Effects of Alloying Elements upon Austenite

Decomposition in High Strength Low Alloy Steels

by

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(ABSTRACT)

The kinetics of austenite decomposition were studied in high purity Fe–0.1 C–0.4 Mn–0.3 Si–X (concentrations in weight percent, X represents 3 Ni, 1 Cr, or 0.5 Mo) steels at temperatures between 500 and 675°C. The transformation stasis phenomenon was found in the Fe–C–Mn–Si–Mo and Fe–C–Mn–Si–Ni alloys isothermally transformed at 650°C and 675°C but not in the Fe–C–Mn–Si and Fe–C–Mn–Si–Cr alloys at any of the temperatures investigated. The occurrence of transformation stasis was explained by synergistic interactions among alloying elements. The paraequilibrium model was applied to calculate the metastable fraction of ferrite in each alloy. This fraction was shown to coincide with cessation of transformation in the Mo alloy transformed at 600°C. Transformation stasis was found in both the Ni and the Mo alloys isothermally reacted at 650°C and 675°C. The interactions among Mn, Si, and Mo as well as interactions among Mn, Si, and Ni appear to decrease the threshold concentrations for occurrence of transformation stasis in Fe–C–Mn–Si systems. The segregation of Mn and Mo to the α/γ boundary assisted by Si was suggested to enhance the drag force and led to transformation stasis. In the Ni alloy, lower driving force for ferrite formation by addition of Ni could be responsible for occurrence of transformation stasis.
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The morphology of ferrite under TEM. No carbide is found during transformation stasis in Ni alloy reacted at 650°C for 3162 sec. (\(\text{M=Martensite, F=Ferrite}\)).  

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INTRODUCTION

The overall kinetics of austenite decomposition have been investigated previously in a series of ternary steels including Fe–C–Mo [1, 2], Fe–C–Cr [3, 4], Fe–C–Ni, Fe–C–Mn, Fe–C–Cu, and Fe–C–Si [4]. These efforts concentrated on the effects of the substitutional alloying elements on the morphology and the kinetics of ferrite formation to the carbon steels. It was found that the incomplete transformation phenomenon, often presumed to be characteristic of the bainite reaction [5], is absent in many ternary alloys. The occurrence of incomplete transformation, or transformation stasis [6], required minimum concentrations of C and Mo, Cr or Mn. It was not observed in Fe–C–Ni or Fe–C–Si alloys. Since many commercial steels exhibit time-temperature-transformation (TTT) diagrams that suggest the possibility of transformation stasis, it is possible that occurrence of the phenomenon is enhanced by interactions among substitutional alloying elements. Some data from Fe–C–Mn–Si alloys support this view [7, 8, 9, 10].

It has been recognized for some time that TTT diagrams of plain carbon steels exhibit a single C-curve and some high-alloy steels have two C-curves [5]. The two C-curves result from a change with temperature in the mechanisms of ferrite formation [2, 11]. The change in mechanism with decreasing reaction temperature occurs at a characteristic temperature designated as the bay temperature, $T_b$. This is the temperature at which the two C-curves
for initiation of transformation intersect. The bay temperature has also been referred to as the bainite start temperature [5]. However, this usage relies upon an ambiguous definition of bainite [4, 8, 12], so it will not be employed here.

During transformation stasis [6], both ferrite nucleation and growth stop completely, and the fraction transformed displays a plateau when plotted versus the logarithm of the reaction time. Cessation of ferrite formation can result from thermodynamic or kinetic factors. From a thermodynamic standpoint, transformation can cease in the absence of carbide precipitation when the metastable fraction of ferrite forms [1]. Thermodynamic models can be used to calculate this fraction of ferrite at a given temperature.

If cessation of ferrite formation occurs before the metastable fraction is reached, then the cause must be kinetic in origin. The term, transformation stasis, will be used to refer to this form of cessation. Investigations of Fe-C-X alloys have led to the view that transformation stasis [2, 3, 4, 13] as well as anomalously slow ferrite growth kinetics [1, 14, 15, 16] and highly degenerate ferrite morphologies [2, 16, 17] can be ascribed to a solute drag-like effect (SDLE) [12, 18].

On the SDLE hypothesis, nonequilibrium absorption of a substitutional alloying element occurs to ferrite:austenite boundaries. When the element is one that markedly reduces the activity of carbon, the effective carbon concentration gradient in austenite ahead of a growing ferrite crystal is reduced. Since this gradient is responsible for driving ferrite growth, absorption of the solute element reduces ferrite growth kinetics. In extreme cases, ferrite growth ceases altogether.

Transformation stasis can be explained by considering the influence of the SDLE upon ferrite growth together with the change in the mechanism of ferrite nucleation at the bay
temperature [2]. At temperatures below $T_b$, ferrite growth is greatly restricted by the SDLE. Transformation proceeds by the nucleation of a ferrite crystal on a pre-existing ferrite grain (sympathetic nucleation) followed by a limited amount of growth. Once the SDLE inhibits the growth of the sympathetic nucleated crystal, a new ferrite crystal nucleates and grows until the SDLE inhibits migration of its boundaries. However, since ferrite growth is accompanied by carbon partitioning, the driving force for sympathetic nucleation rapidly declines with the amount of ferrite formed. Transformation stasis begins when there is no longer sufficient driving force to support sympathetic nucleation of ferrite. Transformation does not resume until carbides form and the driving force for ferrite nucleation and growth is restored [2, 4, 19].

Four types of overall reaction kinetics behavior (Figure 1) were observed in alloys presumed to have a strong SDLE [13]. When austenite transformation ceases completely below the metastable ferrite fraction (transformation stasis), the transformation curve shows a zero slope. This is recognized as type IV transformation. At lower temperatures or in materials with lower concentrations of carbon and alloying elements, transformation is impeded but does not stop completely resulting in type II and type III transformation behaviors (Figure 1). Type I transformation results from little or no SDLE, and it also appears at temperatures above $T_b$.

In four or more component steels, complication of the SDLE is expected by interactions among the alloying elements. However, the nature of alloying element interactions is not clear. In recent work on the nucleation and growth of ferrite in an Fe–C–Mn–Si alloy, no strong interaction between Mn and Si was found [20]. There is also evidence that transformation stasis occurs in an Fe–0.35 C–2.27 Mn–2.34 Si alloy but not in either the
Figure 1: Four types of transformation behavior observed in Fe–C–X alloys. [1]
Fe–C–Mn or Fe–C–Si alloys with similar alloy concentrations [8, 10, 12]. The interactions between alloying elements are thus important to the overall transformation behavior, and systematic studies on transformation stasis in multi-component alloys are needed.

In the present study, austenite decomposition kinetics, primarily to ferrite and carbide, are investigated in four multicomponent steels. An Fe–0.1 C–0.4 Mn–0.3 Si steel is employed as a reference alloy, and the effects of small additions of Ni, Cr or Mo on overall transformation kinetics are determined.
2

EXPERIMENTAL PROCEDURE

2.1 Measurement of CCT Diagrams

Alloys for this study were vacuum induction melted, cast into 35 kg ingots and redundant hot worked. Bars $12 \times 12 \times 150$ mm in size were machined from the hot worked stock and homogenized in quartz under $1/3$ atm $\text{Ar}$ for three days at $1250^\circ \text{C}$. An Fe–0.1 C–0.4 Mn–0.3 Si (concentrations in weight percent) steel was chosen as a reference alloy. Three additional alloys were made by adding $3 \text{Ni}$, $1 \text{Cr}$, or $0.5 \text{Mo}$ to the reference alloy (Table 1). Henceforth, these alloys are referred to as the reference, Ni, Cr, and Mo alloys, respectively.

Carbon combustion analysis was performed on each alloy before and after homogenization to ensure that decarburization did not occur. Dilatometer samples $3$ mm in diameter $\times 10$ mm long were machined from homogenized material. These were heated to $1200^\circ \text{C}$ at a rate of $40^\circ \text{C}$ per minute and held for 15 minutes before cooling. The continuous-cooling-transformation (CCT) diagram for each alloy was measured dilatometrically using 15 cooling rates.
2.2 Isothermal Heat Treatment and Measurement of Transformation Curves

The homogenized materials were cold rolled and cut into $5 \times 5 \times 0.38$ mm coupons for isothermal heat treatment. They were first austenitized at 1200°C for 15 min in the graphite-deoxidized BaCl$_2$ salt bath. Following austenization the samples were transferred to a deoxidized lead bath for isothermal reaction. Isothermal transformation was carried out at temperatures between 500°C and 675°C, and the reaction time ranged from 1 sec to 10,000 sec (about 3 hrs). The samples were then quenched into ice brine. Carbon analysis was also performed after these procedures to verify that decarburization did not take place during austenization or isothermal heat treatment.

Isothermal transformation curves were determined by quantitative metallography [21, 22, 23]. The fraction of austenite transformed to ferrite (or ferrite + carbides) was determined for each transformation time and temperature to within approximately ±2%. The etchant used was 5g FeCl$_3$, 5 drops of HCl, and H$_2$O to make 100 ml of solution; the etching time was about 10 sec [24]. This procedure produced good contrast suitable for point counting. Subgrain boundaries between sympathetically nucleated ferrite could also be revealed. An overetch with 2% Nital or an 8% sodium metabisulfate etch for 10 sec followed by a 2% Nital etch for 5 sec were used in some cases [11, 25]. Both of these methods reveal subgrain boundaries between ferrite plates.

2.3 TEM Sample Preparations

Transmission electron microscope (TEM) specimens were prepared by grinding heat treated samples to a thickness of 100 μm and punching 3 mm disks. These were then
mechanically dimpled by a depth of 30 µm and jet polished to perforation in a South Bay Model 550C single jet thinning instrument using a 30% HNO₃, 70% methanol solution at −50°C and 20–30 V. TEM observations were carried out with a Philips EM420 operated at 120 KV.
Table 1: Compositions of the four alloys.

<table>
<thead>
<tr>
<th>Alloys (in w/o)</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Alloy</td>
<td>0.11</td>
<td>0.41</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>Ni Alloy</td>
<td>0.11</td>
<td>0.42</td>
<td>0.31</td>
<td>3.03 Ni</td>
</tr>
<tr>
<td>Cr Alloy</td>
<td>0.11</td>
<td>0.41</td>
<td>0.31</td>
<td>0.99 Cr</td>
</tr>
<tr>
<td>Mo Alloy</td>
<td>0.11</td>
<td>0.42</td>
<td>0.31</td>
<td>0.50 Mo</td>
</tr>
</tbody>
</table>
3

RESULTS

3.1 CCT Diagrams

CCT diagrams were measured dilatometrically for each alloy (Figure 2). These curves provided a relatively easy way to select the temperatures and times for isothermal heat treatments.

The CCT diagrams of the reference alloy, Figure 2(a), and of the Cr alloy, Figure 2(b), are quite similar. They both show a discontinuity in the initiation curve of transformation at about 750°C for a cooling time of approximately 60 sec. This discontinuity is likely to be due to the same change in mechanism responsible for the bay in TTT diagrams of low carbon alloy steels.

On the other hand, in the Ni alloy, the discontinuity in the initiation curve can not be found with any rate of cooling to 700°C in less than 10,000 sec (Figure 2(c)). In the Mo alloy, the CCT diagram (Figure 2(d)) shows a well defined discontinuity between two C-curves at 625°C.

3.2 Isothermal Transformation Curves

For each alloy, isothermal transformation curves were measured at 500, 550, 600, and 650°C (and 675°C for Ni and Mo alloys) for reaction times between 1 sec and 10,000
Figure 2: CCT diagrams for (a) the reference alloy, (b) Cr alloy, (c) Ni alloy, and (d) Mo alloy.
Figure 2, cont.
Figure 2, cont.
Figure 2, cont.
These temperatures and reaction times were chosen to correspond roughly to the time and temperature range of the discontinuities in the CCT diagrams. The isothermal transformation curves, Figure 3–6, were categorized according to the types of behavior shown in Figure 1 [13].

The transformation curves of the reference alloy and the Cr alloy (Figure 3 and 4) exhibit type I curves at all temperatures investigated. Austenite starts to transform in less than 10 sec and the transformation proceeds rapidly to completion. Transformation at higher temperatures initiates at longer time and proceeds with slower kinetics. The delay in the start of transformation at higher temperature coincides with the trend in their corresponding CCT initiation curves within this temperature range.

As for Ni and Mo alloys, their isothermal transformation curves (Figure 5 and 6) showed similar shapes as those of the reference and Cr alloys below 600°C, i.e. type I transformation. However, after 1000 sec at 650°C, the Ni alloy exhibits a cessation of transformation at about 75% transformation. In the Mo alloy, the transformation curve at 650°C shows an obvious change in the slope at about 18 sec (log (t) = 1.25) and the slope is approximately zero between 18 and 178 sec. Cessation of transformation at this temperature occurs at a transformation level of 70%. Both of these curves are categorized as type IV transformation (Figure 1). Transformation curves of 675°C for Ni and Mo alloy are shown in Figure 3(e) and 4(e), respectively. Transformation cessation is also found in both alloys at 675°C with similar transformation levels as found at 650°C. One apparent difference between the Ni and Mo alloys is that transformation in the Ni alloy does not reach completion within 10,000 sec at 650°C and 675°C, but it does resume following transformation stasis in the Mo alloy and eventually reaches ~ 95%.
Figure 3: Overall transformation kinetics of the reference alloy isothermally reacted at (a) 500°C, (b) 550°C, (c) 600°C, and (d) 650°C.
Figure 4: Overall transformation kinetics of the Cr alloy isothermally reacted at (a) 500°C, (b) 550°C, (c) 600°C, and (d) 650°C.
Figure 5: Overall transformation kinetics of the Ni alloy isothermally reacted at (a) 500°C, (b) 550°C, (c) 600°C, (d) 650°C, (e) 675°C.
Figure 6: Overall transformation kinetics of the Mo alloy isothermally reacted at (a) 500°C, (b) 550°C, (c) 600°C, (d) 650°C, (e) 675°C.
The transformation curve of the Mo alloy reacted at 600°C (Figure 6(c)) shows that the transformation slows at a level of about 93% after 100 sec; however, this curve appears more like type I than type IV behavior since the transformation is nearly complete at this level.

3.3 Microstructure

3.3.1 Optical Morphology of Ferrite and Carbides

Optical micrographs of the proeutectoid ferrite morphology are shown in Figure 7(a) - (d). The general features found in each alloys are considered separately.

