SOME UNRESOLVED ISSUES IN PHASE TRANSFORMATIONS - THE ROLE OF MICROANALYSIS

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Abstract – A few of the current difficulties associated with first order phase transformations are reviewed in the context of the facilities offered by fine scale microanalytical techniques. The aim is to stimulate cooperation between those who are experts in field ion microscopy and associated techniques, and others involved in the modelling of phase transformations and microstructures.

1 – INTRODUCTION

There has been remarkable progress in the past thirty years or so, in the use of experimental thermodynamic data combined with clever methods of solving complicated systems of nonlinear equations, towards the calculation of phase diagrams for metals and alloys [1]. There are now several systems capable of estimating the phase diagram as a function of pressure, temperature and the combined effect of numerous alloying elements, given a starting set of possible phases [1]. Since the thermodynamic properties of a metastable phase are continuous with its properties under equilibrium conditions, the calculations can be used to extrapolate the phase boundaries into regimes where the phases are not thermodynamically stable. This is an important facility, since kinetic barriers in reality often allow a phase to exist happily even though it may be unstable.

Phase diagrams *per se* are of considerable value in the design of alloys [1,2], but in many applications, kinetic considerations are of overriding importance and control the development of microstructure, and hence the properties, of metals. Consequently, the next major advance in the theory of materials is likely to be in the development of kinetic models, which enable the estimation of *microstructure* as a function of chemistry and thermomechanical treatments. Of course, kinetic theory itself is already well advanced [3], but it often relies on assumptions such as the existence of local equilibrium at the interface, which may not be realistic when considering transformations at high supersaturations [4]. Many large scale industrial processes are now tending towards conditions of high supercooling, since it is in those circumstances that ultrafine grained microstructures, phases with nonequilibrium solute concentrations, etc. can be produced [5].

The purpose of this review is to identify a small number of problems related to the modelling of microstructure, which could in principle benefit from carefully designed microanalysis experiments. Metals, and in particular steels, are probably the best disposed of all materials to benefit from developments in kinetic theory, since metallurgy is a relatively advanced science, with a large experimental database. Such a database is necessary to allow discrimination between different theories. For this reason, and because of the author's personal interests, the review focuses on metals, although it will become evident that the problems and solutions are of general applicability.

2 – EQUILIBRIUM TO PARAEQUILIBRIUM TRANSITION

As pointed out earlier, it is a common assumption that local equilibrium exists at the transformation during diffusion controlled growth. For binary alloys, this means that the compositions $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ of the product (α) and parent (γ) phases respectively, at the interface, are specified by a tie-line of the ($\alpha + \gamma$) two-phase field of the phase diagram; see for example, [3,6]. Conservation of mass then requires that the amount of solute being partitioned between the phases per unit of time is balanced by the solute diffusion flux at the interface:

$$(x^{\alpha\gamma} - x^{\gamma\alpha})v = D(\partial x/\partial z)$$

where D is the solute diffusivity, v is the interfacial velocity and z the coordinate normal to the interface. Note that the concentration gradient is evaluated in the parent phase at the interface.

For the local equilibrium assumption to be viable, there must exist sufficient atomic mobility at the transformation temperature. In an alloy in which there is some atomic mobility within the parent phase, the reconstruction of the crystal structure may provide an opportunity for the solvent and solute atoms to redistribute between the two phases. However, in a system such as Fe-C-X (where X represents a substitutional solute), the diffusion rate of carbon in the austenite may be many orders of magnitude greater than that of a substitutional atom in the temperature range of interest and these very different rates of atomic migration mean that true equilibrium segregation with regard to all components may not be produced at a migrating interface. If the interaction between the fluxes of the two species is neglected, then in terms of the mass conservation conditions, there are two equations to be satisfied simultaneously:

$$(x_1^{\alpha\gamma} - x_1^{\gamma\alpha})v = D_1(\partial x_1/\partial z)$$

$$(x_2^{\alpha\gamma} - x_2^{\gamma\alpha})v = D_2(\partial x_2/\partial z)$$

where the subscripts 1 and 2 identify the interstitial and substitutional solute species respectively. Since the diffusivities differ by many orders of magnitude, simultaneous solution is in general impossible for the case where the tie-line passes through the average composition of the alloy concerned.

