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Considerations of solute-drag in relation to transformations in steels

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In recent years, solute-drag theory has been widely quoted to explain apparent discrepancies in kinetic measurements of transformations in steels. Since conventional impurity drag theory is concerned solely with drag at grain boundaries, many new, or "special" drag models have been developed to apply at interphase interfaces. An assessment is made of these special drag theories, and of the experimental evidence claimed in their support. It is found that our understanding of solute-drag at interphase interfaces is very weak, and that the experimental evidence for the existence of solute drag at transformation interfaces in steels is very doubtful.

1. Introduction

Experiments in recrystallization have convincingly demonstrated the existence of solute-induced diffusional drag on grain boundary motion [1–11]. The addition of small quantities of "impurities" can be shown to lead to large changes in the recrystallization temperatures of deformed materials. Such results can be qualitatively rationalized in terms of the association of solute atoms with moving grain boundaries [13, 14], the solute-boundary interaction energy E being negative or positive, depending on whether there is adsorption or desorption (respectively) of the "impurity" at the boundary. Under certain circumstances, the solute atoms can be expected to be "dragged" along ($E < 0$) with, or pushed ahead ($E > 0$) of the boundary, reducing its rate of migration, relative to that expected in a pure material.

While the main purpose of this paper* is not concerned solely with the segregation-induced effects, it is these drag phenomena which are theoretically well established, and which might provide some insight into the special effects to be discussed later. Hence, it is useful to begin by emphasizing and briefly reviewing some of the relevant aspects of "conventional" drag theories.

2. Conventional solute-drag theories

2.1. The identification of an appropriate diffusion coefficient

All the conventional theories on solute-drag [12–19] require segregation (or desegregation) of solute atoms to the interface (to a level which differs from the bulk solute concentration C_0). The interface itself is assumed to have a finite width δ, usually defined as the distance normal to the interface plane, over which the solute–interface interaction free energy E is non-zero. (It should be noted that the δ of [16] is defined to be twice as large as that of [13].) The drag force (P) on the boundary is obviously zero when segregation does not occur, or when the composition profile due to the segregation is symmetrical with respect to the centre plane of the interface. For a moving boundary, the existence of a finite drag requires the diffusion of solute atoms in the direction of boundary motion; one of the major difficulties in applying solute-drag theory to real

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*Throughout this paper, a deliberate attempt is made to focus attention strictly on the solute drag problem, and to avoid detailed excursions into the well established theories of diffusion and interface controlled growth. However, relevant references to such theory are included at appropriate positions in the text.

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problems is the suitable choice of a diffusion coefficient describing this process.

In his theoretical paper on drag effects [13], Cahn took the diffusivity to be some function of the distance from the centre of the boundary*, presumably approaching the value of the bulk (or volume) diffusivity ($D(\infty)$) at large distances normal to the interface. At the centre plane of the boundary, the diffusion coefficient would be given by the grain boundary diffusivity (D_b). By referring to the results of Turnbull and Hoffman [20], Cahn suggested that the diffusivity would increase typically by a factor of 10^6 as the centre of the boundary was approached. However, the work of Turnbull and Hoffman was concerned with solute transport along the grain boundary, rather than across it; solute-drag on the other hand relies on impurity diffusion in the direction of boundary motion, and across the boundary itself. The diffusivity of an interface must in general be considered to be highly anisotropic, reflecting the nature of its defect structure. Hence, it is not surprising [20] that the movement of atoms along the interface is easier than that in the bulk of matter; interface dislocations should act as pipes for the channelling of atoms. However, the transport of atoms across the interface may be a very different problem [21]; it is now well established that the boundary structure can in general be described in terms of areas of good fit (and hence little free volume, relative to an ideal crystal) separated by localized regions of higher distortion (e.g., interface dislocations). Under these circumstances (at least for coherent and semi-coherent interfaces), the diffusion coefficient describing the movement of atoms across the interface, D_a, must be more closely related to $D(\infty)$. (This suggestion is somewhat in line with the original paper of Leuke and Detert [12], where the diffusivity was taken to be $D(\infty)$.) These problems are further emphasized by the fact that the boundary width δ in the solute drag theories is usually assumed to be equal to a few interatomic distances. Such a large δ is probably acceptable when δ is defined as the region over which E is non-zero. However, it is not obvious that the diffusivity D_a should differ from $D(\infty)$ over the same distance δ.