The Reference Alloy

Figure 7(a) shows the ferrite morphology of the reference alloy isothermally reacted at 500°C for 2 sec. Long ferrite plates consist of an array of smaller sympathetically nucleated crystals [11]. Ferrite branches develop extensively in this alloy, and the ferrite plates have a degenerate [26] appearance.

A nonlamellar mixture of carbide and ferrite forms between groups of ferrite crystals (Figure 7(a)). Similar structures in other alloys have been termed “nodular bainite” (see for example Figure 3 of Reference [2] and Figure 1 of Reference [27]). For reaction temperatures between 500°C and 650°C, nodular bainite typically forms in less than 10 sec. At 500°C for example, nodular bainite starts to form after approximate 2 sec or at about 30% transformation. Figure 8 shows the microstructure after isothermal heat treatment at 650°C for 10 sec; the transformation is close to completion.
Figure 7: Morphology of sympathetic nucleated ferrite for (a) the reference alloy (reacted at 500°C for 2 sec. NB=Nodular Bainite), (b) the Cr alloy (reacted at 600°C for 3 sec), (c) the Ni alloy (reacted at 600°C 10 sec), and (d) the Mo alloy (reacted at 650°C for 10 sec). Etchant: 5g FeCl₃, 5 drops of HCl, with H₂O to make 100 ml
Figure 7, cont.
Figure 7, cont.
Figure 7, cont.
Figure 8: Carbides are observed in the reference alloy reacted at 650°C for 10 sec. No transformation stasis is found in the transformation curves at any temperatures investigated in this alloy. (NB=Nodular Bainite)
**Cr Alloy**

The microstructure of the Cr alloy after isothermal reaction at 600°C for 3 sec is shown in Figure 7(b). Sympathetic nucleated ferrite appears to dominate the microstructure. The ferrite crystals are thinner and longer than those of the reference alloy even though the reaction temperature of Figure 7(b) is 100°C higher than Figure 7(a). Figure 9 shows the microstructure of the Cr alloy reacted at 650°C for 18 sec. The formation of carbides does not start as early as in the reference alloy, and carbide formation initiates at grain boundaries rather than between ferrite plates. The formation of nodular bainite occurs at a comparatively higher percentage transformation than in the reference alloy (Figure 7(a)).

**Ni Alloy**

The morphology of ferrite in the Ni alloy isothermally reacted at 600°C for 10 sec is shown in Figure 7(c). Both sympathetic nucleated ferrite plates and grain boundary ferrite appear to be more equiaxed than those found in the reference alloy. Aggregates of sympathetic nucleated ferrite crystals are also found to be comparatively larger than those in the other alloys with the same amount of transformation.

As in the reference alloy, nodular bainite is observed at early stages of transformation at temperatures below 600°C. Carbides form at about 24% transformation or after as little as 3 sec at 500°C (Figure 10). At 550 and 600°C, nodular bainite forms after 10 sec and 18 sec, respectively. The transformation level where carbides start to form at these temperatures appears to be approximately 60%.

Isothermal transformation at 650°C or 675°C does not produce carbides in the Ni alloy.
Figure 9: Microstructure of the Cr alloy reacted at 650°C for 18 sec; carbides start forming on the grain boundaries. (NB=Nodular Bainite, M=Martensite)
Figure 10: (a) Carbides are found in the microstructure of the Ni alloy when transformation stasis is absent. (reacted at 500°C for 3 sec, NB=Nodular Bainite) (b) The structure of Ni alloy during transformation stasis (reacted at 675°C for 10000 sec), and no carbide is observed.
Figure 10, cont.
for reaction times up to 10,000 sec, and the ferrite morphology is shown to be blocky (Figure 10(b)) rather than plate-like. The apparent size of blocky ferrite grains appears to be about 50 μm. It should be noted that cessation of transformation is observed at 650°C and at 675°C in the Ni alloy at about 70% transformation, and the blocky ferrite morphology is the one present at these temperatures during transformation stasis.

Mo Alloy

The morphology of ferrite in the Mo alloy is shown in Figure 7(d). The ferrite plates appear very degenerate, and the ratio of the ferrite plate length to thickness is larger than that found in the reference and the Ni alloys. Sympathetic nucleated ferrite is the predominant ferrite morphology.

No nodular bainite was found at any temperatures including those with transformation stasis. The microstructure of the Mo alloy during transformation stasis is shown in Figure 11.

3.3.2 Ferrite Morphology under Transmission Electron Microscope

The purpose of the TEM work was to determine whether carbides are present during transformation cessation in the Ni and the Mo alloys. Isothermal reaction at 650°C for 3162 sec ( log(t)=3.5 ) was selected for Ni alloy. The blocky ferrite produced by this heat treatment consists of numerous subgrains several microns in size (Figure 12). Two possible mechanisms might generate such a structure: sympathetic nucleation or polygonization. Although the subgrains are generally misoriented by a few degrees or less and thus resemble a polygonalized structure, the individual sub-boundaries produce deep cusps
Figure 11: Carbide is not observed in Mo alloy during transformation stasis (reacted at 650°C for 178 sec. M=Martensite).
in the ferrite:austenite or ferrite:martensite boundaries (Figure 12). These suggest that the sub-boundaries result from sympathetic nucleation since low-angle ferrite-ferrite boundaries formed during polygonalization should produce a shallow triple point configuration when they intersect ferrite:austenite boundaries.

The heat treatment for the Mo alloy was 650°C for 178 sec (within the range of transformation cessation). Compared with the ferrite morphology of the Ni alloy, the ferrite in the Mo alloy (Figure 13) appears to be less equiaxed and the boundaries between ferrite grains are more faceted. The ferrite plated in the Mo alloy are also thinner and longer. No carbide was found in either the Ni or the Mo alloy for the conditions chosen in the transformation cessation regimes.

3.4 Thermodynamic Calculation

Several statistical thermodynamic models are available to evaluate the thermodynamic properties of ferrous alloys. Among them, the quasi-chemical approximation [28, 29], the Hillert-Staffansson [30] model, and the central atoms model by Lupis and Elliott [31] are the most widely used. The central atoms model is selected for this study because the parameters required by the model are readily available or can be derived theoretically from data in the literature [32, 33, 34]. Not only is it more convenient to use for complicated systems, it is capable of treating solutions with nonrandom mixing and can include vibrational and translational contributions to the free energy [35, 36].

The central atoms model, is employed to calculate the $\alpha/(\alpha + \gamma)$ and $\gamma/(\gamma + \alpha)$ tie-lines for each alloy. These tie-lines are used to determine metastable fractions of ferrite in austenite at the isothermal transformation temperatures via the lever rule. The metastable
Figure 12: The morphology of ferrite under TEM. No carbide is found during transformation stasis in Ni alloy reacted at 650°C for 3162 sec. (M=Martensite, F=Ferrite)
Figure 13: The morphology of ferrite under TEM. No carbide is found during transformation stasis in the Mo alloy reacted at 650°C for 178 sec. (M=Martensite, F=Ferrite)
fractions of ferrite are then compared to the observed fractions of ferrite in cases where transformation ceases before reaching 100%.

Two different kinds of equilibrium conditions are considered: orthoequilibrium and paraequilibrium. Under orthoequilibrium [37], or full equilibrium, the chemical potential of each element is equal in the ferrite and austenite phases. That is:

$$\mu_i^{\alpha} = \mu_i^\gamma$$
where $i = \text{Fe, C, Mn, Si, or } X$ \hspace{1cm} (3.1)

Paraequilibrium [37, 38] is a constrained equilibrium in which only the mobile interstitial species, such as carbon, is allowed to partition between ferrite and austenite. This type of equilibrium simulates the conditions during ferrite growth from austenite [15, 39, 40, 41]. In materials like Fe–C–Mn–Si–X alloys, the ratios of the substitutional alloying elements (Mn, Si, or X) to the concentration of the solvent, Fe, are the same in both phases. The paraequilibrium condition can be written for an alloy with $t$ substitutional components as [42]:

$$\mu_i^{\alpha} = \mu_i^\gamma$$
$$\mu_i^{\alpha} + \sum_{i=2}^{t} \theta_i \mu_i^\alpha = \frac{\mu_i^{\alpha}}{\mu_i^{\gamma}} + \sum_{i=2}^{t} \theta_i \mu_i^\gamma$$ \hspace{1cm} (3.3)

$$\theta_i = \frac{X_i^{\alpha}}{X_i^{\alpha}} = \frac{X_i^{\gamma}}{X_i^{\alpha}} \quad (i = 2 \sim t)$$ \hspace{1cm} (3.4)

The total free energy of a mixture of $\alpha$ and $\gamma$ with the alloy composition is minimized subject to the orthoequilibrium conditions or the paraequilibrium constraints of Equation 3.4 [43, 44]. The minimization procedure was performed using the simplex method developed by Nelder and Mead [45, 46, 47]. A program for calculating the phase boundaries in multicomponent steels was coded using the symbolic manipulator software, Mathematica [48].
The details of central atoms model and the minimization procedures are included in the Appendix.

The results of the thermodynamic calculations are listed in Table 2. Ortho- and paraequilibrium tie-lines between austenite and ferrite were calculated for all the alloys at temperatures between 500°C and 650°C. Orthonequilibrium yields a lower metastable fraction of ferrite than paraequilibrium in all alloys except the Cr alloy, and the ferrite fraction increases with decreasing temperature.

Comparing the calculated phase boundaries, the Ni alloy shows the lowest carbon concentration in the \( \gamma / (\gamma + \alpha) \) boundary at all the temperatures investigated. The carbon concentration in austenite under paraequilibrium in the Ni alloy at 650°C is about 4.61 at% compared to 6.13, 5.84, and 6.19 at% C in the reference, Cr, and Mo alloys, respectively. The paraequilibrium ferrite fraction in the Ni alloy is also lower than that in the other alloys.
Figure 14: (a) Schematic isothermal free energy surfaces of alpha and gamma in a ternary system with an orthoequilibrium tie-line shown. (b) Paraequilibrium tie-line [42]
Figure 14, cont.
Table 2: The calculated \((\alpha/(\alpha + \gamma)\) and \(\gamma/(\gamma + \alpha)\)) tie-lines of the four alloys under orthoequilibrium and under paraequilibrium at 500, 550, 600, and 650°C. (all concentrations in atomic percentage)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Orthoequilibrium ((a/o))</th>
<th>Paraequilibrium ((a/o))</th>
<th>Ferrite %</th>
<th>Ferrite %</th>
<th>Ferrite %</th>
<th>Ferrite %</th>
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<tr>
<td>C Mn Si X</td>
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<td>C Mn Si X</td>
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<td></td>
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</tr>
<tr>
<td>500°C</td>
<td>(\alpha/(\alpha + \gamma))</td>
<td>0.10 0.28 0.61</td>
<td>0.14 0.41 0.60</td>
<td>0.10 0.28 0.61</td>
<td>97.0 11.95 0.36 0.54</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>(\gamma/(\gamma + \alpha))</td>
<td>12.35 4.57 0.05</td>
<td>-</td>
<td>0.15 0.41 0.60</td>
<td>-</td>
<td>96.8</td>
</tr>
<tr>
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<td>(\alpha/(\alpha + \gamma))</td>
<td>0.11 0.30 0.61</td>
<td>0.14 0.41 0.60</td>
<td>0.11 0.30 0.61</td>
<td>96.5 11.03 0.37 0.54</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>(\gamma/(\gamma + \alpha))</td>
<td>0.11 0.30 0.61</td>
<td>0.14 0.41 0.60</td>
<td>0.11 0.30 0.61</td>
<td>96.5 11.03 0.37 0.54</td>
<td>96.0</td>
</tr>
<tr>
<td>600°C</td>
<td>(\alpha/(\alpha + \gamma))</td>
<td>6.06 1.70 0.22</td>
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<table>
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<tr>
<th>Temperature</th>
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<th>Paraequilibrium ((a/o))</th>
<th>Ferrite %</th>
<th>Ferrite %</th>
<th>Ferrite %</th>
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<tr>
<td>C Mn Si Cr</td>
<td>C Mn Si Cr</td>
<td>C Mn Si Cr</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>500°C</td>
<td>(\alpha/(\alpha + \gamma))</td>
<td>- - -</td>
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<td>- - -</td>
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<td>11.58 0.36 0.54 0.95</td>
<td>- - -</td>
<td>11.58 0.36 0.54 0.95</td>
<td>96.9</td>
</tr>
<tr>
<td>550°C</td>
<td>(\alpha/(\alpha + \gamma))</td>
<td>- - -</td>
<td>0.11 0.41 0.60 1.07</td>
<td>- - -</td>
<td>0.11 0.41 0.60 1.07</td>
<td>96.3</td>
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<td></td>
<td>(\gamma/(\gamma + \alpha))</td>
<td>- - -</td>
<td>0.11 0.41 0.60 1.07</td>
<td>- - -</td>
<td>0.11 0.41 0.60 1.07</td>
<td>96.3</td>
</tr>
<tr>
<td>600°C</td>
<td>(\alpha/(\alpha + \gamma))</td>
<td>13.25 2.71 0.06 10.63</td>
<td>97.0 0.11 0.41 0.60 1.07</td>
<td>13.25 2.71 0.06 10.63</td>
<td>97.0 0.11 0.41 0.60 1.07</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>(\gamma/(\gamma + \alpha))</td>
<td>6.59 1.67 0.20 3.72</td>
<td>94.0 0.11 0.41 0.60 1.07</td>
<td>6.59 1.67 0.20 3.72</td>
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Table 2 cont.