It is, however, possible to envisage growth under diffusion control with local equilibrium at the interface in the sense that the compositions of the two phases are joined by a tie line of the equilibrium diagram, even though this tie line does not pass through the point representing the initial (or average) composition of the alloy. When these kinetic restrictions apply, the two phases may differ either significantly or negligibly in substitutional solute content. A qualitative analysis for ternary steels was first developed by Hillert /7/, and a simplified quantitative theory in which diffusion cross terms are neglected was developed by Kirkaldy /8/, Purdy et al. /9/, and Coates /10/; the effect of the cross terms was later examined by Coates /11,12/. The simple theory shows that for the diffusion-controlled growth of ferrite from austenite in an Fe-C-X alloy with initial composition near the $\gamma/(\gamma+\alpha)$ phase boundary (i.e. with a small supersaturation), the tie line selected will have the carbon composition of the austenite at the interface almost equal to that of the bulk alloy so that the activity of carbon is nearly constant in the austenite, thus reducing the driving force for carbon diffusion almost to zero. There will be a concentration gradient of the substitutional solute ahead of the interface, resulting in appreciable partition, and the relatively slow growth rate will be determined by the diffusion rate of this solute. For large supersaturations, the tie line will have the Fe+X composition of the ferrite virtually identical with that of the bulk austenite, partitioning of the substitutional solute will be extremely small, with a relatively fast growth rate. These are referred to as the partitioning local equilibrium (P-LE) and negligible partitioning local equilibrium (NP-LE) growth modes respectively /9,12,5/, and for a high ratio of the diffusivities, the theory predicts an abrupt transition from one to the other as the supersaturation increases.

In the NP-LE mode, the concentration of X is uniform except for a small "spike" in the parent phase adjacent to the interface. As the ratio of interstitial: substitutional diffusion rates increases, the width of this spike decreases, and when it becomes of the order of atomic dimensions, the concept of local equilibrium at the interface is invalid and has to be replaced (assuming the growth is nevertheless diffusion-controlled) by that of paraequilibrium /13-17/. In conditions of paraequilibrium, there is no redistribution of Fe + X atoms between the phases, the Fe/X ratio remaining uniform right up to the interface. One interpretation of the paraequilibrium limit is that reconstructive transformation occurs with all displacements of the Fe+X atoms taking place in the incoherent interface; another interpretation might be that only displacive transformation can occur. In either case, to quote from Coates, "the slow diffuser and the solvent participate only in the change of crystal structure". Paraequilibrium implies that the growth rate is controlled by the interstitial diffusivity, the interface compositions now being given by the tie lines of the pseudo-equilibrium between the two phases under the constraint of a constant Fe-X ratio.

3 – TASK NUMBER ONE

To summarise the discussion, when Fe-C-X alloys are transformed at low supersaturations, there is bulk partitioning of the slow diffuser, the activity gradient of the fast diffuser being reduced to a negligible level (the P-LE mode, Fig. 1). At high supersaturations, there is negligible partitioning of the slow diffuser, so that its activity gradient in the parent phase is large enough to allow it to keep pace with the faster diffusing element. Paraequilibrium transformation involves zero partitioning of substitutional elements
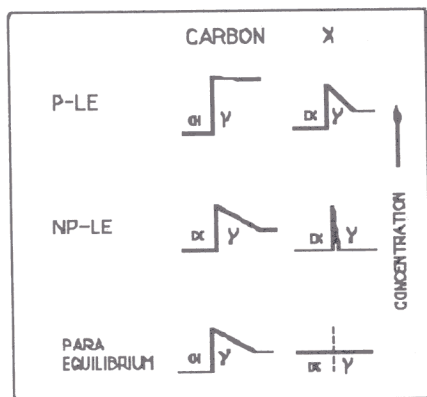
Fig. 1 –Diagrams illustrating the concentration profiles at the transformation interfaces, for the P-LE, NP-LE, and paraequilibrium modes.

during transformation, the ratio of substitutional solute to iron atoms being constant everywhere, even on the finest conceivable scale.

