Application of a New Model to the Interphase Precipitation Reaction in Vanadium Steels

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A new model has been applied to the precipitation of vanadium carbide (VC) particles in sheets at austenite/ferrite interphase boundaries during the isothermal transformation of Fe-C-V steels. Linear relationships between the intersheet spacings, the VC particle sizes, and the square root of the vanadium diffusivity in ferrite have been identified. The model establishes predictive correlations between the interphase precipitate sheet widths, intersheet spacings, and boundary migration speeds as a function of isothermal transformation temperature, and shows that the time associated with the interphase precipitate repeat period is a constant for each alloy over the temperature ranges studied. From a single measurement of interphase boundary velocity in a volume where the intersheet spacing is known, it is possible to predict the intersheet spacing and width as a function of temperature.

I. INTRODUCTION

HIGH strength low alloy and micro-alloyed vanadium steels can be significantly strengthened by precipitation of vanadium carbide particles at the austenite/ferrite interphase boundaries during the transformation of austenite to ferrite. The interphase precipitation reaction can occur during both isothermal and continuous cooling transformations after austenitization, and results in a characteristic microstructure of sheets of vanadium carbide (VC) precipitates containing predominantly one variant of VC. The strength and toughness of the resulting microstructures have recently been shown by Todd and Li[1] to depend on the austenitization temperature, VC solubility in austenite, volume fraction of VC available for precipitation in ferrite, the size and spacing of the resulting precipitates, and the ferrite grain size. Optimum combinations of strength and toughness were achieved in a Fe-0.2C-1V alloy by isothermal transformation at temperatures above the nose of the ferrite C-curve. In contrast, transformations at temperatures below the ferrite C-curve nose resulted in high strength but catastrophically brittle microstructures. The mechanical properties could be correlated with the spacings between the sheets of interphase precipitates and the size of the VC particles. Yield strengths correlated well with Melander's model for critical resolved shear stress when all the available vanadium and carbon precipitated as interphase vanadium carbide. [2]

In order to optimize the strengths and toughnesses of vanadium containing steels, it is essential to understand the mechanisms governing the formation of the interphase precipitates and to predict their sizes and spacings as a function of transformation temperature. The existing theories of interphase precipitation in vanadium steels have not yet adequately addressed this problem.[1,4,10]

This paper re-examines the current mechanisms and models for the interphase precipitation reaction and shows how a new solute balance model, developed recently by Todd, Li, and Copley,[2] can be applied to explain many aspects of the interphase precipitation of vanadium carbide in ferritic steels.

II. EXPERIMENTAL PROCEDURE

The chemical compositions (wt pct) of the steels used in this study were Fe-0.19C-1.14V-0.45Mn-0.001N and Fe-0.2C-1.0V-3.0Ni-0.5Mn. The alloys were prepared from high purity elements (99.9+ wt pct) and induction melted in high purity elements (99.9+ wt pct) and induction melted under argon in a magnesium oxide crucible. A 10 kg, 7 cm diameter ingot was cast in a copper mold in an argon atmosphere. The ingots were upset forged at 1200 °C in air and cross-rolled to rectangular sections 7 cm wide by 1.5 cm thick. Specimens were isothermally transformed at temperatures in the range 600 °C to 750 °C. The isothermal time temperature transformation (TTT) and mechanical property data for these treatments have been reported earlier.[11] Thin foils were prepared for transmission electron microscopy from 0.5 mm slices by chemically thinning to approximately 0.15 mm using a solution of HF and H2O2. Discs, 3 mm in diameter, were punched and ground to 0.06 mm thickness, followed by jet polishing in Cr2O3(CH3)COOH solution. The foils were examined with a 120 kV Philips 420T scanning transmission electron microscope in the Center for Electron Microscopy and Microanalysis (CEMMA) at USC.

III. INTERPHASE PRECIPITATION MODELS

Six mechanisms or models have been proposed for the interphase precipitation reaction and are now reviewed briefly in relationship to the present study.

A. Ledge Mechanism

Interphase precipitation of vanadium, molybdenum, and chromium carbides was first reported in 1968 by Davenport et al.[3] (for Fe-0.2 wt pct C alloys containing 1.5 wt pct of the carbide-forming elements vanadium, molybdenum, and chromium, respectively) and by Gray and Yeo[4] (for niobium containing steels). Davenport and Honeycombe[5] subsequently proposed that the sheets of vanadium carbide platelets precipitated on the austenite-ferrite boundaries during transformation, pinning them, and that local breakaway of the boundary led to the formation of mobile ledges or steps. A ledge mechanism has been well established by Aaronson et al.[13,14] and Kinsman and Aaronson[15] for growth of ferrite from austenite in the absence of precipitate and has led to the conclusion that, "for most of the transfor-
mation temperature range, austenite-ferrite boundaries associated with interphase precipitation grow predominantly, but not exclusively, by the ledge mechanism.\[6\]

A schematic representation of the nucleation and growth of vanadium carbide on austenite-ferrite interphase boundaries migrating with regular and irregular ledge heights is shown in Figure 1.\[5\] This model assumes that precipitation occurs on planar, low energy, semicoherent, immobile interfaces formed by the passage of a high energy ledge, which is moving too fast to act as a nucleation site.\[16\] The lateral passage of the mobile ledges results in a macroscopic motion of the planar austenite/ferrite boundary which is normal to the direction of ledge migration. The nucleation of the precipitates on the straight semi-coherent interface should be in sheets which have spacings equal to the ledge height. The precipitate sizes are expected to decrease close to the mobile ledge due to the shorter time available for growth.

Evidence to support this model has been provided by thermionic emission studies\[14\] and photo emission electron microscopy,\[17\] both of which gave only occasional resolution of the precipitate particles, and transmission electron microscopy observations of 50 to 400 nm ledges in a Fe-12Cr-0.2C steel.\[18\] The concept of a ledge mechanism is consistent with the work of Hillert,\[19\] which indicates that Kurdjumov-Sachs (K-S) related ferrite, with faceted, planar austenite-ferrite boundaries, is favored by high supersaturations and low isothermal transformation temperatures. However, the ledge mechanism has not yet provided a quantitative explanation for the factors governing (1) the repeated nucleation of precipitates along the planar γ/α boundary; (2) the uniform size of precipitates along the sheets; and (3) the intersheet spacings.

