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THE INFLUENCE OF ELASTIC STRAIN ON THE SHAPE OF PARTICLES SEGREGATING IN AN ALLOY

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ABSTRACT. An estimate is given of the way in which the strain energy associated with a particle of precipitate depends upon the shape of the particle. It is shown that the energy can only be reduced if the precipitate forms in flat plates, and then only in the case of particles which have broken away from the lattice of the matrix. This dependence of strain energy on shape causes the precipitate to consist of plates of a shape similar to that observed in Widmanstätten structures.

When small quantities of a second phase precipitate out in an alloy, the internal strains set up affect both the hardness of the material and the nature of the precipitating particles. To fix ideas we may consider the precipitate to have the greater atomic volume. Without going further into the mechanism of diffusion, it is assumed that diffusion can only result in the interchange of pairs of atoms occupying definite lattice sites. In the process of segregation, particles of silver are formed which are larger than the vacant regions of the copper lattice which they occupy*. The elastic energies involved are large, and may exceed the chemical heat of solution of one phase in the other. Previous contributions to this discussion have shown that in the case of spherical particles the strain cannot be released by a simple agglomeration of the particles into larger spheres, and from general dimensional considerations it is clear that this result remains true whatever the type of strain, provided only that the distance between particles is large compared with their size, and that their size is large compared with a single atom. It will also be shown that even in the form of a sheet the silver atoms retain a large part of their elastic energy until the sheet breaks away.

What are the possible ways in which the strain energy can be released? The particle of precipitate is too big for the hole in which it is situated, and this misfit may be adjusted partly by compressing the silver and partly by increasing the size of the hole in the copper. The energy required to compress the silver until it fits the hole depends only on the size of the particle and not on its shape, so that changes in shape will not influence the accommodation of the precipitate. But, as W. L. Bragg has suggested, a disk-shaped hole in the copper can quite easily be expanded to accommodate the silver, for the faces of the disk will yield readily to internal pressure. The way in which the disk yields is shown by figure 1. What is now

* We use the Ag–Cu system as an example throughout.

needed is a calculation of the energy required to take a hole of volume of 1 cm^3 in a block of copper and increase its volume 1 per cent. This energy E depends upon the shape of the hole: the family of ellipsoids with semi-axes a, a, c represents disks, spheres or needles according to the value of c/a, and for this model the value of $E(c/a)$ is sketched as a function of c/a in figure 2. The details of the function are not yet known, but it is certain that the energy needed to enlarge the hole is greatest in the case of a sphere ($c=a$), and that it decreases to $\frac{3}{4}$ of this value as the sphere elongates to a needle ($c/a \to \infty$). For a very flat disk the energy tends to zero, and upper and lower limits for the slope of the tangent at the origin have been determined. An approximate value is taken in the following discussion.



Figure 1. Under internal pressure the rectangular section of a flat disk becomes lenticular.

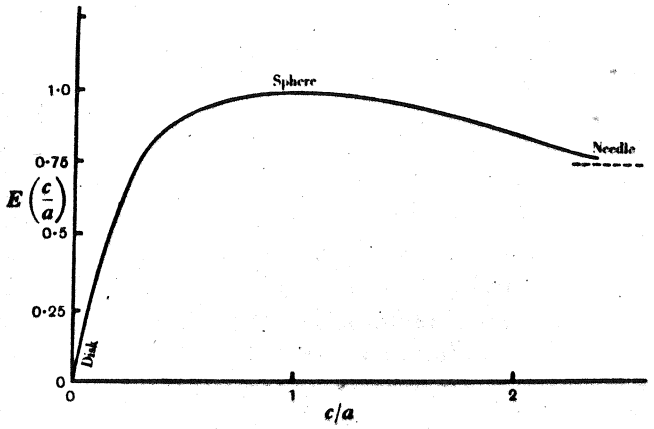

Figure 2. The elastic energy E of a particle of precipitate as a function of its shape. a is the equatorial diameter, c the polar diameter.

These considerations of elastic strain-energy seem to provide at least a qualitative explanation of the laminar precipitation which is observed in the Widmanstätten structures.

It is also possible to predict the influence of the degree of supersaturation of the silver on the shape of the particles which precipitate. The general nature of the effect is obvious. For suppose the alloy is so heavily supersaturated that every silver atom which diffuses to a nucleus sticks to it: then a nucleus originally long and thin gathers uniform coatings till its axes become nearly equal. On the other hand, in an alloy which is only slightly supersaturated, atoms can only precipitate on the edges of a disk-shaped nucleus, where they do not add much to the elastic energy. A layer of atoms precipitating on the face of the disk would cause an increase in the ratio c/a, and so an increase in the elastic energy of the particle which might be greater than the chemical free energy available.

