

# A model for interphase precipitation in stoichiometrically balanced vanadium steels

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A model has been developed which provides a fairly simple rationale for interphase precipitation in the stoichiometrically balanced Fe–V–C and Fe–V–N–C steels. The model assumes that interphase precipitation takes place by the steady-state migration of a stepped interface. Quantitative relationships between ledge velocity, ledge height, transformation temperature and carbide volume fraction, are obtained. The influence of growth kinetics upon the formation of interphase precipitation is also briefly discussed.

## 1. Introduction

Ferrite in steels may grow by the movement of ledges accompanied by carbide precipitation on the ledge terraces [1–3]. Such a mechanism is normally called “interphase precipitation” [1–6] and has been subjected to extensive experimental investigation [1–3, 5, 7]. However, comparatively less work has been done to establish quantitative relationships between growth kinetics and the morphology of interphase precipitation [8–14].

Todd *et al.* [8] have given a detailed quantitative description of interphase precipitation of alloy carbides (IPAC). They maintained that IPAC formed by the consecutive passage of carbide-free ferrite ledges. The ferrite ledge height, in their model, was not necessarily equal to the intersheet spacing. They assumed that carbide precipitation on the ledge terrace took place periodically after the passage of a certain number of ferrite ledges. In their view, the alternating ferrite and carbide layer formed one after the other, so that the ferrite/austenite interface moved in the direction normal to the ledge velocity.

Often, however, “trains” of ferrite ledges are observed to move together so that a stepped interface migrates in the direction of ledge velocity. In this case the ferrite ledge height is equal to the intersheet spacing. Experimental evidence for such a mechanism can be found in many alloys [1–4, 15–17]. A well-known micrograph illustrating that is presented by Campbell and Honeycombe [16] (see Fig. 7 of [16] or Fig. 10 of [1]). One detail of this micrograph is of particular relevance, namely, the size of the carbide particles on a given ledge terrace decreases as they are closer to the riser of the same ledge. A schematic view of such a situation, as well as a morphological study of IPAC in microalloyed steels, can be found in Rios [12].

When the steel is stoichiometrically balanced and all the carbon and the carbide former element go into

the carbides, probably the most simple situation exists in which IPAC can occur because the matrix composition remains constant. As a consequence, it is reasonable to admit that the ledge velocity also remains constant so that a steady-state migration of the stepped interface is obtained. Because of this, the final microstructure is expected to be entirely interphase precipitation with approximately constant ledge height and carbide size.

Such a microstructure was observed in the stoichiometrically balanced Fe–V–C alloys of Batte and Honeycombe [18]. Their work is the only experimental work available in which carbide volume fraction and transformation temperature were systematically varied, with ledge height and carbide size being measured in each case. The work of Balliger and Honeycombe [19] on Fe–V–N–C alloys has also been included in the present analysis. However, even though their alloys were stoichiometrically balanced, their microstructure was not always entirely interphase precipitation. In some cases it also contained precipitation on dislocations and Widmanstätten ferrite.

In this work, a quantitative model has been developed to account for interphase precipitation in the stoichiometrically balanced Fe–V–C and Fe–V–N–C steels studied by Batte and Honeycombe [18] and by Balliger and Honeycombe [19], respectively. In this paper, “carbon” and “carbides” will be used for simplicity. Of course, if nitrogen is present “carbon and nitrogen” and “carbonitrides” would be more appropriate.

## 2. Description of proposed transformation mechanism

The mechanism of the steady-state migration of a stepped interface is shown schematically in Fig. 1. The following assumptions are made.

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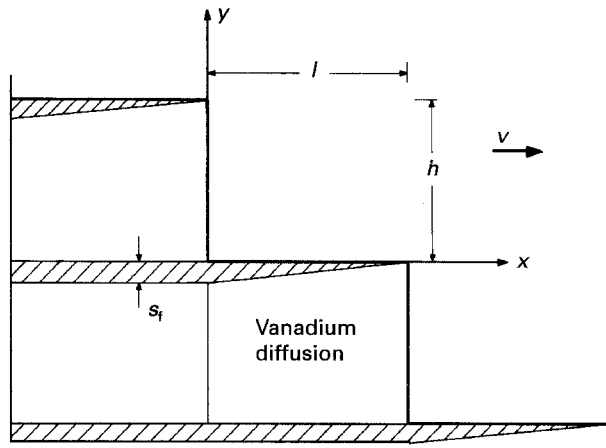


