Modeling and Input Feature Analysis of Alloy Carbides and Austenite in Ultrahigh-Performance Steels

D.M. Field¹, H.A. Murdoch¹, D.J. Magagnosc¹, K.R. Limmer¹, M.C. Rupinen²

¹DEVCOM Army Research Laboratory

²Oak Ridge Associated Universities
6300 Rodman Rd. APG, MD 21005
Phone: 410-306-0742
Email: daniel.m.field6.civ@army.mil

ABSTRACT

Commercial Ni-Co steels with ultra-high strength and toughness were examined using a combination of modeling and experimentation to assess the capabilities of modeling to predict key microstructural features. Parameter studies were used to determine optimum model feature parameters to match carbide and reverted austenite evolution from literature data in a prototypical alloy. It was found that several aspects of both precipitation and diffusion CALPHAD simulations needed to be tuned, particularly the mobility. This work highlights the vital role of experimental results in informing modeling techniques for alloy design.

INTRODUCTION

High Ni-Co alloys (such as AF1410 and AerMet 100) combine high strength and high fracture toughness, Figure 1. The alloying strategy to enhance toughness without sacrificing strength is twofold, first is the promotion of fine laths of stable austenite during tempering for toughness and secondly controlled precipitation of a secondary hardening phase, here M₂C. To achieve this combination, Ni-Co steels require complex heat treatments, which includes either cryogenic cooling or thermal cycling, to trigger the transformation of any metastable retained austenite and Stage III (>450 °C) tempering to both promote the formation of fine M₂C for secondary hardening and the precipitation of fine, highly stable, films of reverted austenite for toughness [1-7].

![Figure 1 Ashby plot highlighting advantageous combination of strength and toughness in high Ni-Co steels.](image-url)
The austenite type and stability are microstructural concerns for strength and toughness. Metastable austenite can provide high work hardening rates (e.g., medium-Mn steels) for improved Charpy V-notch toughness. However, at sub-ambient (< 25 °C) temperatures, the austenite must be sufficiently enriched in alloying elements to prevent the thermal transformation to fresh brittle martensite [8]. This issue is exacerbated in high Ni-Co steels with low martensite start (M_s) temperatures as they typically suffer from incomplete transformation of the austenite upon cooling due to the martensite finish (M_f) being below room temperature. Austenite which remains after quenching due to the incomplete martensite transformation is referred to as retained austenite (\(\gamma_{\text{retain}}\)) and its composition is similar to that of the martensite, making it unstable. Austenite which grows or forms during subsequent tempering heat treatments is referred to as reverted austenite (\(\gamma_{\text{revert}}\)) and is generally enriched in Ni, making it sufficiently stable to provide a benefit to toughness [1-3].

The effects of Co, Mo, and Cr on the precipitation, growth, and coherency of the M_2C phase have been previously investigated [1, 5-7, 9-14]. Cobalt increases the dislocation density in martensite leading to increased diffusion rates of C via pipe diffusion. The increased diffusivity helps promote the formation of the M_2C and decreases the heat treatment time for the peak aged condition. The mixed metal (Cr, Mo)_2C is preferable due to low lattice misfit, enabling a coherent interface [12, 13]; further, the enhanced diffusion of Cr compared to Mo in the martensite matrix improves the formation kinetics. The ratio is also important for the driving force for precipitation [5, 11].

In designing alloys within the Ni-Co family, previous efforts have focused on metrics leveraging time-independent thermodynamic criteria such as the relative driving force for M_2C, the equilibrium phases at austenization temperatures, and the M_s predicted from driving force models [11, 15, 16]. These metrics however do not account for how the microstructure evolves during the various stages of heat treatments and may fail to capture the kinetics of the reactions. The approach in this work attempts to utilize a kinetics-based modeling approach, calibrated to existing experimental data in the literature, to capture the essential design features of Ni-Co steels during processing. The following criteria are considered:

1. Kinetics of martensite formation: to avoid retained austenite, the M_f should be considered in addition to the previous criteria of a high M_s
2. Formation of reverted austenite on lath boundaries during tempering (of a composition that is stable under further heat treatment / in service)
3. Formation of (coherent) secondary hardening carbides, e.g. M_2C
4. Competitive formation of cementite (or other deleterious carbides) that would negatively impact toughness.

