a displacement $\frac{3}{2}\delta r_0^2 r^{-1}$ increases a volume V in the inclusion by $3\delta V$ with an expenditure of energy equal to $\frac{9}{2}\mu V\delta^2$.

2·3. An infinite block of material contains an almost spherical cavity bounded by the surface

$$r = r_0\{1+\epsilon P_\nu(\cos\theta)\}. \tag{2}$$

It is subject to a displacement which is the gradient of a potential

$$U = \kappa r_0^3\left\{\frac{1}{r}+k\frac{r_0^\nu}{r^{\nu+1}}\epsilon P_\nu\right\}. \tag{3}$$

Then (Love 1927) it is in equilibrium under the action of forces acting on the internal surface only.

Expressions for the strains are given by Love, but his non-diagonal components are twice the tensor components used here, and denoted by e_{ij}.

The components of stress p_{ij} are given by

$$p_{ij} = 2\mu e_{ij} + \lambda \delta_{ij} e_{kk}, \tag{4}$$

where the repeated index implies a summation and λ and μ are the usual elastic constants as defined by Love. In this case $e_{kk} = 0$, and at the surface where r is given by (2) the displacements and strains reduce to

$$\begin{aligned}
u_r &= -\kappa r_0 \{1 + (k\overline{\nu+1} - 2)\,\epsilon P_\nu\} + O[\epsilon^2] \\
u_\theta &= -\kappa r_0\, k\epsilon P'_\nu \sin\theta + O[\epsilon^2] \\
u_\phi &= 0 \\
e_{rr} &= \kappa\{2 + (k\overline{\nu+1}\,\overline{\nu+2} - 6)\,\epsilon P_\nu\} + O[\epsilon^2] \\
e_{\theta\theta} &= -\kappa + O[\epsilon] \\
e_{\phi\phi} &= -\kappa + O[\epsilon] \\
e_{\theta\phi} &= 0 \\
e_{\phi r} &= 0 \\
e_{r\theta} &= \kappa\,\overline{\nu+2}\, k\epsilon P'_\nu \sin\theta + O[\epsilon^2].
\end{aligned}$$

The direction cosines of the normal to the surface are

$$g_r = 1 + O[\epsilon^2], \quad g_\theta = -\epsilon P'_\nu \sin\theta + O[\epsilon^2], \quad g_\phi = 0, \tag{5}$$

while the surface element is

$$dS = r_0^2(1 + 2\epsilon P_\nu) \sin\theta\, d\theta\, d\phi + O[\epsilon^2]. \tag{6}$$

The elastic energy of the matrix is equal to the work done by the surface forces, which is

$$-\tfrac{1}{2}\iint p_{ij} g_i u_j\, dS = 8\pi\mu r_0^3 \kappa^2 + O[\epsilon^2]. \tag{7}$$

The normal pressure is $p_{ij} g_i g_j = 2\mu e_{rr} + O[\epsilon^2]$,
and this is independent of θ as far as quantities of the order of ϵ if

$$k\overline{\nu+1}\,\overline{\nu+2} = 6.$$

The original volume is

$$V = \tfrac{1}{3}\iint r^3 \sin\theta\, d\theta\, d\phi = \tfrac{4}{3}\pi r_0^3 + O[\epsilon^2]. \tag{8}$$

The change in volume is

$$\Delta V = \iint u_r r^2 \sin\theta\, d\theta\, d\phi = -4\pi\kappa r_0^3 + O[\epsilon^2]. \tag{9}$$

If, as in §§ 2·1 and 2·2, $\Delta V = 3\delta V$, then $\kappa = -\delta$ and the energy is

$$6\mu V\delta^2 + O[\epsilon^2].$$

2·4. The nature of the strain around a disk-shaped cavity containing a fluid under pressure is a subject which will be of considerable interest in the later discussion. Unfortunately, only an approximate solution has been obtained. An arbitrary displacement is considered, and although this does not correspond to a uniform hydrostatic pressure inside the cavity it is used to obtain an approximate value of the energy required to enlarge the cavity.

It is possible to obtain upper and lower limits for this energy. In the first place we shall prove the general theorem that a given increase in the volume of the cavity is obtained with the least expenditure of energy by the application of a uniform hydrostatic pressure alone.* The arbitrary displacement is then considered, and the forces on the boundary which cause it are found to be of two kinds, a normal pressure and a tangential traction. The normal pressure is constant over most of the surface, and it is shown that the work done by the pressure on those parts of the surface where the pressure differs appreciably from this value is small compared with the total work. The displacements due to the normal and tangential forces cannot be separated analytically, but it is shown that the tangential forces are clearly of a kind to increase the volume of the cavity. Now by the general theorem the whole work done in the displacement is an upper limit for the work which would be done in producing the same increase of volume by hydrostatic pressure alone. But the work done by the normal forces alone produces a greater increase in volume than would be produced by a hydrostatic pressure doing the same amount of work. For suppose that the hydrostatic pressure is proportional to p, while the tangential forces are proportional to t, so that the energy can be expressed in the form $2W = ap^2 + 2bpt + ct^2$. Now a and c are necessarily positive, and since both p and t increase the volume the value of b must also be positive in this case. The co-ordinate corresponding to p, the increase in volume, is $P = ap + bt$. The work done by the pressure is $\frac{1}{2}Pp = \frac{1}{2}(ap^2 + bpt)$. If this work had been done in the absence of t the internal pressure would have risen to $p' = [(ap^2 + bpt)/a]^{\frac{1}{2}}$, leading to an increase in volume $P' = [a(ap^2 + bpt)]^{\frac{1}{2}}$. Thus $P^2 - P'^2 = abpt + b^2t^2$, which is positive, and so the work done by the normal forces only represents a lower limit to the work required to produce the actual increase in volume.