Figure 1 A schematic view of the mechanism proposed here. The stepped interface migrates with a velocity,  $v$ , in the direction indicated by the arrow. Ledge height is  $h$  and interledge distance is  $l$ . "Pseudophase" is the shaded area. Its thickness is  $s_f$  just behind the advancing ledge riser and decreases linearly, being zero at the end of the ledge terrace. A moving  $x$ - $y$  reference framework attached to the riser of the ledge is also shown. Carbon diffusion takes place in the austenite. Vanadium diffusion takes place in ferrite, behind the moving riser, within the region limited by  $0 < x < l$  and  $-h < y < 0$ .

1. The stepped interface migrates with a given constant velocity,  $v$ . The ledge height is  $h$  and the interledge distance is  $l$ . A moving  $x$ - $y$  reference framework attached to the riser of the ledge is also shown in Fig. 1.

2. The carbides can be thought to form as a continuous layer or "pseudophase" [8]. This pseudophase (shaded area in Fig. 1) reaches its final thickness,  $s_f$ , just behind the advancing ledge riser. Ahead of the moving ledge riser the pseudophase thickness is assumed to decrease [1, 16] linearly so that the position of the pseudophase/ferrite interface,  $y_p$ , is  $y_p = -s_f$  at  $x = 0$  and  $y_p = 0$  at  $x = l$ . This implies that half of the carbide volume fraction from the region limited by  $0 < x < l$  and  $-h < y < 0$  has precipitated ahead of the moving riser on the terrace of the "next" ledge. The assumption of a "pseudophase" is not unreasonable, as it has been shown [12] that carbides occupy a significant proportion of the area of the ledge terrace.

3. Carbon diffusion to the carbide takes place through the austenite. The carbon content of austenite remains constant because the stoichiometry requires that all the carbon rejected by the ferrite goes into the carbides.

4. Vanadium diffusion to the carbide takes place through the ferrite behind the moving riser within the diffusion region limited by  $0 < x < l$  and  $-h < y < 0$ . Because of assumption 2, the average vanadium concentration in the ferrite within this region must be equal to  $V_0/2$ , where  $V_0$  is the vanadium concentration of the steel in atoms per unit of volume. If a steady state is maintained, all vanadium that enters the ferrite through the moving riser interface must go into the pseudophase forming on the terrace of the same ledge. The assumption of vanadium diffusion through the ferrite is reasonable, because vanadium diffusivity in ferrite is about three orders of magnitude higher than in austenite [8]. The "pseudophase" is represented in Fig. 1 growing inside

the ferrite, below the ledge terrace, because of the assumption that its growth is controlled by vanadium diffusion in ferrite.

5. Vanadium concentration in ferrite on the ledge riser ferrite/austenite interface (that is, at  $x = l$ , along the  $-y$  direction) is assumed to be equal to the initial vanadium concentration of the steel,  $V_0$ . Vanadium concentration in ferrite on the ferrite/pseudophase interface (that is, at  $y = y_p$ ) is assumed to be equal to zero [8]. Vanadium concentration in austenite remains constant and equal to  $V_0$ .

Based on these assumptions, the steady-state movement of the stepped interface can be related to carbide growth that is determined by the diffusion of the slowest element: vanadium. Therefore, one has to find a steady state solution to the problem of vanadium controlled pseudophase growth in ferrite.

### 3. Steady-state vanadium-controlled carbide growth

A rigorous mathematical solution of the diffusion equation is not attempted. Instead a simplified approach, similar to Zener's linearized gradient [20] is adopted [13]. Here,  $x$  and  $y$  refer to the moving reference framework shown in Fig. 1. It is admitted that within the diffusion region, vanadium concentration in ferrite in atoms per unit of volume,  $V(x, y)$ , can be approximated by a plane

$$V(x, y) = A + Bx + Cy \quad (1)$$

Equation 1 implies that the gradients are constant along the  $x$  and  $y$  direction.

The constants  $A$ ,  $B$  and  $C$  can be determined by using two boundary conditions which are consequences of assumption 5 and mass conservation within the diffusion region.