More recently, curved interphase precipitate sheet morphologies have been observed in many alloy steels, implying precipitation at nonplanar interphase boundaries.\[7,8,20-25\] The presence of curved sheets of precipitates has led to the development of two additional mechanisms, the bowing mechanism and the quasiledge mechanism, described in Sections III-B and III-C, to account for the precipitation of vanadium carbide precipitates on curved austenite/ferrite interphase boundaries.

B. Bowing Mechanism

The bowing mechanism was proposed in 1982 by Ricks and Howell\[7\] to account for the effect of interfacially nucleated precipitation on the mobility of high energy (non K-S related) interphase boundaries. They used an energy balance criterion to model the bowing of interphase boundaries between pinning precipitates and showed that there was a critical precipitate spacing below which it was not energetically possible for a bowing mechanism to operate. Their mechanism, shown in Figure 2, assumes:

1. The interface bows between the particles until unpinning occurs when the bowed segments are semicircular in cross-section (Figures 2(a), 2(b));
2. The interface will then continue to advance until sufficient solute is acquired in the vicinity of the boundary to enable precipitates to renucleate and the bowing process to recommence (Figures 2(c), 2(d)).

However, for a Fe-0.2C-1V steel, the minimum particle spacing along the sheet, calculated by Ricks and Howell,\[7\] virtually always exceeded that measured experimentally, assuming the bowed segment to be a hemispherical bulge (Figure 3). The model was reported as being more successful for the Fe-0.2C-10Cr alloy shown in Figure 3, which

![Fig. 2](image-url)

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has slower transformation kinetics, resulting in coarser precipitates and larger spacings. No readily apparent correlation could be established by Ricks and Howell[18] between the probability of observing the bowing mechanism and the transformation temperature. However, when the precipitate spacing along the boundary was less than the minimum value required for bowing, they proposed that the boundary must then migrate by the “quasiledge” mechanism described in Section III-C.

C. Quasiledge Mechanism

The quasiledge mechanism was proposed for precipitation on high energy, disordered, austenite-ferrite interphase boundaries which have been immobilized by copious precipitation, forming curved sheets of precipitates (Figure 4). For forward migration to occur, it was necessary for steps or ledges to laterally traverse the boundary (Figure 4(b)) in a similar manner to that described for the low energy immobile boundaries (Figure 4(a)). This is shown schematically in Figure 5 where a mobile interface, which has been pinned by precipitates, acts as a source of new ledges by bowing of the interface between widely spaced particles. Subsequent precipitation repins the interface, forcing the ledge to move sideways.

Implicit in this model is the assumption that the interphase precipitates, which nucleate at the austenite-ferrite boundary, pin the boundary and require the passage of a successive ledge for ferrite growth.

D. Eutectoid Decomposition Model

Obara et al.[19] developed a eutectoid decomposition model for an Fe-0.11C-1.95Mo alloy, in which planar and curved boundary interphase precipitation, fibrous precipitate structures, and pearlite were developed, in terms of the following two crystallographic factors:

1. $\theta_1$, the angle between the slowest moving austenite-ferrite boundary orientation and the plane of the grain boundary; and
2. $\theta_2$, the angle between the slowest moving austenite-carbide and the slowest moving austenite-ferrite boundaries (Figure 6(a)).

When both $\theta_1$ and $\theta_2$ were small, a planar interphase boundary carbide structure (i.e., ledge mechanism) developed. As $\theta_1$ and $\theta_2$ increased (Figure 6(b)), a quasiledge or bowing mechanism became dominant, resulting in curved boundary interphase precipitation. Further increase of $\theta_1$ and $\theta_2$ resulted in the fibrous MoC carbide morphology being favored (Figure 6(c)) until for large $\theta_1$, $\theta_2$, the cooperative growth of a pearlite structure evolved (Figure 6(d)).

This mechanism is thermodynamically based and predicts the shapes of the precipitates. Figure 6 shows the carbide phase projecting into the austenite during the decomposition and shows that fibers occur as $\theta_1 = \theta_2$ approaches 90 deg, with the fibers growing parallel to the slowest moving austenite-ferrite boundary. The model does not predict the interphase precipitate sheet spacings.

E. Solute Depletion Model

Roberts[10,11] has proposed a diffusional model in which nucleation of vanadium carbo-nitride precipitates, V(C, N), was assumed to take place immediately behind a smooth migrating interface. Solute depletion of the ferrite matrix, as the precipitates grew, would then be responsible for the repeated coplanar arrays of the interphase precipitates, as shown in Figure 7. If the interface migration rate was slow (e.g., as produced by continuous cooling rates <12 °C/min), it was possible for the interphase precipitates to develop a “fibrous” morphology. Fibers were purported to nucleate...
on smooth non K-S austenite-ferrite boundaries and grow parallel to the direction of the slow motion of the interface.

However, Roberts' model has several shortcomings: (a) the nucleation of VC precipitates homogeneously in the wake of a nonfaceted interface gives no reason to predict a single variant Baker-Nutting orientation relationship between VC and ferrite; (b) the model treats the depletion zone that develops around an isolated spherical particle, and thus Roberts' analysis cannot be applied to calculate the concentration profile produced by the uniformly distributed, closely spaced precipitates in an interphase precipitate sheet; (c) the model ignored the solute diffusivity discontinuity at the γ/α boundary; and (d) the model was applied to continuously cooled vanadium steels, making it very difficult to determine the diffusivities of vanadium in ferrite and also the interphase boundary migration speeds during the cooling treatments.

F. Solute-Drag Nucleation Model

The necessity to account for both the interphase and "fibrous" vanadium carbide morphologies led Edmonds[26] to propose a model for interphase precipitation similar to that suggested earlier by Davenport and Honeycombe.[5] This model, shown in Figure 8, assumed that the build-up of carbon ahead of the moving austenite-ferrite boundary, coupled with the possible collection of vanadium atoms on the interface, exerted a drag on its movement, as described by Kinsman and Aaronson,[27] and slowed the boundary sufficiently to allow nucleation and growth of vanadium carbide precipitates. As the VC growth continued, the carbon and vanadium concentrations at the interface were reduced and the driving force was increased sufficiently to move the transformation front to a position where nucleation was repeated.