**METHODS**

Martensite formation was examined using a Linseis L78 RITA quenching dilatometer. Dilatometry specimens with initial dimensions of 3 × 2 × 10 mm were heated to 885 °C at a rate of 10 °C/s, held at temperature for 5 min, and then quenched at 15 °C/s to room temperature. An additional step, where a liquid nitrogen gas flow attachment was equipped, was used to further cool the samples to -80 °C using a constant 40% gas flow. Phase fractions were measured with X-ray diffraction using a Bruker D2 Phaser diffractometer with a cobalt radiation source operating at a voltage of 30 kV and current of 10 mA. Scans were carried out with a 20 of 45 to 105°, a 0.02° step size, and integrating for 1 s per step. Phase quantification was performed using Rietveld refinement through the TOPAS™ software.

The diffusion (DICTRA) and precipitation (PRISMA) modules of Thermo-Calc [17] are used to model microstructural evolution in high Ni-Co alloys, benchmarking against literature experimental data from AF1410 and AerMet 100. The modeled compositions for all alloys are matched to the cited experimental data for comparison to model predictions. The Thermo-Calc databases TCFE10 and MOBFE5 are used for all calculations. The specific parameters used are discussed in the following sections but in summary, for DICTRA calculations, the parameters needed are the dimension of the martensite lath, dimension of the retained austenite, the initial composition of the martensite, and the initial composition of the retained austenite. For PRISMA calculations, the general parameters needed are the nucleation type and site density, interfacial energy, elastic misfit behavior, and growth model.

**RESULTS AND DISCUSSION**

A comparison between current models for three key microstructural features: retained austenite, reverted austenite, and secondary hardening carbides and experimental data, is presented with discussion of necessary modifications made to the models.

3.1 Retained Austenite

A consequence of the high Ni-Co content in these alloys is a low (≤250 °C) martensite start (M_s) temperature and a sub-ambient (<25 °C) martensite finish (M_f); subsequently at room temperature the martensitic reaction is incomplete resulting in significant
retained austenite. This is usually addressed with a cryogenic treatment after quenching [18, 19] to complete the martensite transformation. Dilatometry of AerMet 100, Figure 2, shows about 2.7 vol.% austenite at 25°C; further cooling to 0°C appeared to fully complete the martensite transformation, indicating that a cryogenic treatment would alleviate the issue of retained austenite, as expected.

In designing a modified alloy to understand thermal treatments, both the $M_s$ as well as the kinetics of the martensite reaction must be predicted with confidence to assess the retained austenite content. Common models for martensite kinetics are Lee-Van Tyne [20] and Koistinen-Marburger (KM) [21] which take the general form:

$$f = 1 - \exp[-\alpha(M_s - T)]$$

where the fraction of martensite, $f$, is predicted as a function of the temperature, $T$, the martensite start, $M_s$, and a constant, $\alpha$. The experimentally measured formation of martensite is plotted in Figure 2 (black dots) using a lever rule on experimental dilatometry data for AerMet 100 for the formation. It is compared to two KM fits, as using the Lee-Van Tyne model led to a very poor fit likely due to the coefficients being determined from low alloy steels. The use of a KM-type model also requires knowledge of the $M_s$; in this case it was experimentally observed at 300 °C, but it can be predicted. The Ghosh-Olsen $M_s$ model [22], for example, predicts 322°C for AerMet 100. However, it is often more relevant to use an offset to the $M_s$ that reflects the undercooling at which significant fraction of martensite begin to form i.e., 250 °C. This is labeled the modified “Mod KM fit”. While the modified KM model fits the kinetics well the necessity for fitting the offset to the experimental data is somewhat contrary to the goal of predicting the $M_s$ and kinetics for these Ni-Co alloys.