The first boundary condition is that the average vanadium concentration in ferrite just behind the ledge riser ferrite/austenite interface (that is at  $x = l$ ) is equal to the initial vanadium concentration,  $V_0$ . This can be written as

$$V_0 = - \frac{\int_0^{-h} V(l, y) dy}{h} \quad (2)$$

The second boundary condition is that the average vanadium concentration in ferrite at the ferrite/pseudophase interface (that is, at  $y = y_p \approx 0$ ) is equal to zero

$$\frac{\int_0^l V(x, 0) dx}{l} = 0 \quad (3)$$

where it was assumed that the thickness of the pseudophase is small compared to the ledge height so that  $y = y_p \approx 0$ . This is justified by the fact that the carbide volume fraction is invariably very small  $< 0.02$ .

The average concentrations were imposed as boundary conditions to try to avoid a difficulty found in the solution of two-dimensional steady state ledge growth [21, 22]: when the gradient at the ledge riser is considered constant one normally obtains

a concentration varying along the ledge height. Specifying an average concentration ensures that, at least on average, the concentration will have the required value.

From assumption 4, the average vanadium concentration in ferrite within the diffusion region must be equal to  $V_0/2$

$$\frac{V_0}{2} = - \frac{\int_0^{-h} \int_0^l V(x, y) dx dy}{lh} \quad (4)$$

Inserting Equation 1 into Equations 2–4, gives

$$V(x, y) = V_0 \left( -\frac{1}{2} + \frac{x}{l} - \frac{y}{h} \right) \quad (5)$$

This is admittedly a crude approximation but can be used because the main interest is in *average* quantities, not on the concentration profile itself.

As a steady-state has been assumed, all vanadium atoms that enter the ferrite through the ledge riser per unit of time must enter the growing pseudophase. Therefore, a flux balance gives

$$l \left[ \frac{\partial V(x, y)}{\partial y} \right]_{y=0} + h \left[ \frac{\partial V(x, y)}{\partial x} \right]_{x=l} = 0 \quad (6)$$

From Equations 5 and 6,  $h = l$ .

Noticing that the average vanadium concentration at  $y = y_p \approx 0$ , is equal to zero, the average velocity of the pseudophase/ferrite interface,  $v_p$ , can be calculated from

$$v_p(0 - kV_p) = -D \left[ \frac{\partial V(x, y)}{\partial y} \right]_{y=0} \quad (7)$$

where  $D$  is the vanadium diffusion coefficient in ferrite,  $V_p$  is the vanadium concentration in the carbide,  $kV_p$  is the vanadium concentration in the pseudophase, and  $k$  is a constant.

From Equation 7

$$v_p = -\frac{fD}{kh} \quad (8)$$

where  $f = V_0/V_p$  is the volume fraction of carbides, and  $v_p < 0$  because the pseudophase grows in the  $-y$  direction.

The ledge velocity,  $v$ , can be calculated by noticing that as the ledge riser moves from  $x = 0$  to  $x = h$  (recalling that  $h = l$ ) in a time,  $\tau$ , the pseudophase average interface position moves from  $y_p = -s_f/2$  to  $y_p = -s_f$ . Therefore

$$\tau = -\frac{s_f}{2v_p} = \frac{h}{v} \quad (9)$$

where  $\tau$  is the time it takes for the riser to move a distance  $h$  (which is equal to  $l$ ).

If all vanadium goes into the carbide and then  $s_f(kV_p) = hV_0$  or  $f = (ks_f)/h$ . Using this and Equations 8 and 9 gives

$$v = \frac{2D}{h} \quad (10)$$

Equation 10 shows that ledge velocity is inversely proportional to ledge height. It can be useful to calculate ledge velocity from measured values of  $h$ .

#### 4. Relationship between ledge velocity, carbide volume fraction and transformation temperature

Unfortunately, Equation 10 is not useful to relate ledge velocity to transformation temperature and carbide volume fraction because how the ledge height depends on these is not known.

Using Equations 8–10,

$$\frac{ks_f}{D^{1/2}} = f(2\tau)^{1/2} \quad (11)$$

and

$$\frac{h}{D^{1/2}} = (2\tau)^{1/2} \quad (12)$$

It can be seen from Equations 11 and 12 that there are two equations for three unknowns, namely,  $ks_f$ ,  $h$  and  $\tau$ . An additional condition is necessary and it is assumed that

$$K = \frac{ks_f}{D^{1/2}} \quad (13)$$

where  $K$  is a model parameter, related to the characteristics of the pseudophase.