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<th>Paraequilibrium (a/o)</th>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Mn</td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α/(α + γ)</td>
<td>0.10</td>
<td>0.28</td>
</tr>
<tr>
<td>γ/(γ + α)</td>
<td>11.45</td>
<td>4.23</td>
</tr>
<tr>
<td>550°C</td>
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<td></td>
</tr>
<tr>
<td>α/(α + γ)</td>
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<td>0.31</td>
</tr>
<tr>
<td>γ/(γ + α)</td>
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<td>2.50</td>
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<tr>
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<tr>
<td>α/(α + γ)</td>
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</tr>
<tr>
<td>γ/(γ + α)</td>
<td>5.75</td>
<td>1.55</td>
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<tr>
<td>650°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α/(α + γ)</td>
<td>0.07</td>
<td>0.32</td>
</tr>
<tr>
<td>γ/(γ + α)</td>
<td>3.55</td>
<td>1.05</td>
</tr>
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<td>675°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α/(α + γ)</td>
<td>0.06</td>
<td>0.51</td>
</tr>
<tr>
<td>γ/(γ + α)</td>
<td>2.61</td>
<td>0.90</td>
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Mo Alloy (or Fe-0.46a/oC-0.41a/oMn-0.60a/oSi-0.23a/oMo) | | |
| | | | | | | | | | | |
| Temperature | Orthoequilibrium (a/o) | Paraequilibrium (a/o) |
| | C | Mn | Si | Mo | Ferrite | C | Mn | Si | Mo | Ferrite |
| 500°C | | | | | | | | | | |
| α/(α + γ) | 0.10 | 0.28 | 0.51 | 0.25 | 0.16 | 0.41 | 0.60 | 0.296 |
| γ/(γ + α) | 15.16 | 4.74 | 0.06 | 1.72 | 97.2 | 11.96 | 0.36 | 0.53 | 0.26 | 97.4 |
| 550°C | | | | | | | | | | |
| α/(α + γ) | 0.12 | 0.31 | 0.61 | 0.27 | 0.16 | 0.41 | 0.60 | 0.29 |
| γ/(γ + α) | 10.58 | 3.33 | 0.10 | 1.80 | 96.7 | 10.06 | 0.37 | 0.54 | 0.26 | 97.0 |
| 600°C | | | | | | | | | | |
| α/(α + γ) | 0.12 | 0.32 | 0.61 | 0.27 | 0.16 | 0.41 | 0.60 | 0.29 |
| γ/(γ + α) | 8.31 | 2.37 | 0.15 | 0.63 | 95.9 | 8.14 | 0.37 | 0.55 | 0.27 | 96.1 |
| 650°C | | | | | | | | | | |
| α/(α + γ) | 0.12 | 0.32 | 0.63 | 0.28 | 0.14 | 0.41 | 0.60 | 0.29 |
| γ/(γ + α) | 6.19 | 1.72 | 0.22 | 0.43 | 94.3 | 6.19 | 0.38 | 0.56 | 0.27 | 94.6 |
| 675°C | | | | | | | | | | |
| α/(α + γ) | 0.11 | 0.32 | 0.62 | 0.28 | 0.12 | 0.41 | 0.60 | 0.29 |
| γ/(γ + α) | 5.15 | 1.47 | 0.26 | 0.37 | 92.9 | 5.20 | 0.39 | 0.57 | 0.28 | 93.3 |
DISCUSSION

4.1 CCT Diagrams and the Transformation Curves

As shown in Figure 2(a) and (b), the CCT diagrams of the reference alloy and the Cr alloy have similar shapes at the initiation of transformation. Although transformation begins slightly later in the Cr alloy, they both have a bay temperature at about 750°C. The isothermal transformation curves (Figure 3(a) – (d) and 4(a) – (d)) of the reference and Cr alloy are also very much alike. The only apparent difference is for isothermal transformation at 650°C, at which temperature the Cr alloy transforms slightly slower than the reference alloy.

The CCT diagram of the Ni alloy is shown in Figure 2(c). The absence of a distinct discontinuity in the transformation initiation curve of the Ni alloy’s CCT diagram at any cooling rate employed prevented identification of a distinct bay temperature. The lack of a discontinuity may be due to an absence of the change in transformation mechanism or to an insufficiently slow cooling rate in the dilatometer. According to Figure 2(c), the time to initiation of transformation increases greatly as the transformation temperature approaches 700°C. If an upper C-curve is not revealed due to an insufficiently slow cooling rate, 700°C might thus be a temperature close to $T_b$. This is supported by the fact that cessation of transformation is found at both 650°C and 675°C (Figure 5(d) – (e)).
The CCT diagram of the Mo alloy is shown in Figure 2(d). The discontinuity in the slope of transformation initiation curve occurs at approximately 625°C. Transformation cessation (Figure 6(d), (e)), however, is found in the Mo alloys isothermally reacted at 650°C and 675°C, somewhat higher than the CCT bay temperature. Since the CCT diagrams generally lie at lower temperatures than TTT diagrams, the $T_b$ in the TTT diagram is probably higher than 625°C. Thus, cessation of transformation in the Mo alloy at 675°C may still be transformation stasis below the TTT $T_b$.

Near-transformation cessation is observed in the transformation curve of the Mo alloy reacted at 600°C (Figure 6(c)). The transformation fraction remains at a level of 93 vol% after approximately 100 sec. As shown in Figure 2(d), the flat secondary curve in the Mo alloy's CCT diagram indicates that the transformation is sluggish at temperatures between 500 and 625°C.

At temperatures between 500°C and 550°C, a delay in the start of transformation (Figure 5(a),(b)) is found in the Ni alloy relative to that in the Mo alloys (Figure 6(a),(b)). A similar trend can be observed in the initiation curves of their CCT diagrams.

In the CCT diagrams of the reference and Cr alloys, the dilatometric measurements exhibit several regions of apparent transformation stasis, but transformation stasis is not observed in these alloys in isothermal transformation experiments. On the other hand, cessation of transformation is found in the Ni and Mo alloys at temperatures above 650°C, but a transformation stasis region is not found in either of their CCT diagrams. Thus, as was noted several years ago [49], dilatometric experiments can sometimes give qualitatively different results from those obtained with isothermal heat treatments and quantitative metallography.
4.2 Thermodynamic Calculation Results and Prediction of Stasis Level

To be interpreted as transformation stasis, transformation of austenite to ferrite must cease before the metastable fraction of ferrite is achieved [1]. In the present study, paraequilibrium is employed to interpret the metastable stasis level. Among the possible stasis observations, cessation of transformation in the Mo alloy reacted at 600°C can be eliminated as an occurrence of transformation stasis since the percent transformed is approximately 93 vol% (Figure 6(c)), whereas paraequilibrium predicts a metastable amount of ferrite of 96 at% (Table 2; volume and atomic percentages are equivalent to within the limits of experimental and calculation error).

However, cessation of transformation occurs at about 75 vol% at both 650 and 675°C in Ni alloy (Figure 4(d) – (e)), and the paraequilibrium ferrite fractions are considerably higher (92 at% and 89 at%, respectively). The Mo alloy stops transforming at about 70% at 650 and 675°C (Figure 5(d) – (e)), but the calculated paraequilibrium ferrite fractions are 95% and 93%, respectively (Table 2). The calculated values are evidently higher than the experimental values in these cases, so the cessation found in the Ni and Mo alloys at 650°C and 675°C does not correspond to the metastable fraction of ferrite. The plateau found in the transformation curves of these alloys and temperatures can thus be recognized as transformation stasis.

4.3 Solute Drag-Like Effect (SDLE) and Transformation Stasis

The SDLE was originally proposed by Aaronson et al. [12, 18] to explain sluggish ferrite growth kinetics in steels containing specific alloying elements. It maintains that
these alloying elements are swept up by ferrite:austenite boundaries in a nonequilibrium fashion and reduce the activity of carbon in austenite such that the effective concentration gradient in austenite driving growth is diminished. Although a quantitative SDLE theory is unavailable and a direct test of the hypothesis has not been done, a number of indirect experiments and observations support the basic concept [2, 4, 13]. In the context of the present experiment, the SDLE can be used to explain the presence of transformation stasis. The mechanism through which the SDLE causes transformation stasis is described in several recent reviews [13, 19].

For alloys containing elements producing a strong SDLE, the segregated alloying elements at ferrite:austenite boundaries impede ferrite growth enough that renucleation of ferrite is necessary for the transformation to proceed. Renucleation requires sufficient undercooling to allow sympathetic nucleation of ferrite. Sympathetic nucleation continues until the surrounding austenite becomes sufficiently enriched in carbon to prevent further ferrite nucleation. Transformation stasis then begins, since overall transformation effectively ceases when both nucleation and growth of ferrite stop. The transformation does not resume until carbide precipitation or the volume diffusion of the substitutional species relieves the SDLE on ferrite:austenite boundaries.

In order to test the applicability of this hypothesis to the present alloys, the microstructures during transformation stasis were investigated with optical microscope and TEM. As shown in Figure 10(b), 11, 12, and 13, carbides are not present in either the Ni or the Mo alloy during transformation stasis. In contrast, carbide precipitation occurs during the early stages of transformation in the Cr and reference alloys, and these steels do not exhibit transformation stasis (Figure 8 and 9). In addition, carbides form in the Ni alloy at
temperatures that do not produce transformation stasis (Figure 10(a)). These observations are consistent with the model for transformation stasis based on the SDLE hypothesis.

4.4 The Effects of Alloying Elements and their Interactions on the Transformation Curves

Previous work in Fe–C–X alloys indicates that transformation stasis occurs at 555°C in Fe–0.13C–2.99Cr [3], below $T_b$ and above the minimum threshold concentrations of $C$ and Mo in Fe–C–Mo alloys [2], and at 550°C in Fe–0.1C–2.99Mn [4]. Transformation stasis was not observed in several Fe–C–Ni or Fe–C–Si alloys nor in an Fe–0.38C–3.11Mn alloy. The appearance of stasis on the current hypothesis requires: (1) a strong SDLE to inhibit ferrite growth, and (2) the absence of carbide formation so that the supersaturation for the sympathetic nucleation of ferrite is reduced during ferrite formation.

On the most recent model for the SDLE [2], a solute drag like effect results when the chemical potential of carbon in the ferrite:austenite boundary is significantly less than the paraequilibrium value. Predicting this condition requires knowledge of the boundary concentrations of carbon and the solute species, and a thermodynamic description of the boundary. Since very little of this information is available, one must resort to generalities. It is likely, as has been suggested before [1, 15], that elements capable of reducing the carbon activity should produce a SDLE. This may not be a requirement, but it is a reasonable starting assumption. Mo, Mn and Cr, whose interaction parameters with C are negative, should produce a SDLE, and Ni and Si, whose interaction parameters are positive, should not.

In an alloy with more than one alloying element, interactions among the substitutional
species in the ferrite:austenite boundary must also be considered. Of the quaternary steels, Fe–C–Mn–Si has been investigated the most. Bhadeshia et al. [7] claim that Fe–0.43 C–3.00 Mn–2.12 Si shows transformation stasis. As described previously, both Fe–0.38C–3.11Mn and Fe–0.38 C–1.73 Si [8] steels do not exhibit transformation stasis (Table 3). However, the methods and results of Reference [7] have been challenged on experimental grounds and are thus not definitive [8, 9]. Chen and coworkers [10] appear to have identified transformation stasis in Fe–0.35C–2.27Mn–2.34Si reacted between 450 and 535°C. Thus, the interactions of Mn and Si could produce transformation stasis. The large temperature range over which stasis is found suggests that Si enhances the SDiE when combined with Mn. This possibility has been suggested to result from enhanced Mn segregation to ferrite:austenite boundaries caused by Si [8]. It is also likely that inhibition of cementite formation by Si at higher carbon concentrations (0.35 C) in Fe–C–Si–Mn alloys encourages the development of transformation stasis.

Since Fe–C–Mn–Si alloys exhibit stasis under some conditions, the absence of transformation stasis in the reference alloy may be a consequence of the low concentrations of C, Mn and Si in the alloy (Table 3). That is, these elements are below the threshold [2] concentrations for the Fe–C–Mn–Si system.

In this work, transformation curves of an Fe–0.12 C–3.28 Ni alloy isothermal reacted at 650°C and 675°C are also determined (Figure 15). Transformation stasis is absent in this alloy at temperatures between 550°C and 675°C [4]. Therefore, the interactions among Mn, Si, and Ni lead to transformation stasis in the Ni alloy (Table 3). The addition of Ni to the reference alloy apparently lowers $T_b$ from 750°C in the reference alloy to 700°C. This decrease could be related to the fact that Ni is an austenite stabilizer. The reduction
in driving force for ferrite formation caused by Ni could, in effect, lower the threshold concentrations of C, Mn, and Si required to cause transformation stasis.

The reduction in driving force for ferrite precipitation engendered by Ni may also explain the differences in the microstructures of the Ni alloy from the other alloys studied. Two features are found in the microstructure survey of the Ni alloy: the grain boundary ferrite at the early stage of transformation is relatively thicker than the other alloys studied (Figure 7(c)), and blocky ferrite is formed during transformation stasis (Figure 10(a)). Since the driving force for ferrite formation is decreased by Ni, the sympathetic nucleated ferrite is comparatively more difficult to form than in the other alloys. The alloying elements that produce a SDLE may also affect the interfacial structure of ferrite:austenite boundaries in such a way as to lead to subtle changes in ferrite morphology.

In contrast to a Ni addition, Mo is a ferrite stabilizer [50] and increases the driving force for ferrite precipitation. However, it also produces a strong SDLE as is evidenced by the anomalously slow ferrite growth kinetics [1] and transformation stasis [2] in Fe–C–Mo alloys (Table 4). Since transformation stasis is not found in an Fe–0.13 C–0.46 Mo steel [2] and the reference alloy, the combined effects of Mo, Mn and Si in the Mo alloy result in transformation stasis at substantially lower threshold concentrations of C and Mo than required to produce stasis in a ternary Fe–C–Mo alloy.
Figure 15: Overall transformation kinetics of Fe–0.12 C–3.28 Ni alloy isothermally reacted at (a) 650°C, (b) 675°C.
Table 3: Transformation stasis and interactions of Mn, Si, and Ni

<table>
<thead>
<tr>
<th>Alloys (in w/o)</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>X</th>
<th>Stasis</th>
<th>Reference</th>
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<td>–</td>
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<tr>
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<td>1.73</td>
<td>–</td>
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<td>0.31</td>
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<td>this work</td>
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<tr>
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<td>0.42</td>
<td>0.31</td>
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<td>–</td>
<td>3.28 Ni</td>
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Table 4: Transformation stasis and interactions of Mn, Si, and Mo

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<th>Si</th>
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<th>Stasis</th>
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<td>0.31</td>
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<td>0.31</td>
<td>–</td>
<td>No</td>
<td>this work</td>
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<tr>
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<td>–</td>
<td>–</td>
<td>0.46 Mo</td>
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CONCLUSIONS

The overall kinetics of proeutectoid ferrite transformation were investigated in a series of Fe-0.1 C-0.4 Mn-0.3 Si-X alloys where X stands for 3 Ni, 1 Cr, or 0.5 Mo, and Fe-0.1 C-0.4 Mn-0.3 Si was served as the reference alloy. At temperatures between 500 and 650°C, no transformation stasis is found in the reference and the Cr alloys. Transformation stasis is observed at 650°C and 675°C in the Ni alloy and in the Mo alloy. The fraction of ferrite present during transformation stasis is significantly less than the calculated metastable (paraequilibrium) fraction of ferrite at these isothermal reaction temperatures.