The kinetics of martensite formation near the martensite finish temperature is of greatest interest for these Ni-Co alloys due to the potentially detrimental effects of retained austenite on properties. Both the KM and Mod-KM models predict that the retained austenite does not fully decompose until below room temperature; however, neither adequately captures the entirety of the kinetics of the reaction. While the KM model appears to capture the conclusion of the reaction, the Mod-KM does a better job of predicting the initial transformation kinetics. At the temperature of a typical cryogenic treatment (-73°C) they predict between 1.7-2.9 vol.% retained austenite. This is consistent with the 2.5 vol.% measured via XRD in AerMet 100 after quenching and cryogenic treatment. However, XRD quantification below 5 vol.% is highly subjective to the fitting procedure. Furthermore, even the calculations of martensite fraction from dilatometry are limited. In the AerMet 100 alloy, discerning a true $M_f$ at ambient temperatures is not possible and a cryo-quench apparatus was necessary to cool the sample to sub-ambient temperatures to calculate the martensite fraction formed. The difficulties in fitting the current empirical models and in collecting the experimental data both highlight the need for a more predictive and accurate model for martensite kinetics especially in higher alloyed steels.

![Figure 2 Martensite transformation kinetics in AerMet 100; experimentally measured (black points) compared to the KM and modified KM models.](image.png)
3.2 Reverted Austenite

After the quench, the potential formation of reverted austenite is modeled with the diffusion based DICTRA module. The simulation cell is a half-width dimension of a martensite lath with the reverted austenite phase allowed to form at the lath boundaries. The composition of the martensite phase is assumed to be equal to the bulk composition in this work which assumes complete solutionization of secondary phases during austenitizing (partial austenitization can lead to compositional variation between the bulk alloy and the martensite formed due to the presence of high temperature carbides). Diffusion simulations usually assume there is some retained austenite as a seed for the reverted austenite, and that the retained austenite is the same composition as the martensite [3, 23, 24]. The reverted austenite that is formed is a distinct composition; chemical measurements (Figure 3) consistently show enrichment of Ni and depletion of Co in the reverted austenite relative to the global composition across various temper temperatures and different measurement methods in both AF1410 and AerMet 100 [1-3, 13]. Carbon content is not indicated on the plot due to difficulties in quantitative spectroscopy of carbon and because DICTRA simulations of austenite do not generally consider carbon. This is mainly due to the difficulty in modeling diffusion with both substitutional and interstitial elements simultaneously because of the orders of magnitude difference in the time/length scales for the different type of alloying elements. Further, it is the substitutional elements that are the rate limiting step for the formation and dissolution of austenite. Simulations of AerMet 100 at 482°C show that the reverted austenite composition aligns better with experimental observations when retained austenite is initially present even in very small quantities, Figure 3. When no retained austenite is present in the simulation cell, the reverted austenite formed has a consistent composition of Ni (dashed lines) across the reverted austenite film that is higher than observed. When a small amount of retained austenite is considered in the initial cell (here shown for 1 vol.%, but true for smaller fractions as well), the compositions are shown in solid lines. The average Ni composition across the $\gamma_{\text{revert}}$ film is 29 wt.% compared to the 31 wt.% measured by atom probe (compared to 38 wt.% for the no retained austenite case). Further, the shape of the chemical distribution is in line with observations, as opposed to the sharp, constant composition seen with the dashed lines (no retained austenite case).

![Figure 3](image-url)  
Figure 3 (left) Measured compositions of reverted austenite in AerMet 100 and AF1410. Gruber Atom Probe Tomography (@50 hours) [3]; Ayer TEM EDS (@5hr) [1]; Gruber TEM EDS (@5hrs) [2]; AF1410 APT (@8hrs)[13]. Dotted lines are global AerMet100 composition for comparison. (right) Predicted compositions from DICTRA simulations assuming no retained austenite exists at onset of temper (dashed line) compared to minimal (1 vol.%) retained austenite at onset of temper. Predicted composition is in agreement with measured compositions when retained austenite seed exists for temper.

