Thermodynamic and kinetic modeling of oxide precipitation in nanostructured ferritic alloys

L. Barnard^{1,*}, lbarnard@wisc.edu
N. Cunningham², njc@engineering.ucsb.edu
G. R. Odette², odette@engineering.ucsb.edu
I. Szlufarska¹, szlufarska@wisc.edu
D. Morgan¹, ddmorgan@wisc.edu

¹Materials Science and Engineering, University of Wisconsin-Madison
1509 University Ave
Madison, WI 53706

² Materials Science Department, University of California Santa Barbara
Santa Barbara, CA 93106-5050

*Corresponding author
P: 973.919.6382
3111 Engineering Centers Building
1550 Engineering Drive
Madison, WI 53706

Abstract

The mechanical properties and radiation tolerance of nanostructured ferritic alloys rely on a dense population of nanometer-scale Y-Ti oxides. The stability of these nano-oxides during extended service is critical in high temperature applications. Here, a model framework is developed for the thermodynamics and kinetics of Y-Ti oxide nucleation, growth and coarsening. The model, which is based upon available thermodynamic and kinetic data as well as key density functional theory calculations, shows that nano-oxide nucleation and growth are highly driven and that pipe diffusion is the dominant mode of their coarsening, in agreement with previous analyses of experimental high temperature data. The model predicts that the nano-oxides are thermally stable for 80 or more years below 1175 K. This analysis also provides insights the effect of O and Ti on nano-oxide sizes, and on optimization of alloy microstructure.

1 Introduction

Future advanced nuclear energy systems are expected to place demands on structural materials that lie well beyond the capabilities of materials used in current reactors. Structural materials in proposed fusion and many advanced fission reactor designs would be subject to significantly higher operating temperatures and much larger radiation doses than their counterparts in conventional light water reactors. Nanostructured ferritic alloys (NFAs), which are a variant of oxide dispersion strengthened (ODS) steels, are a uniquely promising candidate alloy class to meet these demanding requirements [1-5].

NFAs typically contain (in wt%) 12-16 Cr and up to 0.5 Mo or 3 W [6] with small additions Ti, Y, and O. The latter solutes precipitate during processing to form a high density of Ti-Y-O nano-oxides. The Y and some O are most often introduced by mechanically alloying

Y_2O_3 with ferritic steel powders using high energy ball milling. The alloy powders are then consolidated by hot isostatic pressing or extrusion.

The Y-Ti oxides are highly effective in pinning dislocations and constitute a high density of point defect sinks that also trap transmutant helium. These functions lead to both outstanding high temperature strength and irradiation tolerance [2]. Thus, the ability to produce optimal nano-oxide distributions during processing, and their subsequent stability and resistance to excessive coarsening during service, are critically important issues [6-8]. Predicting nano-oxide coarsening over decades of service is particularly challenging since such predictions must be based on relatively short-time experiments. Therefore, a primary motivation for the present study is to develop physically-based models that can provide qualitative and quantitative insight into the nano-oxide thermodynamics and kinetics that mediate phase selection, precipitation and coarsening. Due to the complexity of the many interactive processes being treated, a small number of fit parameters are required to fully calibrate the models. The fit parameters include the effective values of the chemical potential of oxygen in solution and the oxide-ferrite interface energies. The fitting strategy is described in detail below. Other parameters have been estimated based on direct experimental measurements or generally observed empirical trends. While this approach leads to some uncertainties in the model predictions, they do not have a significant impact on the major conclusions and mechanistic insights reached in this study related to the active mechanisms during nano-oxide evolutions and how Y-Ti-O composition and thermal history determine precipitate phases, sizes and number densities.

Due to their very small size, there is some uncertainty regarding nano-oxide structures and compositions. Most high-resolution TEM studies show that the nano-oxides are consistent with $\text{Y}_2\text{Ti}_2\text{O}_7$ [6, 9-11]. Combined small angle neutron and x-ray scattering [6, 12, 13] and x-ray

diffraction measurements [14, 15] are also broadly consistent with this conclusion. However, the $\text{Y}_2\text{Ti}_2\text{O}_7$ may not be fully stoichiometric; and a multitude of other observed oxide phases include, but are not limited to, Y_2TiO_5 , Y_2O_3 , CrTiO_3 and TiO_2 , as well as a variety of carbo-nitrides. Atom probe tomography (APT) measurements have been interpreted to indicate that the smallest Y-Ti-O are coherent highly non-stoichiometric sub-oxides with high Ti/Y ratios [1, 12, 16-22]. However, it is likely that the APT atom probe measurements are affected by various artifacts [6]. Furthermore, density functional theory (DFT) calculations of the formation energies of small Y-Ti-O clusters in Fe have shown that small clusters that are structurally similar to bulk Y and T-Ti oxides are far more stable than clusters that are coherent with the ferrite matrix [23]. Here, we assume that the nano-oxides are known equilibrium Y-Ti-O phases during their entire evolution.

