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Some geometrical aspects of microstructural stability

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Microstructural instability commonly arises from a progressive decrease in interfacial area and thus in free energy. Particle coarsening processes provide an example of this but most of the work on microstructural instability has concentrated attention on particles within grains and at grain boundary surfaces. Despite the fact that the geometrical principles are well documented and understood, little consideration has been given to the coarsening processes of particles at grain edges and grain corners beyond the general recognition that such sites present favourable situations for preferential growth. It is noted here that certain specific features arise for particular values of the ratio between the interfacial and grain-boundary energies. Within a specific range of values of this ratio which are not very common in practice, there is a possibility of preferential growth of particles at grain corners and their stabilization independently of their initial size. More particularly and over a wider range of this ratio, a gross change in particle morphology, effectively as a spreading as a second phase along grain edges, can occur with the special characteristics that there is an advantage to such spreading with a small cross-section perpendicular to the grain edge at the expense of some reduction in the cross-section of a thicker section of material spread along a neighbouring grain edge. From these considerations, it is suggested that a particularly stable form of microstructure may be developed which could conceivably form a good basis for fibre reinforcement.

1. Introduction

Over many years, much attention has been given to the geometrical aspects of the shapes of grains and phases present in solid systems. Such studies have been thoroughly reviewed [1] and, on a macroscopic scale, there now exists a complete picture of all the requirements for space filling and of the physical conditions that are required to establish equilibrium shapes or equilibrium conditions at junctions by minimizing surface free-energy [2, 3].

More recently, the need to obtain reasonably stable structures, maintaining properties over a considerable period of time at elevated temperatures, has led to strong interest in the conditions for microstructural stability [4]. At an atomic level, much remains to be learned. At a macroscopic level, although the principles are firmly established, there does not appear to be a wide general appreciation of all their consequences, some of which may possibly be helpful for use in the practical aspects of materials design.

2. Some principles of microstructural stability

In many solid systems, phase transformations are incomplete and in such cases free energy reduction can arise progressively by continued phase transformation, where the bulk energy is provided by changes in the amounts of the respective phases involved. This aspect will not be dealt with in this work; instead, consideration will be restricted to two additional features, firstly, the driving force for change related to the lack of attainment of equilibrium where interfaces meet and, secondly, the driving force for instability that arises through surface curvature. These two features are interrelated in so far as they influence microstructural stability.

Where equilibrium is established at junctions

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between a grain boundary of energy, γ_g, per unit area and two interfacial boundaries, each of energy γ_i per unit area between two phases, the well known relationship

$$\gamma_g = 2\gamma_i \cos(\theta/2), \qquad (1)$$

applies, where θ is the dehedral angle [1]. It is a further requirement of equilibrium conditions for isotropic phases with some solubility in the matrix phase that the surface curvature of a discrete phase or particle is everywhere constant, except at these junctions. This follows from the equilibrium relationship between curvature and solubility [2] which can be given as

$$S_r/S_\infty = \exp(2\gamma_i V_m/RTr), \qquad (2)$$

where S_r is the solubility of a particle with surface of radius r, S_∞ is the solubility at infinite radius at temperature T, V_m is the molar volume of the material of the particle and R is the gas constant.

These principles are illustrated in Fig. 1 where the three particles shown, within a grain, at a grain boundary and at a grain edge, all have the same radius of curvature. This immediately implies that all three particles have the same solubility and so none of these particles will compete with another for growth at the expense of the others. Conversely, if similar volumes of material are placed at each of these three positions, as shown in Fig. 2, then it is apparent that the radius of curvature of the particle at the grain edge is greatest and has the lowest solubility and that of the particle within the grain is smallest and has the highest solubility. This arises simply because the greatest area of grain boundary has been removed for the particle at the grain edge and for the particle within the grain there is no compensating reduction in grain-boundary area. The argument can be further extended to show that, for similar reasons and for the same volume of material, the particle radius of curvature is still greater for a particle situated at a grain corner.

