Coupled diffusional and displacive transformations
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SYNOPSIS

Transformations involving crystals containing both substitutional and interstitial elements have been studied theoretically with a view to establishing the conditions under which plates can form with just partial redistribution of the interstitial element during non-equilibrium nucleation and growth.

INTRODUCTION

The rate at which an interface moves depends both on its intrinsic mobility (related to the process of atom transfer across the interface) and on the ease with which any alloying elements partitioned during transformation diffuse ahead of the moving interface. The two processes are in series so that the *interface velocity as calculated from the interface mobility always equals that computed from the diffusion of solute ahead of the interface.*

Both of these processes dissipate the net free energy (ΔG, which does not include stored energy terms) available for interface motion (Fig. 1), G_{id} being the amount dissipated in the interface process and G_{dd} the quantity dissipated in the diffusion process (G_{surf} is stored during the creation of new interface area and G_{el} because of any shape deformation due to phase change; the free energy G_α of α includes G_{el} and G_{surf}, so that ΔG is the free energy available for interface motion after allowing for $G_{el} + G_{surf}$). The two dissipations are related by the equation:

$$\Delta G = G_{id} + G_{dd} \tag{1}$$

When $\Delta G \approx G_{dd}$, growth is said to be diffusion-controlled. Interface-controlled growth occurs when $\Delta G \approx G_{id}$. Mixed control arises when neither process dominates.

Hence, there are two ways of calculating the interface velocity V:

$$V_i = \xi\{G_{id}\} \tag{2}$$
$$V_d = \psi\{G_{dd}\} \tag{3}$$

where ξ and ψ are functions relating V to the appropriate dissipation. Substitution of the correct values of G_{id} and G_{dd} into these equations makes $V = V_i = V_d$. This provides a method for fixing G_{id} and G_{dd} for a given value of ΔG.

To calculate V_d, we consider a disc shaped particle with a curved edge of radius equal to the semi-thickness of the disc. Capillarity is then accounted for by increasing the stored energy of the ferrite by the term G_{surf}, V_d is determined by the diffusion of carbon in the γ ahead of the interface; it can be calculated using the Ivantsov [1] equation:

$$(\bar{x} - x_I)/(x_\alpha - x_I) = (\pi p)^{0.5} \exp\{p\} \operatorname{erfc}\{p^{0.5}\} \tag{4}$$

where p is the Péclet number (a dimensionless velocity) given by $p = V_d r/2\bar{D}$, and ρ is the effective plate tip radius consistent with the parabolic approximation to our model of the plate. The diffusion coefficient D of carbon in austenite depends on the carbon concentration x so a weighted average diffusivity $\bar{D}$ is used [2]:

$$\bar{D} = \int_{x_I}^{\bar{x}} D\{x, T\}\, dx/(\bar{x} - x_I) \tag{5}$$

The function D{x,T} used is according to [3,4]. x_I is the carbon concentration in γ at the γ/α interface; for a given carbon concentration in α at the α/γ interface (i.e., x_α), x_I can have a maximum value x_m.

In order to calculate V_d as a function of G_{dd}, it remains to determine how x_I varies with x_α and G_{dd}. For a given value of x_α, x_m (Fig. 1) can be obtained by solving:

$$(1 - x_\alpha)[\Delta G_{Fe}^{\gamma\alpha} + RT \ln\{(a_{Fe}^\alpha\{1-x_\alpha\})/(a_{Fe}^\gamma\{1-x_m\})\}]$$
$$+ x_\alpha[RT \ln\{(a_C^\alpha\{x_\alpha\})/(a_C^\gamma\{x_m\})\}] + G_{el} + G_{surf} = 0 \tag{6}$$

where $\Delta G_{Fe}^{\gamma\alpha}$ is the Gibbs free energy change accompanying the $\gamma \to \alpha$ transformation in pure iron. a_{Fe}^γ and a_C^γ are the respective activities of Fe and C in γ, that of C being defined relative to graphite as the standard state. R is the universal gas constant. Thus, for the special case where $G_{id} = 0$, eq.6 can be used to calculate x_I ($= x_m$) for a given value of x_α. We note that G_{dd}, equal to ΔG, is then given by:

$$\Delta G = G_{dd} = G_1\{x_\alpha, \bar{x}\} - G_\alpha\{x_\alpha\} \tag{7}$$

where $G_1\{x_\alpha, \bar{x}\}$ is the Gibbs free energy at the point x_α on the tangent to the point $\bar{x}$ on the γ free energy curve. γ free energy curve.