We shall now prove the general theorem quoted above. Suppose the cavity is enlarged by the application of arbitrary surface forces. Fill the enlarged cavity with an incompressible fluid, and release the surface forces. If the system is in equilibrium, the forces reduce to a uniform pressure. If not, the system moves to another state where the cavity has the same volume, while the incompressible fluid necessarily has the same (zero) elastic potential

* This was pointed out to me by Professor Mott.

energy. But the system as a whole has gained kinetic energy, so that the original enlargement of the hole cannot have been conducted with the least possible expenditure of work.

The arbitrary displacement which will be considered is obtained as follows. The gravitational potential of an ellipsoid of semi-axes a, b, c at external points is (Thomson and Tait 1883)

$$U = -\kappa abc \int_q^\infty \left(1 - \Sigma \frac{x^2}{a^2+u}\right) \frac{du}{\Pi(a^2+u)^{\frac{1}{2}}}, \tag{10}$$

where q is the greatest root in θ of

$$\Sigma \frac{x^2}{a^2+\theta} = 1. \tag{11}$$

The direction cosines of the normal to the ellipsoid at a point on its surface are

$$g_{nx} = \frac{x}{a^2}\left(\Sigma \frac{x^2}{a^4}\right)^{-\frac{1}{2}}, \text{ etc.} \tag{12}$$

Since U is a potential function, its gradient represents an elastic displacement which is in equilibrium under the action of forces at the surface of the ellipsoid $\theta = 0$ alone. The components of displacement are

$$u_x = \frac{\partial U}{\partial x} = 4\kappa abc A^2 x, \text{ etc.}, \tag{13}$$

and the tensor components of strain are

$$\left.\begin{aligned} e_{xx} &= \frac{\partial^2 U}{\partial x^2} = 4\kappa abc A^2 - 4\kappa \frac{x^2}{a^4}\left(\Sigma \frac{x^2}{a^4}\right)^{-1} \\ e_{yz} &= \frac{\partial^2 U}{\partial y \partial z} = -4\kappa \frac{yz}{b^2 c^2}\left(\Sigma \frac{x^2}{a^4}\right)^{-1}, \text{ etc.}, \end{aligned}\right\} \tag{14}$$

where

$$A^2 = \frac{1}{2}\int_0^\infty \frac{1}{a^2+u} \frac{du}{\Pi(a^2+u)^{\frac{1}{2}}}, \text{ etc.} \tag{15}$$

The normal displacement of a point on the surface $\theta = q = 0$ is $u_n = g_{nx} u_x$, and the normal strain is $e_{nn} = g_{ny}\, g_{nz}\, e_{yz}$. The dilatation represented by the sum e_{kk} vanishes, and so from (4) the components of stress are given by $p_{ij} = 2\mu e_{ij}$ and the normal stress is

$$p_{nn} = -8\kappa\mu\left[1 - abc\left(\Sigma \frac{x^2}{a^4}\right)^{-1} \Sigma \frac{x^2}{a^4} A^2\right].$$

The work done by the normal stress is

$$W_1 = -\tfrac{1}{2}\iint p_{nn} u_n \, dS. \tag{16}$$

These general formulae will now be applied to the special case of an oblate spheroid $a = b > c$. A suitable co-ordinate system is provided by the transformation

$$x = at\cos\theta\cos\phi, \quad y = at\cos\theta\sin\phi, \quad z = ct\sin\theta. \tag{17}$$

The energy given by (16) can now be evaluated. The increase in volume is

$$\Delta V = \iint u_n \, dS = \tfrac{16}{3}\pi\kappa a^2 c. \tag{18}$$

The volume is $V = \frac{4}{3}\pi a^2 c$, and in the previous notation $\Delta V = 3\delta V$, so $\kappa = 3\delta/4$. In the case $c = a$ the substitution of this in (16) leads to the expression $6\mu V\delta^2$ already obtained for the work required to enlarge a sphere. When $c < a$ the energy may be expanded as a power series in c/a. The first term is of order $a^2 c$, which is the volume of the inclusion, but its coefficient vanishes, and the expansion is of the form

$$W_1 = \tfrac{9}{2}\pi\frac{c}{a}\mu V\delta^2 + O[c^3]. \tag{19}$$

When $a \gg c$, the normal pressure p_{nn} is given by

$$p_{nn} \sim \frac{\frac{1}{2}\pi ac + c^2\cot^2\theta + O[c^3]}{a^2 + c^2\cot^2\theta}. \tag{20}$$

Since $a \gg c$, this remains nearly constant when $\sin\theta > (c/a)^{\frac{1}{2}}$, and it changes value again when $\sin\theta = c/a$. The only appreciable contribution to the integral (16) for W_1 comes from the region where the pressure is constant. For in this region $|\sin\theta| > (c/a)^{\frac{1}{2}}$ the expression (20) is of order $\frac{1}{2}\pi c/a$, while $(A^2\cos^2\theta + C^2\sin^2\theta) \sim \sin^2\theta/a^2 c$ and the range of integration is almost $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$, so that the integral with respect to θ is of order $\pi/3a^3$. In the region $|\sin\theta| < (c/a)^{\frac{1}{2}}$ the expression (20) $\leqslant 1$, while

$$(A^2\cos^2\theta + C^2\sin^2\theta) < 2/a^3$$

and the range of integration is $-(c/a)^{\frac{1}{2}}$ to $(c/a)^{\frac{1}{2}}$, so that the contribution of this part of the range to the integral is of order $4(c/a)^{\frac{1}{2}}/a^3$, which is small compared with the whole integral.