If the VC platelets were oriented with a major growth direction parallel to the movement of the interface and if the interfacial movement were slow enough, then a transition to a fibrous carbide would occur. Austenite-ferrite boundary migration rates were thought to be related to their degree of coherency with the most coherent being the most sluggish. Alloying element segregation was also predicted to affect the boundary migration rate. It is now well established that higher manganese contents reduce the mobility of the interface and favor the development of fibrous carbides.[28-31]

Edmonds' research showed single variants of VC precipitates developing into both platelets and "fibrous" carbides. More recently, six morphologies of VC precipitates have been identified by Todd and Li,[1] including an "S-shaped"
short fiber. Todd and Li also suggested that the fibrous morphology develops when a low lattice $\alpha$/VC mismatch direction is parallel to both an easy growth direction in the ferrite and the interphase boundary plane normal.\(^{22}\)

No attempt was made to develop quantitatively Edmonds' model,\(^{23}\) probably due to the earlier conclusion of Davenport and Honeycombe,\(^{24}\) based on diffusion data available at that time, that the observed rates of transformation in vanadium steels could only be achieved by assuming grain boundary diffusion rather than bulk diffusion of vanadium in ferrite.

G. Summary

The models presented above are divided into two categories: the first is an interface boundary energy controlled mechanism and assumes that a stationary K-S or non K-S austenite-ferrite interphase boundary is required for nucleation of the vanadium carbide, while the second is a diffusion controlled mechanism and considers nucleation at or behind a moving interface. The first category is further subdivided into ledge, quasiledge, and bowing mechanisms although the temperature dependencies and transitions between such mechanisms are not well established. However, there are currently no quantitative models which predict the VC inter-sheet spacings and particle sizes.

IV. A NEW MODEL FOR INTERPHASE PRECIPITATION IN VANADIUM STEELS

In this section, a new model proposed by Todd, Li, and Copley\(^{22}\) is applied to interphase precipitation in vanadium steels. The model combines a solute balance approach with the ledge mechanism of ferrite growth in order to establish predictive correlations among the intersheet spacings, precipitate sheet widths, interphase precipitation repeat periods, boundary velocities, and the diffusivity of vanadium in ferrite. The model is applicable to, and will be correlated with, experimental data collected by Balliger and Honeycombe (Fe-C-V-N steel),\(^{25}\) Batte and Honeycombe (Fe-C-V-Nb steels),\(^{26}\) Honeycombe,\(^{22}\) Klenn (Fe-C-V-Ni steel),\(^{27}\) and Wilyman and Honeycombe.\(^{28}\) The new model comprises the following premises:

1. The diffusion profile developed during growth of an interphase precipitate sheet can be represented by that resulting from the growth of a "pseudophase" of constant solute concentration equal to the average concentration of the sheet of interphase precipitates.
2. The solute lost by the depleted layer during growth is exactly equal to the excess solute found in the pseudophase sheet.
3. The average solute concentration in $\alpha$ at the interphase boundary is constant between nucleation events.
4. Nucleation of a sheet of VC precipitates occurs when the local solute concentration at migrating ledges at the interphase boundary reaches a critical value.
5. The nucleation event does not hinder the migration of the $\gamma$/$\alpha$ interphase boundary, e.g., by pinning the boundary.
6. The nucleation time for a sheet of precipitates is short once the critical solute concentration is reached.
7. Precipitation has been completed but significant coarsening has not occurred.

These premises will now be considered with respect to vanadium steels. The crystallography of the interphase precipitation reaction in vanadium steels has been addressed separately by Li\(^{29}\) and Li and Todd.\(^{30}\) The analysis is discussed in terms of planar interphase and pseudophase boundaries in order to use Zener’s solution for plate precipitate growth.\(^{31}\) However, the approach can also be applied to the case of curved boundaries if they comprise a series of small ledges.

A. Schematic Representation of the Model

The new model is represented schematically for the precipitation of vanadium carbide in ferritic steels in Figure 9 and can be divided into the following steps:

(a) Heterogeneous nucleation of VC precipitates occurs when a critical solute (vanadium) concentration is reached
Fig. 9—Schematic illustration of the new solute balance model. (a) VC nuclei form at a ferrite ledge on the γ/α boundary. (b) Nucleation of additional VC as a second ledge migrates. The bulk solute diffusion zone around each VC precipitate is much larger in the ferrite than the austenite. (c) The sheet of precipitates is modeled as a planar “pseudophase” with forward growth distance, \( y_p \), and solute concentration, \( c_p \). The solute required for forward growth is exactly supplied by the depleted layer between the pseudophase and the γ/α boundary. (d) Nucleation of the next sheet of precipitates occurs when the interphase and pseudophase boundaries reach \( y' \) and \( y'' \), respectively. (e) Additional growth due to residual solute produces a final spacing and width for the precipitate sheets equal to \( y'_p \) and \( y''_p \), respectively.

(d) As more ferrite steps migrate, the depletion zones around the particles become larger and overlap. Hence, it becomes possible to model the solute concentration at the interphase boundary as a planar front. The sheet of interphase precipitates is modeled as a planar “pseudophase” of width, \( y_p \), with a constant solute concentration, \( c_p \), equal to the average composition of the precipitate sheet (Figure 9(c)). The solute required for growth of the pseudophase in the forward direction is exactly supplied from the depleted layer between the pseudophase and the \( y/α \) boundary.

(e) The pseudophase continues to grow as the \( y/α \) boundary advances with a steadily decreasing velocity, maintaining a constant average vanadium concentration, \( C_{mc} \), in the \( α \) at the \( γ/α \) boundary. When the \( γ/α \) boundary reaches \( y' \), the local vanadium concentration at ledges on the \( γ/α \) boundary required for nucleation of VC is reached and the next sheet of precipitates is nucleated. The pseudophase has grown a distance \( y'_p \) in the forward direction at this point (Figure 9(d)).