The absence of carbide precipitation appears to be a necessary condition for transformation stasis. No carbide forms for the reaction temperatures and times in the stasis regime of the Ni and Mo alloys. However, carbide precipitation does occur in the Ni alloy at lower temperatures where transformation stasis is absent. Stasis is also absent in the reference and the Cr alloys with carbide precipitation.

The transformation kinetics in these alloys are consistent with a previously proposed explanation for transformation stasis [2]. Transformation stasis occurs in alloys with sufficient concentrations of C and solute elements to produce a strong solute drag-like effect with no concurrent carbide formation. At large enough driving forces for ferrite formation, ferrite precipitates via sympathetic nucleation with subsequent growth severely restricted.
by the solute drag-like effect.

The presence of transformation stasis is encouraged in the Mo alloy by the combined presence of Mn and Si. Both Mn and Mo may be segregating to ferrite-austenite boundary to produce an enhanced SDLE.

In the Ni alloy, the temperatures with transformation stasis are within 50° of the CCT bay temperature. Stasis in this alloy is probably due to a reduction in the threshold concentrations of C, Si and Mn required for stasis since Ni greatly reduces the driving force for ferrite formation. Ni may also change the interfacial structure of ferrite causing formation of blocky ferrite rather than the degenerate ferrite found in the other alloys exhibiting transformation stasis.

Even though the reference and the Cr alloys have similar CCT curves as the Ni alloy, transformation stasis is not observed in these alloys due to the formation of carbides. It may also be that these alloys are not above the threshold concentrations of C, Mn, Si (and Cr) required to produce transformation stasis.

Some regions in the CCT diagrams of the reference and Cr alloys are no-transformation areas according to dilatometric data. No such regions are found in the CCT diagrams of the Ni and Mo alloys. However, transformation stasis does occur in the Ni and the Mo alloys but not in the reference and Cr alloy. This implies that dilatometry is not a reliable indicator of isothermal transformation stasis.
REFERENCES


Appendix A

Calculation of Phase Boundaries by Central Atoms Model

A.1 Derivation of Central Atoms Model Activity Functions

Central atoms model was employed to calculate the tie-line, or the compositions of \( \alpha/(\alpha + \gamma) \) and \( \gamma/(\gamma + \alpha) \) phase boundaries, in the investigated alloys and temperatures. In a \( m \)-component alloy steel, \( Fe - C - X_2 - \cdots - X_t \), two sublattices are defined as the substitutional and interstitial sublattices. Different number is assigned to each element for convenience and generality of expressions. The solvent, Fe, is numbered as 1. \( t \) stands for the total number of substitutional solutes. The interstitial solutes then begin with \( t + 1 \), i.e. carbon is assigned with number \( t + 1 \). \( m \) is equal to \( t + 1 \) in this specific system of alloys with only one interstitial component, C. Vacancies are counted as the rest of interstitial sites, \( m + 1 \). The activity functions were derived by Foo and Lupis [32] as follows. For solvent 1 (Fe):

\[
ln a_1 = ln Y_1 + r ln Y_{m+1} - ln P_k - r ln P_{m+1} - \frac{\mu^0_1}{RT} \quad (A.1)
\]

for the substitutional solute \( k (k = 2 \sim t \) hereafter):

\[
ln a_k = ln Y_k + r ln Y_{m+1} + (Z\Delta_k + z\Delta'_k) - ln P_k - r ln P_{m+1} - \frac{\mu^0_k}{RT} \quad (A.2)
\]
and for the interstitial solute \( l(l = t + 1 \sim m \text{ hereafter}) \):

\[
\ln a_l = \ln y_l + (Z' \Lambda_l + z' \Lambda'_l) - \ln P_l + \ln P_{m+1} - \frac{\mu_i^c}{RT}
\]  \hspace{1cm} (A.3)

\( Z \) and \( z \) are the number of substitutional and interstitial nearest neighbors to a substitutional site, while \( Z' \) and \( z' \) are the coordinate numbers of an interstitial site. The ratio of interstitial sites to substitutional sites, \( r \), is thus \( z/Z' \). For austenite or fcc phase, \( Z = z' = 12, z = Z' = 6 \), and \( r = 1 \). For ferrite or bcc phase, \( Z = 8, z = 6, Z' = 2, z' = 4 \), and \( r = 3 \). Also, let \( X_i \) be the molar fraction of \( i \)th element in the alloy. \( Y_i \) is defined as the site fraction of \( i \)th component in its corresponding sublattice.

\[
Y_k = \frac{X_k}{1 - \sum_{i=t+1}^{m} X_i}
\]

\[
Y_l = \frac{1}{r} \cdot \frac{X_l}{1 - \sum_{i=t+1}^{m} X_i}
\]  \hspace{1cm} (A.4)

\( y_i \) is then the site ratio of \( i \)th component to the number of solvent or vacancies in substitutional or interstitial sublattices, respectively.

\[
y_k = \frac{X_k}{1 - \sum_{i=2}^{m} X_i}
\]

\[
y_l = \frac{1}{r} \cdot \frac{X_l}{1 - \sum_{i=t+1}^{m} X_l(1 + \frac{1}{r})}
\]  \hspace{1cm} (A.5)

\( \mu_i^c \) is the chemical potential of the \( i \)th component. \( \Lambda_i \) and \( \Lambda'_i \) are Lagrangian multipliers to obtain the most probable configuration of atoms by maximizing the partition function and satisfying the mass balance equations. They can be rewritten as follows to simplify in later expressions.

\[
\omega^{(k)}_i = \omega_i = \exp(\Lambda_k - \delta \varphi^{(1)}_i)
\]

\[
\omega^{(l)}_i = \omega'_i = \exp(\Lambda'_k)
\]  \hspace{1cm} (A.6)
where $\delta \varphi_{1k}^{(1)}$ is the difference in energy when one kth atom appears around the Fe central atom compared to all nearest neighbors being Fe atoms. New interaction parameters are also defined to simplify the equations:

$$
\lambda_{k-i} = 1 - \exp(-\delta \varphi_{1i}^{(k)} + \delta \varphi_{1i}^{(1)})
$$

$$
\lambda_{i-i} = 1 - \exp(-\delta \varphi_{1i}^{(1)})
$$

(A.7)

The newly defined interaction parameters, $\lambda_{i-j}$, can be related to the conventional Wagner interaction parameter, $\varepsilon_i^j$, by [20, 32, 33, 34]

$$
\lambda_{i-j} = \frac{1}{2Z^2} \varepsilon_i^j
$$

$$
\lambda_{i-C} = \frac{1}{2Z^2} \varepsilon_C^i
$$

$$
\lambda_{C-i} = \frac{1}{2Z^2} [\varepsilon_C^i - (1 + \frac{1}{r})]
$$

(A.8)

through the definition of $\varepsilon_i^j = \frac{\partial \ln(a_i/X_j)}{\partial x_j} |_{X_{j-i}}$. It is noted that $\lambda_{i-j} = \lambda_{j-i}$, since $\varepsilon_i^j = \varepsilon_j^i$.

$P_i$ in Equation A.1 is a normalization factor for the probability of distribution of ith atom [35].

$$
P_i = Y_1^Z_1 Y_{m+1}^{Z_i} \exp(-\varphi_{00}^{(i)})
\cdot [1 + \sum_{k=2}^{t} y_k \omega_k^{(i)} (1 - \lambda_{i-k_i})]^Z_i
\cdot [1 + \sum_{l=i+1}^{m} y_l \omega_l^{(i)} (1 - \lambda_{i-l_i})]^Z_i
$$

(A.9)

Since $\lambda_{i-j}$ can be obtained through Wagner’s interaction parameters, $\omega_i$ and $\omega_i'$ can also be solved as function of $X_i$ through the mass balance equations.

$$
\psi_k = \sum_{j=1}^{t} N_j \frac{Z y_k \omega_k (1 - \lambda_{j-k})}{1 + \sum_{k'=2}^{t} y_{k'} \omega_{k'} (1 - \lambda_{j-k'})} - Z n_k = 0
$$

(A.10)
\[ \psi_i = \sum_{j=1}^{i} n_j \frac{z \gamma_j \omega_j (1 - \lambda_{j-l})}{1 + \sum_{l'=l+1}^{m} \gamma_{l'} \omega_{l'} (1 - \lambda_{j-l'})} - z' n_i = 0 \]  
(A.11)

\[ \psi_k' = \sum_{j=1}^{n+1} n_j \frac{Z' \gamma_k \omega_k' (1 - \lambda_{j-k})}{1 + \sum_{l'=l+1}^{i} \gamma_{l'} \omega_{l'} (1 - \lambda_{j-l'})} - z n_k = 0 \]  
(A.12)

\[ \psi_i' = \sum_{j=1}^{n+1} n_j \frac{z' \gamma_i \omega_i' (1 - \lambda_{j-l})}{1 + \sum_{l'=l+1}^{i} \gamma_{l'} \omega_{l'} (1 - \lambda_{j-l'})} - z' n_i = 0 \]  
(A.13)

where \( n_i \) was the site fraction of solute \( i \).

In Equation A.1 – A.3, parameters, such as \( \delta \varphi_{1,k}^{(1)} \), can be generated by substituting the Lagrangian multipliers, and \( \varphi_{0,0}^k \) is obtained by taking the logarithm of \( P_i \). All these can be eliminated by substituting the expressions of \( \ln \gamma_i^\infty \):

\[ \ln \gamma_i^\infty = Z \delta \varphi_{1,k}^{(1)} + \varphi_{0,0}^k - \frac{\mu_i^0}{RT} \]

\[ \ln \tau \gamma_c^\infty = Z' \delta \varphi_{1,c}^{(1)} + \varphi_{0,0}^c - \frac{\mu_c^0}{RT} \]  
(A.14)

where \( \gamma_i^\infty \) is the activity coefficients as solute \( i \) is in an infinitively dilute solution. These are available in the literature.

### A.2 Equilibrium Conditions

#### A.2.1 Orthoequilibrium

To satisfy the orthoequilibrium condition (Equation 3.1), the ferrite growth rate must depend on the volume diffusion of alloying element, since the volume diffusion of carbon is four or more orders of magnitude faster than other alloying elements. It is shown [15, 39] in several alloys that the growth kinetics predicted by orthoequilibrium is as many as five orders of magnitude below the experimental data. Orthoequilibrium is thus not practical to describe the phase boundaries during the austenite transformation [40, 41].

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In Equation 3.1, \( \mu_i^{\alpha-\gamma} \) is the standard chemical potential change of solute \( i \) from \( \alpha \) to \( \gamma \) phase which is available in references [20, 35, 50, 51, 52, 63]. Choice of thermodynamic data has been individually checked by calculating the phase boundaries in the relative binary and ternary systems to fit the available phase diagrams.

At any temperature, there are a total of \( 2(m-1) \) unknowns in orthoequilibrium (\( X_{2-m}^\alpha \text{ and } \gamma \)); however, only \( m \) equations (Equation A.1 – A.3) are available. There is accordingly \( m-2 \) degrees of freedom. These can be eliminated by setting \( m-2 \) compositions in \( \alpha \) or \( \gamma \).

Given \( m-2 \) components in the phase boundaries, one unique tie-line should be attained. For example, in binary system, there is only one tie-line between \( \alpha \) and \( \gamma \) phases at any temperatures without knowing what the alloy is. In ternary system, one composition of the phase boundaries, such as \( X_C \) in the \( \gamma/(\gamma+\alpha) \) boundary, must be known to find the unique tie-line satisfying this requirement.

### A.2.2 Paraequilibrium

Paraequilibrium [37, 38, 42] avoids the drawback of underestimating ferrite growth kinetics by allowing metastable equilibrium at the ferrite:austenite interface. It requires that only carbon diffuses while alloying elements do not. The phenomenon that no alloying element is partitioning during the transformation has been observed in several alloys [40, 41] through electron microprobe analysis, such as Fe–C–Si, Fe–C–Mo, or Fe–C–Cr at temperatures investigated, and Fe–C–Mn or Fe–C–Ni at below a certain temperature depending on the composition. Since the alloying element does not partition during the growth, the growth kinetics in paraequilibrium is carbon diffusion controlled. It has been found [15, 39] in Fe–C–Mn, Fe–C–Si, Fe–C–Cr, and Fe–C–Ni alloys that the difference between measured
and predicted ferrite growth kinetics data by paraequilibrium is within one order of magnitude.

The condition of paraequilibrium is shown in Equation 3.2–3.4. Equation 3.4 represent the constraint to the phase boundaries. It restricts partitioning of the alloying element \((2 \sim t)\) between the two phases, since the ratio of the \(i\)th solute to solvent, Fe, is the same in both phases.

In paraequilibrium, there are only two independent equations (Eqns. 3.2 and 3.3). In these equations, \(\theta_i\)'s are obtained from the compositions of the alloy, and the tie-line is calculated to satisfy Equation 3.4. As a result, \(X_C^{a/(a+y)}\) and \(X_C^{y/(y+a)}\) are the only independent variables to be solved. \(X_{Fe}\) can then be obtained by

\[
1 = X_{Fe} + \sum_{i=2}^{1} \theta_i X_{Fe} + X_C \tag{A.15}
\]

and \(X_i = \theta_i X_{Fe}\) in both phases.

A.2.3 Equilibrium through Minimization of Free Energy

The total free energy can be written as

\[
G = n_o G^o + n_\gamma G^\gamma \\
= \left[ \sum_{i=1}^{n} (n_o X_i^o \mu_i^o + n_\gamma X_i^\gamma \mu_i^\gamma) \right] \tag{A.16}
\]

where \(n_o\) and \(n_\gamma\) are the molar fraction of \(o\) and \(\gamma\) phases respectively \((n_o + n_\gamma = 1)\).

With an initial guess of tie-line knowing the interstitial composition in one of the phase boundaries, \(G\) can be minimized by iteration. The tie-line with minimum \(G\) will be tangent to both \(o\) and \(\gamma\) free energy surfaces as shown in Figure 14(a). In paraequilibrium, the
tie-line lies on a plane satisfying Equation 3.4 and is tangent to the intersections of this plane with two free energy surfaces (Figure 14(b)).