A second major complication in developing a model is associated with the fact that O contents in NFAs are far in excess of equilibrium values. Indeed, non-equilibrium O concentrations in excess of that added by Y_2O_3 are needed to produce optimal Y-Ti nano-oxides [24]. As the concentration of O within the alloy is difficult to control, and likely fluctuates over the course of alloy processing, we use the O chemical potential within the alloy as an adjustable parameter in the model. Values representing equilibrium with possible Cr, Fe, and Ti oxides provide a plausible range of values for this parameter, along with precipitation and aging kinetics that are consistent with experimental observations. While these assumptions and approximations do not capture all of the potentially important physics, such as the precise nucleation pathway through compositional space, or the appearance of metastable phases, they provide a well-defined foundation to begin to understand the complex multicomponent precipitation process in nanostructured ferritic alloys.

The remainder of this paper is organized as follows: Section 2 details the thermodynamic model used to evaluate the necessary driving forces for modeling nano-oxide precipitation and coarsening. The kinetic model for simulating nano-oxide precipitation is then briefly described, with additional details found in the Appendix. Section 3 presents the predictions of the thermodynamic model and the results of fitting the kinetic model to experimental measurements of nanoparticle size as a function of aging time. The predictions of the best-fit model for both coarsening kinetics and alloy composition effects on nanoparticle size are then described. Finally, section 4 provides concluding remarks and commentary on paths that can lead to more advanced models.

2 Methods

2.1 Thermodynamic Model

The model developed in this study describes phase separation of Y and Ti nano-oxide phases from a bcc Fe-Cr-Y-Ti solid solution. The thermodynamic model used to describe this process includes the following phases: bixbyite Y_2O_3 , rutile TiO_2 , pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$, orthorhombic Y_2TiO_5 , and ferrite Fe-Cr-Y-Ti solid solution. These oxides are the equilibrium phases in the $\text{Y}_2\text{O}_3 - \text{TiO}_2$ pseudobinary system [25] over the temperature range of interest (900 to 1573 K), while ferrite is the matrix phase in the NFAs considered in this study with Cr contents lying outside the gamma loop [2, 26].

The thermodynamic equilibrium phase separated state of a given NFA can be determined by first computing the free energies of the individual phases listed above and then minimizing the total free energy of the system as mediated by the fractions of each phase. Numerous thermodynamic assessments in the CALPHAD formalism were used to describe these free energies. The necessary parameters for these descriptions are summarized in Table 1.

The total free energy to be minimized may be written as

$$G^{tot} = f^{\alpha} G^{\alpha} + f^{203} G^{203} + f^{227} G^{227} + f^{215} G^{215} + f^{012} G^{012} \quad \text{Eqn. 1}$$

where $f^i G^i$ is the product of the mole fraction of phase i and the molar free energy of phase i .

The superscripts 203, 227, 215, and 012 refer to the oxide phases Y_2O_3 , $Y_2Ti_2O_7$, Y_2TiO_5 , and TiO_2 respectively. The free energy of the solid solution phase is computed using the following equation

$$G^{\alpha} = \sum_i x_i {}^0G_i^{\alpha} + RT \sum_i x_i \ln x_i + {}^{ex}G^{\alpha} \quad \text{Eqn. 2}$$

where x_i is the mole fraction of component i in the ferrite phase α ($i = Y$ or Ti), and ${}^0G_i^{\alpha}$ is the molar free energy of pure component i in the structure of α . The term ${}^{ex}G^{\alpha}$ is the excess free energy of mixing, described by the Redlich-Kister polynomial

$${}^{ex}G^{\alpha} = x_m x_n \sum_j (x_m - x_n)^j {}^{(j)}L_{mn}^{\alpha} \quad \text{Eqn. 3}$$

where $m = Fe, Cr$ and $n = Y, Ti$. The parameters ${}^{(j)}L_{mn}^{\alpha}$ are the Redlich-Kister polynomial expansion coefficients and are evaluated in in Table 1. Because the mole fractions of Ti and Y in NFAs are generally dilute (typically less than 1 at%), Y - Y , Y - Ti , and Ti - Ti interactions in the solid solution phase are neglected. Furthermore, because their mole fractions in solution do not change significantly during the precipitation of the Y and Ti oxide phases, the Fe and Cr contributions to total free energy are approximately the same before and after the phase separation, and thus are neglected. Finally, it is assumed that O exists in the alloy at a constant chemical potential throughout phase separation. This chemical potential value determines the driving force for oxide precipitation, and the detailed interactions of O within the solid solution phase are not required. This assumption is discussed further below.