##### 4.1. Phenomenological determination of $K$

The model parameter  $K$  is now determined from a phenomenological analysis of the data of Batte and Honeycombe and Balliger and Honeycombe shown in Tables I and II, respectively.

The carbide/nitride volume fraction,  $f$ , was calculated admitting that all carbon, nitrogen and vanadium formed carbides/nitrides [12]. The density of ferrite was taken to be equal to 7.86, that of vanadium carbide equal to 5.77 and that of vanadium nitride equal to 6.13 [23].

The quantity  $I_0/I_{in}$  (shown in Tables I and II) is the ratio of the total interstitial element content in the alloy,  $I_0$ , to the amount of interstitial,  $I_{in}$ , which is insoluble in the austenite with vanadium content equal to  $V_0$ .

For Fe–V–C alloys (Table I) with carbon content equal to  $C_0$  the amount of soluble carbon,  $C_s$ , can be calculated from

$$C_s = \frac{K_{VC}}{V_0} \quad (14)$$

where  $K_{VC}$  is the solubility product of vanadium carbide in austenite. Consequently,

$$\frac{I_0}{I_{in}} = \frac{C_0}{C_0 - C_s} \quad (15)$$

For Fe–V–C–N alloys (Table II) containing  $C_0$  and  $N_0$  of carbon and nitrogen, the methodology developed by Rios [24, 25] can be used. The solubility

TABLE I Data of Batte and Honeycombe [18]:  $T$  is the transformation temperature,  $h$  is the ledge height,  $n$  is a number associated with a particular data point for further reference,  $I_0/I_{in}$  is the ratio of the total interstitial element content in the alloy,  $I_0$ , to the amount of interstitial,  $I_{in}$ , which is insoluble in the austenite with vanadium content equal to  $V_0$ . Alloy compositions in wt %

Alloy 1, Fe-1.04V-0.20C-0.02Nb, $f = 1.69$ vol %				Alloy 2, Fe-0.75V-0.15C-0.02Nb, $f = 1.23$ vol %				Alloy 3, Fe-0.48V-0.09C-0.02Nb, $f = 0.78$ vol %			
$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$	$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$	$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$
1	725	7.5	1.01	6	730	10	1.02	11	730	18	1.04
2	750	10	1.01	7	755	13	1.03	12	755	21	1.08
3	755	16	1.02	8	780	20	1.05	13	780	35	1.13
4	800	20	1.04	9	806	24	1.08	14	806	62	1.24
5	825	30	1.06	10	830	52	1.13	15	830	73	1.42

TABLE II Data of Balliger and Honeycombe [19]:  $T$  is the transformation temperature,  $h$  is the ledge height,  $n$  is a number associated with a particular data point for further reference,  $I_0/I_{in}$  is the ratio of the total interstitial element content in the alloy,  $I_0$ , to the amount of interstitial,  $I_{in}$ , which is insoluble in the austenite with vanadium content equal to  $V_0$ . Alloy compositions in wt %

Alloy 4, Fe-0.27V-0.05C-0.0002N, $f = 0.44$ vol %				Alloy 5, Fe-0.26V-0.020C-0.022N, $f = 0.4$ vol %				Alloy 6, Fe-0.29V-0.004C-0.032N, $f = 0.42$ vol %			
$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$	$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$	$n$	$T(^{\circ}\text{C})$	$h(\text{nm})$	$I_0/I_{in}$
16	720	21	1.08	21	740	18	1	25	760	35	1
17	740	44	1.13	22	760	42	1.01	26	810	85	1.01
18	760	57	1.2	23	790	50	1.01	27	850	149	1.01
19	790	103	1.41	24	830	120	1.01	—	—	—	—
20	810	114	1.71	—	—	—	—	—	—	—	—

product for the carbonitride is given by

$$\frac{V_0 C_s}{K_{VC}} + \frac{V_0 N_s}{K_{VN}} = 1 \quad (16)$$

where  $C_s$  and  $N_s$  are the amounts of carbon and nitrogen soluble in austenite with vanadium concentration equal to  $V_0$  and  $K_{VN}$  is the solubility product of vanadium nitride in austenite.

Admitting that  $C_s/N_s \approx C_0/N_0$ , the values of  $C_s$  and  $N_s$  can be calculated from Equation 16. So that

$$\frac{I_0}{I_{in}} = \frac{C_0 + N_0}{C_0 + N_0 - C_s - N_s} \quad (17)$$

The solubility products of vanadium carbide and vanadium nitride were taken from Narita [26] and Roberts and Sandberg [27], respectively [25].