The structure of an incoherent boundary is not very clear, and it is possible that D_a may approach D_b for such interfaces. It is interesting that the drag effect generally diminishes [19], at any particular interface velocity, as the ratio $D_a/D(\infty)$ increases (although this trend may be different for the very low velocity regime, see Fig. 5, [19]).

Finally, there have been suggestions [22, 23] that the diffusivity of a moving boundary is higher than that of a stationary one. It is not at all obvious how this might influence the concepts of the solute drag theory.

2.2. The problem of evaluating the interaction free energy $E(y)$

While Cahn's solute drag theory is general, in the sense that both D_a and E can be expressed as functions of the distance y, it is usually necessary to make simplifying assumptions about the forms of $D(y)$ and $E(y)$. The way in which the drag force P varies with $E(y)$ has been considered by Hillert and Sundman [19]. For cases where E varies gently from zero (at $y = \pm(\delta/2)$) to some other value within the boundary, the drag force P goes through a maximum as the interface velocity increases. However, if E changes discontinuously from a constant value within the boundary to zero at $y = \pm(\delta/2)$, P never decreases with increasing velocity. As Hillert [16] pointed out, the former choice of $E(y)$ is probably more realistic, especially when the discrete nature of lattices is taken into account. Nevertheless, it is recognized that in the absence of detailed knowledge on solute/interface interactions, the choice of $E(y)$ must be somewhat uncertain. The situation is additionally worrying because the form of $E(y)$ also determines the region of the boundary from which the main component of the drag force originates [13, 19]. The value of D in those particular regions would then control the drag effect [13]. This problem would, of course, be minimized if D_a was always close to $D(\infty)$, as was suggested earlier for the case of semi-coherent interfaces.

3. The composition profile at the boundary

The drag theories either predict [13], or are designed [16, 19] so that the solute concentration behind (trailing) the interface, during steady state motion, is always equal to the bulk solute level C_0, as if the boundary did not exist. The solute concentration at $y < (-\delta/2)$ is thus always C_0. For a stationary boundary, the concentration of solute differs from C_0 within the region $(-\delta/2) < y <$

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*This distance, y, is measured from the centre plane of the boundary (where $y = 0$), in a direction normal to the interface plane. The positive values of y occur in the region ahead of the interface, in the direction of interface motion.

$(\delta/2)$. For a moving boundary, the composition differs from C_0 not only within the boundary, but also in front of it, irrespective of whether E is less than or greater than zero. The extent of penetration into the region beyond $y = (\delta/2)$ depends on interface velocity amongst other factors.

4. Drag at interphase interfaces

The theory for solute segregation-induced drag on transformation interfaces is not well established, and the experimental evidence in this area is all the more difficult to interpret.

Hillert [16, 17] and Hillert and Sundman [19] first extended the concepts of grain boundary drag theory to apply to certain special cases of interphase interfaces. They considered transformations in which the product (ferrite) formed from the parent (austenite) without any change in composition: however, the transformation considered was not martensitic, because substitutional solute atoms (i.e. 'X' atoms) were allowed to segregate within the interface, with a solute concentration spike in the austenite adjacent to the interface. The height of this extremely narrow concentration spike was chosen to be consistent with the existence of local equilibrium* at the interface. Free energy is thus dissipated in driving the X atom spike ahead of the interface, and in driving the diffusion of X atoms which have segregated in the boundary itself. This dissipation of free energy manifests itself as a drag force on the interface.

As the velocity of the interface increases, the height of the solute spike in the austenite deviates from local equilibrium; it follows [19] that less free energy is dissipated in driving this reduced spike and so its contribution to the total drag force diminishes. Eventually, at high enough velocities, only the atoms segregated within the interface contribute to the drag force.