The total work done by all the surface forces is

$$W_2 = -\tfrac{1}{2}\iint p_{ij} u_i g_{nj} \, dS.$$

For a spheroid this becomes

$$W_2 = 64\pi\kappa^2 a^4 c^2 \mu[\tfrac{2}{3}A^2 + \tfrac{1}{3}C^2 - a^2 c(\tfrac{2}{3}A^4 + \tfrac{1}{3}C^4)]. \tag{21}$$

When $a = c$ this again reduces to $6\mu V\delta^2$, but when $c < a$ it can be expanded in the form

$$W_2 = 9\pi \frac{c}{a} \mu V \delta^2 + O[c^3]. \tag{22}$$

It only remains to be shown that the tangential stresses produce an increase in volume. There are two principal tangents, the one which is also tangent to a circle of latitude, whose direction cosines are

$$\left.\begin{aligned} g_{lx} &= -\sin\phi = -y(x^2+y^2)^{-\frac{1}{2}}, \\ g_{ly} &= \cos\phi = x(x^2+y^2)^{-\frac{1}{2}}, \\ g_{lz} &= 0, \end{aligned}\right\} \tag{23}$$

and the meridional tangent whose direction cosines are

$$\left.\begin{aligned} g_{mx} &= -\frac{xz}{c^2}\left(\Sigma\frac{x^2}{a^4}\right)^{-\frac{1}{2}}(x^2+y^2)^{-\frac{1}{2}}, \\ g_{my} &= -\frac{yz}{c^2}\left(\Sigma\frac{x^2}{a^4}\right)^{-\frac{1}{2}}(x^2+y^2)^{-\frac{1}{2}}, \\ g_{mz} &= \frac{x^2+y^2}{a^2}\left(\Sigma\frac{x^2}{a^4}\right)^{-\frac{1}{2}}(x^2+y^2)^{-\frac{1}{2}}. \end{aligned}\right\} \tag{24}$$

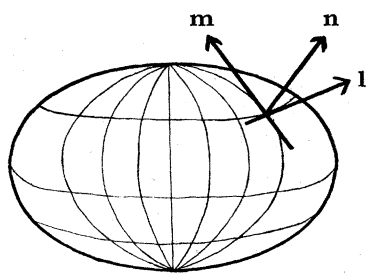

FIGURE 1. The principal directions **l**, **m**, **n** on a spheroid.

From a simple calculation or from the symmetry of the problem it follows that the strain e_{ln} and so the corresponding stress p_{ln} vanish. The meridional stress is

$$\begin{aligned} p_{mn} &= 2\mu e_{mn} = 2\mu e_{ij} g_{mi} g_{nj} \\ &= 8\kappa\mu(C^2 - A^2)\frac{(x^2+y^2)^{\frac{1}{2}} z}{c\Sigma x^2/a^4}. \end{aligned} \tag{25}$$

This vanishes, as it should, for a sphere where $c = a$ and $C = A$. But when $c < a$ this expression has the sign of $(x^2 + y^2)^{\frac{1}{2}} z$, so that the stress on the surface is always directed from the pole to the equator. The stress is proportional to $\sin\theta \cos\theta/(a^2 \sin^2\theta + c^2 \cos^2\theta)$. The angle χ between $\mathbf{m}$ and the z axis is given by $c \tan\chi = -a \tan\theta$, and as long as $\theta > c/a$ the tangential stress represents a force roughly parallel to the equatorial plane, and tending to enlarge the cavity. When $\theta > (c/a)^{\frac{1}{2}}$ the stress is of order $1/a^2$, and acts over an area of order a^2. The resultant force vanishes, and the stress can thus be represented by two "dipoles" each formed by forces of the order unity separated by a distance of the order of a, so that the strength of the dipoles is of order a. When $(c/a)^{\frac{1}{2}} > \theta > (c/a)$ the stress is of order $1/a^2c$ and acts over an area of order ac, so that the dipole strength is of order a again. When $\theta < c/a$ the tangential stress has a considerable component parallel to the axis and tending to reduce the volume. The stress is of order $1/c^2$ and acts over an area of order c^2. But while the resultant component of force again vanishes, for this axial component the force on each element is balanced, not by the force which is its image in the axis and so is a distance of the order a away, but by the force on the element which is its image in the equatorial plane and so is a distance of the order c^2/a away. Thus the forces tending to reduce the volume form a dipole spread along the equator, the strength of which is only of order c^2/a, and produce deformations which are only appreciable in the equatorial belt. That is to say, the stresses tending to reduce the volume are confined to the equatorial belt. They are large, but as they act only over a small area they represent forces of the same order as those tending to increase the volume. Since, moreover, each force is balanced by an opposite force only a short distance away they produce only local deformations which cannot appreciably reduce the volume.