(f) After precipitation is completed, residual solute has caused additional growth to occur at the ends of the precipitates forming the pseudophase layers. The final spacing of the precipitate sheets is \( y''_p = y'_p \) and their width is \( y''_p \) (Figure 9(e)).

B. Boundary Pinning

The sixth model premise, which assumes that the nucleation of vanadium carbide does not interfere with the migration of the \( γ/α \) boundary, can be established by considering the energetics of the interphase precipitation reaction.

The energy of interest is that involved in transforming a thin layer of austenite of height, \( h \), to ferrite at the interface between a VC nucleus and austenite, by the passage of a ferrite step (Figures 10(a) and 10(b)). This energy is given by the equation

\[
\Delta U = Ah(F_v - F_{v}) + A\Gamma_{α/γ} + A\Gamma_{VC/α} - A\Gamma_{VC/γ} + \varepsilon_1
\]  

at the ferrite ledges migrating across a semi-coherent planar austenite/ferrite interphase boundary. Growth of the ferrite is envisaged to occur by the migration of a series of small steps or ledges (which could initially range from a single atomic plane to a small multiple of atomic planes), rather than a single macroscopic step.\[37-40\] Figure 9(a) shows the nucleation of VC precipitates at ledge corners on such a migrating step.

(b) Nucleation may occur during the passage of several atomic steps. Figure 9(b) shows increased nucleation as additional steps of ferrite migrate. The precipitates in the layer may grow by interphase boundary and bulk diffusion of solutes. It should be noted, however, that at 825 °C the diffusivity of vanadium in ferrite is 300 times that in austenite. The precipitates are, therefore, likely to grow in the ferrite with, for example, the Baker-Nutting orientation relationship.\[41\]

(c) The nucleation event locally depletes the boundary region of solutes, causing a significant increase in ledge velocity. Hence, the time available for precipitate growth by interphase boundary solute diffusion is expected to be very small, and the accelerated ledge growth will leave the precipitates entirely in the ferrite matrix.
where $A = \text{interface area}$, $F^V = \text{volumetric free energy}$, $\Gamma = \text{surface energy}$, $K_{S} = \text{Kurdjumov-Sachs orientation}$, and $\varepsilon_1 = \text{strain energy associated with incorporating the VC nucleus at the } \gamma/\alpha \text{ boundary into the ferrite}.$

1. Consider the energy of formation of an identical volume of ferrite at a $\gamma/\gamma$ grain boundary (Figure 10(c)). At the isothermal transformation temperature, this must be a large negative number given by

$$Ah(F_a^V - F_a^\gamma) + (A + 4h\sqrt{A})\Gamma_{\alpha\gamma}^{K_S} + \Delta\Gamma_{\alpha\gamma}^{K_S} - \Delta\Gamma_{\gamma\gamma} + \varepsilon_2 < 0 \quad [2]$$

where $NC = \text{noncoherent}$ and $\varepsilon_2 = \text{strain energy associated with the ferrite formation}$. Since $\Gamma_{\alpha\gamma}^{K_S} < \Gamma_{\alpha\gamma}^{NC}$, and $\varepsilon_2 > 0$, we have

$$Ah(F_a^V - F_a^\gamma) + 2(A + 2h\sqrt{A})\Gamma_{\alpha\gamma}^{K_S} - \Delta\Gamma_{\gamma\gamma} < 0 \quad [3]$$

2. Consider the energy of formation of an identical volume of VC homogeneously in ferrite (Figure 10(d)). Since such nucleation occurs, the energy is considered to be negative, giving

$$Ah(F_{VC}^V - F_a^V) + 2(A + 2h\sqrt{A})\Gamma_{VCa} + \varepsilon_3 < 0 \quad [4]$$

where $\varepsilon_3 = \text{strain energy associated with the formation of VC in ferrite}$.  

3. Consider the energy of formation of an identical volume of VC at a $\gamma/\gamma$ grain boundary (Figure 10(e)). This value is assumed to be more positive than the left side of Eq. [4] because observations of isothermally transformed or tempered vanadium steels indicate that ferrite matrix precipitation is favored over grain boundary precipitation for a prior austenitization temperature of 1200 °C. The difficulty of nucleating VC in austenite has also been referenced by Woodhead. This energy is given by

$$Ah(F_{VC}^V - F_a^V) + 2(A + 2h\sqrt{A})\Gamma_{VCa} - \Delta\Gamma_{\gamma\gamma} + \varepsilon_4 < 0 \quad [5]$$

where $\varepsilon_4 = \text{strain energy for the formation of VC at a } \gamma/\gamma \text{ boundary}$.  


$$-Ah(F_{VC}^V - F_a^V) + 2(A + 2h\sqrt{A}) \cdot (\Gamma_{VCa} - \Gamma_{VCy}) + \Delta\Gamma_{\gamma\gamma} + \varepsilon_3 - \varepsilon_4 < 0 \quad [6]$$


$$2(A + 2h\sqrt{A})\Gamma_{\alpha\gamma}^{K_S} + \Gamma_{VCa} - \Gamma_{VCy} + \varepsilon_3 - \varepsilon_4 < 0 \quad [7]$$

6. If $\varepsilon_i \equiv \varepsilon$, and recognizing that $(A + 2h\sqrt{A}) > A > 0$, Eq. [7] becomes

$$\Delta\Gamma_{\alpha\gamma}^{K_S} + \Delta\Gamma_{VCa} - \Delta\Gamma_{VCy} < 0 \quad [8]$$

Referring to Eq. [1], since $Ah(F_a^V - F_a^\gamma)$ is large and negative under the conditions of interest, $\Delta\Gamma_{\alpha\gamma}^{K_S} + \Delta\Gamma_{VCa} - \Delta\Gamma_{VCy} < 0$, and the strain energy $\varepsilon_1$ is estimated to be small, then

$$\Delta U < 0$$

This argument concludes that the migration of a ferrite step would not be impeded by the presence of a vanadium carbide precipitate at a planar interphase boundary.