As a matter of interest, the segregation profile within the interphase interface should be asymmetric, since the interface region is bounded by two phases with different thermodynamic properties.

In many ways, the theory relies heavily on the local equilibrium concept, and in addition, is acknowledged [19] to be restricted in applicability to transformations whose parent and product phases have identical compositions. It is not clear whether interface segregation-induced solute drag would significantly contribute in circumstances where the parent and product phases differ in composition, and hence require the long range diffusion and redistribution of solute during transformation.

Recently, there have been a number of suggestions implying the existence of significant interactions between substitutional alloying elements (in steels) and austenite–ferrite transformation interfaces. These have all been referred to as "special" drag effects, since it is claimed that they operate when the transport of solute atoms in the direction of boundary movement can be ruled out. None of these ideas have been developed in any detail, either theoretically or experimentally, but have nevertheless been widely quoted in the literature to explain away apparent discrepancies in the kinetics of transformations in steels, often without paying proper attention to the mechanisms involved. The purpose of this paper is to critically examine the proposed special drag effects, and the experimental evidence on which they rely.

5. Special solute drag effects

5.1. Interaction of carbide-forming elements with interfaces

One of the first special drag effects was proposed by Kinsman and Aaronson [25] who found the growth rate of allotriomorphic ferrite (in a Fe–Mo–C alloy) to be lower than that expected from paraequilibrium† transformation theory,

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*Coates has discussed this in a very thorough paper on diffusional transformations [24]. The local equilibrium concept is an alternative (to the paraequilibrium mode [16]) mechanism of transformation in which the ratio of X/iron atoms is identical in both the parent and product phases. A very narrow X atom spike is allowed to exist in the austenite immediately adjacent to the interface, such that the X atoms at the interface, in both the phases have the same partial molar free energy, i.e. local equilibrium exists, even though the narrowness of the spike prevents long range diffusion of X atoms. The spike is such that the growth rate of the ferrite is controlled by the diffusion of carbon in the austenite, and not by the need to diffuse X atoms in the austenite. The end product is thus similar to that of paraequilibrium transformation, i.e. carbon diffusion controlled growth, and equal X/iron atom ratios in both phases.

†Paraequilibrium transformation [16] refers to the formation of ferrite from alloyed austenite, without any redistribution of substitutional alloying elements, even on the finest conceivable scale. Carbon does partition during transformation, such that its partial molar free energy is equal in both the phases at the interface. Growth, therefore, occurs at a carbon diffusion controlled rate, with the ratio of substitutional/iron atoms being constant throughout the material, including at any interface regions.

although the observed interface velocities seemed too large to be consistent with the dragging of molybdenum atoms "along with the interface", by any "volume diffusion or volume diffusion like processes" [25]. On the other hand, steels containing ternary additions of manganese or silicon exhibited allotriomorphic ferrite growth kinetics somewhat more consistent with paraequilibrium transformation. This stimulated the suggestion that elements which are strong carbide formers have a tendency to "be bound" to "disordered" austenite–ferrite interfaces, due to the higher carbon concentration that would be expected to exist in the austenite at the transformation interface, during growth involving the partitioning of carbon between the parent and product phases. Presumably, this binding between the molybdenum atoms in the interface and the carbon atoms in the adjacent austenite would hinder the transfer of the molybdenum atoms into the ferrite lattice. Kinsman and Aaronson further suggested that the molybdenum atoms may be required to diffuse short distances along the interphase interface before completing their transfer into the ferrite, or alternatively, may simply serve as "pinning points"* around which the boundary must bend before it can break away.

Before discussing these ideas in detail, it seems that in the original version of the proposal [25], the segregation of molybdenum (or other substitutional alloying elements) atoms to the interphase interfaces concerned was not implied (although a later paper [26] mentions the "segregation of certain alloying elements to austenite–ferrite interfaces"). However, the time of stay of the molybdenum atoms in the interface was said to be greater than that of weaker carbide formers, so that the iron atoms in the same alloy can be expected to move relatively more rapidly into the ferrite. This must lead to an enrichment of molybdenum in the interface. Because of these difficulties of interpretation, it was felt necessary to examine the implications of "special drag effects" both in circumstances where the ratio of substitutional (or "X") atoms to iron atoms is constant throughout the transforming material (absolutely no segregation anywhere), and for cases where interfacial segregation of X atoms is envisaged.