When G_{id} is finite (i.e., when $\bar{x} < x_I < x_m$), its value is given by:

$$G_{id} = G_1\{x_\alpha, x_I\} - G_\alpha\{x_\alpha\} \tag{8}$$
$$G_{dd} = \Delta G - G_{id} \tag{9}$$

The variation of G_{id} with x_I is illustrated in Fig. 2.

The theory for thermally activated dislocation motion can be adapted to represent the motion of the α/γ interface, using dislocation models of interfacial structure [5-8]; V_i is then given by:

$$V_i = V_o \exp\{-G^*/(kT)\} \tag{10}$$

where G^* = Gibbs free energy of activation, V_o is the dislocation velocity as limited by lattice friction (in the absence of any significant inertial effects), and is taken to be 30m/s based on experimental data obtained from single-interface martensitic transformations [6]. k is the Boltzmann constant and T is the absolute temperature.

$$G^* = \int_{G_{id}}^{\bar{G}_{id}} V^*\, dG \tag{11}$$

$\bar{G}_{id}$ is the maximum glide resistance presented by obstacles to interface motion, V^* is the activation volume swept by the

interface during a thermally activated event. For a wide range of obstacle interactions, the function $G^*\{G_{id}\}$ can be represented by:

$$G^* = G_o\{1 - (G_{id} / \overline{G}_{id})^y\}^z \qquad (12)$$

where G_o is the total activation free energy necessary to overcome the resistance to dislocation motion without the aid of external work. The constants y and z define the shape of the force-distance function and for solid solution interactions in the Labusch limit, we assume that y=0.5 and z=1.

Kinetic data for the interface-controlled barrierless nucleation of martensite give (unpublished research) $G_o = 0.31\mu\Omega$ where μ is the shear modulus of the matrix and Ω is the volume per atom. Similarly, $\overline{G}_{id}$ is found to be $\overline{G}_{id} = 1.22 \times 10^{-3}\mu$.

Calculations were carried out for an Fe-0.4C wt.% alloy transformed at temperatures within the range 410-530°C. For this alloy, the martensite start temperature calculated thermodynamically [9] is 397°C.

The results are presented in Fig. 3, in which the ordinate begins at 700 J/mol because this is a reasonable representation of the term $(G_{el} + G_{surf})$ during the growth of martensite; this term in effect represents the stored energy of martensite and is assumed independent of temperature. During nucleation, the stored energy term exceeds 700 J/mol and is taken to be $2 \times 10^{-3}\mu$, based on previous work on the nucleation of martensite. The temperature dependence of the elastic constants of γ was taken into account for the nucleation part of the problem. In Fig. 3, every intersection of the function ξ with ψ corresponds to a solution for the actual growth velocity, since V_i then equals V_d. It is not surprising that in all circumstances, the growth rate during nucleation is lower than that during growth. As the particle grows and the $G_{el}+G_{surf}$ term diminishes, the velocity should smoothly move between these limits.

The solutions for V, as obtained from Fig. 3, are plotted in Fig. 4, as a function x_α, the level of carbon in the α. If we next assume that the transformation occurs at a value of x_α corresponding to a maximum growth rate (i.e., $V = V_{max}$), the growth rate of a plate, V_{max}, increases monotonically as the transformation temperature decreases from 530-410°C. At the same time, the ratio $x_\alpha/\overline{x}$ increases from 0.12 to 0.65 as the temperature decreases from 530°C to 460°C. For transformation at 440°C and below, $(x_\alpha/\overline{x}) = 1$, the plates *growing* with a full supersaturation of carbon. The increase in V_{max} with decreasing temperature occurs in spite of the accompanying decrease in the diffusivity of carbon in γ.