In practical systems it is well known that the equilibrium conditions at grain edges and corners are not generally established overall since, in a three dimensional case, space-filling polyhedra with plane surfaces do not everywhere have the angles between the grain faces of 120° and angles between the grain edges of 109.5°. The variability found in real situations and often the influence of anisotropy leading to the need to introduce torque terms [5] have tended to limit the attention given to phases along grain edges and at grain corners, although some phenomena, such as liquid metal embrittlement [6], have been considered in this respect. More recently, however, further considerations have been reported, including the proposal [7] of a space-filling polyhedron having faces with distributions of four-, five- and six-sided faces similar to the observed morphology of separated crystallites and derived from the Kelvin α-tetrakaidecahedron [8]. Some interest has also been focussed on the geometrical aspects of phases at grain boundaries in relation to dihedral angle [9]. These aspects have come into prominence in practical situations such as the removal of porosity in uranium dioxide during sintering and its reoccurrence and development to permit the release of gases [10–12].

Such considerations prompt the attention to the relative stabilities of condensed phases at grain corners, edges and faces that could have a bearing on microstructural development.

3. Particle coarsening processes and the importance of particle location

In the many cases where particle coarsening processes have been extensively analysed [13], the rates of growth of "large" particles have been calculated with the simultaneous decrease of "smaller" ones. When specific particle locations are taken into account, a more precise definition of the terms "large" and "small" becomes necessary since it is clear from Figs 1 and 2 that a particle on a grain boundary, which is somewhat smaller in volume than one in the matrix, may grow preferentially. Moreover, grain edges and especially grain corners are particularly well favoured sites for growth and can eventually deplete the particle concentration in other regions. The terms "large" and "small" should invariably refer to the particle radii of surface curvature for then, without any more features of the geometry becoming involved, it is evident that a particle on a grain surface, edge or corner can only grow providing it is of larger radius than its neighbours.

Some further consequences of these features seem rarely to have been appreciated for all ratios of γ_g/γ_i, although they are implicit in detailed analyses of geometrical features of two-phase aggregates [14]. For a particle at a grain corner where the grain edges each meet at 109.5° and when $\gamma_g/\gamma_i = 2\sqrt{\frac{2}{3}}$, so that $\theta = 70.5°$, the particle takes the form of a regular tetrahedron. This may

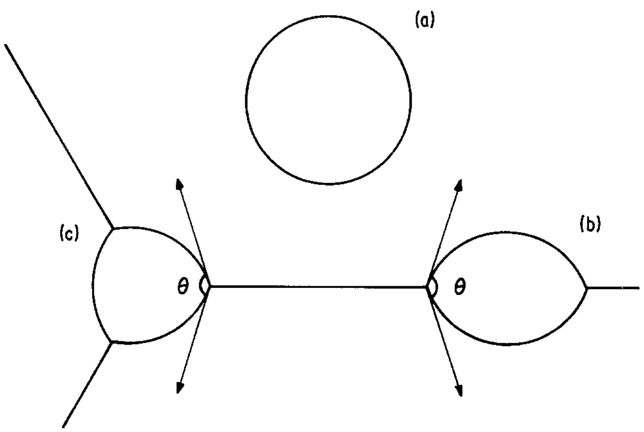

Figure 1 Three particles, all having the same radius of curvature, are schematically illustrated which are situated (a) within the grain (b) on a grain boundary and (c) at a grain edge. The same dihedral angle, θ, greater than 60°, is subtended by the particle–matrix interfaces at all intersections with the grain boundaries. Despite differences in their volume, all three particles have the same solubility.