5.1.1 The zero-segregation case

Clearly, the conventional solute-drag theories are not applicable in such cases, and the special drag effect [25] involves the concept that the molybdenum atoms should experience a binding force with the high-carbon region in the austenite at the interface. It might intuitively seem reasonable that a strong carbide-former such as molybdenum should behave in this manner. Nevertheless, such an approach does not take proper account of all the other more subtle interactions that must exist between the molybdenum atoms and the α-iron, γ-iron and α-carbon atoms, respectively.

The net effect on the molybdenum atom can be treated in terms of Einstein's [27] proposal that the virtual force acting on a diffusing species may be regarded as the negative gradient of its partial molar free energy. This is simply a formal statement of the fact that diffusion (or alternatively, atomic jumps in an overall non-random direction) will tend to occur in the direction which leads to thermodynamic stability. To apply Einstein's condition, the species need not actually be able to diffuse (this would depend on the mobility of the atom in its environment); the condition does, however, give the preferred tendency of movement; in the present context, it enables us to deduce whether or not the molybdenum atoms really prefer to be associated with the high-carbon regions in the austenite.

Calculations of the type described above require a knowledge of the carbon content of the austenite at the interface (i.e. $x_{\gamma}^{\gamma\alpha}$), when transformation is occurring under paraequilibrium conditions. These are presented in Fig. 1, calculated according to [28], for the Fe–0.11C–1.95Mo alloy in wt% (used by Kinsman and Aaronson [25]). The molybdenum/iron ratio in both the austenite and ferrite is of course contant. To a very good approximation, we may assume that the carbon content of the ferrite is zero, for the remainder of the calculations. The activity coefficients of molybdenum in austenite and in ferrite, as a function of phase composition, were obtained from [29].

Fig. 2 shows the difference $(\bar{G}_{\mathrm{Mo}}^{\gamma} - \bar{G}_{\mathrm{Mo}}^{\alpha})$ between the partial molar free energies of molybdenum in ferrite (Mo = 1.95 wt%, $C = 0$) and in

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*Here we can only assume that the pinning referred to is due to the extra effect of the binding between the Mo and C atoms, and not simply a solid solution hardening effect, which in itself cannot be expected to be specific to carbide formers. Hence it is not clear how the pinning is meant to be an alternative effect to the 'binding' mentioned earlier.

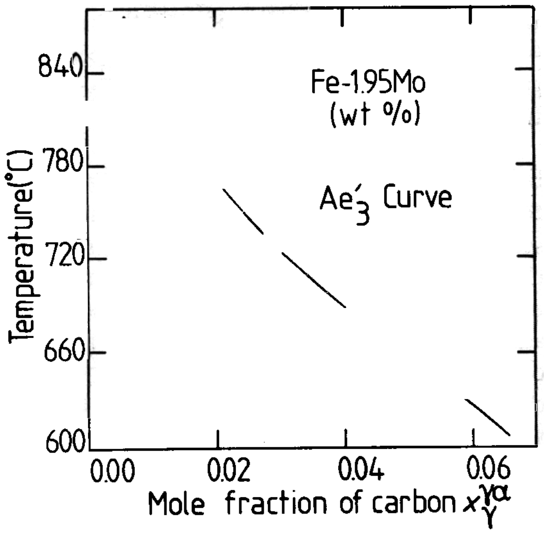

Figure 1 The $\gamma/(\gamma+\alpha)$ paraequilibrium Ae$_3$′ phase boundary for Fe–1.95Mo (wt/%).