C. The Relationship between Solute Diffusivity and the Interphase Precipitate Sheet Spacings

In the interest of correlating data on interphase precipitation in the Fe-0.19C-1.14V-0.48Mn and Fe-0.2C-1.0V-3.0Ni-0.5Mn steels used in this study with the diffusion controlled mechanisms discussed in the introduction, the observed VC intersheet spacings were compared with the diffusivities of the three major solutes, C, V, and Ni, in ferrite and austenite (Tables I, II). These data suggested that the measured intersheet spacings may be related to the square root of the diffusion coefficient for vanadium in ferrite.

$y'_x = K_{x}(D_v)^{1/2}$ \[9\]

This was a surprising result but did tend to support the hypothesis that interphase precipitation of vanadium carbide was controlled by diffusion of vanadium in ferrite. The constant of proportionality, $K_x$, was higher for the nickel, aluminum, and manganese containing alloys than for the niobium containing alloys and also appeared to depend on the austenitizing temperature.

The intersheet spacings were then plotted as a function of $(1/T)K^{-1}$ in Figure 12 and again a linear relationship was apparent in all cases. An activation energy equal to 123 KJ/mol, approximately half the activation energy for diffusion of vanadium in ferrite (242 KJ/mol), was determined from

| Table I. Diffusion Data for V, C, and Ni in Ferrite and Austenite |
|-----------------------------|-------------------|-----------------|----------------|
| Matrix | Solute | $D_0$ (mm$^2$ s$^{-1}$) | $Q$ (KJ mol$^{-1}$) | Reference |
| Ferrite | | | | |
| V | | 398 | 242 | 42, 43 |
| C (616 °C to 844 °C) | | 220 | 122 | 44 to 46 |
| C | | 2 | 84 | 47 |
| Ni | | 130 | 56 | 48 |
| V | | 365 | 293 | 42 |
| Austenite | | | | |
| V | | 365 | 293 | 42 |
| C (800 °C to 1400 °C) | | 20 | 142 | 48, 49 |
| Ni | | 44 | 283 | 48 |
Table II. Comparison of the Diffusivities of V, C, and Ni in Ferrite and Austenite with the Intersheet VC Spacings Observed in Isothermally Transformed Vanadium Steels

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_m$ (°C)</th>
<th>Solute</th>
<th>$D_s^a$ (nm$^2$s$^{-1}$)</th>
<th>$\sqrt{D_s^a}$ (nmms$^{-1/2}$)</th>
<th>$D_f^a$ (nm$^2$s$^{-1}$)</th>
<th>$\sqrt{D_f^a}$ (nmms$^{-1/2}$)</th>
<th>$y'$ (nm)</th>
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<tbody>
<tr>
<td>Fe-0.19C-</td>
<td>740</td>
<td>V</td>
<td>1.32 $\times$ 10$^{-10}$</td>
<td>11.43</td>
<td>2.84 $\times$ 10$^{-13}$</td>
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<td>20</td>
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<td>1.14V-0.48Mn</td>
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<td>C</td>
<td>1.12 $\times$ 10$^{-4}$</td>
<td>1.06 $\times$ 10$^4$</td>
<td>9.47 $\times$ 10$^{-7}$</td>
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<td>1200 °C $T_v$</td>
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<td>Ni</td>
<td>1.68 $\times$ 10$^{-1}$</td>
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<td>V</td>
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<td>14</td>
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<td>C</td>
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<tr>
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<tr>
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Fig. 11 — Linear relationship between the intersheet spacings, $y'$, and the square root of vanadium diffusivity in ferrite.

the slope. These results will now be discussed in the context of the new solute balance model.

D. Application of the New Solute Balance Model

The new model assumes that when the interphase precipitates nucleate, they are small and uniformly distributed along the interphase boundary. This enables the growth of the sheet of interphase precipitates, once the $y/\alpha$ interphase boundary has moved on, to be approximated by the planar growth of a "pseudophase", which is assumed to have a constant solute concentration equal to the average concentration in the sheet containing the interphase precipitates.

According to the model, the concentration in front of the advancing pseudophase can be represented by the equation

$$C_m - C_m^o = 1 - \text{erf}(y/2\sqrt{Dt})$$

where

$$y_p = s\sqrt{Dt}$$

$D = \text{solute diffusivity in the matrix (\(\alpha\) phase), } t = \text{time, } C_m = \text{solute concentration in the matrix at position } y(t), C_m^o = \text{initial concentration of solute in the matrix, } C_m^{cp} = \text{concentration of solute in ferrite at the pseudophase/matrix interface (which is equivalent to the concentration of vanadium in ferrite at the } \alpha/VC \text{ interface and is approximated to zero in the present analysis), and } y_p = \text{forward growth distance of the pseudophase.}$

Zener showed that a good approximation of the parameter, $s$, was given by the equation

$$y_p = s\sqrt{Dt}$$
If it is assumed that the increased solute in the pseudophase is provided only from a depleted layer between the pseudophase boundary at the instant the next sheet is nucleated and the position where the next sheet is nucleated, then Todd, Li, and Copley\textsuperscript{12} show that the parameter $\Omega$ is given by the equation

$$
\Omega = \left[ \frac{1}{2} \left( \frac{y'_p}{y'_e} - 1 \right) + 1 \right]^{-1}
$$

where $y'_e$ and $y'_p$ are the interphase precipitate sheet spacing and pseudophase width, respectively, at the instant a new sheet of nuclei is formed. This assumption is appropriate for vanadium steels where the diffusivity of vanadium is 10 to 1000 times greater in austenite than in ferrite.

The concentration of solute in the pseudophase, $C_p$, is given by the equation

$$
C_p = \frac{1}{2} \left( C^{mc} - C^{mp} \right) \left( \frac{y'_p}{y'_e} - 1 \right) + C^{mp}
$$

The intersheet spacing is given by the equation

$$
y''_p = y'_e \sqrt{\frac{t'_c}{\Omega}} = A t'_c^{1/2} D_0^{1/2} e^{-\Delta H_v/2RT}
$$

where $t'_c$ is the interphase precipitate repeat period, and $A$ is given by

$$
A = \frac{2 - \Omega}{\sqrt{1 - \Omega}}
$$

This provides a theoretical basis for the correlation between the intersheet spacing and the square root of vanadium diffusivity in ferrite, providing $A t'_c^{1/2}$ is a temperature independent constant, which appears to be supported by the experimental data.