The equilibrium oxide phase separation in a given NFA is found by minimizing Eq. 1 under the constraints of constant mole fractions of Fe, Cr, Y, and Ti, and a constant chemical potential of O. These constraints are equivalent to assuming that the system is closed with respect to the metallic constituents, but open with respect to O. The assumption of openness is based on ubiquitous observations that the initially dissolved O in NFA significantly exceeds the nominal solubility in equilibrium with the oxides of Fe, Ti and Cr [4-10]. The precise value of this O chemical potential is unknown. However, there are two important empirical constraints on the magnitude of the O chemical potential: a) consistency with observed oxide phases in NFAs, which have well established *minimum* O potential limits of stability: and, b) consistency with observed kinetics of oxide nanoprecipitate nucleation, growth and coarsening. Together, these constraints impose a range of O potential values for which both the correct oxide phases and the correct coarsening behavior can be reproduced by the model.

The high dissolved O concentrations are not entirely unexpected since ball milling defect structures, such as high dislocation densities [19], fine grains and excess vacancies [20], lower the solution energy of O, thus increasing its effective mole fraction solubility. Furthermore, it is known that O in excess of the amount added in the form of the Y_2O_3 powder is needed to form fine complex oxide nanoprecipitates [15, 27]. Cunningham et al. recently demonstrated that improved impurity control during powder milling reduces the amount of excess O [24], and that nano-oxide formation is inhibited for very low O contents. The O potentials in equilibrium with known Fe and Cr oxides correspond to O partial pressures (hereafter denoted P_{O_2}) in the range of 10^{-23} to 10^{-15} atm and O solubility values in the range of 10^{-4} to 10^{-2} at% over the temperature range of interest here, based on the calculated phase diagrams [28]. Meanwhile, atom probe tomography (APT) characterization of both total atomic and matrix O tend to be much higher

than these nominal equilibrium values. For example, APT measurements show the matrix O content in the NFA MA957 is 0.11 ± 0.014 at.% [11]. These data are clear evidence that there is an ample reservoir of total O for forming the complex Y-Ti oxide nanoprecipitates. Further, because the O interstitial diffusion coefficient is many orders of magnitude higher than those for the metallic solutes [16-18], we assume that the free matrix O can instantaneously equilibrate with this O reservoir during Y-Ti oxide nucleation, growth and coarsening. For these reasons, it is convenient to treat the O as existing at a fixed reservoir potential, rather than a fixed total mole number.

2.2 Kinetic model

The Y-Ti oxide precipitation model is based upon Slezov's general model of the kinetics of first order phase transformations [29, 30]. The expressions used to implement this theory are discussed in Appendix 1; a thorough derivation of these expressions may be found in [30] and in chapter 2 of [29]. Slezov's method is based upon solving a master equation of the form of Eqn. A2, which describes the size distribution function of the precipitate ensemble as a function of time.

A number of phenomena and mechanisms related to nucleation and initial growth are neglected in this kinetic model. These phenomena may be important in actual NFAs, such as transient excess vacancies from ball milling, non-uniformities in the solute distributions in the matrix, heterogeneous nucleation on dislocations or other crystal defects, and transient elevated O concentrations that increase the driving force for the initial nanoprecipitate nucleation. In comparison, the purely homogeneous treatment of the nucleation process in this study is highly idealized. However, since the focus of our study is predominantly on the long-term thermal stability of the nanoprecipitates, the simulated initial nucleation and growth processes have been

used primarily to generate an as-processed particle size distribution that is consistent with experimental measurements. This particle size distribution was then subjected to simulated coarsening by both bulk and dislocation pipe diffusion mechanisms, as outlined in Appendix 1.

2.2.1 Summary of model parameters

A number of physical parameters are required as input to enable use of this model, which may be generally categorized into kinetic, thermodynamic and geometric quantities. These quantities are summarized in Table 2. The kinetic quantities are the diffusion coefficients of the Y and Ti monomers. For normal bulk diffusion, D_{Ti} has been taken from experimental measurement [31], and D_Y has been taken from first principles-based diffusion theory [32]. While no experimental value of D_Y is available, surface depletion measurements [6] have been found to be reasonably consistent with the first principles-based value. Arrhenius parameters for all the diffusion coefficients are given in Table 2. No value for the diffusion coefficient of Y in a dislocation D_Y^D has yet been determined, however in many metals it has been found that using the value of the bulk diffusion coefficient with a reduction of 40-60% in the activation energy is a reasonable approximation of this parameter [33-37]. Therefore, we will assume that D_Y^D has the same Arrhenius form as D_Y except with one-half the bulk activation energy. In addition to the parameters listed in Table 1, the thermodynamic quantities required by this model include the specific interfacial energies σ_0^ϕ and the Y dislocation binding energy E_Y^D . The former is treated as an adjustable parameter, as described in Sec. 2.2.3, while the latter is calculated in this study by DFT (see Sec. 2.2.2). Finally, the geometric quantities include principally molar volumes of the various phases in the system. These values are summarized in Table 2. The parameterized

model differential equations were numerically integrated using the CVODE module of the SUNDIALS package [38].