A.3 Numerical Methods and Programming

A.3.1 Iteration Methods of Solving $\omega$ Parameters

It should be noted that $\omega_i$ and $\omega'_i$ are not known until $X_i^0$ and $X_i'$ are obtained. To make the program as general as possible, the authors did not use the approximation function, $A_{ij}$, as in Reference [32]; instead, a numerical method was employed to find $\omega_i$ and $\omega'_i$. Jacobian method is applied to obtain $2(m-1)$ of the $\omega$ and $\omega'$ parameters by fixing $X_i$ in $2(m-1)$ mass balance equations (Equation A.11 - A.13). For $\psi(\omega_i) = 0$, the Jacobian matrix can be defined: $J \equiv p \frac{\partial \psi}{\partial \omega_j}$, and

\[
J(\Omega_n) \quad D_n = \psi(\Omega_n)
\]

\[
\Omega_{n+1} = \Omega_n - Dn
\]  \hspace{1cm} (A.17)

where $\Omega_n$ is a vector consisting of all $\omega_i$ in the nth iteration. It is iterated until

\[
\left| \frac{\Omega_{n+1} - \Omega_n}{\Omega_n} \right| < \delta
\]  \hspace{1cm} (A.18)

where $\delta$ is set to be a small number for sufficient accuracy.

A.3.2 Minimization by Simplex Method

The procedure chosen for optimization is a simplex method developed by Nelder and Mead [45, 46, 47]. To minimize a function with $n$ variables, an initial simplex containing $(n+1)$ points in $n-$dimensional space is arbitrarily chosen. The method follows the direction in

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the simplex with lowest value to find next lower points by three basic operations: reflection, contraction and expansion. The iteration does not stop until the size of simplex converges to a small area indicating that the minimum value has been obtained. The detail of the minimization procedures can be obtained in Reference [45].

A.3.3 Program Descriptions

The program was written with a symbolic mathematic software, Mathematica [48]. Through this software, the iteration is operated in a fashion of vectors, and all the polynomials or functions can be manipulated symbolically which make the program more friendly and more readable. The current version of program, MultiAlloy.ma, is able to calculate the phase boundaries in any $Fe-C-X_2\cdots-X_t$ systems at any temperatures for either para-equilibrium or orthoequilibrium as long as the required interaction parameters are provided. The code consists of four parts: the definition and input of parameters and thermodynamic data such as $Y_i$ and $\lambda_{i-j}$; the expressions of polynomials and functions to be solved; the iteration procedures needed to solve $\omega_i$ and $\omega_i'$; and the simplex method to minimize the system free energy. The computer time depends greatly upon the number of components in the alloy. Less than 100 iterations was typical for systems less than four components. Up to 200 iterations might be required for five component systems. The delay of calculation is attributed to the numerical solving procedures of $\omega_i$ and $\omega_i'$.

A.4 Thermodynamic Data

The following table lists the thermodynamic data and their variables being employed in MultiAlloy.ma program.
Table 5: Thermodynamic data

<table>
<thead>
<tr>
<th>Notation</th>
<th>Variables</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^\infty_{\text{Fe}}$</td>
<td>$\Delta G^\infty_{\text{C}}$</td>
<td>Interpolated from [51]</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Mn}}$</td>
<td>$\Delta G^\infty_{\text{Si}}$</td>
<td>0 [20]</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$\Delta G^\infty_{\text{Cr}}$</td>
<td>$3477 - 0.514T - 2.742 \times 10^{-3}T^2 + 1.653 \times 10^{-6}T^3$ [20]</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$\Delta G^\infty_{\text{Mo}}$</td>
<td>9590 - 0.58T</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$-3932.96 - 4.1087 \times 10^{-3}T^2 + 4.853 \times 10^{-6}T^3 - 1.41 \times 10^{-9}T^4$ [20]</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$\Delta G^\infty_{\text{Cr}}$</td>
<td>$10460 + 0.6276T$ [50]</td>
</tr>
<tr>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$\Delta G^\infty_{\text{Ni}}$</td>
<td>$10460 + 0.637$ [53]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Notation</th>
<th>Variables</th>
<th>$\ln \gamma_t^{\infty}$</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln \gamma_t^{\infty}$</td>
<td>loggamma$[1/2,\text{CC},1,\text{CC}]$</td>
<td>$-5.151 + 12431T$</td>
<td>$-2.1 + 5300/T$ [20]</td>
</tr>
<tr>
<td>$\ln \gamma_M^{\infty}$</td>
<td>loggamma$[1/2,\text{MN},1,\text{MN}]$</td>
<td>0.5636 + 493.1/T</td>
<td>$2.042 - 2270/T$ [35]</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{Si}}^{\infty}$</td>
<td>loggamma$[1/2,\text{SI},1,\text{SI}]$</td>
<td>$-129704 + 7.95T/RT$</td>
<td>$(-136917 + 7.95T)/RT$ [20]</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{Ni}}^{\infty}$</td>
<td>loggamma$[1/2,\text{NI},1,\text{NI}]$</td>
<td>$1339 + 1.3275 \times 10^{-3}T^2$</td>
<td>$(2092 - 3.8314 \times 10^{-3}T^2)/RT$ (2092 - 3.8314 \times 10^{-3}T^2)/RT</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{Cr}}^{\infty}$</td>
<td>loggamma$[1/2,\text{CR},1,\text{CR}]$</td>
<td>$-1.358 + 3019.5/T$</td>
<td>$-0.7549 + 890.7/T$</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{Ni}}^{\infty}$</td>
<td>loggamma$[1/2,\text{MO},1,\text{MO}]$</td>
<td>$-1.006 + 3875/T$</td>
<td>$-1.006 + 2982/T$ [35]</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{Si}}^{\infty}$</td>
<td>loggamma$[1/2,\text{SI},1,\text{SI}]$</td>
<td>$-92885 - 23.012T/RT$</td>
<td>$(-104184 - 23.012T)/RT$ [20]</td>
</tr>
<tr>
<td>$\ln \gamma_{\text{NI}}^{\infty}$</td>
<td>loggamma$[1/2,\text{NI},1,\text{NI}]$</td>
<td>$45606 + 3.64T/RT$</td>
<td>$(51882 + 10.878T)/RT$ [20]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda_{i,j}$</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{C} \rightarrow \text{C}}$</td>
<td>$\text{lambda}[1/2,\text{CC},\text{CC}]$</td>
</tr>
<tr>
<td>$\lambda_{\text{Mn} \rightarrow \text{Mn}}$</td>
<td>$\text{lambda}[1/2,\text{MN},\text{MN}]$</td>
</tr>
<tr>
<td>$\lambda_{\text{Si} \rightarrow \text{Si}}$</td>
<td>$\text{lambda}[1/2,\text{SI},\text{SI}]$</td>
</tr>
<tr>
<td>$\lambda_{\text{Cr} \rightarrow \text{Cr}}$</td>
<td>$\text{lambda}[1/2,\text{CC},\text{CC}]$</td>
</tr>
<tr>
<td>$\lambda_{\text{Ni} \rightarrow \text{Ni}}$</td>
<td>$\text{lambda}[1/2,\text{NI},\text{NI}]$</td>
</tr>
<tr>
<td>$\lambda_{\text{Ni} \rightarrow \text{Cr}}$</td>
<td>$\text{lambda}[1/2,\text{CC},\text{CC}]$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\epsilon_{i,j}$</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{\text{Cr} \rightarrow \text{Cr}}$</td>
<td>$\text{epsilon}[1/2,\text{CR},\text{CR}]$</td>
</tr>
<tr>
<td>$\epsilon_{\text{Mn} \rightarrow \text{Mn}}$</td>
<td>$\text{epsilon}[1/2,\text{MO},\text{MO}]$</td>
</tr>
<tr>
<td>$\epsilon_{\text{Cr} \rightarrow \text{Cr}}$</td>
<td>$\text{epsilon}[1/2,\text{CC},\text{CC}]$</td>
</tr>
<tr>
<td>$\epsilon_{\text{Cr} \rightarrow \text{Cr}}$</td>
<td>$\text{epsilon}[1/2,\text{CR},\text{CC}]$</td>
</tr>
</tbody>
</table>
This is a part of Appendix in Jhewn-kuang Chen's Thesis. The object of this program is to calculate the phase boundaries between ferrite and austenite phases which will be utilized to evaluate the thermodynamic dependence of the stasis level.

This program allows users to calculate either ortho- or para-equilibrium for most alloys containing Fe and C as long as sufficient thermodynamic data are properly implanted. Currently, the data are available for Fe-C-Mn-Si, Fe-C-Mn-Si-Ni, Fe-C-Mn-Si-Cr, and Fe-C-Mn-Si-Mo alloys, and the following example coding is being set to calculate the orthoequilibrium tie-line of Fe-0.1C-0.4Mn-0.3Si-1Cr at 600 C. Comments can be found in between (* and *).

Last modified on September 19, 1992.

Definition of Parameters and Thermodynamic Data
(* PARA=1 stands for doing paraequilibrium calculation. PARA is set to zero in this example for orthoequilibrium calculation. *)
PARA=0;
ORTHO=1-PARA

(* In Central Atom Model, substitutional elements are always numbered starting with 1 for the solvent, Iron, and then other substitutional components. Interstitial elements are numbered after the substitutional elements. *)
t stands for the total no. of substitutional elements, and m is the total no. of the system. Therefore, carbon should always be numbered as $t+1$. It may result in failed calculation, if C had not been numbered as $t+1$ while it is in the alloy. *)
t=4;
m=5;

(* Components in the alloy to be calculated : Fe-C-Mn-Si-Cr. Substitutional sublattice - #1:Fe, #2:Mn, #3:Si, #4:Cr. Interstitial sublattice - #5:C. All others not being used in this calculation, such as Ni and Mo, are assigned #0. *)
FE=1;
MN=2;
SI=3;
NI=0;
CR=4;
MO=0;
CC=t+1;

(* IT - Calculating temperature (C)*)
IT=600;
(* Note on notations and units:
A. SI system units are employed, such as Joule/mole.
   Temperature is in Kelvin's scale.
B. Generally, matrices of 2 rows are used, and they are respectively:
   1- Alpha Phase.
   2- Gamma Phase.

Zi[[2]], z[[2]] - Z and z for alpha and gamma phases.
Zp[[2]], zp[[2]] - Z' and z' for alpha and gamma phases.
r[[2]] - r for alpha and gamma phases.
logamma[[2,m,m,m]] - logarithmic activity coefficients for alpha and gamma phases.
lambda[[2,m+1,m+1]] - lambda(i,j) for alpha and gamma phases.
epsi[[2,m,m]] - epsilon(i,j) for alpha and gamma phases.
Y[[2,m+1]] - Y(i) for alpha and gamma phases.
y[[2,m+1]] - y(i) for alpha and gamma phases.
phai[2,m] - Phai(i) in the mass balance equations.
phai[2,m] - Phai'(i) in the mass balance equations.
delph[2,m+1,m+1] - delta phi(i,i) (alpha, gamma)
eqns1[[1,m-1]] - Mass Balance Eqns. Set #1 for ferrite.
vars1[[1,m-1]] - Variables in Mass Balance in set #1.
eqns2[[1,m-1]] - Mass Balance Eqns. Set #2 for austenite.
vars2[[1,m-1]] - Variables in Mass Balance in set #2
L[[2,m]] - Lagrange's multipliers (for substitutional components).
Lp[[2,m]] - Lagrange's multipliers (for interstitial components).
P[[2,m+1]] - P(i) Total probability or normalization factors for both phases.
loga[[2,m]] - log a ; logarithm of activity of component i for both phases.
deltageo[m] - Standard free energy change of each component from alpha to gamma phase.
w[[2,m]] - omega in ferrite and austenite.
w_{p[[2,m]]} - omega' in ferrite and austenite. *)
(* Matrices and variables initialization *)

Unprotect[In, Out, All];
Clear[In, Out, All];
R=8.31431; (* Joule/mole/K *)
c2j=4.184;
RT=R T;

Z={8,12};
z={6,6};
Zp={2,6};
zp={4,12};
r=Table[z[[i]]/Zp[[i]],{i,2}];

Array[nii,2];
Array[nt,2];
Array[ns,2];
Array[X,{2,m+1}];
Array[n,{2,m}];

Array[w,{2,m}];
Array[wp,{2,m}];

Array[deltago,{m}];
Array[delph,{2,m+1,m+1}];
Array[phioo,{2,m+1}];
Array[vuo,{2,m}];

(* theta(i) used for substitutional components in para-equilibrium calculation.*)
Array[theta,t];
(* Para-equilibrium requires that \( X(i) = \theta(i) \) X(Fe) *)

Switch[PARA,1,
   Do[
      X[i,m]=1.00-X[i,1];
      X[i,m+1]=0;
      phioo[i,m+1]=0;
      Do[
         X[i,j]=\theta[j] X[i,1];
         X[i,m]=X[i,j]{j,2,m-1}],
      {i,2}],
   0,
   Do[
      X[i,1]=1;X[i,m+1]=0;
      phioo[i,m+1]=0;
      Do[X[i,1]=X[i,j]{j,2,m}],{i,2}]
   ]
]

(* Calculating the site fraction of component from #1 to m+1 (n[i,j]), substitutional components (ns[i]), and interstitial components (nt[i]) *)

Do[ns[i]=0; nt[i]=0;
   Do[n[i,j]=X[i,j];ns[i]+=n[i,j]{j,1,t}];
   nt[i]+=ns[i]{i,2}];

Do[nii[i]=0;
   Do[n[i,j]=X[i,j];nii[i]+=n[i,j]{j,t+1,m}];
   nt[i]+=nii[i]{i,2}];

Do[ni=r[i] ns[i]; n[i,m+1]=ni-nii[i];
   nt[i]+=n[i,m+1]{i,2}];