The diffusion information for DICTRA simulations are derived from a mobility database which only considers bulk diffusion through a bcc lattice. However, diffusion through martensite will be accelerated relative to bulk diffusion due to the additional diffusion pathways (e.g., pipe diffusion) stemming from the highly dislocated structure of martensite. The dislocation density of martensite is well documented as being on the order of $10^{15}$ m$^{-2}$ [25, 26]. As such, to better model the physically observed phenomena the mobility should be enhanced in the simulations. Balluffi proposed [27] that the activation energy for pipe diffusion can range from 0.4 to 0.7 of the bulk value within a dislocation core. In a maraging steel with the same alloying elements as the current UHSS of interest (Cr, Ni, Co, Mo) [28], a mobility prefactor of 3,000x was applied to all substitutional elements in order to match experimentally observed increases in austenite fraction and the approximate width of the austenite laths. Simulations in a stainless (Cr, Ni, Mo, Mn) [29] and medium-Mn steels [23, 30, 31] similarly required mobility enhancements to match experimental results. For alloys incorporating cementite even higher mobility enhancements may be required [30]. However, the cementite phase lacks significant experimentally derived diffusion data and there has been little work to calibrate the database. Regardless, this shows that for improved modeling fidelity the mobility must be enhanced, regardless of the steel alloy system.
In order to assess the necessary mobility prefactor for the high Ni-Co steels studied, a parameter study using the work of Yoo et al. [7] on AerMet 100, who measured the fraction of reverted austenite after heat treatments of up to 200 hours at 3 different temperatures, was performed. A planar geometry cell was used in DICTRA with a closed boundary condition. Martensite laths were estimated at 1 μm wide from the micrographs in [7]. Thus, the size of the DICTRA cell was set as 500 nm (half the width). The initial (after quench and cryogenic treatment) volume of retained austenite was reported to be 0.0428 vol.%, which corresponds to a dimension of 0.2 nm wide in the cell. A geometric grid of 50 points is used for the martensite region (BCC phase) and 20 points for the initial retained austenite region (FCC phase). The mobility prefactor is varied in this study and applied to all elements equally in the martensite region; mobility is not enhanced in the austenite, as it is not highly dislocated.

Figure 4(a) shows the results of the mobility prefactor parameter study for the heat treatment at 482°C. The default mobility (1x) of the database produces essentially zero reverted austenite even at very long times (200 hours), failing to capture the observed phenomenon. These results illustrate the need for a parametric investigation utilizing experimental data, and it is seen in Figure 4(a) that a mobility > 2000x is required to approach the measured content of reverted austenite. Selecting a mobility factor of 3000x from reasonable agreement at 482°C, the formation of reverted austenite at lower and higher tempering temperatures is examined. It is assumed that a single mobility prefactor for the present study is sufficient. The dislocation density is not expected to significantly evolve thereby limiting changes in pipe diffusion. Furthermore, the range of tempering temperatures is limited. Hence any variation between bulk and dislocation diffusion as a function of temperature is minimal [32]. From the results in Figure 4(b), it is seen that applying the mobility prefactor fit to experimental data at one temperature is not particularly adept at describing other temperatures at short times; however, the trend is qualitatively correct in that increasing temperature increases reverted austenite.

![Figure 4 (a) DICTRA mobility study using data from Yoo [7] heat treatment at 482 °C. (b) Mobility prefactor of 3000x for multiple temperature](image)

It should be noted that, as we are applying the mobility enhancement to all elements equally (assuming the enhancement is due to increased dislocation density and pipe diffusion in the martensite phase), that regardless of mobility factor the composition of the reverted austenite is essentially consistent, only the volume fraction (and dimension) of the laths is affected.