It has thus been shown that the tangential forces produce an increase in the volume of the cavity, and so it is established that the values W_1 and W_2 given by (19) and (22) do represent lower and upper limits for the least work required to increase the volume of an oblate spheroid. It seems likely that the work done by the traction will be rather ineffective in increasing the volume, so that probably the true value lies considerably nearer to W_1 than to W_2.

2·5. A further case which will be considered is that of the disturbance caused by inserting into a cavity in the matrix a body of the same shape but of the wrong size, and of the same rigidity. The natural volume of the hole is V, while that of the inclusion is $V(1 + 3\delta)$. The elastic equations are satisfied if the displacement in the matrix is given by $u_x = \gamma \dfrac{\partial U}{\partial x}$, etc., and that in the

inclusion by $u_x = \gamma \frac{\partial U}{\partial x} + \delta x$, etc., where U is the gravitational potential of the inclusion and γ is a suitable constant.The energy in this case is given by (1) whatever the shape of the hole.*

3. The influence of the strain on the process of precipitation

The energies associated with these internal strains are large, of the order of the chemical heats of solution of one metal in another. For whatever may be the nature of the precipitation process there can be little doubt that it is primarily one of diffusion, and while the mechanism of diffusion is in its turn not yet fully understood it seems certain that diffusion simply results in the interchange of pairs of atoms occupying definite lattice sites. If an island of one metal is formed by diffusion in a matrix of the same crystal structure but having an atomic spacing smaller by δ, it behaves as a strained inclusion whose elastic energy is given by a formula of the type (1). The value of δ is in many cases of the order 3–4 %, while the elastic constants of a pure metal are of the order 10^{12} dynes/cm.^{2}. The energy is thus of the order 4×10^9 ergs/cm.^{3} of precipitate, or taking the density of the metal as 5, the energy is 20 cal./g. of precipitate. In the case of silver precipitating from copper, δ has the unusually high value of 12 %, so that the energy may be of the order of 100 cal./g. Unless these large energies were released the process of precipitation would be impossible, for it would involve an increase in the energy of the system and a decrease in its entropy, so that the free energy would necessarily increase.

3·1. If precipitation takes place solely at the crystal boundaries or if the original crystal lattice breaks up into crystallites, these strains are not produced, for the lattice of the precipitate is free to expand, and there is ample evidence (e.g. Ageew, Hansen and Sachs 1930; Cohen 1936) that both of these methods of releasing the strain are effective. But there is also evidence (e.g. Derge, Kommel and Mehl 1937; Calvet, Jacquet and Guinier 1939) that particles of precipitate are formed within single crystals, which remain apparently continuous. In the latter case it is possible that the strain has been released by some recrystallization of the matrix in the neighbourhood of the inclusions, for it is well known that strain will induce recrystallization at temperatures considerably lower than those at which it can occur in the unstrained metal (Burgers 1934).

If, as Wagner suggests (Wagner and Schottky 1930), the mechanism of

* This result is due to Mr M. M. Crum.

diffusion is provided by the empty lattice sites which must always arise in a metal in thermodynamical equilibrium, it would be possible for the strain around a particle of silver in copper to be released by the migration of the holes in the copper to the boundaries of the silver inclusion. Since these holes can only be formed at the surface of a crystal, and the number originally present is extremely small, such an explanation of over-ageing and softening would require that a large crystal softened much more slowly than a small. There does not seem to be explicit evidence against such a relation, but it seems to be generally agreed that crystal size is in fact not an important factor in determining the rate of softening.

It is commonly stated that the strain is relieved by the agglomeration of the precipitate into large particles. However, all the formulae obtained in § 2 show that the energy of an isolated inclusion of given shape is proportional to its volume, so that in a dilute solution where the particles of precipitate are separated by distances large compared with their size the total strain energy associated with particles of a definite form depends only on the total volume of the precipitate and not on the volumes of the individual particles. For spherical particles of radius r_0 separated by distances r the mean minimum strain which in Taylor's theory determines the strength is $\epsilon r_0^3 r^{-3}$, where ϵ is given in I as a constant depending only on the properties of the two phases concerned. But $r_0^3 r^{-3}$ is simply the volume concentration of the precipitated phase, and so the hardness is independent of the size of the individual particles if their total volume remains constant. General dimensional considerations show that this must also be true for particles of any definite shape. This statement is apparently incompatible with the existence of precipitation hardening in the usual sense, and provides an example of the limitations of the theory, which obviously loses all quantitative value if an attempt is made to apply it to the solid solution in which the included particles are single atoms. The principal factor which reduces the hardness of the solid solution below that of the precipitation-hardened alloy into which it may be converted is probably that a dislocation is not seriously impeded by an adverse strain spread over a region small compared with its own "wave-length". Such a small obstacle may be surmounted in two ways, either by the dislocation breaking and reforming on the far side, or by thermal fluctuations momentarily reducing the adverse strain. The recent calculation of Peierls (1940) that the wave-length of a dislocation is only a few atomic distances shows that the detailed consideration of these effects is likely to be somewhat difficult.