The first step of the phenomenological analysis is to obtain an expression for  $h$  from Equations 12 and 13

$$h = K \frac{D^{1/2}}{f} \quad (18)$$

Equation 18 suggests plotting experimentally determined values of  $h$  against  $D^{1/2}/f$ . The vanadium diffusion coefficient in ferrite,  $D$ , was taken from other works [28, 29].

Fig. 2 shows a plot of ledge height,  $h$  (nm) against  $D^{1/2}/f$  with  $D$  expressed in  $\text{nm}^2 \text{s}^{-1}$  and  $f$  given in vol % for Alloys 1-4 (Tables I and II) which are essentially vanadium carbon alloys. Visual inspection of Fig. 2 suggests that points 1-9, 11-13 and 16 (see Tables I and II) lie on a straight line. Linear regression analysis of these points gives a best-fit straight

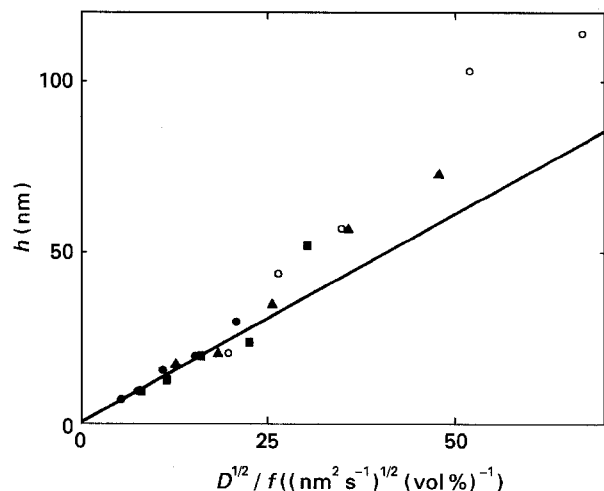


Figure 2 Plot of ledge height,  $h$ , against  $D^{1/2}/f$ . The best-fit straight line is also shown. Its intercept is small, 0.6 nm, and its slope is  $1.22 \text{ s}^{1/2} \text{ vol \%}$ . The correlation coefficient is 0.95. Data points are from Alloys 1-4 given in Tables I and II. Only points 1-9, 11-13 and 16 from Tables I and II were included in the linear regression analysis. It can be seen that the excluded points lie systematically above the best-fit straight line. Alloy: (●) 1, (■) 2, (▲) 3, (○) 4.

line (shown in Fig. 2) which has a small intercept equal to 0.6 nm and a slope, which corresponds to  $K$  in Equation 18, equal to  $1.22 \text{ s}^{1/2} \text{ vol \%}$ . The correlation coefficient is equal to 0.95. For remaining points: 10, 14-15 and 17-20, the measured values of  $h$  lie systematically above the best-fit line. Moreover, the deviation from the best-fit line appears to increase for points with the highest transformation temperatures and lowest alloy contents.

Further examination of Fig. 2 and Tables I and II suggests that higher deviations from the best-fit straight line can be associated with increasing values of  $I_0/I_{in}$ . Thus,  $K$  can be considered constant for  $I_0/I_{in} \approx 1$  but appears to increase as  $I_0/I_{in}$  increases. This observation suggests that to a first approximation

$$K = K_s \frac{I_0}{I_{in}} \quad (19)$$

Introducing Equation 19 into Equation 18 gives

$$h = K_s \left( \frac{I_0}{I_{in}} \right) \frac{D^{1/2}}{f} \quad (20)$$

A plausible physical interpretation can be given of the quantity  $I_{in}/I_0$ . If the supersaturation for carbide nucleation from austenite on the ledge terraces is high, a large number of carbides can nucleate per unit of area, resulting in fine, closely spaced carbides. On the other hand, if the supersaturation is low, fewer nuclei and consequently coarser and more widely spaced carbides will be formed. In a previous work [12] it was shown that carbide size is directly proportional to ledge height, so that finer carbides will result in smaller ledge heights. The quantity  $I_{in}/I_0$  may be associated with the supersaturation available to carbide precipitation. Thus, lower values of  $I_{in}/I_0$  will result in coarser carbides and, consequently, larger ledge heights. As a consequence, if carbide size depends on  $I_{in}/I_0$ , ledge height must depend on  $I_0/I_{in}$  as shown in Equation 20.