Altering the mobility (e.g. incorporating any prefactor) increases the simulation time substantially. Due to the increased computational costs to run these simulations, it is ideal to have a rapid means of assessing that austenite can form by making sure the heat treatment is above the $A_{\text{c1}}$ temperature, where austenite is thermodynamically stable. Using an in-house algorithm, we predict an $A_{\text{c1}}$ of ~435°C for AerMet 100 from the equilibrium phase fractions. (It should be noted that the equilibrium $A_{\text{c1}}$ cannot generally be extracted from a dilatometry curve unless the heating rate is slower than 28 °C / hour [33] so a quick modeling prediction is advantageous). In Ayer [1], reverted austenite was observed at temperatures of ≥ 468°C in AerMet 100; at 427 and 454°C cementite was observed at grain boundaries instead of reverted austenite. Thus, the $A_{\text{c1}}$ prediction/calculation is a good means of determining the viability of a heat treatment in producing reverted austenite.

### 3.3 M₂C

While the reverted austenite is engineered to provide toughness, M₂C is desired to provide strength through secondary hardening. The M₂C carbides in these alloys at peak hardness are usually on the order of ~2 nm wide needles with aspect ratio of ~3 and are described as coherent at the peak hardening tempers [1, 5, 7, 9, 10, 12, 13, 34]. This is to provide the optimum combination of strengthening without being deleterious to the toughness. The Cr:Mo ratio of AF1410 and AerMet 100 is aimed at promoting the formation of a mixed metal carbide to minimize lattice mismatch as can be seen in Figure 5(e); (Cr, Mo)₂C has an $\epsilon_{\text{11}}$ mismatch close to zero, compared to the pure Mo₂C and Cr₂C carbides. The (Cr, Mo)₂C carbide nucleates coherently and remains coherent until ~10 hours (see lattice strain increase in Figure 5(c and d)) and then is semi-coherent until ~100 hours when it becomes incoherent. In contrast, Mo₂C may nucleate coherently, but it is semi-coherent at the prescribed aging
times, and becomes incoherent within the 10–16-hour range [12]. It can be seen in Figure 5(b) that the size of the carbides cannot be used to determine coherency, as the Mo2C carbide is smaller than the mixed carbide at the same tempering temperature of 510°C despite being semi-coherent (before dotted line) and then incoherent (after dotted line). There is no obvious shift in the size for either the Mo2C or mixed carbide. In Figure 5(a), the aspect ratio of the Mo2C does appear to shift significantly at the loss of coherence (dotted line) but not for the mixed carbide (dashed line) where the aspect ratio is generally unchanged.

Figure 5 (a) Measured aspect ratio of M2C carbides in AerMet100 [1, 7] and AF1410 [5]. Points are colored by tempering temperature. (b) Evolution of M2C phase as a function of tempering time at 510 °C in AF1410 [5] - with (Cr,Mo)2C - and modified AF1410 [12] - with Mo2C. (c and d) Elastic mismatch of M2C carbides in α-Fe matrix; solid points are calculated from experimental measurements of lattice parameter while open points are calculated from lattice constants from JCPDS files.

Ideally, modeling the carbides would capture the change in lattice parameter, which is a function of composition, since aspect ratio or size are not reliable metrics for determining coherency. However, for many precipitate phases, including M2C, the Thermo-Calc database considers the precipitate composition stagnant as a function of time, Figure 6. The predicted composition of M2C for the AF1410 alloy is shown as solid lines in Figure 6 (Fe content is ~0.003 at.% excluded for simplicity) and is generally congruent with compositions measured via APFIM [13] at intermediate times. The predicted composition does change with overall alloy composition and with temperature, allowing for comparison of phase formation between alloys and temper conditions, but not between coherency states within an individual alloy or temper with time.
Coherency is also important to consider in the interfacial energy used for the precipitation calculation, as an important component to the nucleation condition; the Gibbs energy of formation of a critical nucleus is:

$$\Delta G^* = \frac{16\pi \sigma^3}{3(\Delta G_m^{\alpha \rightarrow \beta} / V_m^\beta)^2}$$