austenite (Mo = 1.95 wt%, $C = x_\gamma^{\gamma\alpha}$). If a co-ordinate Z is defined with an origin in the austenite, and in a direction normal to the interface plane, then the gradient (with respect to Z) of partial molar free energy of molybdenum across the interface is proportional to $-(\bar{G}^{\gamma}_{\mathrm{Mo}} - \bar{G}^{\alpha}_{\mathrm{Mo}})$, and the virtual force on the molybdenum atoms, being related to the negative of this gradient therefore acts in the direction of Z if $(\bar{G}^{\gamma}_{\mathrm{Mo}} - \bar{G}^{\alpha}_{\mathrm{Mo}})$ is positive, and $-Z$ if $(\bar{G}^{\gamma}_{\mathrm{Mo}} - \bar{G}^{\alpha}_{\mathrm{Mo}})$ is negative.

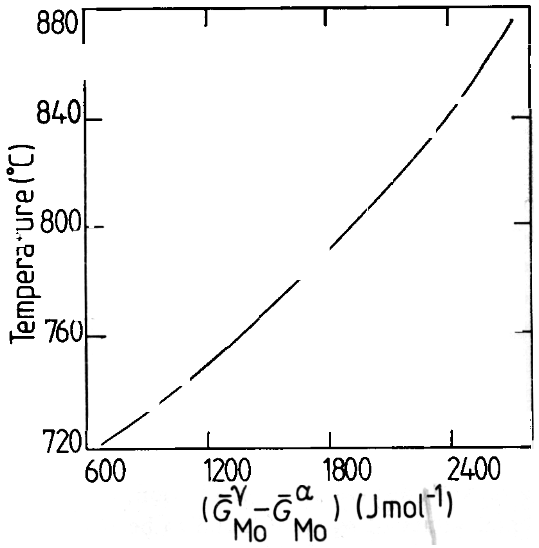

Figure 2 Plot of the difference $(\bar{G}^{\gamma}_{\mathrm{Mo}} - \bar{G}^{\alpha}_{\mathrm{Mo}})$ in partial molar free energy of molybdenum in austenite and in ferrite, assuming that the compositions of these two phases is that obtained at the interface during paraequilibrium transformation, as a function of transformation temperature. See text for detailed explanation.

It is clear that despite the high carbon concentration in the austenite at the interface, the molybdenum atoms prefer to be in the ferrite lattice, at least for the conditions of the experiments reported by Kinsman and Aaronson. In hindsight, this conclusion would seem obvious, since at equilibrium the ferrite should contain more molybdenum than austenite. However, care must be exercised in reaching such conclusions from equilibrium phase diagrams, since the extent of the austenite + ferrite phase field is always more restricted under conditions of paraequilibrium transformation.

5.1.2. Special drag with segregation at the interface

More recent developments [26, 30–32] of the original [25] special drag theory have definitely involved the segregation of X elements at the austenite–ferrite transformation interface. Such segregation is supposed to occur [31] "through a sweeping up" of the X atoms, rather than by the diffusion of these atoms through the austenite and/or ferrite* to these boundaries. The segregated X atoms are then meant to significantly effect the activity of carbon in the austenite which is in contact with these interfaces, thereby altering the carbon concentration profile (and hence the interface migration rate) in the austenite ahead of the interface.

X elements which reduce the activity of carbon in austenite are claimed, therefore, to decrease the carbon concentration gradient in the austenite, leading to a drop in the rate of boundary movement. On the other hand, X elements which increase the activity of carbon in austenite would then have the opposite effect on growth kinetics (referred to as an "inverse solute drag-like effect" [33]).

There are a number of difficulties with these concepts. Firstly, the proposal that the segregation profile of X elements, at the interface, should be solely confined to the interface, and not extend into the austenite (since X is not supposed to diffuse through the volume of the austenite) may not be correct for a moving interface (for a stationary interface the drag force P is zero anyway). Chan's

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*As pointed out earlier, drag theory indicates that the trailing composition is always equal to C_0, so that for an austenite to ferrite transformation we probably need not worry about diffusion through the ferrite.

theory [13] clearly shows, for the grain boundary case, that the solute profile in the vicinity of the moving interface always extends into the region beyond the interface (i.e. in the region $y > \delta/2$). It is interesting that when $E < 0$ in the boundary, there is expected to be a decrease in solute concentration, in the austenite just ahead of the interface (see Fig. 2, [13]).