The phenomenological analysis thus suggests that the characteristics and formation of the pseudophase can be associated with carbide nucleation on the ledge terraces.

Equation 20 suggests that  $h$  is plotted against  $(I_0/I_{in})D^{1/2}/f$ . This is shown in Fig. 3 which includes all data shown in Tables I and II. Linear regression analysis gives a correlation coefficient of 0.96. The best-fit straight line shown in Fig. 2 has a very small intercept equal to  $-0.25$  nm and a slope, which corresponds to  $K_s$ , equal to  $1.22 \text{ s}^{1/2} \text{ vol } \%$ . That is, Equation 20 reduces to Equation 18 for  $I_0/I_{in} \approx 1$ .

Therefore, the regression analysis shows that Equation 20 provides a good and very simple description of ledge height for both Fe-V-C and Fe-V-C-N stoichiometric alloys.

It is worthy of note that Equation 20 encompasses ledge heights ranging from 7.5–149 nm. Another point is that the left-hand side of Equation 20 contains only one adjustable parameter, namely,  $K_s$ . All other quantities can be calculated from composition and transformation temperature.

In principle,  $K_s$  could be estimated from a single measurement of ledge height at a certain transformation temperature and composition and this value used to estimate other ledge heights at other transformation temperatures and compositions. However theoretically possible, this would not be recommended, because in this case too much reliance would be placed on the precision of this single measurement of ledge height.

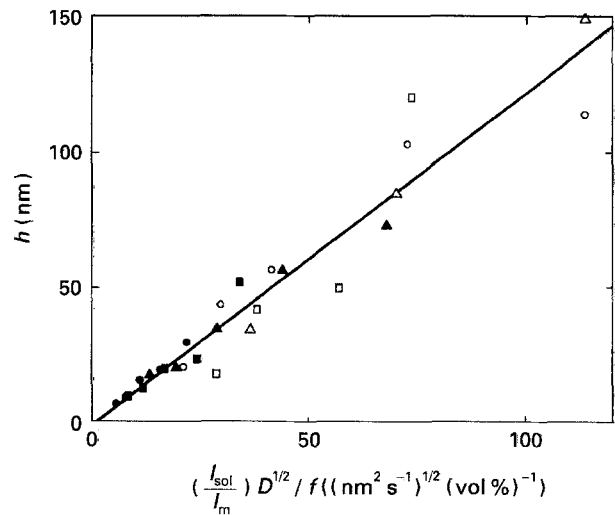


Figure 3 Plot of ledge height,  $h$ , against  $(I_0/I_{in})D^{1/2}/f$ . The quantity  $I_0/I_{in}$  is the ratio of the total interstitial element content in the alloy,  $I_0$ , to the amount of interstitial,  $I_{in}$ , which is insoluble in the austenite with vanadium content equal to  $V_0$ . The best-fit straight line is also shown. Its intercept is very small,  $-0.25$  nm, and its slope is  $1.22 \text{ s}^{1/2} \text{ vol } \%$ . The correlation coefficient is 0.96. Data points are from Alloys 1–6 given in Tables I and II. Alloy: (●) 1, (■) 2, (▲) 3, (○) 4, (□) 5, (△) 6.

Moreover, by using Equation 20 together with a relationship between carbide size and ledge height developed in a previous work (Equation 3 of [12]) one would be able to estimate values of ledge height and carbide size for other transformation temperatures and compositions.

#### 4.2. Expression for ledge velocity

In view of the above, one can substitute Equation 20 into Equation 10 and obtain another expression for the ledge velocity, namely

$$v = \left( \frac{2}{K_s} \right) \left( \frac{I_{in}}{I_0} \right) f D^{1/2} \quad (21)$$

From Equation 21 it can now be seen that ledge velocity decreases with transformation temperature, decreases with carbide volume fraction, and decreases as the solubility of the carbides increases. In addition, if the carbide solubility decreases too much so that  $I_{in}/I_0$  becomes very small, carbide nucleation may not be able to occur. So that at highest temperatures, carbide-free proeutectoid ferrite may occur. This was confirmed in Alloy 4 in which above  $810^\circ\text{C}$  Balliger and Honeycombe report that proeutectoid ferrite formed.