Provided the precipitated particle does not break away from the matrix its energy can only be reduced to a limited extent by changes of shape. For

the particular case in which the inclusion has the same rigidity as the matrix Crum's calculation in § 2·5 shows that the strain energy is entirely independent of the shape, and it is reasonable to infer that as long as the rigidity of the inclusion remains comparable with that of the matrix its energy will not depend greatly on its shape.

W. L. Bragg has pointed out that a precipitate of flat sheets is likely to have a smaller strain energy than almost any other because the faces of the sheets are nearly free to expand, and that in an anisotropic material this lowering of energy will be particularly effective if the sheets are formed in a plane in which the lattice of the precipitate is easily stretched. It is interesting to estimate how great this reduction of strain energy would be in some particular case if the precipitate did *not* break away from the lattice. Silver precipitates from copper in sheets lying in the {100} planes of the copper. If the precipitate has not broken away these must also be {100} planes of the silver, and the calculation of II shows that in this case the energy is reduced by a factor less than 6.

It seems, then, that the strain can only be effectively released by allowing the precipitate to break away; that is to say, by allowing its lattice to become discontinuous with that of the matrix. In the further growth of the particle there need no longer be 1 : 1 correspondence between the points of the lattice of the particle and the lattice points of that part of the matrix which originally occupied the same space. The total number of atoms in the particle must, however, be equal to the number of missing points in the matrix lattice, for the interchange of atoms still takes place by simple diffusion in the main bulk of the matrix. This in fact means that the particle recrystallizes in such a way that the shear strain in it vanishes, and only a uniform compression remains; for example, the walls of a disk-shaped cavity bulge outwards owing to the increased volume of the atoms lying within it, and the inclusion recrystallizes so that atoms are removed from the compressed regions near the rim and replaced in the less strained central regions. That this internal recrystallization should occur at rather low temperatures is not surprising, for a particle of precipitate provides just the type of strained region which appears to act as a nucleus of recrystallization.

For any type of precipitate the misfit between the particle and the cavity which it occupies is accommodated partly by the deformation of the matrix and partly by that of the particle. For an inclusion which is effectively fluid the relative accommodations can easily be calculated. For suppose W_3 is the energy when the whole volume misfit 3δ is taken up by compressing the inclusion, and W_4 is the energy when the whole misfit is taken up by the matrix. Let the actual compression of the inclusion be $3x$, so that the enlargement of

the cavity is $3(\delta - x)$. The total energy is $[x^2 W_3 + (\delta - x)^2 W_4]/\delta^2$, which has its minimum value W_5, given by

$$\frac{1}{W_5} = \frac{1}{W_3} + \frac{1}{W_4}, \tag{26}$$

when $x = W_4\delta/(W_3 + W_4)$. If $W_4 \ll W_3$ then $x \approx 0$, $W_5 \approx W_4$ and the compressibility of the inclusion is unimportant.

To see how W_4 varies with the shape of the inclusion, it may be determined as a function of c/a for the spheroids with semi-axes a, a, c, which provide models of several simple figures of revolution—disks, spheres and needles. It may be written in the form

$$W_4 = 6\mu V \delta^2 E\left(\frac{c}{a}\right); \tag{27}$$

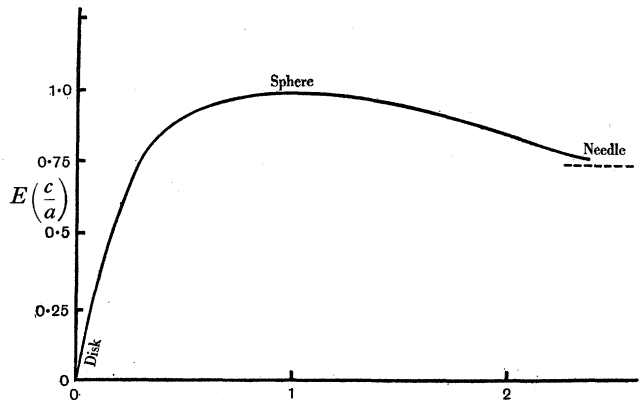

FIGURE 2. The elastic energy E of a particle of precipitate as a function of its shape. a is the equatorial diameter, c the polar diameter.

for the values of c/a for which it has been possible to calculate W_4 the energy does not depend on the elastic constant λ of the matrix, and any possible dependence of W_4 on this constant when c/a takes more general values will be neglected. When $c/a = \infty$, § 2·2 shows that $E = 3/4$. In § 2·3 put $n = 2$, when the cavity considered becomes a spheroid of semi-axes $r_0(1 - \frac{1}{2}\epsilon)$, $r_0(1 - \frac{1}{2}\epsilon)$, $r_0(1 + \epsilon)$, so that when $c/a = 1 + \frac{3}{2}\epsilon + O[\epsilon^2]$ then $E = 1 + O[\epsilon^2]$. Finally, when $c/a \ll 1$, § 2·4 shows that $W_1 < W_4 < W_2$, and taking $W_4 = W_1$ leads from (19) and (27) to $E \approx \frac{3}{4}\pi c/a$. A smooth curve through these points gives the graph of $E(c/a)$ shown in figure 2.

The explanation of the Widmanstätten structure (Derge, Kommel and Mehl 1937) and of the laminar structures observed by Chao and Taylor (1940) and Bradley (1940) is now apparent, for provided that the precipitate or

second phase has broken away its strain energy can be reduced to any extent simply by causing the precipitate to form in sufficiently flat plates or sheets.