be viewed as a particle of zero surface curvature or rather as one of infinite radius. The significance of this is that, regardless of its actual dimensions, the particle will always grow competitively at the expense of any other particle, no matter how large, which has a convex but finite radius of curvature. This may be illustrated in Fig. 3, where the tetrahedron of edge length, x, has a total area of its four faces of $4(\sqrt{3}x^2/4)$ but six triangular areas are removed with their total area of $6(x^2/4\sqrt{2})$. The net change in free energy, E (due to a change in these areas through growth) with respect to a small change in edge length x, is thus

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left[\sqrt{3}\gamma_\mathrm{i} - \left(\frac{3\gamma_\mathrm{g}}{2\sqrt{2}}\right)\right] x^2, \qquad (3)$$

which equals zero when $\gamma_\mathrm{g} = \gamma_\mathrm{i} 2\sqrt{\frac{2}{3}}$. This implies that an increase in particle surface free energy on growth is exactly compensated for by loss of grain-boundary free energy because of the area of grain boundary removed.

An interesting situation arises if the dihedral angle, θ, is less than 70.5° but is rather greater

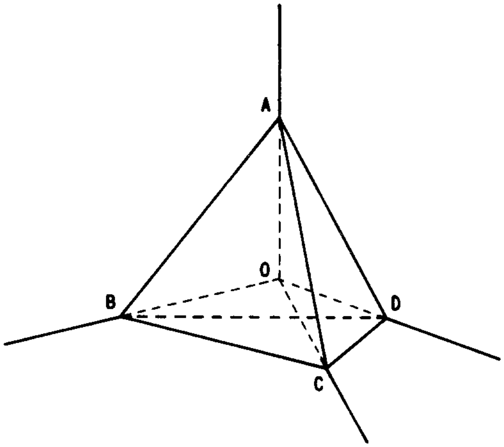

Figure 3 For a particle at a grain corner where grain edges each meet at 109.5° and where the dihedral angle between faces of the particle is 70.5°, then the particle takes the form of a regular tetrahedron. This implies that the particle has plain surfaces. It follows that, regardless of its actual dimensions, this particle at the grain corner will always grow competitively at the expense of any other particle, no matter how large, which has a convex but finite radius of curvature. A small change in size of the grain corner particle does not lead to any total increase or decrease of interfacial energy. The interfacial energy of the particle made up of the four faces of the type ABC, leads to $4(\sqrt{3}x^2/4)\gamma_\mathrm{i}$ but the particle in this position actually removes six triangular areas of grain boundary such as AOB with a total energy of $6(x^2/4\sqrt{2})\gamma_\mathrm{g}$.

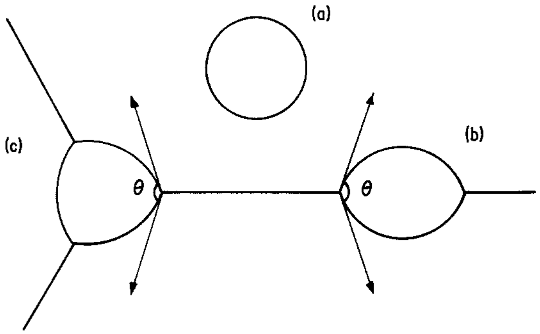

Figure 2 Particles are again situated (a) within the grain, (b) on a grain boundary and (c) at a grain edge. In this instance all the particles have the same volume and the dihedral angle at intersections with grain boundaries has the same value, θ. In this instance it is apparent that the radius of curvature of the particle within the grain is the smallest. Where the particles have some solubility, it follows that the particle at (c) at the grain edge will grow at the expense of the other particles. This situation arises because the greatest area of grain boundary has been removed in case (c) whereas in case (b) there is less and in (a) there is no compensating reduction in the total grain-boundary area.

than 60° (by an amount depending on the volume-fraction [14] of the phases where different features arise to be dealt with later). The relationship between surface curvature and solubility holds for both positive (convex) and negative (concave) radii curvature. For a low volume-fraction of second phase it is clear from the foregoing considerations that, for discrete particles with concave surfaces at grain corners, for $70.5° > \theta > 60°$, as in Fig. 4, the particle with the larger dimensions has the lower solubility. Thus, for a number of such particles, each at grain corners, the more usual particle coarsening phenomena would not occur. Instead, there would be a tendency for the particles of smaller dimensions to grow at the expense of the larger particles with a consequent overall equalization of particle size. This assessment is well founded but this situation is unlikely to occur to a significant extent in most practical circumstances, for, as well as satisfying the condition for the dihedral angle, θ, it is also required that a polycrystalline material consists of grains whose angles between grain edges are everywhere 109.5°, and such grains rarely exist in practice.