Where $\sigma$ is the interfacial energy, $\Delta G_m^{\alpha \rightarrow \beta}$ is the molar Gibbs energy change for the formation of the $\beta$ precipitate of the critical composition from the matrix, $\alpha$, (maximum driving force for the $\alpha \rightarrow \beta$ phase transformation), and $V_m^\beta$ is the molar volume of the precipitate phase. The built-in calculation for interfacial energy in Thermo-Calc utilizes Becker’s model [35] which considers only chemical contributions to interfacial energy (no elastic strain energy) and further is using the composition in Figure 6 which is not reflective of the initial state at the onset of tempering. Unsurprisingly, it predicts a value of ~0.5 J/m² for the M_{2}C/$\alpha$ interface, which reflects the incoherency at long times (i.e. equilibrium) but fails to capture the nucleation process during which the interface is coherent. Interfacial energies of 0.099 J/m² at short times and 0.19 J/m² at intermediate times were back-calculated from experimental results in AF1410 [5] and 0.2 J/m² was assumed in modeling Mo_{2}C to align with experimental measurements [14]. These values align with the coherency observed as discussed above. In our parameter study we chose 0.1 J/m² for expected coherent nucleation in the mixed carbides of AF1410.

As in the DICTRA simulations, the mobility enhancement of dislocations within martensite should be considered. Mobility was enhanced in precipitation simulations of maraging steels by a factor of 4 [36] and by a factor of 45 in med-Mn steels to match atom probe data [37]. Predictions using methods other than Thermo-Calc also require adjustments to the mobility to account for dislocations as a short circuit path for diffusion[32]. Interestingly, decreases in mobility have also been successful at modifying simulations to reproduce experimental measurements, as in the case of boron segregation reducing grain boundary mobility, however those simulations investigated the effect of alloying on impeding kinetics, not accelerating the formation of desired phases[24].

To calculate the impact of elastic energy due to misfit on the nucleation and growth of precipitates, Thermo-Calc can utilize an elastic mismatch matrix, $\varepsilon_{ij}$ in conjunction with the elastic properties of the matrix (e.g. stiffness tensor $C_{ij}$). The $\varepsilon_{11}$ and $\varepsilon_{33}$ components of the elastic mismatch matrix for M_{2}C are discussed above, and both misfit calculations from experimental lattice parameters [5] and ab-inito methods [38] report the $\varepsilon_{22}$ value as approximately double the $\varepsilon_{33}$. Therefore, in the parameter study $\varepsilon_{11}$ and $\varepsilon_{33}$ are varied across reasonable ranges and the assumption that $\varepsilon_{22} = 2\varepsilon_{33}$ is made for simplification as well as all other components of the $\varepsilon_{ij}$ matrix are zero.

The nucleation sites for M_{2}C are generally agreed to be dislocations [5, 9, 10, 34] within the martensitic laths or plates; the nucleation site density is therefore calculated as: $N_d = \rho_d (N_A / V_m^\alpha)^{1/3}$ where $\rho_d$ is the dislocation density, $N_A$ is Avogadro’s number, and $V_m^\alpha$ is the molar volume of the matrix. Typical dislocation densities are on the order of $10^{15}$ m^{-2} [25, 26] but have been estimated as high as $10^{16}$ m^{-2} [5].

Figure 7 shows results of the parameter study for AF1410 composition starting with a dislocation density of $10^{15}$ m^{-2} and using the simplified growth model. The same parameter study was performed using the “general” growth model, but the results were
similar, except the calculations often failed to converge with no discernable cause for the model crash. In the hatched regions of Figure 7 it was predicted that the nucleation barrier was too high for M2C to form ($\Delta G_m^{\alpha-\beta}$ includes a chemical and elastic term, presumably here the elastic term is driving the high barrier). Interestingly, this is the region of measured $\epsilon_{33}$ within experiments, e.g. Figure 5(d). Typical experimental values for aspect ratio (3), particle length (17nm) and number density (7$^{10^{25}}$) are indicated by a cyan contour line. It can be seen again that the mobility database (1x) grossly underpredicted the size of the M2C phase and only predicted an aspect ratio of 1, a spherical particle, even for very high misfit strain values.