3·2. The breaking away of a precipitate is hindered by the same forces which cause the formation of a regular lattice. To produce the discontinuity of the lattice requires roughly the same energy as the melting of a monatomic layer of metal at the surface of the inclusion. If the latent heat of melting is Λ and the density is ρ, the energy of melting is $\Lambda\rho$ cal./cm.^{3}. The surface energy of such a discontinuity is thus $d\Lambda J\rho$ ergs/cm.^{2}, where d is the interatomic distance and J the mechanical equivalent of heat. For copper this is equal to 410 ergs/cm.^{2}. This surface energy is most important for small particles of precipitate, and tends to make them spherical in shape, while the elastic energy favours an inclusion in the form of a thin sheet. It follows that there must be an equilibrium form which is the more flattened the larger the grain. Since the elastic energy is of order 4×10^9 ergs/cm.^{3} the tendency to form spherical grains becomes marked in the case of particles of linear dimensions less than about 10^{-7} cm., a few atomic distances.

Even in grains so large that surface energy no longer has any effect there is a dynamic equilibrium form which is determined by the rate of precipitation. If the grain is in the form of a moderately thick plate, the energy required to increase its thickness may be so large as to prevent precipitation on the faces, while precipitation at the edges still occurs, so that the plate elongates. For a very thin sheet the elastic energy is negligible even if the thickness is somewhat increased, while the rate at which precipitating atoms reach the faces is far greater than the rate at which they reach the edge, so that the sheet thickens. It is clear that the differential effect of the elastic energy in promoting elongation of the plate will be most effective when the average rate of precipitation is low, and so flat sheets should be formed especially in solutions which are only slightly supersaturated.

In a mathematical treatment of the growth of a flat inclusion it is again convenient to consider it as a prolate spheroid of semi-axes a, a, c. Its surface area is

$$S = 2\pi a^2 + O[c^2 \log a/c]. \tag{28}$$

If $a \gg c$ its elastic energy is W_4, which is equal to W_1, as given by equation (19), for W_3, the energy required to compress the inclusion into the original volume of the hole, is of order a^2c and is so large that practically all the misfit is taken up by shear in the matrix.

Suppose that when the concentration of precipitating atoms in the matrix is c their flux (number of atoms crossing unit area in either direction in unit

time) is cf, where it is assumed for simplicity that f is independent of c. The concentration (ratio of filled to total available lattice points) in the precipitate is 1. Let the heat of solution of the pure metal unstrained be U. Then in its solution the concentration is $e^{-U/kT}$ and the flux is $fe^{-U/kT}$. The outward flux from a surface such that the addition of a single atom requires strain energy $\overline{W}$ is $fe^{(\overline{W}-U)/kT}$. Let the "relative humidity" defined as (concentration)/(vapour pressure of unstrained metal) in the matrix be H. Then the inward flux from the matrix is $Hfe^{-U/kT}$ and the rate of deposition is

$$fe^{-U/kT}(H-e^{-\overline{W}/kT}) = fe^{-U/kT}(s-\overline{W}/kT), \tag{29}$$

if $\overline{W}$ is small compared with kT, and s, the "supersaturation", is $H-1$.

Let the inclusion be $2\mathscr{N}$ atoms thick and $2\mathscr{R}$ atoms in diameter. Then $a = d\mathscr{R}$, $c = d\mathscr{N}$, and the energy is

$$W = 2\pi d^3(3\pi\mu\delta^2\mathscr{N}^2\mathscr{R} + \Lambda J\rho\,\mathscr{R}^2). \tag{30}$$

The total number of atoms is $\frac{4}{3}\pi\mathscr{N}\mathscr{R}^2$, and so the average energy per atom required to increase the width is

$$\frac{3}{8\pi\mathscr{N}\mathscr{R}}\frac{\partial W}{\partial\mathscr{R}} = \frac{3d^3}{4}\left(3\pi\mu\delta^2\frac{\mathscr{N}}{\mathscr{R}} + 2\Lambda J\rho\frac{1}{\mathscr{N}}\right), \tag{31}$$

while for an increase in thickness it is

$$\frac{3}{4\pi\mathscr{R}^2}\frac{\partial W}{\partial\mathscr{N}} = \frac{3d^3}{4}3\pi\mu\delta^2\frac{4\mathscr{N}}{\mathscr{R}}. \tag{32}$$

So from (29)

$$\left.\begin{aligned}\frac{d\mathscr{R}}{dt} &= fe^{-U/kT}\left[s-\frac{3d^3}{4kT}\left(3\pi\mu\delta^2\frac{\mathscr{N}}{\mathscr{R}}+2\Lambda J\rho\frac{1}{\mathscr{N}}\right)\right],\\ \frac{d\mathscr{N}}{dt} &= fe^{-U/kT}\left[s-\frac{3d^3}{4kT}3\pi\mu\delta^2\frac{4\mathscr{N}}{\mathscr{R}}\right].\end{aligned}\right\} \tag{33}$$

These may be expressed in the form

$$\frac{d\mathscr{R}}{dt} = a - b\frac{\mathscr{N}}{\mathscr{R}} - c\frac{1}{\mathscr{N}},$$

$$\frac{d\mathscr{N}}{dt} = a - 4b\frac{\mathscr{N}}{\mathscr{R}}:$$

it is possible to sketch the solutions of (33) in the plane of $\mathscr{R}$ and $\mathscr{N}$, t being a parameter measured along the curves. This is done in figure 3, for arbitrary values of a, b, c, and it will be seen that the heavily drawn curve separates the

plane into two regions representing particles which can ultimately grow indefinitely and particles which ultimately vanish.