Do[Do[(n[i,j] /=nt[i]){j,m+1}],{i,2}];
(* Standard Gibbs free energy change of iron transformation from ferrite to austenite as function of temperature. Data are compiled by Orr and Chipmann. *)

ghTFeAlpha={298.15,6.52},{300,6.5202},{400,6.7615},
{500,7.2355},{600,7.7892},{700,8.3675},
{800,8.9494},{850,9.2394},{900,9.5285},
{950,9.8174},{1000,10.1073},{1020,10.2241},
{1030,10.2827},{1042,10.3535},{1050,10.4011},
{1060,10.4607},{1080,10.5796},{1100,10.6982},
{1184,11.1876},{1200,11.2790},{1300,11.8335},
{1400,12.3599},{1500,12.8602},{1600,13.3372},
{1665,13.6363});

ghTFegamma={500,5.4958},{600,6.6602},{700,7.6575},
{800,8.5332},{850,8.9349},{900,9.3162},
{950,9.6795},{1000,10.0265},{1020,10.1612},
{1030,10.2276},{1042,10.3067},{1050,10.3589},
{1060,10.4238},{1080,10.5519},{1100,10.6780},
{1184,11.1876},{1200,11.2810},{1300,11.8434},
{1400,12.3714},{1500,12.8695},{1600,13.3417},
{1665,13.6363});

ghalpha=Table[ghTFeAlpha[[i,1]]-1,ghTFeAlpha[[i,2]]),(i,25)];
ghgamma=Table[ghTFegamma[[i,1]]-1,ghTFegamma[[i,2]]),(i,22)];
ghalga=Table[ghalpha[[i+3,1]],ghalpha[[i+3,2]]-
ghgamma[[i,2]]),(i,22]};
\texttt{deltagFe[T_] := Block[{},
    For[tpos = 1, tpos <= 21, tpos++,
        If[{T > ghalga[[tpos, 1]] && 
          T < ghalga[[tpos + 1, 1]]}
          \&\& tpos == 21 \&\& T > ghalga[[tpos + 1, 1]]]
        , Return[c2j ((ghalga[[tpos + 1, 2]] - 
          ghalga[[tpos, 2]])/(ghalga[[tpos + 1, 1]] - 
          ghalga[[tpos, 1]])*(T - ghalga[[tpos, 1]]) + 
          ghalga[[tpos, 2]])]
        ];
    ];

If[T > ghalga[[22, 1]],
    Print["T > 1665 K is not covered in this calculation."]];

For[tpos = 1, tpos <= 3, tpos++,
    If[T > ghalpha[[tpos, 1]] && 
        T < ghalpha[[tpos + 1, 1]]
        , Return[c2j ((ghalpha[[tpos + 1, 2]] - 
          ghalpha[[tpos, 2]])/(ghalpha[[tpos + 1, 1]] - 
          ghalpha[[tpos, 1]])*(T - ghalpha[[tpos, 1]]) + 
          ghalpha[[tpos, 2]]) - ((ghgamma[[2, 2]] - 
          gghamma[[1, 1]])*(T - gghamma[[1, 1]]) + 
          gghamma[[1, 2]])]
        ];
    ];

If[T <= ghalpha[[1, 1]],
    Return[c2j ((ghalpha[[2, 2]] - ghalpha[[1, 2]])/
        (ghalpha[[2, 1]] - ghalpha[[1, 1]])* 
        (T - ghalpha[[1, 1]]) + ghalpha[[1, 2]] - 
        ((ghgamma[[2, 2]] - gghamma[[1, 2]])/
        (ghgamma[[2, 1]] - gghamma[[1, 1]])* 
        (T - gghamma[[1, 1]]) + gghamma[[1, 2]]))];
]

(* Standard free energy change of alloy elements. *)

deltagMn = 3477.0 - 0.5140*T - 2.742 10^-3 T^2 + 1.653 10^-6 T^3;

deltagSi = 9590 - 0.58 T;

deltagCo = 0;

deltagNi = (-3932.96 - 4.1087 10^-3 T^2 + 4.853 10^-6 T^3 - 
            1.41 10^-9 T^4);

deltagCr = 10460 + 0.6276 T;

deltagMo = 10460 + 0.63 T;
If[MN!=0, deltago[MN]=deltagoMn];
If[SI!=0, deltago[SI]=deltagoSi];
If[NI!=0, deltago[NI]=deltagoNi];
If[CR!=0, deltago[CR]=deltagoCr];
If[MO!=0, deltago[MO]=deltagoMo];
If[CC!=0, deltago[CC]=deltagoC];

(* Set logarithmic activity coefficients. *)
Clear[logamma];
logamma=Table[Null,{i,2},{j,m},{k,m},{l,m}];
logamma[[1,1,1,1]]=0;
logamma[[2,1,1,1]]=0;

(* Fe-Mn *)
If[MN!=0,
  logamma[[1,MN,1,MN]]=0.5636+493.1/T;
  logamma[[2,MN,1,MN]]=2.042-2270/T;
];

(* Fe-Si *)
If[SI!=0,
  logamma[[1,SI,1,SI]]=(-129704+7.95 T)/RT;
  logamma[[2,SI,1,SI]]=(-136817+7.95 T)/RT;
  If[MN!=0,
    logamma[[1,SI,MN,SI]]=(-92885-23.012 T)/RT;
    logamma[[2,SI,MN,SI]]=(-104184-23.012 T)/RT;
  ];
]

(* Fe-Ni *)
If[NI!=0,
  logamma[[1,NI,1,NI]]=(1339+1.3275 10^-3 * T^2-
    1.587 10^-6 * T^3)/RT;
  logamma[[2,NI,1,NI]]=(2092-3.8314 10^-3 T^2 +
    1.6338 10^-6 T^3)/RT;
  If[MN!=0,
    logamma[[1,NI,MN,NI]]=(45606+3.64 T)/RT;
    logamma[[2,NI,MN,NI]]=(51882+10.878 T)/RT;
  ];
]

(* Fe-Cr *)
If[CR!=0,
  logamma[[1,CR,1,CR]]=1.258+3019.5/T;
  logamma[[2,CR,1,CR]]=0.7549+890.7/T;


(* Fe-Mo *)
If[MO!=0,
   logamma[[1,MO,1,MO]]=-1.006+3875/T;
   logamma[[2,MO,1,MO]]=-1.006+2982/T;
];

If[CC!=0,
   logamma[[1,CC,1,CC]]=(-5.191+12431/T);
   logamma[[2,CC,1,CC]]=(-2.1+5300/T);
];

logamma;

(* Interaction parameters, lambda[[i,j,k]]:  
   i = 1:ferrite, 2:austenite  
   j,k = interaction between j and k atoms  
lambda=Table[,{i,2},{j,m+1},{k,m+1}];

(* C *)
If[CC!=0,
   lambda[[1,CC,CC]]=0;
   lambda[[2,CC,CC]]=1-Exp[-0.1-290/T];
];

(* Mn *)
If[MN!=0,
   lambda[[1,MN,MN]]=(-376.5-0.983 T)/RT;
   lambda[[2,MN,MN]]=(1572.5-1.416T)/RT;
   If[CC!=0,
      lambda[[2,MN,CC]]=0.155-650/T;
   ];
];

(* Si *)
If[SI!=0,
   lambda[[1,SI,SI]]=(-4707+15.12 T) /RT;
   lambda[[2,SI,SI]]=(-2545.25+10.08 T) /RT;
   If[CC!=0,
      lambda[[1,CC,SI]]=lambda[[1,SI,CC]]=3.7-3750/T;
      lambda[[2,CC,SI]]=lambda[[2,SI,CC]]=0.403+614/T;
   ];
   If[MN!=0,
      lambda[[1,SI,MN]]=lambda[[1,MN,SI]]=
      (2045-2.228T)/RT;
      lambda[[2,SI,MN]]=lambda[[2,MN,SI]]=
   ];

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(2146-1.999T)/RT;
];
];
(* Ni *)
If[NI!=0,
  lambda[[1,NI,NI]]=(-2369+4.095 10^-3*T^2 -
    1.252 10^-6*T^3)/RT;
  lambda[[2,NI,NI]]=(-3255+2.672 10^-3*T^2-
    1.139 10^-6*T^3)/RT;
If[MN!=0,
  lambda[[1,NI,MN]]=lambda[[1,MN,NI]]=
    (2510-6.538 10^-2 T - 8.297 10^-5*T^2 +
     9.919 10^-8 T^3)/RT;
  lambda[[1,NI,MN]]=lambda[[2,MN,NI]]=
    (2861-2.545 10^-1 T - 1.596 10^-4 T^2 -
     6.808 10^-8 T^3)/RT;
];
If[CC!=0,
  lambda[[2,CC,NI]]=lambda[[2,NI,CC]]=
    -0.183+633/T;
];
]

Do[Do[
  lambda[[p,j,i]]=lambda[[p,i,j]],[j,i+1,m+1]],[i,m+1],[{p,2}];
lambda;

(* Wagner's interaction parameters being used to help finding
lambda. *)
Clear[eps, p, i, j];
eps=Table[, (p,2), {i,m}, {j,m}];
For[p=1,p<=2,p++,
  For[i=1,i<=m,i++,
    For[j=1,j<=m,j++,
      If[loggamma[[p,j,i,j]]==Null,
        (epsi[[p,i,j]]=Null),
        epsi[[p,i,j]]=loggamma[[p,j,i,j]]-
          loggamma[[p,i,1,i]]- loggamma[[p,j,1,j]]
      ]
    ]
  ]
];

(* Mn *)
If[MN!=0,
  epsi[[1,MN,MN]]=1.8928-724.6/T;
epsi[[2, MN, MN]] = -4.0872 + 4510.8/T;
(* Mn-C *)
If[CC! = 0,
   epsi[[1, CC, MN]] = epsi[[1, MN, CC]] = 0.;
   epsi[[2, CC, MN]] = epsi[[2, MN, CC]] = 1.86 - 7800/T;
]

(* Ni *)
If[NI! = 0 && SI! = 0,
   epsi[[1, SI, NI]] = epsi[[2, SI, NI]] = epsi[[1, NI, SI]] =
   epsi[[2, NI, SI]] = 0;
]

(* Cr *)
If[CR! = 0,
   epsi[[1, CR, CR]] = 2.516 - 6039/T;
   epsi[[2, CR, CR]] = 1.5098 - 1781.3/T;
   If[CC! = 0,
      epsi[[1, CR, CC]] = 0.0;
      epsi[[2, CR, CC]] = 24.4 - 38400/T;
   ];
(* Mn-Cr *)
If[MN! = 0,
   epsi[[1, CR, MN]] = epsi[[1, MN, CR]] = epsi[[2, CR, MN]] =
   epsi[[2, MN, CR]] = 0
]

(* Si-Cr *)
If[SI! = 0,
   epsi[[1, CR, SI]] = epsi[[1, SI, CR]] = epsi[[2, CR, SI]] =
   epsi[[2, SI, CR]] = 0
]

(* Mo *)
If[MO! = 0,
   epsi[[1, MO, MO]] = 4.026 - 7460/T;
   epsi[[2, MO, MO]] = 4.026 - 5822/T;
(* Mo-C *)
If[CC! = 0,
   epsi[[2, CC, MO]] = epsi[[2, MO, CC]] = 3.855 - 17870/T;
   epsi[[1, CC, MO]] = epsi[[1, MO, CC]] = 58.0 - 91700/T;
]
(* Si-Mo *)
If[SI! = 0,
\[\varepsilon_i[[1, MO, SI]] = \varepsilon_i[[2, MO, SI]] = \varepsilon_i[[1, SI, MO]] = \varepsilon_i[[2, SI, MO]] = 0;\]

Clear[p, i, j];
Do[Do[\[\varepsilon_i[[p, j, i]] = \varepsilon_i[[p, i, j]], \{j, i + 1, m\}, \{i, m - 1\}, {p, 2}];

(* This paragraph is to evaluate unknown lambda from Wagner's interaction parameters : *)
\[\lambda_i(i, j) = 1/2Z * \varepsilon_i(i, j)\]
\[\lambda_i(i, C) = 1/2Z' * \varepsilon_i(C, i)\]
\[\lambda_i(C, C) = (r/2Z') * (\varepsilon_i(C, C) - (1 + 1/r))\]
)

Do[Do[Do[
    \varepsilon_i[[p, i, j]] = Null,\,, \lambda_i[[p, i, j]] = 1/2Z[[p]] * \varepsilon_i[[p, i, j]], \{j, i, t\}, {i, t}, {p, 2}];
    If[CC != 0, Do[
            If[\lambda_i[[p, i, CC]] = Null, If[\varepsilon_i[[p, CC, i]] = Null,\,, 
                                 \lambda_i[[p, i, CC]] = 1/2Zp[[p]] * \varepsilon_i[[p, CC, i]]]]
            , {i, m}, {p, 2}];
            Do[ If[\varepsilon_i[[p, CC, CC]] = Null,\,, \lambda_i[[p, CC, CC]] = r[[p]]/2Zp[[p]] ( \varepsilon_i[[p, CC, CC]] - 1 - 1/r[[p]])), {p, 2}]
            ];
            \lambda_i[[1, CC, CC]] = 0;
            Do[Do[
                    If[k > j, \lambda_i[[i, k, j]] = \lambda_i[[i, j, k]]];
                    If[\lambda_i[[i, j, k]] = Null, \lambda_i[[i, j, k]] = 0], {k, 1, m + 1}, {j, 1, m + 1}, {i, 2}];
            \lambda_i;\]

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(* Y and y setting for both phases. *)
Y=Table[ Join[
Table[X[i,k]/(1-Sum[X[i,11],{ll,t+1,m}]),{k,1,t}],
Table[1/r[i]] (X[i,1]/(1-Sum[X[i,11],{ll,t+1,m}])),
{i,2}];
Do[Y[[i,m+1]]=1;
Do[Y[[i,m+1]]=Y[[i,j]],{j,t+1,m}],{i,2}];
]

y=Table[ Join[
Table[X[i,k]/(1-Sum[X[i,kk],{kk,2,m}]),{k,1,t}],
Table[1/r[i]] (X[i,1]/(1-(1+1/r[i])) Sum[X[i,11] ,
{ll,t+1,m}]),{l,t+1,m+1}],{i,2}];
Do[y[[i,m+1]]=1,{i,2}];

Definitions of Polynomials and Functions to be Used

This paragraph is to write down the mass balance equations
through phi and phai.

phai=Table[ Join[{Null}, Table[
Sum[n[i,j] z[i] y[i,k] w[i,k] (1-
lambda[i,j,k]) / (1+ Sum[y[i,kp]] w[i,kp] (1-
lambda[i,j,kp])),{kp,2,t} ),{j,t}] -
Z[i] n[i,k],[k,2,t]],
Table[
Sum[n[i,j] z[i] y[i,1] w[i,1] (1-
lambda[i,j,1]) / (1+ Sum[y[i,lp]] w[i,lp] (1-
lambda[i,j,lp])),{lp,t+1,m} ),{j,t}] -
Zp[i] n[i,l],[l,t+1,m] ],{i,2}];

phai=Table[ Join[{Null}, Table[
Sum[n[i,j] zp[i] y[i,k] wp[i,k] (1-
lambda[i,j,k]) / (1+ Sum[y[i,kp]] wp[i,kp] (1-
lambda[i,j,kp])),{kp,2,t} ) ,{j,t+1,m+1} -
z[i] n[i,k],[k,2,t]],
Table[
Sum[n[i,j] zp[i] y[i,1] wp[i,1] (1-
lambda[i,j,1]) / (1+ Sum[y[i,lp]] wp[i,lp] (1-
lambda[i,j,lp])),{lp,t+1,m} ) ,{j,t+1,m+1} -
zp[i] n[i,l],[l,t+1,m] ],{i,2}];
(* Here is to generate two sets of mass balance equations. *)
eqns1=Join[Table[Simplify[phai[[1,j]]]==0,{j,2,m}],
    Table[Simplify[phai[[2,j]]]==0,{j,2,m}]];
vars1 = Join[Table[w[1,j],{j,2,m}],Table[wp[1,j],{j,2,m}]];

eqns2=Join[Table[Simplify[phai[[2,j]]]==0,{j,2,m}],
    Table[Simplify[phai[[2,j]]]==0,{j,2,m-1}],
    {phai[[2,m]]=0}];
vars2 =Join[Table[w[2,j],{j,2,m}],Table[wp[2,j],{j,2,m}]];