Secondly, the concept that an X element which is segregated into the interface will have an effect on the carbon activity in the adjacent austenite is itself doubtful*. The proposal ignores the fact that the segregation of X will only occur to the extent that the partial molar free energy of X in the interface equals that in the austenite, and it fails to treat the boundary as a thermodynamically separate phase. Even though the concentration of X in the interface may be different from that in the bulk of the austenite, its influence on the activity of carbon in austenite will be identical to that of the X atoms present in the bulk of the austenite.

There is a further difficulty in the concept that the segregating X elements which reduce the activity of carbon in austenite would lead to a decrease in the carbon concentration gradient ahead of the interface, and hence reduce the growth rate. The limiting carbon concentrations in each of the phases (normally referred to as $x_\alpha^{\alpha\gamma}$ and $x_\gamma^{\gamma\alpha}$, for ferrite and austenite, respectively, see Fig. 10 [34]), at the interface during diffusion controlled growth, are calculated from the condition that the partial molar free energy of carbon in each phase is equal. If an X element reduces the activity of carbon in austenite, then to maintain this equality of partial molar free energies, the concentration (and hence concentration gradient) of carbon (i.e. $x_\gamma^{\gamma\alpha}$) must correspondingly increase, in contradiction with Kinsman and Aaronson's hypothesis.

Finally, it should be noted that the diffusivity of carbon in austenite is influenced by the activity coefficient describing the solution of carbon in austenite, and by the carbon–carbon interaction energy [35, 36]. Both these factors depend on substitutional alloying element concentrations [37–39], so that the rate of growth cannot be discussed simply in terms of concentration gradients ahead of the interface; the effect on diffusivity must also be taken into account.

5.2. Interaction of clusters with interfaces

Sharma and Purdy [40] proposed that special solute-drag effects may arise if elements such as chromium or molybdenum tended to form clusters in the austenite, such that carbon atoms became associated with these clusters. Since ferrite can only accommodate a very limited amount of carbon, the motion of the transformation interface would be hindered by the need to strip these clusters from their carbon atmospheres.

In trying to explain various features of time-temperature-transformation curves, Sharma and Purdy [40] went on to suggest that since the formation of clusters (by volume diffusion in the austenite) would be most difficult at lower temperatures, the proposed drag effect should also be more pronounced at low temperatures. This, however, seems illogical since the less easy formation of clusters at low temperatures should reduce any hindrance to interface motion.

Finally, it is approriate to note that (for low-alloy steels, at least) the activity coefficients of both molybdenum and chromium in austenite [29] are less than unity, implying that these elements do not tend to cluster in austenite.

5.3. Experimental evidence for special drag effects in steels

Some of the most widely quoted evidence for special drag effects on steels is deduced from measurements of the growth rate of allotriomorphic ferrite in steels†. Kinsman and Aaronson [25] found that in a Fe–1.95Mo–0.11C wt % steel, α_1 went through a maximum with decreasing transformation temperature (T), even though theoretical calculations (assuming paraequilibrium transformation) indicated a monotonically increasing α_1 with decreasing T. In addition, the experimental values of α_1 were found to be lower than the calculated values for $T < 800°$ C, the experiments being confined to $T > 720°$ C. On the other

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*This effect is meant to be an additional phenomenon due to the segregation of X, its influence being beyond that of the bulk concentration of X (which would alter the thermodynamics of transformation even in the absence of any interface segregation).

†The growth rate is usually described in terms of the parabolic rate constant α_1, [41], from the relation $s = \alpha_1 t^{1/2}$, where s = allotriomorph half-thickness, t = time at transformation temperature, after the nucleation event. The growth of the allotriomorph is usually treated in terms of the diffusion controlled advance of a planar interface.