For nucleation, where $G_{el}+G_{surf}$ is greater, the interface velocity passes through a maximum as the temperature decreases, giving C-curve nucleation kinetics. As with growth, the trend for nucleation is for increasing supersaturation with decreasing T, except for an anomalous reduction in supersaturation around 440°C where the variation of V_d with x_α is complex.

In contrast to the case of completely diffusionless martensitic transformation, all of the transformation temperatures considered thus far involve some solute partitioning during nucleation. The results for 410°C indicate that diffusionless nucleation must follow just below 410°C given that ξ for nucleation below this temperature is to the left of the crossover region of the ψ curves. The model is therefore consistent with the definition of martensite as involving diffusionless nucleation and growth. The other results are consistent with the hypothesis [10] that transformations at temperatures above the M_s temperature (i.e., to bainite and Widmanstätten ferrite) involve displacive nucleation in which $x_\alpha < \overline{x}$. Growth occurs at lower values of x_α as the transformation temperature is increased. An approximation which should be modified in future work is that the stored energy of martensite during growth remains independent of transformation temperature. It is known that this is not the case because the aspect ratio of bainite plates is considerably smaller than that of martensite formed at lower temperatures. These features can be incorporated using a model for the dynamic evolution of the shape and stored energy of a growing plate in a plastic matrix, recently applied to martensite

growth [11]. This can account for the cessation of individual growth events (subunits) through plastic accommodation.

CONCLUSIONS

A model has been established which allows a calculation of the plate lengthening velocity for mixed diffusion and interface control, during displacive transformation of $\gamma\rightarrow\alpha$. By considering velocity functions for different levels of carbon supersaturations in α, and by assuming a maximum velocity criterion, the model has been used to predict the level of supersaturation at different transformation temperatures during both nucleation and growth.
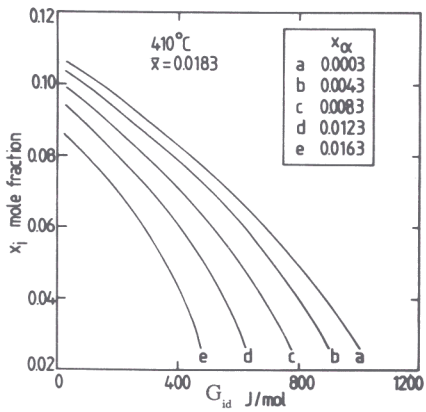
It is found that for an Fe-0.4C wt.% alloy, the model predicts an increasing interfacial velocity and supersaturation during growth with decreasing transformation temperature, while nucleation velocity passes through a maximum giving C-curve kinetics. The supersaturation during nucleation increases with undercooling, the nucleus becoming fully supersaturated at the M_s temperature. Growth with a full supersaturation is found possible above the M_s temperature. The coupled transformation model thus provides a possible rationale for all the displacive transformations in steels (martensite, bainite and Widmanstätten ferrite).

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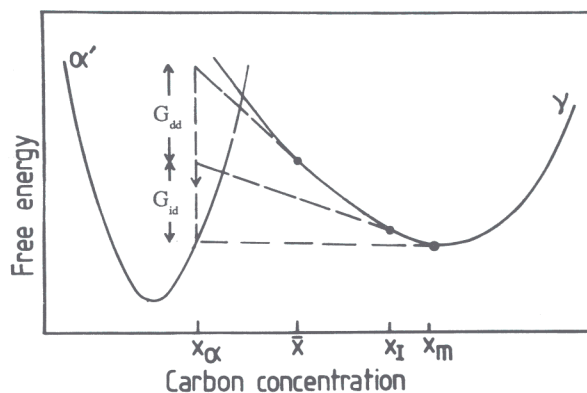
1 Constant temperature free energy curves showing the quantities ΔG, G_{dd} and G_{id} for the case where the interface compositions are x_I and x_α in γ and α respectively. ΔG is exclusive of the stored energy terms $G_{el} + G_{surf}$.