(* Lagrange's multipliers. *)
L=Table[Table[Log[w[i,k]]+delph[i,k,1],{k,1,m}],{i,2}];
Lp=Table[Table[Log[wp[i,k]],{k,1,m}],{i,2}];

(* Summed probability or normalization factor. *)
P=Table[Join[Table[
    Y[[i,1]]^Z[[i]] Y[[i,m+1]]^z[[i]]^* 
    Exp[- phi0[[i,j]]] * (1+ Sum[ y[[i,k]] w[i,k]*
      (1-lambda[[i,j,k]]))\{k,2,t}\)^Z[[i]]^* 
    (1+Sum[y[i,1]] w[i,1] (1-lambda[[i,j,1]]),
    {l,1,t+1,m})]^z[[i]], {j,t}],
    Table[
    Y[[i,1]]^Zp[[i]] Y[[i,m+1]]^zp[[i]]^* 
    Exp[- phi0[[i,j]]] * (1+ Sum[ y[[i,k]] wp[i,k]*
      (1-lambda[[i,j,k]]))\{k,2,t}\)^Zp[[i]]^* 
    (1+Sum[y[i,1]] wp[i,1] (1-lambda[[i,j,1]]),
    {l,1,t+1,m})]^zp[[i]], {j,t+1,m+1}],
    {1,2}]];

Unprotect[Log];
Log[x_ y_]=:Log[x]+Log[y];
Log[Exp[y_]]:=y;
Log[x^y_] := y Log[x];
Protect[Log];
(* Expressions for \( \ln a(i) \):
\[ vu[i] = vuo[i] + \ln a[i] \] for both phases by
known delta vuo[i] from ferrite to austenite.
*)
Clear[loga];
Do[phioo[i,1]=0;
vuo[i,1]=0,{i,2}]
loga=Table[Join[
{Log[Y[[i,1]]]+ r[[i]] Log[Y[[i,m+1]]] -
Log[P[[i,1]]] - r[[i]] Log[P[[i,m+1]]] -
vuo[i,1]/RT},
Table[ Log[Y[[i,k]]] + r[[i]] Log[Y[[i,m+1]]] +
Z[[i]] L[[i,k]] + z[[i]] Lp[[i,k]] -
Log[P[[i,k]]] - r[[i]] Log[P[[i,m+1]]] -
vuo[i,k]/RT, {k,2,t}},
Table[ Log[y[[i,1]]] + Zp[[i]] L[[i,1]] + Zp[[i]]*
Lp[[i,1]] - Log[P[[i,1]]] + Log[P[[i,m+1]]] -
vuo[i,1]/RT, {l,t+1,m}] },{i,2}];
(* NOTE : 
The following commands are to substitute 
loggamma[i,j,1,j] with delph(j,1),phico(j),
and vuo(j). They can only be executed once.
*)
rul=Table[Join[Table[Z[[i]]] delph[i,j,1]+phico[i,j] -
vuo[i,j]/RT,{j,t}],
Table[Zp[[i]] delph[i,j,1]+phico[i,j]-vuo[i,j]/
RT,{j,t+1,m} ] },{i,2}];
Do[Do[loga[[i,j]]=Together[loga[[i,j]]-rul[[i,j]]+
loggamma[[i,j,1,j]],{j,2,t}],{i,2}];
Do[Do[loga[[i,j]]=Together[loga[[i,j]]-rul[[i,j]]+
Log[r[[i]]] + loggamma[[i,j,1,j]],{j,t+1,m}],{i,2}];
(* Calculation status and the composition functions printout.*)
If[PARA==1,
Print["Paraequilibrium Calculation :"],
Print["Othoequilibrium Calculation :"];
]
Print[" ";
Do[Print[X[i,j]],[i,2],[j,m]];

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Orthoequilibrium Calculation:

\[
X[1, 2] \\
X[1, 3] \\
X[1, 4] \\
X[1, 5] \\
X[2, 2] \\
X[2, 3] \\
X[2, 4] \\
X[2, 5]
\]

**Iteration on solving w and w’**

The followings are the third and fourth parts of CAM calculation. It will solve the tie-line where allows equilibrium conditions for the interested alloy. The "Simplex" method is being employed for Gibbs free energy function minimization. This version of MultiAlloy.ma also allows to solve omega and omega’ (w and w’) by a numerical method, Jacobian method. There are 4(m-1) w and w’ to be solved. Its advantage is that omega and omega’ can be solved numerically from nonlinear equations for any systems; for example, 5-component systems in this calculation. Generally, w and w’ are mostly close to unity. It is accordingly set to be the initial value of this subroutine, and the convergence rate can thus be reduced as a result. Moreover, the influence of w and w’ may not be very big to the free energy calculation, so the problems of precision is relieved.

(* Number of parameter: 
  \( X(\alpha, i=2-m) \) and \( X(\gamma, 1) \) for Orthoequilibrium, so no=m. 
  And no=2+m-(t+1) for Paraequilibrium *)

Switch[PARA,1,no=2+m-t-1,0,no=m];
(* For Simplex method:
    alpha : reflection coefficient,
    beta  : contraction coefficient,
    gamma : expansion coefficient.
*)
alpha=1;
beta=0.5;
gamma=2;
(*
Initialvalue expressions:

**Basically, these two initial values do not influence**
the calculation results at all. However, it must contain
the information of the interested compositions.

Initialvalue =
{ { X(alpha, 2), X(alpha, 3),......,X(alpha, m) },
{ X(gamma, 2), X(gamma, 3),......,X(gamma, m) } }
for orthoequilibrium

Initialvalue =
{ {X(alpha, i), X(alpha, i+1),......, X(alpha, m-1) },
{ X(gamma, i), X(gamma, i+1),......, X(gamma, m-1) } }
for paraequilibrium

Rules to generate initial values for the same Xu:

Xu - The interested composition.
We are looking for a tie-line minimizing delta G
at this composition - "u" composition.
nu - Hypothetical molar fraction of alpha phase in u alloy.

initialvalue[[1]] = (1-nu) Xu;
initialvalue[[2]] = (1+nu) Xu;
( 0 < nu < 1 )

So the information of Xu is contained in the
initialvalue, where Xu= { X(i) } (i=2 to m)
*)

(* theta(i) setting for paraequilibrium only.*)
If[PARA==1,
paracndts={theta[FE]->1.000,theta[MN]->0.40362/
97.47433, theta[SI]->0.59397/97.47433,
theta[CR]->1.06610/97.47433};
]

(* Initialvalue settings. *)
Initialvalue={{0.00334097,0.00610303,0.0077028,0.000667701},
{0.0265228,0.000657012,0.106342,0.132448}};

nu=0.9700;

(* Double check the composition being calculated. *)
Xu=N[nu Initialvalue[[1]]+ (1-nu) Initialvalue[[2]], 20]
Equilibrium conditions and constraints setting

(* Temperature being calculated put in "constraint" *)
Switch[PARA, 1, (* paraequilibrium *)
    constraint = Join[paracnds, {T -> IT + 273}];
    (* orthoequilibrium *)
    , 0, constraint = {T -> IT + 273};
];
solve1 = Together[eqns1] /. constraint;
solve2 = Together[eqns2] /. constraint;

(* Mass balance equations containing omega and omega' to be solved. *)
weqns = Join[solve1, solve2];

la1 = Table[loga[[1, i]], {i, 1, m}] /. constraint;
la2 = Table[loga[[2, i]], {i, 1, m}] /. constraint;

(* standard free energy change at this temperature. *)
deltag = Join[{deltagFe[T] /. constraint}, Table[deltago[i, {i, 2, m}] /. constraint]//N

{952.52, 2038.33, 9083.66, 11007.9, 0.}

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la=la1-la2;
(* "potentialFe" is only for paraequilibrium calculation. If vu(i) stands for the chemical potential change from ferrite to austenite. "potentialFe" is equal to vu(1) + theta(2) vu(2) + .... theta(i) vu(i) (i=2 - t, i.e. all substitutional elements) and has to be zero for paraequilibrium. *)
Switch[PARA,1,
(*paraequilibrium*)
potentialFe=Together[RT la[[1]]-
deltagFe[T/.constraint]]/.constraint;
Do[ potentialFe += theta[i] (Together[RT la[[i]]-
deltago[i]],{i,2,t})/.constraint;
eqlcndt=Join[ {potentialFe},
 Table[Together[RT la[[i]]-deltago[i]]
 /.constraint, {i,t+1,m}] ],

(*orthoequilibrium*)
0, eqlcndt=Join[ {Together[RT la[[1]]-
deltagFe[T/.constraint]]/.constraint},
 Table[Together[RT la[[i]]-deltago[i]],{i,2,m}]/. constraint];
];

(* equilibrium conditions and variables settings. *)
ortho=Table[eqlcndt[[i]]==0,{i,no}];
orthoeqns=Join[ortho,weqns];
Unprotect[In,Out,All];
ClearAll[In,Out,All];
Protect[In,Out,All];
Switch[PARA,1,  
(* paraequilibrium *)
  varbl=Join[{{X[1,1]},
  Table[X[1,j],{j,t+1,m-1}],
  {X[2,1]},Table[X[2,j],{j,t+1,m-1}]}],
  (* orthoequilibrium *)
  0, varbl=Join[Table[X[1,j],
  {j,2,m}],Table[X[2,j],{j,2,m}]];  
];

(* variable list *)
orthovarbl=Join[varbl,vars1,vars2]
{X[1, 2], X[1, 3], X[1, 4], X[1, 5], X[2, 2], X[2, 3],
  X[2, 4], X[2, 5], w[1, 2], w[1, 3], w[1, 4], w[1, 5],
  wp[1, 2], wp[1, 3], wp[1, 4], wp[1, 5], w[2, 2],
  w[2, 3], w[2, 4], w[2, 5], wp[2, 2], wp[2, 3],
  wp[2, 4], wp[2, 5]}
F=Table[orthoeqns[i,1]],{i,no4(m-1)};  
varbln=Table[orthovarbl[[i]]->0.,{i,no4 (m-1)}];
(* Jacobian Method solving w and w' as functions of X(i).
There are totally, 4(m-1) unknown and 4(m-1) equations. *)
vars=Join[vars1,vars2];
eqns=Join[Table[{eqns1[[i,1]]/.constraint},{i,2(m-1)}],
Table[{eqns2[[i,1]]/.constraint},{i,2(m-1)}]];

(* Jacobian matrix *)
J=Table[D[eqns[[i,1]]/.constraint,vars[[j]]],
{i,4(m-1)},{j,4(m-1)}];
tempx=Table[{1.},{4(m-1)}];
wsolve[varbln_]:=Block[{n,xn,error,varln,ij,f,d,
flag,return},
n=4(m-1);
xn=tempx;
error=1;
While(error>1.0 10^-4,
flag=0;
varln=Join[varbln,Table[vars[[i]]->xn[[i,1]],{i,n}]];

(* Inverse of J matrix *)
ij=Inverse[J/.varln//N];

(* Value of equations to solved in this guess*)
f=(eqns/.varln//N);

(* Tentative deviation of this guess from the solution.*)
d=ij.f//N;
error=0;
Do[
  xn[[i,1]]=d[[i,1]]//N;
  (* If[xn[[i,1]]<=0. || xn[[i,1]]>=3.0,
    flag=1]; *)
  error += d[[i,1]]^2;
  ,{i,n}];
If[flag==1,return=0,
  return=Join[varbln,
    Table[vars[[i]]->xn[[i,1]],{i,n}]]];
tempx=xn;
Return[return];
]
Simplex Method for Minimization of Free Energy

(*
Free energy surface value setup:

Minimizing \[ N(\alpha) \ln(\alpha) + N(\gamma) \ln(\gamma) \]
= \[ N(\alpha) \text{Sum} [x(i,\alpha)] + N(\gamma) \text{Sum} [x(i,\gamma)] \]

\[ = \text{Sum} [N(\alpha) \alpha(i) + N(\gamma) \gamma(i)] \]
\[ + \text{Sum} [\ln(\alpha(i),\gamma(i))] \]
\[ + \text{Sum} [\ln(\alpha(i),\gamma(i))] \]

op : Original \( X \) and \( N(\alpha) \).
p : Transformed \( X \) and \( N \), i.e. \( p(i) = \exp(-p(i)^2) \)

So there is no limitation on \( p(i) \) even that
\( 0 < p < 1. \)
*)

\[ yvalue[p_] := \text{Block} \{ \{ i, j, op, flag, nalpha, return \}, \]
\[ \text{varbln}=\text{Take} [\text{varbln}, 2 \ no-2]; \]
\[ \text{op}=\text{Table} [\exp [-\{ p[i] \}], \{ i, \text{no} \}]; \]
\[ \text{flag}=0; \]
\[ \text{nalpha}=(\text{Xu}[1]-\text{op}[\text{no}])/(\text{op}[1]-\text{op}[\text{no}])); \]
\[ \text{If}[\text{nalpha}>1.0 \ || \ \text{nalpha}<0.0, \ \text{flag}=1]; \]
\[ \text{Do}[\text{varbln}[i,2]=\text{op}[1]]; \]
\[ \text{If}[\text{varbln}[[i,2]]>1 \ || \ \text{varbln}[[i,2]]<0., \ \text{flag}=1]; \]
\[ ,\{ i, \text{no} \}]; \]

\[ \text{Do}[\text{varbln}[\text{no+j-1,2}]=\text{Xu}[j]-\text{nalpha} \ \text{op}[[j]]/ \]
\[ (1-\text{nalpha}); \]
\[ \text{If}[\text{varbln}[[\text{no+j-1,2}]]>1.0 \ || \ \text{varbln}[[\text{no+j-1,2}]]<0., \]
\[ \ \text{flag}=1]; \]
\[ ,\{ j, 2, \text{no}-1 \}]; \]

\[ \text{If}[\text{flag}=1, \ \text{Return}[9 10^99]]; \]
\[ \text{temp}=\text{wsolve} [\text{varbln}]; \]
\[ \text{varbln}=\text{temp}; \]
\[ \text{If}[\text{varbln}=0, \text{flag}=1; \text{Print} [\text{varbln}, \text{flag}] ]; \]
\[ \text{varbln}=\text{Join} [\text{varbln}, \text{constraint}]; \]
\[ \text{return}=\text{N} \left[ (1-\text{nalpha}) \ \text{Sum} [x[2, i] \]
\[ \text{deltag}[[i]], \{ i, m \} ] + \]
\[ \text{RT} \ \text{Sum} [\text{nalpha} \ X[1, i] \ \text{laa}[[i]] ] + \]