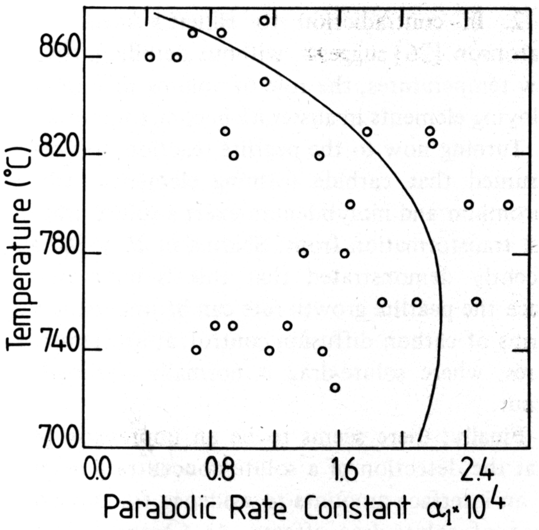

Figure 3 Plot of the parabolic rate constant (calculated for paraequilibrium transformation conditions) as a function of the transformation temperature. The experimental points are due to Kinsman and Aaronson [25].

hand, such difficulties were not encountered in the case of a plain carbon steel and a Fe–Mn–C steel. The lower than expected growth rate in the Fe–Mo–C alloy was thus attributed to a molybdenum-induced special drag effect, as discussed earlier. However, there are problems with this interpretation.

The original theoretical analysis [25] of the growth rate did not allow for the concentration dependence of the diffusivity of carbon in austenite; Fig. 3 presents a reanalysis (using Equation 2 of [25]), taking account of the concentration dependence of diffusivity according to [36]. Better agreement is obtained with the experimental data of Kinsman and Aaronson [25], and a maximum is obtained in the plot of α_1 against T. The agreement with experimental α_1 values is not good for $T < 750°$ C, but there are additional important difficulties, as follows:

1. It is now well established [42–46] that substantial amounts of molybdenum carbides precipitate at the austenite–ferrite interface during ferrite formation in molybdenum containing steels. It is notable that the Fe–Mo–C alloy of [25] was transformed within the ferrite + alloy carbide or ferrite + austenite + alloy carbide phase fields of the equilibrium phase diagram [47]. The formation of such "interphase" carbides requires the long range diffusion of substitutional atoms, and must have a significant effect on the transformation kinetics. The role of such diffusion has been ignored in a recent study [33], which proposed that such carbides only act to increase the driving force for transformation. The effect of the substitutional atom diffusion necessary to form the alloy carbides may be even more pronounced if the diffusion is confined to the vicinity of the transformation front [48]. Hence, disagreement with calculations based on paraequilibrium transformation models is only to be expected, especially at low temperatures, where the driving force for carbide precipitation is highest.

2. It is clear [42–44] that the formation of allotriomorphic ferrite in steels usually occurs by some kind of a ledge mechanism [49], rather than by the continuous displacement of every element of the interface. There are circumstances [50] when the indirect net rate of normal displacement of an interface by a ledge mechanism occurs at a slower rate than would be the case if a ledge mechanism did not operate. It may not be, therefore, realistic to treat the growth kinetics in terms of the advancement of a planar interface.

3. The role of interface faceting [51] on the kinetics of transformation is not clear, and somewhat arbitrary procedures are sometimes used [31] to "correct" for faceting. These corrections can often be very substantial, and reduce the confidence with which experiment and theory may be compared. Furthermore, it is often not obvious that comparative studies involve identical interfaces.

4. In any diffusional transformation, the role of the thermally activated interface attachment processes [52] must become more important as T decreases, ultimately leading to interface controlled growth. Very little is known about the mechanism of interface attachment, and it is possible that departures from diffusion controlled growth might occur, especially at low T.

In recent years there has been an unjustified tendency to extend the solute-drag arguments deduced from observations on allotriomorphic ferrite, to temperature ranges where bainite forms, without taking proper account of the accompanying change in the mechanism of interface motion. The growth of allotriomorphic ferrite is generally accepted to occur by a diffusional mechanism, involving only a volume change on transformation. The formation of bainitic ferrite on the other hand, leads to a surface relief effect which is an invariant-plane strain with a significant shear component, so that the transformation interface is expected to be much more glissile than that responsible for the diffusional growth of allotriomorphic ferrite.