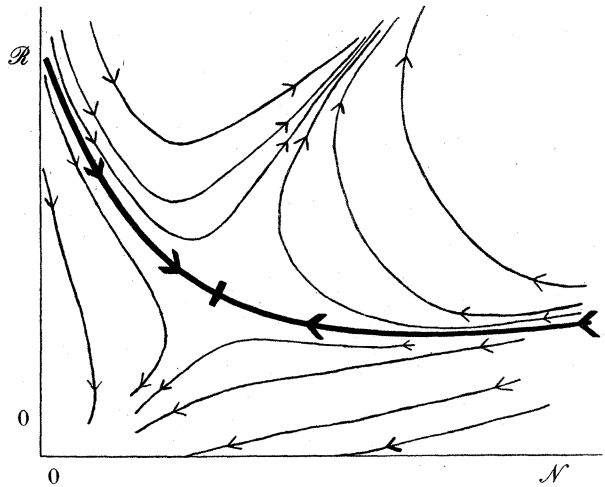

FIGURE 3. Curves showing the growth of particles of precipitate having various radii R and thicknesses $2n$, drawn for arbitrary values of the constants involved. The scale of n is much greater than that of R. Time is a parameter increasing along each curve in the direction marked by the arrows, and the heavily drawn curve separates the values of R and n representing particles which ultimately grow indefinitely from those representing particles which redissolve.

Even a large inclusion cannot grow unless the ratio of its breadth to its thickness is greater than $(p-q)/2a$, and it tends finally to grow with the constant ratio $\mathscr{R}/\mathscr{N} = (p+q)/2a$, where $p = a+4b$ and $q = (a^2+4ab+16b^2)^{\frac{1}{2}}$. The size of particle for which surface effects are important is given by $\mathscr{N} \leqslant 2c/a$. For such metals as copper or silver it will be sufficiently accurate to take the general values

$$d = 2{\cdot}7 \times 10^{-8}\ \text{cm.}, \qquad \mu = 3 \times 10^{11}\ \text{dynes/cm.}^2,$$

$$T = 600^\circ\ \text{K}, \qquad \Lambda\rho = 300\ \text{cal./cm.}^3,$$

while $$k = 1{\cdot}37 \times 10^{-16}\ \text{ergs/}^\circ\text{K.}, \qquad J = 4{\cdot}2 \times 10^7\ \text{ergs/cal.},$$

leading to

$$a = sfe^{-U/kT}, \quad b = 510\delta^2 fe^{-U/kT}, \quad c = 4{\cdot}55fe^{-U/kT}.$$

Since s is necessarily less than unity, and in fact is usually between 3 and 15 %, while δ is rarely as small as 1 % and may be as large as 12 %, it is clear that normally $b \gg a$. In this case the limiting ratio of breadth to thickness at which growth can occur is formally $\mathscr{R}/\mathscr{N} = 1/4$, which is not a flat disk.

This means that any sufficiently large flat disk will ultimately grow, although unless $\mathscr{R}/\mathscr{N} > 4b/a \approx 2000\delta^2/s$ its thickness will at first diminish. This value $\mathscr{R}/\mathscr{N} \approx 2000\delta^2/s$ is also the final dynamical equilibrium axial ratio for a large grain growing in a solution of supersaturation s. Surface effects are important as long as the thickness is less than $10/s$ atoms. The final limiting form is in its order of magnitude quite a good representation of the ratio of length to breadth actually observed in the Widmanstätten structures. For example, if the atomic volumes differ by 15% and the solubility at the temperature of anneal is 5% less than the solubility at the temperature at which the alloy is prepared, $3\delta = 0{\cdot}15$ and $s = 0{\cdot}05$, so that this expression predicts the formation of particles for which

$$\frac{\mathscr{R}}{\mathscr{N}} = \frac{2000 \times 0{\cdot}05^2}{0{\cdot}05} \approx 100,$$

so that the sheets are a hundred times as broad as they are thick. Experimental verification of the relation $\mathscr{R}/\mathscr{N} \sim \delta^2/s$ would be difficult, as the effective value of s in the neighbourhood of an inclusion is not immediately available to experiment, and also there is the risk that the results may be upset by recrystallization in small regions of the matrix on the boundary of the inclusion. It is certainly true that the structures observed by Mehl (Barrett, Kaiser and Mehl 1935) in copper-silver, where δ is large and s was small, were much finer than those formed in most other alloys.

These considerations alone in some cases explain the observed form of the age-hardening curves, particularly at low temperatures. The initial induction period is due to the difficulty of forming a nucleus of precipitation owing to the relatively large influence of surface effects. These effects have been discussed in more detail by Dehlinger (1932) and Becker (1940). (Dehlinger has also given a discussion (Dehlinger 1933) of precipitation and diffusion in which equations of the type of (33) are used.) Once precipitation has started the particles grow rapidly, and since s is fairly large they take the form of rather thick disks. This gives rise to a rapid increase in the hardness of the alloy. As the precipitation continues s decreases, and so the rate of hardening decreases. At the same time the disk can only continue to grow by taking the form of flatter disks or sheets, so causing a further reduction in the rate of hardening. Ultimately when s becomes small the increase of strain due to the slow increase in the total volume of the disks is not great enough to compensate for the decrease due to the changing shape of the disks, and a slow softening sets in. As the sheets become thinner their elastic energy becomes less important, so that the excess of vapour pressure near the face of a disk over that near the edge becomes smaller. The rate at which

the disks flatten becomes very slow, and so the softening process also becomes very slow.