The forward growth distance of the pseudophase at the instant a new sheet of nuclei is formed is given by the equation

$$
y'_p = \frac{\Omega}{\sqrt{1 - \Omega}} \sqrt{\frac{t'_c}{D t'_c}}
$$

The average velocity for the $\gamma/\alpha$ boundary is given by the equation

$$
V_b = \frac{y'_e}{t'_c} = A \frac{D^{1/2}}{t'_c^{1/2}} = A t'_c^{1/2} D_0^{1/2} e^{-\Delta H_v/2RT}
$$

According to Todd, Li, and Copley\textsuperscript{12} the average boundary solute concentration, $C^{mc}$ (i.e., the average concentration of vanadium in ferrite at the time $t = t'_c$, and the position $y = y'_e$, where the next sheet nucleates), which must be lower than the linear approximation of $C^{mp}$ at $y'_e$, is given for the quasi-stationary solution by the equation

$$
C^{mc} - C^{mp} = \frac{\text{erfc}(y'_e/2\sqrt{Dt'_c})}{\text{erfc} \sqrt{2\Omega/1 - \Omega}}
$$

where $y'_e/\sqrt{Dt'_c}$ is given by Eq. [15].

This equation may be rearranged to describe the position where the concentration equals $C^{mc}$ as a function of time, which according to the model is also equal to $y_e$ and is given by

$$
y_e = 2\sqrt{Dt} \text{ erfc} \left( 1 - \frac{C^{mc} - C^{mp}}{C^{mp} - C^{mc}} \text{ erfc} \left( \frac{\Omega}{2\Omega/1 - \Omega} \right) \right)
$$

Comparing Eqs. [15], [16], and [20], it follows that for a specific $C^{mc}$, $y''_p/y'_p$ must be the root of the equation

$$
2\text{ erfc} \left( 1 - \frac{C^{mc} - C^{mp}}{C^{mp} - C^{mc}} \text{ erfc} \left( \frac{\Omega}{2\Omega/1 - \Omega} \right) \right) = 0
$$

V. CORRELATION OF THE MODEL WITH EXPERIMENTAL DATA

In addition to correlating intersheet spacings with temperature and $\sqrt{D_y}$, the new model can be used to relate measured quantities such as sheet spacing ($y''_p$), sheet width ($y'_p$), diffusivity ($D$), alloy concentration ($C^{mp}$), and activation energies, to model quantities such as the sheet repeat period ($t'_c$), the solute concentration of the pseudophase ($C_p$), the average $\gamma/\alpha$ interphase boundary velocity ($V_b$), and the critical supersaturation ($C^{mc}$). Indeed, from a knowledge of $y''_p$ and $y'_p$ for a specific alloy and isothermal annealing temperature, all model quantities can be determined. An analysis of data for all of the alloys included in this investigation is presented in Tables III, IV, and V.

Statistically based investigations by Honeycombe and coworkers\textsuperscript{28,31,33} and Klenn\textsuperscript{22} have established the validity of determining mean values for the intersheet spacing and sheet width for a volume of material in which interphase precipitation has occurred as a function of alloy composition, austenitization temperature, and isothermal annealing temperature. Measured values of $y''_p$ and, where available $y'_p$, are listed at various isothermal transformation temperatures in Table III, columns 4 and 5. Two correlations are apparent from these data. One has already been pointed out, namely

$$
y''_p = K_v \sqrt{D_v} = K_v D_0^{1/2} e^{-\Delta H_v/2RT}
$$

The second is apparent in the data of Batte and Honeycombe,\textsuperscript{32} who measured both $y''_p$ and $y'_p$, namely

$$
y''_p/y'_p = K
$$

where $K$ is a constant that is independent of isothermal annealing temperature but varies with alloy composition and probably with austenitization temperature. This ratio is listed in column 6, Table III.

Todd, Li, and Copley\textsuperscript{12} have shown that $y'_e = y''_p$ and that $y'_p$ can be calculated with the equation

$$
y'_p = \frac{y'_e y''_p}{2y''_p - y'_p}
$$

Values for $y'_e/y'_p$ and $y'_p$ are listed in Table III, columns 7 and 8. From the values for $y'_e$ and $y'_p$, the following parameters were calculated and are listed in Table IV, columns 3 to 5: (i) $\Omega$ calculated with Eq. [13]; (ii) $C_p$ calculated with
<table>
<thead>
<tr>
<th>Column 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>( T_{\text{Aus}} ) (°C)</td>
<td>( T_{\text{iso}} ) (°C)</td>
<td>( \gamma'' ) (exp) nm</td>
<td>( \gamma'' ) (exp) nm</td>
<td>( \gamma''/\gamma' ) (exp)</td>
<td>( \gamma''/\gamma' ) (calc)</td>
<td>( \gamma' ) (calc) nm</td>
</tr>
<tr>
<td>Fe-0.20C-1.04V-0.023Nb</td>
<td>1200</td>
<td>825</td>
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<td>15.0</td>
<td>2.00</td>
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<td>10.0</td>
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<td>800</td>
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<td>2.80</td>
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<tr>
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<td>4.00</td>
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<td>35.0</td>
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<td>2.50*</td>
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<td>2.8</td>
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<td>21.0</td>
<td>—</td>
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<td>5.5</td>
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<td>710</td>
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<td>2.50*</td>
<td>4.00</td>
<td>5.5</td>
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<tr>
<td>Klenn[25]</td>
<td>650</td>
<td>10.0</td>
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<td>2.50*</td>
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<td>—</td>
<td>2.50*</td>
<td>4.00</td>
<td>2.3</td>
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</tbody>
</table>

*limited data available

Eq. [14]: and (iii) A with Eq. [16]. In calculating \( C'' \), \( C''_{mp} \) was taken to be the concentration of vanadium in equilibrium with VC, which is small for the temperature range of interest, hence, \( C''_{mp} \) was set equal to 0. These three parameters are independent of isothermal transformation temperature because they depend only on \( \gamma''/\gamma' \). In alloys where values of \( \gamma'' \) were based on limited measurements or not available (labeled * in Tables III through V), the ratio of \( \gamma''/\gamma' \) was assumed to be 2.5, giving \( \gamma''/\gamma' = 4.0 \).