#### 5. Comparison with the model of Todd *et al.*

Even though Todd *et al.* [8] took a different view on interface migration, it is interesting to compare the ledge speeds obtained here with their "average velocity of the interphase boundary",  $\bar{v}_b$ , shown in Table IV of [9]. Such a comparison shows that the ledge speeds obtained here are about half those obtained by them. Moreover,  $\bar{v}_b$  exhibits the same trends predicted from Equation 21: it decreases with transformation

temperature and carbide volume fraction. The reason for such a similarity is that the assumption that vanadium carbide growth is controlled by vanadium diffusion in ferrite is made in both models. Such an assumption appears to be so "strong" that it appears to influence the resultant trends more than the other assumptions on the transformation mechanism.

Li and Todd [9] attempted to compare  $\bar{v}_b$  with the TTT curves given by Batte and Honeycombe. However, it is fair to say that TTT curves cannot be explained only by the calculated velocities for the following reasons:

1. in both models the velocity decreases with transformation temperature whereas the TTT curves exhibit their characteristic C-shape;

2. in both models the velocity increases with carbide volume fraction whereas the TTT curves are slightly displaced to longer times as the carbide volume fraction increases.

It is well-known that TTT curves depend not only on growth kinetics but also on nucleation kinetics. It is always difficult to separate these factors from TTT data only. As a consequence, reliable comparisons can only be made with directly measured interface velocities which are not available. Moreover, in view of the many simplifying assumptions made in both models, one cannot expect too much precision of the absolute values of velocities. It would probably be more realistic to expect that they are within the correct order of magnitude.

On the whole, the present model offers a much more simple explanation and more simple and general expressions for interphase precipitation in stoichiometrically balanced alloys than the model of Todd *et al.* [8].

## 6. Discussion

It is very important to discuss the physical meaning of Equations 10 and 21. It was admitted in the first place that the stepped interface migrates with a given velocity  $v$ . From this it was established how carbide precipitation should take place so that a steady state could be maintained. As a consequence, ledge velocity could be related to carbide precipitation. Therefore, Equations 10 or 21 can be used to calculate ledge velocity from ledge height, vanadium diffusivity in ferrite and alloy composition.

However, Equations 10 and 21 cannot be interpreted as meaning that the growth kinetics is *controlled* or *determined* by carbide precipitation or vanadium diffusion in ferrite. The opposite is perhaps more likely. It is carbide precipitation and, consequently, ledge height that probably depends on growth kinetics. To illustrate this point, take, for example, the alloy Fe-0.96 wt % V-0.21 wt % C-0.97 wt % Al studied by Wilyman and Honeycombe [30]. The ratio of  $K_{Al}$  determined from this alloy to the  $K$  obtained here is about 4. Consequently, the ratio of the ledge velocity of the aluminium alloy to the ledge velocity of an alloy with the same carbon and vanadium content but without aluminium is about 0.25. This indicates that aluminium substantially retards growth kinetics. As a consequence, carbide

precipitation "adjusts" to this growth kinetics so that the ledge height is increased. For example, at 750 °C the ledge height obtained for the aluminium alloy was 35 nm whereas Batte and Honeycombe obtained a value of 10 nm for an alloy of similar composition: Fe-1.04 wt % V-0.2 wt % C but without aluminium.

If such an "adjustment" is not possible it is likely that another transformation morphology will be adopted, such as fibrous precipitation or precipitation on dislocations [1-3]. This is consistent with Honeycombe's observation [1, 13] that when the growth kinetics is slowed down by the addition of a further alloying element interphase precipitation becomes coarser and the amount of fibrous precipitation increases.

What determines growth kinetics and how different transformation morphologies are selected are still open questions which have been discussed for a long time [1, 7, 14].

Finally, it is worth pointing out that when the matrix composition changes with time, a steady state is not expected to be maintained. In these circumstances, it is not easy to predict what will happen. It is not unlikely that many of the "irregular" interphase precipitation morphologies often reported (e.g. [31]) may be caused by such non-steady-state situations.

## 7. Conclusions

The model developed provides a fairly simple rationale for interphase precipitation in the stoichiometrically balanced Fe-V-C and Fe-V-C-N alloys of Batte and Honeycombe [18] and Balliger and Honeycombe [19]. The following quantitative relationships have been obtained.