A new situation develops for $\theta < 60°$, that is, for $\gamma_g/\gamma_i > \sqrt{3}$, since discrete particles with concave surfaces occupying grain corners are no longer geometrically feasible. In these circumstances the particles then spread along the grain edges to form a complete interconnected network of second phase as rods of three-sided cross-section. When the dihedral angle is precisely 60°, and the grain boundaries each meet at 120°, the rods have plane surfaces and the cross-sections of the rods are then equilateral triangles except near grain corners where a double curvature exists near intersections. With $\theta < 60°$ the rod faces are concave, though now having an axis of curvature with each face being cylindrical rather than with the spherical curvature that is characteristic of the discrete particle distribution which formed under the conditions described earlier. This modifies the relationship between solubility and curvature to the form

$$S_c/S_\infty = \exp(\gamma_i V_m/RTc), \qquad (4)$$

where S_c is now the solubility when the cylindrical faces have a radius of curvature c, c being positive for a convex surface and negative when the surface is concave. This leaves unaltered, however, the principle that the smaller the concave radius of curvature, the less is the solubility, thus indicating that the rods of second-phase at grain edges having a small area of cross-section are more stable than those of larger area. It again follows that solubility and diffusional processes will tend to favour an equalization of the sections of rods. This feature is clearly apparent to the extent that the second-phase tends to spread over all the grain edges thus tending towards the thinnest and most uniform cross-section. In the general case, the geometry is somewhat less simple because, with random three-dimensional grain distribution, the grain boundaries cannot everywhere meet at 120°. Such conditions are reserved for structures of a two-dimensional form where the structure in the third dimension is independent of distance. The possible practical implications of some geometrical forms in the latter case are suggested in Section 4.

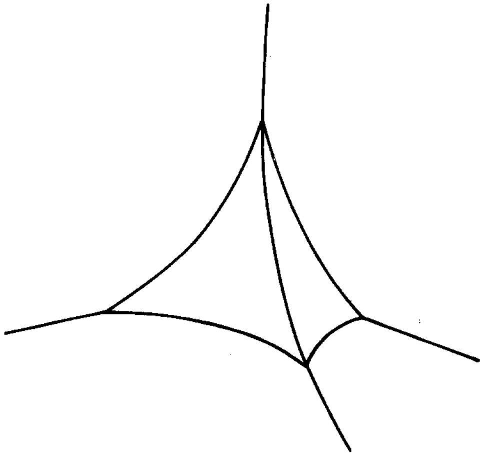

Figure 4 In this case the regular tetrahedron is modified in that its four faces are now concave. This negative curvature implies that the smaller particles of this geometrical form are more stable than the larger ones of a similar form. Hence, there is a tendency for such particles to reach a uniform size but this occurrence is unlikely in practice because, in real systems, grain edges do not everywhere meet at 109.5°.