Several calculated parameters depend on \( D^{1/2} \), which is listed in column 6 of Table IV. Values for these parameters are listed in columns 7 through 9 and include (i) \( t'' \) calculated with Eq. [15]; (ii) \( \bar{V}_s = \gamma''/t'' \), and (iii) \( C''_{mc} \) calculated with Eq. [19]. The parameter \( C''_{mc} \) gives the average concentration at the boundary at the instant the new sheet is nucleated.

The use of Eq. [15] to explain the correlation expressed by Eq. [22] requires that \( \gamma''/t'' \) be independent of isothermal annealing temperature. Values for \( \gamma''/t'' \) are listed in column 10. Although some scatter is apparent in the values listed for each alloy, there is no systematic variation of these values with isothermal annealing temperature.

The value used for \( C''_{mc} \) for each alloy is listed in column 1 of Table V. In all of the alloys listed, V and C were added in the stoichiometric ratio to form VC.

Several parameters listed in Tables III and IV at various isothermal transformation temperatures are independent of isothermal transformation temperature. Values for these parameters, which include \( \gamma''/\gamma' \), \( \Omega \), \( C'' \), \( A \), \( \gamma''/\gamma' \), and \( A_{c''}^{1/2} \), do exhibit experimental scatter and thus their averages are listed in columns 2 through 7 of Table V. The average values of \( K_s (= A_{c''}^{1/2}) \) calculated for the individual measurements at each isothermal annealing temperature match closely, of course, the values obtained graphically from Figure 12, which are listed in column 8.

**VI. DISCUSSION**

This discussion focuses on values of measured parameters and calculated model parameters based mainly on the data of Batte and Honeycombe\[28\] for three vanadium steels, Fe-0.2C-1.04V-0.023Nb, Fe-0.15C-0.75V-0.02Nb, and Fe-0.09C-0.48V-0.016Nb, and data of Klenn\[25\] for a Fe-0.17C-1.03V-1.5Ni steel; see Tables III through V. Two questions are considered. (1) Are values calculated for the model parameters reasonable? (2) Can relationships among measured parameters be deduced that would serve as a test of the model?

**A. Model Parameters**

The following model parameters are discussed: the intersheet repeat period, \( t'' \), the average interphase boundary
Table IV. Model Parameters

<table>
<thead>
<tr>
<th>Column 1</th>
<th>2 T (°C)</th>
<th>3 Ω</th>
<th>4 C\textsuperscript{P} Atoms cm\textsuperscript{-3} × 10\textsuperscript{20}</th>
<th>5 A</th>
<th>6 √D nm s\textsuperscript{-1/2}</th>
<th>7 t_0' s</th>
<th>8 V_0 nm s\textsuperscript{-1}</th>
<th>9 C\textsuperscript{∞} Atoms cm\textsuperscript{-3} × 10\textsuperscript{20}</th>
<th>10 A t_0'\textsuperscript{1/2}</th>
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<td>95</td>
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<td>95</td>
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*limited data available

Table V. Average Values of the Model Parameters

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<th>2 C\textsuperscript{∞} Atoms cm\textsuperscript{-3} × 10\textsuperscript{20}</th>
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<th>4 Ω</th>
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<th>6 A</th>
<th>7 t_0' s</th>
<th>8 V_0 nm s\textsuperscript{-1}</th>
<th>9 C\textsuperscript{∞} Atoms cm\textsuperscript{-3} × 10\textsuperscript{20}</th>
<th>10 A t_0'\textsuperscript{1/2}</th>
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<td>19.0</td>
<td>2.13</td>
<td>0.15</td>
<td>0.82</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Fe-0.15C-0.75V-0.02Nb</td>
<td>6.96</td>
<td>4.30</td>
<td>0.39</td>
<td>18.5</td>
<td>2.06</td>
<td>1.06</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.09C-0.48V-0.016Nb</td>
<td>4.46</td>
<td>4.40</td>
<td>0.38</td>
<td>12.0</td>
<td>2.06</td>
<td>1.36</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.05C-0.27V-0.0002N</td>
<td>2.51</td>
<td>4.00*</td>
<td>0.40</td>
<td>6.3</td>
<td>2.07</td>
<td>3.31</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.21C-0.96V-0.97Al</td>
<td>8.91</td>
<td>4.00*</td>
<td>0.40</td>
<td>22.3</td>
<td>2.07</td>
<td>3.31</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.17C-1.03V-1.5Ni</td>
<td>9.49</td>
<td>4.00</td>
<td>0.40</td>
<td>23.7</td>
<td>2.07</td>
<td>3.31</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.20C-0.96V-1.5Ni</td>
<td>8.90</td>
<td>4.00</td>
<td>0.40</td>
<td>22.3</td>
<td>2.07</td>
<td>3.31</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*limited data available

velocity, V_0; the parameter, A √t_0'; the solute concentration of the pseudophase, C\textsuperscript{P}; and the average solute concentration of ferrite at the interphase boundary, C\textsuperscript{∞}.  