1. The ledge velocity,  $v$ , was found (Equation 21) to be proportional to  $(I_{in}/I_0) f D^{1/2}$  where  $f$  is the carbide volume fraction, and  $D$  the diffusion coefficient of vanadium in ferrite. The quantity  $I_{in}/I_0$  is the ratio of the amount of interstitial,  $I_{in}$ , which is insoluble in the austenite with vanadium content equal to  $V_0$  to the total interstitial element content in the alloy,  $I_0$ . If the ledge height is known,  $v$  can be calculated (Equation 10) from  $v = 2D/h$ .

2. The ledge height was found (Equation 20) to be proportional to  $(I_0/I_{in}) D^{1/2}/f$ . This latter result can be used, together with a previously developed relationship between ledge height and carbide size [12]. With these the ledge height (and of course ledge velocity) and carbide size at other transformation temperatures and carbide volume fractions, can be calculated.

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## References

1. R. W. K. HONEYCOMBE, *Metall. Trans.* **7A** (1976) 915.
2. *Idem*, *Metal Sci.* **14** (1980) 201.
3. *Idem*, in "Phase Transformations in Ferrous Alloys", edited by A. R. Marder and J. I. Goldstein (TMS-AIME, Warrendale, PA, 1984) p. 259.
4. M. MANNERKOSKI, *Metal Sci.* **3** (1969) 54.
5. H. I. AARONSON, M. R. PLICHTA, G. W. FRANTI and K. C. RUSSEL, *Metall. Trans.* **9A** (1978) 363.
6. F. G. BERRY and R. W. K. HONEYCOMBE, *ibid.* **1** (1970) 3279.
7. T. OBARA, G. T. SHIFLET and H. I. AARONSON, *ibid.* **10A** (1979) 1049.
8. J. A. TODD, P. LI and S. M. COPLEY, *ibid.* **19A** (1988) 2133.
9. P. LI and J. A. TODD, *ibid.* **19A** (1988) 2139.
10. J. M. GRAY and R. G. B. YEO, *Trans. ASM* **61** (1966) 256.
11. H. K. D. H. BHADESHIA, *Phys. Status Solidi (A)* **69** (1982) 745.
12. P. R. RIOS, *J. Mater. Sci. Lett.* **10** (1991) 981.
13. *Idem*, *ibid.*, 1993, in press.
14. G. J. SHIFLET and H. I. AARONSON, *Metall. Trans.* **21A** (1990) 1413.
15. A. T. DAVENPORT and R. W. K. HONEYCOMBE, *Proc. R. Soc. Lond.* **A322** (1971) 191.
16. K. CAMPBELL and R. W. K. HONEYCOMBE, *Metal Sci.* **8** (1974) 197.
17. D. V. EDMONDS and R. W. K. HONEYCOMBE, *J. Iron Steel Inst.* **211** (1973) 209.
18. A. D. BATTE and R. W. K. HONEYCOMBE, *ibid.* **211** (1973) 284.
19. N. K. BALLIGER and R. W. K. HONEYCOMBE, *Metall. Trans.* **11A** (1980) 421.
20. C. ZENER, *J. Appl. Phys.* **20** (1949) 950.
21. G. J. JONES and R. K. TRIVEDI, *ibid.* **42** (1971) 4299.
22. C. ATKINSON, *Proc. R. Soc.* **A378** (1981) 351.
23. "Handbook of Chemistry and Physics", 60th Edn, edited by R. C. Weast (CRC Press, Boca Raton, FL, 1979).
24. P. R. RIOS, *Mater. Sci. Technol.* **4** (1988) 324.
25. *Idem*, *Mater. Sci. Eng.* **A142** (1991) 87.
26. K. NARITA, *Trans. Iron Steel Inst. Jpn* **15** (1975) 145.
27. W. ROBERTS and A. SANDBERGH, Swedish Institute for Metals Research, Report no. IM-1489, Stockholm (1980).
28. J. H. WOODHEAD, in "Vanadium in High Strength Steels", VANITEC publication no. V140 (1979).
29. C. D. MORTON, PhD thesis, University of Sheffield (1975).
30. P. R. WILYMAN and R. W. K. HONEYCOMBE, *Metall. Sci.* **16** (1982) 295.
31. P. R. RIOS and R. W. K. HONEYCOMBE, *Mater. Sci. Technol.* **6** (1990) 838.

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