![Figure 7 Predicted aspect ratio, length, and number density of M2C in AF1410 for 5hr at 510°C as a function of misfit values using a dislocation density of 1e15, simplified growth model, $\sigma$=0.1 J/m$^2$, mobility factors of 1x, 10x and 25x.](image)

From the parameter study, it can be seen that several combinations of reasonable parameters can achieve the desired microstructural feature at the conclusion of the temper (e.g. after 5h at 510°C). In Figure 8, the evolution of the M2C phase with time is shown for two selected sets of misfit parameters and mobility enhancement. It is often possible to achieve excellent agreement with one microstructural characteristic but poor agreement with other features, e.g. well predicting the M2C length as shown by the red line in Figure 8 but not the volume fraction or aspect ratio. Generally, good alignment with the length and volume fraction overpredicts the aspect ratio. The expected misfit parameters for M2C in AF1410 are better modeled according to the 25x mobility, while not as exact a fit for the length, are better at describing the combination of both length and volume fraction evolution concurrently.
This parameter study only accounts for the nucleation and growth of M2C from a solute saturated martensite matrix; however, M2C is generally understood to form in competition with cementite, e.g., cementite initially forming in para-equilibrium and then dissolving in favor of M2C [14]. Some works show some small amount of cementite remains present even under optimized tempering conditions [5]. The alloy composition affects the cementite/M2C balance, e.g., Cr has been shown to both promote early dissolution of cementite [39] or stabilize it [40] depending on the overall alloy system; Ni can also promote cementite dissolution [40]. Preliminary work on introducing cementite to the precipitation model (using para-equilibrium growth of cementite) does show the expected early precipitation behavior of cementite; however, using the parameters described above (e.g. nucleation site density, interfacial energy, misfit energies) for M2C in competition with the cementite, the cementite is the only carbide formed even at the peak hardening temperatures. Further study is needed to determine whether there is a combination of appropriate kinetic parameters where cementite dissolves in favor of M2C or whether there is some adjustment to the free energies that needs to be made in these high alloy systems. Accurately assessing the competition of cementite (and other phases) is important for understanding the progression of the microstructure and selecting the appropriate tempering temperature and time to optimize the strength-toughness balance. Alloying design components like Ni and Cr have non-trivial effects on the formation and dissolution of cementite, as-well as effecting the austenite stability. Preliminary DICTRA studies do show prioritization of reverted austenite formation over cementite; it may be better to determine the competitive balance of the phases in DICTRA simulations while modeling the evolution of M2C when it wins out over cementite using the precipitation module.

**CONCLUSION**

A combination of modeling methods utilizing the multipurpose CALPHAD software tool Thermo-Calc were investigated to predict the microstructural features of high alloy Ni-Co steels, namely austenite (retained and reverted) and the secondary hardening precipitate, M2C. Parameter studies showed that the complexity of the Ni-Co steels does not easily lend itself to accurate microstructural modeling in the absence of experimental data. Specific experimentally informed adjustments to Ni-Co steel microstructure models were:
- Improved estimates of \( M_s \) and \( M_f \) which account for the high Co content. The quantity and stability of retained directly impacts both the mechanical properties (i.e., toughness) and subsequent formation of reverted austenite.
- Adjustments to diffusivity in the martensite to reflect the prevalence of pipe diffusion required to capture reverted austenite formation. This is accomplished by introducing a prefactor derived from matching experimental data on reverted austenite.
- Determination of shape and lattice mismatch of \( M_2C \) carbides.
- Understanding of model limitations in predicting the concurrent and competing precipitation behavior of cementite along with \( M_2C \).

In developing the modeling techniques for each microstructural feature, the vital role of reliable experimental data was established. While thermodynamic and kinetic modeling are powerful tools, they must be performed in conjunction with, and not in lieu of, experiments in order to understand and predict the microstructural features. To that end, significant progress has been made towards creating data-informed modeling techniques for the design of Ni-Co steels.

REFERENCES