If we insert approximate numerical values in the formula which is obtained, we find that for two phases whose atomic radii differ by 1 per cent and in which the precipitate is forming from an alloy 5 per cent supersaturated, the ratio of thickness to width should be about 1 to 25, which is very reasonable. But for Cu and Ag where the misfit is about 12 per cent a particle would apparently have to be 300 times as wide as it was thick before it could even begin to grow from an alloy 10 per cent supersaturated. It seems likely that the formation of nuclei of precipitation in such cases cannot be explained in terms of pure elasticity alone, but requires a special discussion of the matching of crystal planes in the two phases for each particular precipitation, such as has been carried out by Mehl and by Preston.

These considerations also supply a possible explanation of the {hardness, time} curves found in age-hardening. In the early stages the alloy is considerably supersaturated, and the particles of precipitate take the form of thick disks, growing rapidly. The strain energy and the hardness increase rapidly with time. But as time goes on the alloy becomes impoverished, and the rate of growth of the particles of precipitate diminishes. At the same time the thick particles tend to take up a more favourable thin sheet-like form, and so the strain energy and the hardness reach a maximum and diminish again.

Another possible cause of the softening, and the one which is probably effective in those cases where the Widmanstätten disks coagulate into globules on prolonged ageing, is recrystallization in the matrix. Returning again to spherical particles of silver, we note that the greatest strain in the copper matrix occurs just outside the particles of silver and that these regions will act as nuclei of recrystallization. Most of the energy of the copper is concentrated in a thin shell round the disturbing particle, so that most of the energy is released before the recrystallization has proceeded far. But the strain in the least strained regions of the copper, those farthest from particles of silver, is not released until practically the whole mass has recrystallized, so that the drop in hardness should occur some time after the crystal has given up its elastic energy. This effect may be the explanation of the secondary minimum of specific heat observed by Sykes in alloys near their maximum hardness.

As we have seen, a spherical precipitate will be compressed or expanded uniformly, while a thin sheet will have negligible strain energy. This will of course only be the case if the sheet has broken away; it is interesting to compare the strain energy of a sheet which has *not* broken away with that of a spherical precipitate.

Confining ourselves to crystals of cubic symmetry, we may take the tensor components of strain to be e_{ij}, when the energy in unit volume W is given by

$$\begin{aligned} 2W &= c_{ijkl}e_{ij}e_{kl} \\ &= c_{11}(e^2_{xx}+e^2_{yy}+e^2_{zz})+2c_{12}(e_{yy}e_{zz}+e_{zz}e_{xx}+e_{xx}e_{yy})+4c_{44}(e^2_{yz}+e^2_{zx}+e^2_{xy}). \end{aligned}$$

With these definitions the condition for isotropy is

$$2c_{44}=c_{11}-c_{12},$$

so that c_{11}, c_{12} and c_{44} agree with the constants tabulated by Schmid and Boas.

We define the components of stress F_{ij} by

$$F_{ij}=\partial W/\partial e_{ij},$$

and then

$$e_{xx}=\frac{(c_{11}+c_{12})\,F_{xx}-c_{12}F_{yy}-c_{12}F_{zz}}{(c_{11}+2c_{12})\,(c_{11}-c_{12})},$$

$$e_{yz}=F_{yz}/2c_{44}.$$

For uniform compression we may take $F_{ij}=F\delta_{ij}$, giving $e_{ij}=F\delta_{ij}/(c_{11}+2c_{12})$. If the linear dimensions of the particle of precipitate are altered in the ratio $1+\epsilon:1$, we must have $e_{ij}=\epsilon\delta_{ij}$ and $W=\frac{3}{2}(c_{11}+2c_{12})\,\epsilon^2$.

For a sheet lying along 100 and contracted in this plane the only components of stress which do not vanish are $F_{yy}=F_{zz}=F$, giving

$$e_{yy}=e_{zz}=\frac{c_{11}F}{(c_{11}+2c_{12})\,(c_{11}-c_{12})}.$$

Again putting $e_{yy}=\epsilon$ we find

$$W=\frac{(c_{11}+2c_{12})\,(c_{11}-c_{12})\,\epsilon^2}{c_{11}}.$$

The ratio of the work required for the sheet to that required for the sphere is

$$2\,(c_{11}-c_{12})/3c_{11}.$$

For silver we may take

$$c_{11}=12{\cdot}0\times10^{11},$$

$$c_{12}=8{\cdot}97\times10^{11},$$

and the ratio is approximately $\frac{1}{6}$. Taking ϵ equal to 12 per cent, the actual energy stored in a sheet of silver is 25 cal./g.

Before these results can be applied we must briefly consider the behaviour of the matrix. In the case of a spherical particle the pressure of the precipitate causes the matrix to expand, and so the energy of the whole system is reduced to something of the order of half the quantity calculated above. But if the particle takes the form of a sheet, it is clear that most of the accommodation is accounted for by a contraction of the sheet in its plane, for any stretching of the matrix parallel to this plane would involve an equally great strain spread over a much larger volume. Moreover we have assumed that the faces of the sheet are free to expand, but in fact unless the sheet is extremely broad and thin the necessary displacement of the matrix requires a further expenditure of energy which may not be negligible. So it seems that until the precipitate breaks away its elastic energy must always be quite large, of the order of the chemical energy released in the case of Ag-Cu.