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\[(1-\text{alpha}) \times [2,i] \text{ la2}[[i],\{i,m\}] / \text{varbln},20]\];

\[\text{If[Im[return]!\neq 0,flag=1];}
\text{If[flag==1,return=9 \times 10^{99}];}
\]

\text{Return[return];}
\]
\]

\[
\text{(*}
\text{For orthoequilibrium, varbl0 is a list of m elements}
\text{containing those independent values in the Initialvalue:}
\text{first m-1 elements from Initialvalue[[1]],}
\text{plus the first element of Initialvalue[[2]]}
\text{varbl0 contains 2 elements in paraequilibrium calculation. *)}
\]
\text{varbl0=Join[Initialvalue[[1]],{Initialvalue[[2,1]]}]}

\{0.00334097, 0.00610303, 0.0077028, 0.000667701,

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(* Maximum and Minimum of the initial simplex *)

y_h=Max[yy];
h=Position[yy,y_h][[1,1]];
y_l=Min[yy];
l=Position[yy,y_l][[1,1]];
Print["h= ",h,"; max = ",y_h];
Print["l= ",l,"; min = ",y_l];

h= 4, max = -1361.41553188396
l= 2, min = -1361.424947093909

(* Centroid - pbar and ybar *)

sum=0;
it=0;
Do[If[i!=h, sum+=p[[i]]],{i,no+1}];
pbar=sum/no;
ybar=yvalue[pbar];
de=Sum[(yy[[i]]-ybar)^2,{i,no+1}]/no

de=0.00502368

Simplex Iteration

While[!(deviation<= 1.0 10^-7 && y_l<10^99),

(* Reflection *)

p_star = -alpha p[[h]] + (1+alpha) pbar;
y_star=yvalue[p_star];

flag=0;
If[y_star>=y_l && y_star<y_h,
 (* Then *)
  p[[h]]=p_star;
yy[[h]]=y_star;
y_h=Max[yy];
hnew=Position[yy,y_h][[1,1]];
If[hnew==h,flag=1,h=hnew;y_h=yy[[h]]];
 (* If the maximum Ph is replaced by the reflection P*, then do contraction.
Otherwise, change the maximum location *)
,
(* Else *)
If[y_star<y_l,
  p2_star=gamma p_star + (1-gamma) pbar;
  (* Expansion *)
  y2_star=yvalue[p2_star];
]
If[y2star<=y1,
   p[[h]]=p2star;yy[[h]]=y2star;
   l=h; yl=yy[[l]];,
   (* Failed Expansion *)
   p[[h]]=pstar;yy[[h]]=ystar;
];
yh=Max[yy];h=Position[yy,yh][[1,1]],

If[ystar>=yh,flag=1;
   (* If F* is worse than Ph, do contraction *)
];
]

If[flag==1, (* Contraction *)
   p2star = beta p[[h]] + (1-beta) pbar;
y2star=yvalue[p2star];
   If[y2star>yh,
      Do[p[[i]]=(p[[i]]+p[[l]])/2;
         yy[[i]]=yvalue[p[[i]]];
         ,{i,no+1}]);
   (* If contraction failed. *)
   p[[h]]=p2star; yy[[h]]=y2star;
];
yh=Max[yy];
h=Position[yy,yh][[1,1]];
yl=Min[yy];
l=Position[yy,yl][[1,1]];

sum=0;
Do[If[i!=h, sum+=p[[i]]],{i,no+1}];
pbar=sum/no;
ybar=yvalue[pbar];
deprivation=Sqrt[Sum[(yy[[i]]-ybar)^2,{i,no+1}]/no];
iter++;
(*If[Mod[iter,10]==0,
      *)

(* Iteration results printout *)
Print["Iteration = ",iter];
Print["Deviation = ",deviation];
Print["Solution = ",p];
Print["Simplex at Minimum of Function = ",yy];
Iteration = 207

Deviation = 9.33909 10
Solution = {{2.38967, 2.25796, 2.20744, 2.72474,
              1.89956}, {2.38967, 2.25796, 2.20743, 2.72473,
              1.89957}, {2.38967, 2.25796, 2.20744, 2.72474,
              1.89956}, {2.38967, 2.25796, 2.20744, 2.72473,
              1.89956}, {2.38967, 2.25796, 2.20743, 2.72474,
              1.89957}, {2.38967, 2.25796, 2.20743, 2.72474,
              1.89956}, {2.38967, 2.25796, 2.20743, 2.72474,
              1.89956}}
Simplex at Minimum of Function =

{-1361.457110582867, -1361.457110582086,
  -1361.457110582011, -1361.457110582734,
  -1361.457110581954, -1361.457110582139}

pl=p[[1]];
varbln=Take[varbln,2 no-2];
op=Table[Exp[-(pl[[i]]^2)],{i, no}];
Do[varbln[[i,2]]=op[[i]],{i, no}];
If[PARA==0,
   nalpha=(Xu[[1]]-op[[no]])/(op[[1]]-op[[no]]);
   Do[varbln[[no+j-1,2]]=(Xu[[j]]-nalpha op[[j]])/
      (1-nalpha);,{j,2, no-1}];
];
varbln=wsolve[varbln];
(* Putting variables together *)
varbln=Join[varbln,constraint]
\{ X[1, 2] \rightarrow 0.00331093, X[1, 3] \rightarrow 0.00610666, \\
X[1, 4] \rightarrow 0.00765214, X[1, 5] \rightarrow 0.000596642, \\
X[2, 2] \rightarrow 0.0270968, X[2, 3] \rightarrow 0.000630989, \\
X[2, 4] \rightarrow 0.106331, X[2, 5] \rightarrow 0.132541, \\
w[1, 2] \rightarrow 0.999521, w[1, 3] \rightarrow 1.0073, \\
w[1, 4] \rightarrow 0.997903, w[1, 5] \rightarrow 0.996375, \\
wp[1, 2] \rightarrow 1., wp[1, 3] \rightarrow 0.999882, wp[1, 4] \rightarrow 1., \\
wp[1, 5] \rightarrow 1., w[2, 2] \rightarrow 1.00145, w[2, 3] \rightarrow 1.00237, \\
w[2, 4] \rightarrow 0.997304, w[2, 5] \rightarrow 0.843774, \\
wp[2, 2] \rightarrow 0.92776, wp[2, 3] \rightarrow 1.17112, \\
wp[2, 4] \rightarrow 0.822659, wp[2, 5] \rightarrow 1.05966, T \rightarrow 873\}
(* F/.varbln gives a reference how good the calculation is close to the solutions. It plugs the results from minimization of system free energy into the equal-chemical potential conditions. Therefore, for the correct answers, they should be as small as possible (or close to zero). It also depends on the error allowed in the iteration which is set to be $10^{-4} - 10^{-6}$. Error below 100 may be fine for the first $m$ equations, since they stands for the chemical potentials of $m$ components.

It has been found that if the bulk composition is out of the phase boundaries, the error is going to be very big which can not be accepted. Hence, it has then to be sure that the bulk composition is lying between the phase boundaries.

The other questionable result is when the composition of one of the phase boundaries is sitting on the bulk composition. It indicates that there is no space for phase boundaries to converge to.

It is also possible that gamma phase actually has higher composition than the alpha phase, e.g. in the case of Si alloy. The difficulties of solving this kind of behavior can be expected. The best way to handle this problem may be to check with binary system phase diagrams first and to decide what should be put in the Initialvalue.

*)

F/.varbln//N
{(−0.00195198), (−0.025939), (−0.0376585), (−0.0173083),
−19
(−0.0145575), (8.67362 10
−18
}, {0.}, {1.73472 10
−20
−19
−18
−18
(−5.42101 10
−17
−19
(1.73472 10
−14
−15
{0.}, {−2.14273 10
−14
−14
(1.60896 10
−14
−14
(−2.79776 10
−14
(−1.07692 10
)}

(* Maximum error from the equal-chemical potential method*)
mxf=Max[Abs[F/.varbln//N]]
0.0376585

Solution Print Out
(*
  M - atomic Weight
  NM - element name
  Phase - phase name
  totalwt - total weight from atomic fraction * M
  at - atomic fraction
  wt - weight fraction
*)
  Array[M,no];
  Array[NM,no];
  Array[Phase,2];
  Array[totalwt,2];
  Array[at,2,m];
  Array[wt,2,m];
  totalwt[1]=0.0000000000;
  totalwt[2]=0.0000000000;
  at[1,1]=1.0000000000;
  at[2,1]=1.0000000000;
  Phase[1]=Alpha;
  para[i]=Para;
  para[2]=Ortho;
  M[MN]=54.94;  NM[MN]=Mn;
  M[SI]=28.00;  NM[SI]=Si;
  M[NI]=58.70;  NM[NI]=Ni;
  M[CR]=52.00;  NM[CR]=Cr;
  M[MO]=95.94;  NM[MO]=Mo;
  M[CC]=12.00;  NM[CC]=C;
Grabsing data from varbln list. i.e. the composition of two phases.

ph - phase
cm - component no.
x - composition

*)
Switch[PARA,1,
     (* paraequilibrium *)
     Do[
        ph=i;
        cm=j;
        x=X[i,j]/.varbln;
        totalwt[ph]= totalwt[ph] + x M[cm];
        wt[ph,cm]=x M[cm];
        at[ph,cm]=x;
        {i,2},{j,m}
    ],

    (* orthoequilibrium *)
    0,
    For[pos=1,pos<=2 m-2,pos++,
        ph=varbln[[pos,1,1]];
        cm=varbln[[pos,1,2]];
        x=varbln[[pos,2]];
        totalwt[ph]= totalwt[ph] + x M[cm];
        wt[ph,cm]=x M[cm];
        at[ph,1]=at[ph,1]-x;
        at[ph,cm]=x;
    ]
    Do[totalwt[i]= totalwt[i]+at[i,1] M[1];
        wt[i,1]=at[i,1] M[1],{i,2}]
    ];

Array[tieX,m];
Array[tiewX,m];
Switch[PARA,1,
     (* paraequilibrium *)
     tieX[m]=1.00;
     tieX[1]=Xu[[1]];
     tieX[m]-=tieX[1];
     Do[tieX[i]=theta[i] Xu[[1]] / constraint;
        tieX[m]-=tieX[i],{i,2,t}];
     Do[tieX[i]=Xu[[i]]];
tieX[m] = tieX[i], {i, t+1, m-1};;

(* orthoequilibrium *)
0,
tieX[1] = 1.00;
Do[tieX[i] = Xu[[i-1]],
   tieX[1] = tieX[i], {i, 2, m}];

tieTotwt = 0;
Do[tieTotwt += M[i] tieX[i], {i, m}];
Do[tieX[i] = tieX[i] M[i]/tieTotwt, {i, m}];
Print[StringForm["'-equilibrium tie line calculation for ":,
   para[2-PARA]]];
Do[
   Print[StringForm["'' at% - '' wt% - ''",
      NM[i], 100 tieX[i], 100 tiewX[i]] ],
   {i, m}];

Print[" ];
Print[StringForm["Temperature (K) = '' ('' C)",
   T/.constraint, T-273/.constraint]];" ];
Print[StringForm["Simplex size = '', deviation];
Print[StringForm["Max. error in chemical driving force = '',
   maxf]];"
Print[StringForm["System Free Energy = '' Joule/mole", yl]]];

Do[
   Print["
   Print[StringForm["' Phase - ", Phase[i]]];
   For[pos = 1, pos <= m, pos++,
     wt[i, pos] = wt[i, pos]/totalwt[i];
     string = "' at% - '' wt% - ''";
     Print[StringForm[string, NM[pos],
        100 at[i, pos],
        100 wt[i, pos]]];
   ], {i, 2}]
Print[StringForm["alpha phase fraction = '',
   N[(tieX[1]-at[2,1])/(at[1,1]-at[2,1]), 20]]];
Ortho-equilibrium tie line calculation for:

Fe at% - 97.4743   wt% - 98.2
Mn at% - 0.40362   wt% - 0.399999
Si at% - 0.59397    wt% - 0.3
Cr at% - 1.0661    wt% - 0.999999
C at% - 0.461981   wt% - 0.100001

Temperature (K) = 873 (600 °C)

Simplex size = 9.33909 10
Max. error in chemical driving force = 0.0376585
System Free Energy = -1361.457110582867 Joule/mole

Alpha Phase -
Fe at% - 98.2334   wt% - 98.6373
Mn at% - 0.331093  wt% - 0.327038
Si at% - 0.610666   wt% - 0.307412
Cr at% - 0.765214   wt% - 0.715394
C at% - 0.0596642   wt% - 0.0128722

Gamma Phase -
Fe at% - 73.3401   wt% - 82.604
Mn at% - 2.70968   wt% - 3.00222
Si at% - 0.0630989   wt% - 0.0356301
Cr at% - 10.6331   wt% - 11.1506
C at% - 13.2541   wt% - 3.2075

alpha phase fraction = 0.969508489292455
VITA

Mr. Jhewn-Kuang Chen was born as the eldest son of a middle-class family in August, 1967 in Taipei, Taiwan, Republic of China. After graduating from Mining and Metallurgical Engineering Department, National Taipei Institute of Technology in 1987, he attended and satisfactorily passed the National Higher Civil Servant Examination held by the Government in the same year. As a government servant, he was working as a designing engineer in the Foundry of Taiwan Machinery Manufacturing Company from 1989 to 1990 after his two year service in R.O.C. Army where he served as a computer programmer. He came to Virginia Polytechnic Institute and State University in 1990 and started his work toward the master of science in Materials Science and Engineering Department on the austenite transformation in high strength low alloy steels. He will be pursuing his Ph.D degree concentrating on the interfacial structure of solid-solid phase transformation in the same institute under direction of Dr. W. T. Reynolds Jr.