There is as yet no complete theory for the transition from local equilibrium to paraequilibrium. The conjecture /12,18/ that the transition occurs when the calculated extent of the diffusion field of the slow diffuser becomes comparable to atomic dimensions is unlikely to be correct, because the calculations do not included gradient energy terms /12,6/. There is also evidence that the kinetics of some transformations are compatible with local equilibrium even when the extent of the calculated diffusion field is negligible /19/.

The task for the microanalysis expert is clear: there is a need to examine the concentration profiles at the transformation interfaces, firstly to establish the local equilibrium assumption for ternary alloys, and secondly to provide direct experimental data on the conditions under which local equilibrium gives way to paraequilibrium. It may even be the case that the paraequilibrium condition does not exist when the mechanism of transformation is reconstructive. It is also likely that there may be an infinite set of intermediate conditions between the limiting cases of local and paraequilibrium /6/.

4 – MECHANISM OF TRANSFORMATION

The behaviour of the atoms on substitutional sites during transformation is critical in specifying the mechanism of change.

In a *displacive* transformation (Fig. 2), the pattern in which the substitutional atoms are arranged changes in a manner consistent with the change in crystal structure; since the change does not involve any diffusion of these atoms, the shape of the whole crystal changes. This shape deformation has the exact characteristics of an invariant-plane strain with a relatively large shear component. Interstitial atoms may diffuse during transformation without influencing the observed shape deformation /20/. There is however, no significant diffusion of substitutional atoms in a displacive reaction.

During *reconstructive* transformation (Fig. 2), the atoms transfer across the interface in an uncoordinated manner which accomplishes the required lattice change and simultaneously ensures a minimisation of the strain energy. This requires the thermally activated migration (in the interface region at least) of all the atoms, irrespective of whether the transformation occurs in a pure metal or in an alloy. There will normally be a volume change associated with the stress-free change of structure, and at sufficiently high temperatures, this may be compensated by a flux of vacancies (and an opposite flux of atoms) between the growing precipitate and the dislocations, grain boundaries and (ultimately) the free surface of the parent phase. At temperatures where the rate of diffusion in the parent phase is inadequate for such an adjustment, reconstructive growth with minimum strain energy will still be possible if the precipitate has a lenticular (tapered plate) shape, and the reconstruction takes place in such a way that the volume change is simply an expansion or contraction normal to the plane of the lens /21/. This can be achieved by atomic migration entirely within, or in the limit, around the particle. Reconstructive growth

the segregate distribution to be nonuniform *within* the interface, although that concept seems dubious given that the width of an interface is likely to be atomic dimensions. A more realistic proposition, by analogy with well established theory for solute drag at grain boundaries /27/, is that for a moving interface, the concentration profile of the segregate is likely to extend outside of the interface itself.

9 – TASK NUMBER FOUR

Careful measurements of the concentration profiles at the transformation interface should convincingly demonstrate the presence or absence of drag effects, and provide a good database for the development of solute drag theory. The profiles should be measured at the position of the interface, and in the parent and product phases in the vicinity of the interface. It is emphasised again, that the observation of segregation in itself does not demonstrate solute drag, but rather, the observation of nonuniformity in segregate concentration in either direction normal to the plane of the interface. Experiments to detect such effects are long overdue, and are probably best carried out on alloys undergoing massive transformations, since interference with diffusion fields due to partitioning between phases can then be avoided.

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