1. Intersheet repeat period (t_0')

The intersheet repeat period varies from 0.1 to 1.0 seconds in the steels investigated by Batte and Honeycombe to several seconds in the nickel containing steel studied by Klenn. For a specific alloy, this parameter, which is the time between precipitate sheet nucleation events, has a constant value independent of isothermal transformation temperature. A rationale for this result can be based on the premise that the nucleation of a sheet of VC precipitates occurs when the local vanadium concentration at migrating ledges on the interphase boundary reaches a critical value. The local concentration of vanadium, which is attracted to the ledges by the presence of carbon, must vary with ledge migration velocity, even though the average solute concentration, C\textsuperscript{∞}, is constant. Since the interphase boundary velocity decreases with 1/X/t_0', the ledge migration velocity also decreases with time. The intersheet repeat period can be interpreted, therefore, as the time required for the ledge migration velocity to decrease to the point that the critical vanadium concentration at ledges is reached. The intersheet repeat period may be independent of temperature because of the compensating effects of a temperature change on diff-

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fusión y la migración de las fisuras. Disminuyendo la temperatura, por ejemplo, se reduce no sólo la tasa de difusión de vanadio hacia la fisura, sino también la veloci dad de migración de las fisuras dada una longitud de fisura fija. Consecuentemente, el tiempo disponible puede ser requerido en diferentes temperaturas para la migración de las fisuras y a la altura donde la concentración de vanadio es suficiente.

Es interesante notar que en los aleaciones investigadas por Batte y Honeycombe, la repetición del ciclo de crecimiento disminuye con el contenido carbono. Este efecto podría atribuirse a una atracción más fuerte del vanadio hacia las fisuras en las aleaciones con más contenido de carbono. Esto podría explicar que el tiempo crítico de concentración de vanadio se logre.

Consecuentemente, el mismo tiempo podría requerirse en diferentes temperaturas para la migración de las fisuras, con el contenido de carbono más alto.

2. Velocidad de interfase (\(V_c\))

Una estimación cruda de la velocidad de migración de las fisuras se puede obtener a través de diagramas TTT isotermales para altas temperaturas. A medida que la temperatura de transformación aumenta, las fisuras se acortan, lo que permite una mayor difusión alrededor de ella. Por ejemplo, Batte y Honeycombe reportaron que el Fe-0.2C-1.04V-0.023Nb con una grano de 50 µm, tras formado a una temperatura de 800 °C, presenta una longitud de fisura de 3.2 × 10^4 nm, si se considera que la transformación progresa desde la punta de la fisura hasta el centro del grano. Este valor corresponde a un promedio de velocidad de 298 nm s^{-1}, que coincide bien con el valor calculado de 149 nm s^{-1} listado en la Tabla IV. Se agregaron elementos como Ni, Mn y Al que disminuyeron la velocidad de fisuras, lo que se comparó con la velocidad de difusión en la superficie, donde el tiempo de difusión es constante.

3. El parámetro \(A \sqrt{i_c}\)

El valor del parámetro \(A \sqrt{i_c}\) para un aleación específico es independiente de la temperatura de transformación isoterma. Esto ha sido demostrado al comparar la ecuación [15] con la ecuación [22], la cual expresa la correlación ilustrada en la Figura 11. El parámetro \(A\) debe ser independiente de la temperatura de transformación isotherma, ya que la velocidad de transformación en aleaciones con concentraciones de vanadio es un valor único para cada aleación (vea ecuaciones [13] y [16]), independiente de la temperatura de transformación isotherma (vea ecuación [23]). Por lo tanto, se puede concluir que \(i_c\) es independiente de la temperatura de transformación isotherma, y el cálculo de la misma se realiza de acuerdo con el parámetro y la concentración de carbono.

4. Concentración del vanadio en la fase pseudofina (\(C_p\))

La concentración de vanadio en la fase pseudofina en un aleación de vanadio pueden ser determinadas por la fracción de VC. A un tiempo, \(A\) es independiente de la temperatura de transformación isotherma. Según la ecuación [14], \(C_p\) para aleaciones de vanadio depende solo de \(y_p\) y durante un tiempo específico, se puede decir que \(C_p\) es independiente de la temperatura de transformación isotherma. Este resultado es consistente con los datos de alta concentración de pequeñas partículas en hojas precipitadas a altas temperaturas y bajas densidades de partículas grandes en hojas precipitadas a altas temperaturas.

5. Concentración de vanadio en la interfase (\(C_{\infty}\))

Es otra base fundamental del modelo nuevo que el valor constante de \(C_{\infty}\) es mantenido en un punto de interfase de transformación isotherma. Según la ecuación [19], \(C_{\infty}\) para aleaciones de vanadio depende solo de \(y_p\) y durante un tiempo específico, es independiente de la temperatura de transformación isotherma. Por lo tanto, la formación de ferrita con una concentración constante de vanadio a lo largo de la variedad de temperaturas de transformación normalmente investigadas puede ser el factor crítico que determina la razón \(y_p\) y \(C_p\). Si \(C_{\infty}\) es estable, entonces \(y_p\) es determinada por la ecuación [21]. El parámetro, \(C_p\), es determinado por la ecuación [14].

B. Parámetros Medidos

El objetivo final de un modelo para la reacción de precipitación de interfase es, en efecto, no calcular los parámetros de modelo de medidas de parámetros aunque tales cálculos pueden ser útiles para entender el fenómeno. El objetivo es predecir los parámetros de medidas de otros conocidos parámetros. Todd, Li, y Copley\[^{[10]}\] han sugerido que un modelo de reacción de precipitación de interfase proporciona una prueba útil y aplicando el modelo se puede determinar la velocidad de interfase de transformación.

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VII. CONCLUSIÓN

A revisión de los datos de la reacción de precipitación de interfase en aleaciones de vanadio ha revelado dos importantes correlaciones: (1) para un aleación específico, la velocidad de precipitación de interfase es proporcional a la base de raíz cuadrada del contenido de vanadio en ferrita; y (2) para un aleación específico la relación entre la velocidad de precipitación de interfase y la anchura es proporcional a la base de raíz cuadrada del contenido de vanadio en ferrita. Un nuevo modelo de balance de sólidos ha sido aplicado a aleaciones de vanadio y proporciona una interpretación satisfactoria de estas correlaciones. Todas las variables del modelo pueden ser determinadas si la interfase de precipitación de interfase y la anchura es proporcional a la base de raíz cuadrada del contenido de vanadio en ferrita. Desde una sola medición de la velocidad de interfase de transformación, se puede predecir la velocidad de interfase de transformación de un aleación donde la interfase de precipitación de interfase es conocida, así como la interfase de precipitación de interfase y la anchura. De esta forma, la velocidad de interfase de transformación puede ser predecida como una función de la temperatura.

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