Figure 2. Variation of G_{id} with x_I for an Fe-0.4C wt.% carbon alloy transformed at $410^\circ C$.

2 Variation of G_{id} with x_I for an Fe-0.4C wt.% carbon alloy transformed at $410^\circ C$.

3 Example plots of $V\rho$ versus the free energy $(G_{id} + G_{el} + G_{surf})$. The calculations are for an Fe- 0.0183C mol. frac. alloy. The curves numbered 1-10 correspond to V_d calculations for x_α values of 0.0003, 0.0023, 0.0043, 0.0063, 0.0083, 0.0103, 0.0123, 0.0143, 0.0163 and 0.0173 mole fraction of carbon, respectively. The chain link curve corresponds to V_i for growth and the dashed curve to V_i for the nucleation event.
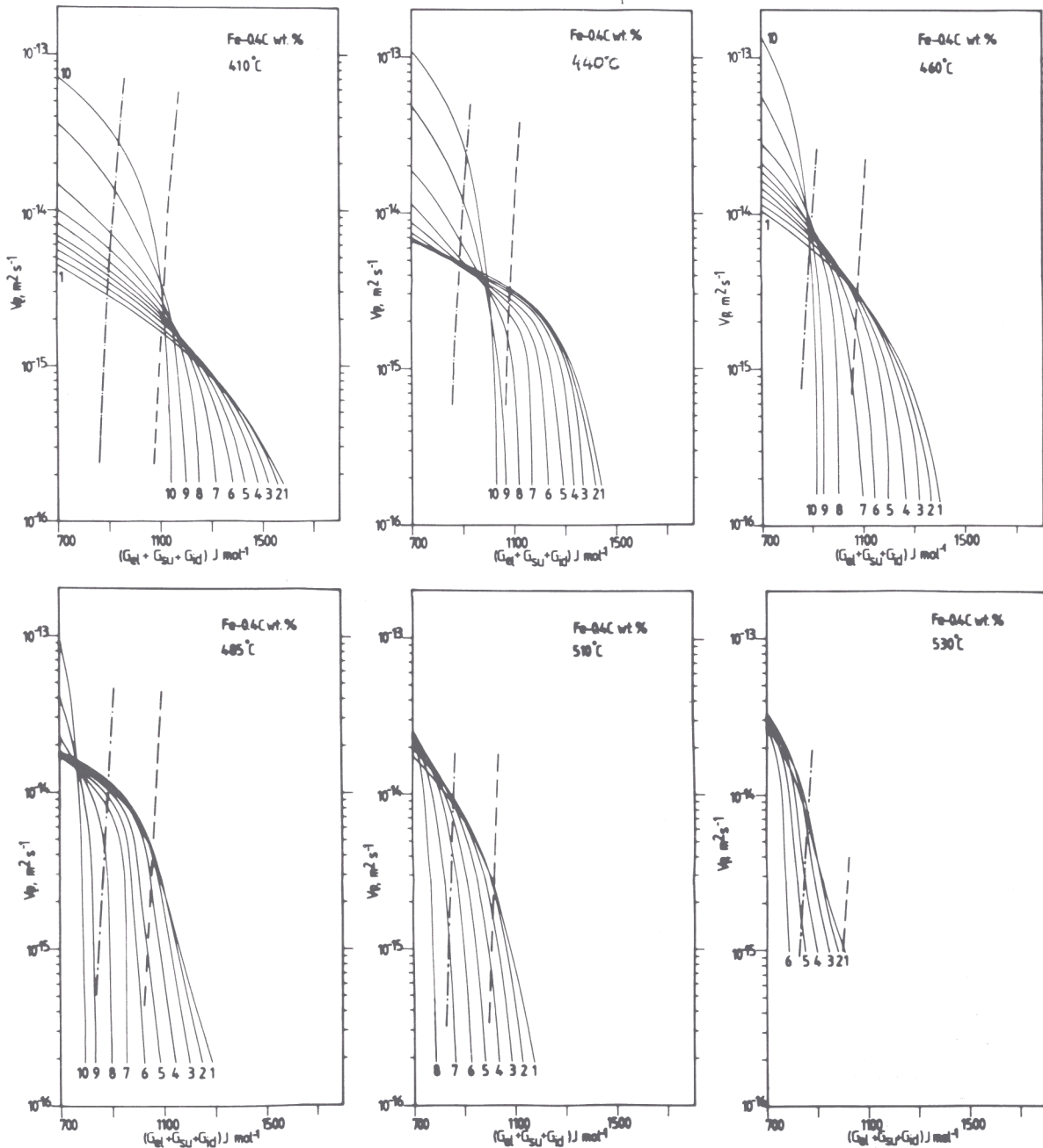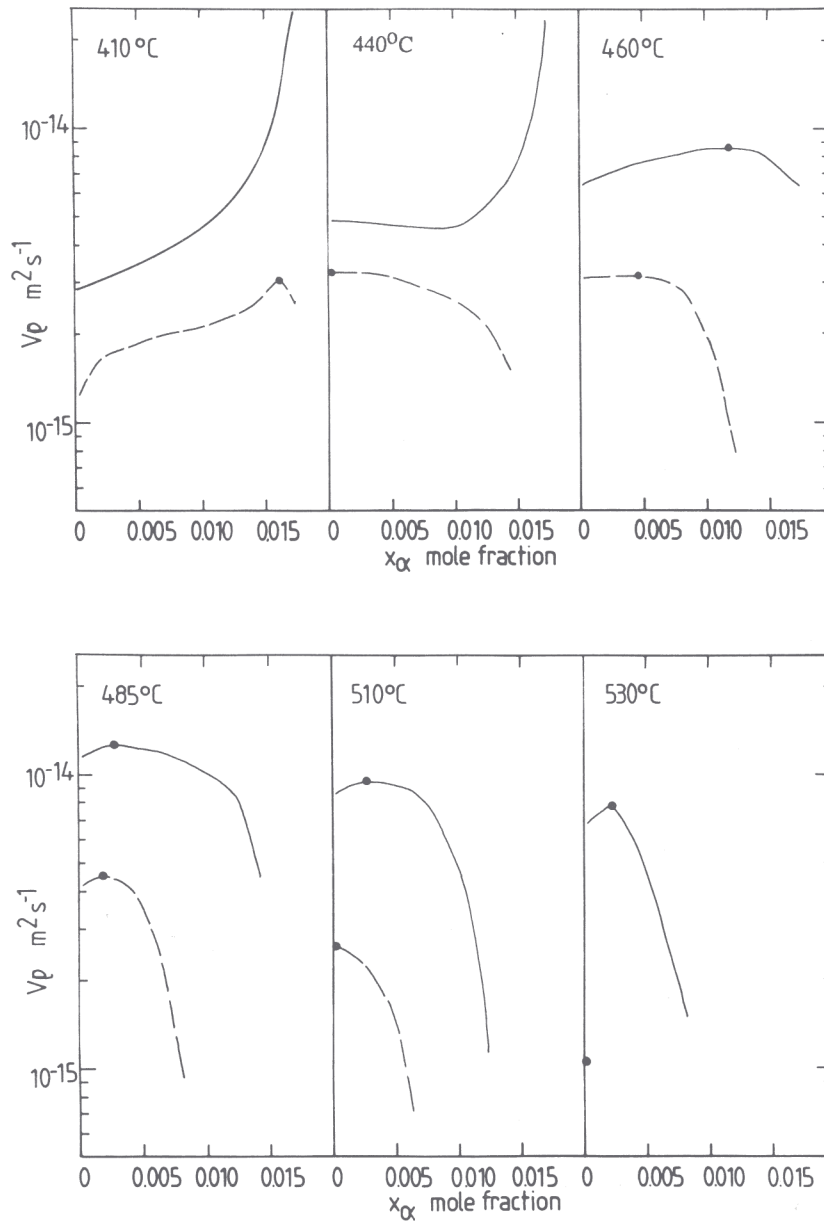
4 Plots of $V\rho$ versus x_α for all cases where $V_i = V_d$. The points indicate the locations of maxima.