This explanation is confirmed by Cohen's result (1936) that the attainment of maximum hardness and so the softening process itself during the precipitation of copper from silver in the temperature range 100–200° C have the same activation energy as the precipitation, which is undoubtedly a diffusion process. But it seems that softening is more usually due to recrystallization, for polished sections in many cases show that on long ageing the Widmanstätten sheets coagulate into globules (e.g. Calvet, Jacquet and Guinier 1939), while the breakdown of the matrix into smaller crystals is clearly shown in the X-ray photographs of Ageew, Hansen and Sachs (1930). Mehl (Barrett, Kaiser and Mehl 1935) observed in the same copper-silver system that a coarse precipitate causes the matrix crystal to break down, while the same amount of precipitate in a fine Widmanstätten structure does not induce recrystallization in the matrix, in agreement with the view adopted here that the two methods of release of strain are alternative.

3·3. These considerations apply to a large inclusion which has broken away, and show why such an inclusion retains a disk-like form as it grows. The orientation of the disk is determined by the processes forming the original nuclei of precipitation, as has been shown by Mehl and his collaborators (Derge, Kommel and Mehl 1937), Preston (1938) and Calvet, Jacquet and Guinier (1938). The latter two workers have carried out a very careful X-ray examination of single crystals of aluminium in which a precipitate of $CuAl_2$ is forming. They find that the copper begins to segregate in regions including between 1 and 5 {100} planes of atoms, and of a breadth increasing from about ten atomic distances in the early stages of the precipitation process to a thousand atomic distances after ageing for a few hours at 200° C or a few weeks at 150° C. After prolonged ageing at 200° C the sheets have become so thick that they diffract as a three-dimensional grating, and the crystal structure and orientation of the $CuAl_2$ phase which has precipitated can be determined. It is found that the two lattices are so orientated that the lattices of the matrix and of the inclusion fit together fairly accurately along the faces of the sheets. This result is confirmed by Mehl's work on other systems, for he finds that the precipitate usually comes out in sheets so orientated and with its own lattice in such a direction that the distributions of atoms in the plane of contact in the matrix and in the precipitate closely match.

The complete process of precipitation may be pictured as follows: Initially atoms of the precipitate segregate in an $(l\,m\,n)$ plane of the original

crystal, where $(l\,m\,n)$ is determined by the condition that there exists a plane $(\bar{l}\,\bar{m}\,\bar{n})$ in the precipitate such that the distribution of atoms in these two layers closely matches. Because of this matching the monatomic sheet of precipitate formed is not greatly stretched in its own plane, while at the same time the lattice is continuous and there is no surface energy of the kind discussed in § 3·2.* Then this region broadens and thickens. If the atomic volume of the precipitate is greater than that of the matrix by a fraction 3δ, while the planes in contact have equal atomic spacings, the separation of these planes in the precipitate must exceed the separation of parallel planes in the matrix by 3δ, so that considerable bulging of the lattice planes in the matrix must occur. But the previous considerations on this type of strain are still valid, and even this large displacement requires little energy if the precipitate is in the form of a sufficiently thin plate. The elastic energy required to keep the two lattices in register along their plane of contact is proportional to the volume of the precipitate, while the surface energy gained thereby is proportional to the surface area of the precipitate, and ultimately becomes smaller than the elastic energy. The lattice of the precipitate breaks away completely from that of the matrix, and the further growth of the particle is governed by the considerations of § 3·2.

It is not difficult to form a rough estimate of the thickness of a sheet when it breaks away. If the misfit between the two lattices in the matched planes is δ', the elastic energy of unit volume is given by a formula in II and the energy of a sheet $\pi\mathscr{R}^2$ atoms in area and $\mathscr{N}$ atoms thick is

$$\pi\mathscr{N}\mathscr{R}^2 d^3 (c_{11}+2c_{12})(c_{11}-c_{12})\delta'^2/c_{11}.$$

The surface energy is $\pi\mathscr{R}^2 d^3 \Lambda J\rho$, and these are equal when

$$\mathscr{N} = c_{11}\Lambda J\rho/(c_{11}+2c_{12})(c_{11}-c_{12})\delta'^2. \tag{34}$$

Taking the values of the constants for silver, this is roughly $\mathscr{N} = 170/\delta''^2$, where δ'' is the percentage misfit, so that a sheet of copper will break away from silver when it is only two atoms thick.

In a eutectic alloy two phases form from the same liquid. Elastic strain is again avoided by precipitation in sheets, but since there is no possibility of matching the precipitate lattice against that of the liquid matrix the sheets are not confined to a few preferred directions, and the typical eutectic structure of thin warped sheets is produced.

This work forms part of an investigation which is being carried out for the Department of Scientific and Industrial Research under the direction of

* The surface energy treated by Becker is due to order-disorder forces, and is present even when the precipitate has not broken away.

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