4. The stability of structures containing parallel rods

Much attention has been given to the development of both metallic and non-metallic fibre composite materials [15] for high-strength applications combined with substantial toughness. There are many processes by which such fibre structures can be made and many possible systems have been considered. Of particular interest is the two-dimensional eutectic growth of two-phase structures [3] because, here, both phases are established in chemical equilibrium and so one of the driving forces for

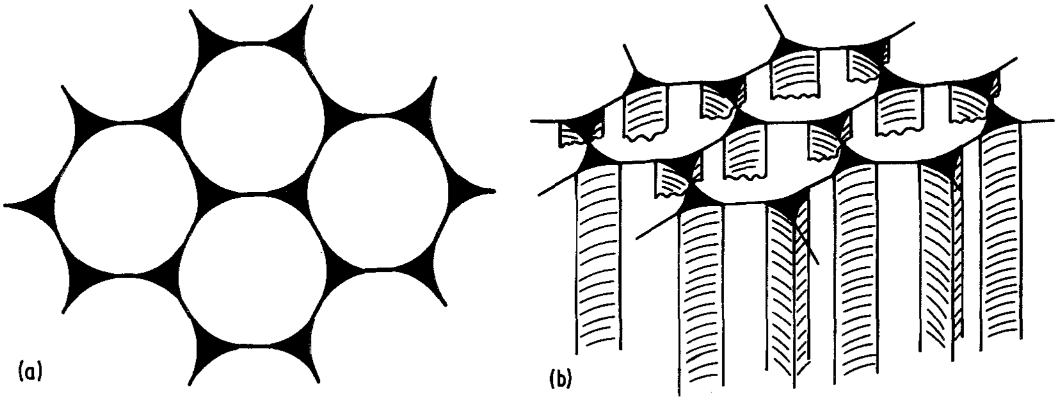

Figure 5 (a) and (b) illustrate a possible form of a two-phase structure which has the characteristics of a fibre composite. The fibres run along the parallel long-grain edges and the cross-sections of the grains are approximately hexagonal. The fibre surfaces are three-sided and are concave. The essence of stability of the fibres lies in the condition that, with some solubility, thicker fibres are less stable than thinner ones and, hence, there is a tendency for all the fibres to become uniform and to resist any competitive growth or spheroidization. In this instance it is necessary to obtain a dihedral angle of less than 60° and to meet this condition in a system where the phase comprising the rods has a high elastic modulus and yield and creep strength with the matrix phase of softer more ductile material in order to obtain the benefits of a stable material at high temperatures with good mechanical properties overall.

instability is immediately removed. They may further have low interfacial energies which assists their thermal stability and such structures have been proposed for elevated temperature applications. Such structures, are of course, only appropriate to withstand stress in a direction along the fibre axes and in many situations an instability arises through processes analogous to particle coarsening where the fibres of small (convex) radius, because of their higher solubility, tend to be dissolved in favour of the growth of the neighbouring fibres of greater radius. Other problems can also arise which relate to crystalline faults in the rods and to the instability of rods in breaking up into droplets (Rayleigh instability). It is conceivable that these difficulties may be overcome by some of the principles outlined above.

It is feasible to form a composite fibre structure as in Fig. 5, where the fibres run along the parallel long-grain edges and where the grain cross-sections are approximately hexagonal. Here, the essence of fibre stability resides in the three-sided concave fibre surfaces where some solubility of fibre in the matrix material serves to increase the uniformity of fibre cross-section because the thicker fibres are less stable than the thinner ones.

In practice, the problem appears to be one of obtaining a dihedral angle, $\theta < 60°$, requiring a value of $\gamma_g > \sqrt{3}\gamma_i$, in a system where the phase comprising the rods has high elastic modulus and yield strength, with the matrix phase of softer, more ductile, material. In systems matching the latter requirement, it appears more common for the phases to have a high interfacial energy per unit area, γ_i, with insufficiently high values of γ_g/γ_i. The wide diversity of methods of manufacture of fibre composite materials and the broad scope in the choice of components may nevertheless imply that suitable systems could be found with their stability as fibre composited based on the above principles. The possibility of appropriate modification to the values of γ_i and γ_g by segregation should not be overlooked.

5. Conclusions

Interfacial effects in relation to second-phases within grains, on grain boundaries, edges and corners may have a profound influence on coarsening phenomena and on stability. Some of these influences may possibly be employed with advantage in the microstructural design of alloys.

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