This extrapolation of the high temperature deductions has led to attempts at explaining the bay that is found to occur in time-temperature-transformation (TTT) diagrams, in terms of solute drag effects*. The detailed arguments differ between authors, but Hillert [16] suggests that the bay is associated with the transition from growth involving a local equilibrium mechanism (at high temperatures above the bay region) to a situation below the bay where the compositions at the interface deviate from the local equilibrium condition, giving a reduced drag effect. It is not clear how this mechanism of bay formation would be specific to carbide forming X elements, and the explanation itself seems self contradictory because it relies on the implicit assumption that interface velocity (v) increases with decreasing T†. Furthermore, the interpretation of TTT curves simply in terms of growth velocities is not satisfactory, since such curves really represent the effects of overall transformation kinetics. For instance, it has not been satisfactorily demonstrated that the nucleation rate remains constant over the temperature range discussed.

Kinsman and Aaronson [25] interpreted the TTT curve of their Fe–Mo–C steel in terms of the special drag theory [25], the details of which have already been discussed. Two main points arise:

1. They consider that alloying elements such as molybdenum, which decrease the activity of carbon in austenite lead to a bay in the TTT diagram. Hehemann [34] and Bhadeshia and Edmonds [53] have pointed out that it is possible to obtain bays even in steels containing X elements which have the opposite effect on the activity of carbon in austenite. Indeed, there are other explanations [54–56], which do not have to rely on any solute-drag effect, for the existence of bays in TTT curves, and there is now direct evidence (on a scale of atomic compositional and spatial resolution) to show that there is no solute-segregation at the bainitic-ferrite/austenite interface [57].

2. In contradiction to Hillert's ideas [16], Aaronson [26] suggests, without detailing, that at low temperatures, the role of volume diffusion of alloying elements in austenite becomes important.

Turning now to the pearlite reaction, it is often assumed that carbide forming elements such as chromium and molybdenum exert a solute-drag on the transformation front. Sharma *et al.* [58] have recently demonstrated that this is unnecessary, since the pearlite growth rate can be understood in terms of carbon diffusion control, at low temperatures, where solute-drag is normally assumed to occur.

Finally, there seems to be an impression [48] that the detection of a solute concentration spike at an interface amounts to evidence for the existence of solute-drag effects. As Coates [24] has pointed out, when transformation occurs by the local equilibrium no partitioning mechanism, an X atoms spike will exist in the austenite at the interface, but will not exert a diffusional drag in spite of its low diffusivity; growth will occur at a carbon diffusion controlled rate. As discussed earlier, the actual shape of any concentration spike is also important, and indeed crucial, since it may help distinguish between the misleading case where segregation occurs after the transformation, from the segregation which must exist during interface motion for drag to occur.

6. Conclusions

It seems that there is currently no solute-drag theory capable of being generally applicable to interphase interfaces. The solute-drag models which have been postulated to account for various kinetic measurements in steels do not seem to be firmly based, and the experimental evidence for solute-drag at transformation interfaces seems very unclear. This is not to suggest that solute–drag effects may not occur during some transformations in steels – simply that convincing experimental evidence for their existence is lacking. It is likely that very high resolution analytical techniques will make a significant contribution to this difficult area of research.

*This bay is a region on the TTT diagram where the overall reaction is much slower than that at temperatures just above or below the statis region, and is the region where the upper and lower 'C' curves intersect.

†See Fig. 30, [16], where the mechanism of interface motion changes as the sequence "long range diffusion → local equilibrium → increasing role of diffusion in interface → deviation from local equilibrium → diffusion in interface only → paraequilibrium" as the interface velocity monotonically increases. Hillert then uses this same sequence to explain TTT curves, despite the fact that he interprets the bay as arising due to a minimum in growth velocity.

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