2.2.2 Calculation of the Y-dislocation binding energy by DFT

In order to incorporate the effects of dislocation pipe diffusion into the kinetic model, the binding energy of a Y atom to a dislocation must be determined. The subject of solute interactions with dislocations in Fe has been well studied, especially for interstitial solutes such as C and N. However, the interaction energy of Y with dislocations in Fe is currently unknown. In this study, DFT calculations have been employed to compute a first approximation for the Y-dislocation binding energy in Fe. To demonstrate that this approach can produce reasonably accurate results, the binding energies of C, O, and N with a dislocation in Fe were also calculated and compared with available values from the literature and from elasticity theory.

A $[100](010)$ edge dislocation was chosen for these calculations because of its structural simplicity. While this type of dislocation is not involved in the predominant slip mechanism in Fe [39], such dislocations are present in Fe and, for example, appear to play an important role in crack nucleation [40]. Figure 1a illustrates the atomistic model of this dislocation structure, viewed along the $[001]$ direction (i.e., along the core of the dislocation). Periodic boundary conditions are employed when calculating the energy of the dislocation structure via DFT, and a supercell was constructed with an array of four dislocations arranged so that their displacement fields are mutually compensated between periodic images. Figure 1b depicts a schematic illustration of the simulation supercell used in these calculations. The solid and dashed lines in Fig. 1b correspond to the planes composed of the light and dark atoms in the atomic model of Fig. 1a, respectively. The supercell was three bcc conventional cubic unit cells in extent along the $[001]$ direction.

Dislocation-solute binding energies were determined using the following expression:

$$\Delta E_i^D = (E_{i+Fe}^D + E_{Fe}^{bulk}) - (E_{Fe}^D + E_{i+Fe}^{bulk}) \quad \text{Eqn. 4}$$

where E_{i+Fe}^D is the DFT-calculated energy of the dislocation structure containing a solute atom of species i , E_{Fe}^D is the energy of the solute-free dislocation structure, E_{i+Fe}^{bulk} is the energy of bulk, undefected Fe with a single solute of species i , and E_{Fe}^{bulk} is the energy of pure, undefected Fe. When calculating E_{i+Fe}^D , the solute Y atom was placed on substitutional sites 1-4 in Fig. 1a, while the C, N, or O atom was placed on octahedral site 5. A 3×3×3 cubic bcc supercell with a single solute atom was used for the bulk Fe calculations.

The calculations were performed using the Vienna Ab Initio Simulations package (VASP) [41-44] in the generalized gradient approximation using the Perdew-Burke-Ernzerhof [45] exchange-correlation functional, and using the projector-augmented wave method [46]. All calculations were spin polarized and used a 3×3×3 k-point mesh and a 400 eV energy cutoff. Cell shape and ionic relaxations were permitted in both the bulk and dislocation structure calculations.

Different sizes of dislocation cells were used to estimate the corresponding size-dependent errors in Y-dislocation binding energy. The basic supercell depicted schematically in Fig. 1b consists nominally of 6 cubic bcc units in the [100] and [010] directions and 3 units in the [001] direction. Three additional supercells were tested with sizes (a) 8×6×3, (b) 6×8×3, and (c) 6×6×4 along the [100]x[010]x[001] directions. The first cell (a) tests convergence with respect to the distance between dislocations in the [100] direction, the second cell (b) with respect to distance between dislocation cores in the [010] direction, and the third cell (c) with respect to

distance between periodic images of the solute atom along the dislocation line in the [001] direction.

2.2.3 Physical quantities used as adjustable parameters

There are two additional quantities used in the present modeling framework that are not precisely known. These are the specific oxide-matrix interfacial energies σ_0^ϕ and the reservoir O chemical potential. Within the model framework, the latter is expressed as the gas phase reference state partial molar free energy, $G_{O_2}^{gas}$, appearing in Table 1. The above quantities are treated as adjustable parameters in the kinetic model used to fit the experimental data, especially focusing on fitting the change in mean precipitate size as a function of aging time. The strategy for performing this fitting is the subject of this section.

In principle, the specific nominal interfacial energies σ_0^ϕ of each oxide phase represent at least four independent parameters as we consider four phases. If all four quantities were used as fitting parameters, then the model would likely have too many degrees of freedom to allow for a unique model fit. Therefore, we have assumed that the interfacial energies of the four oxide phases are related by a simple linear relationship in the Ti fraction of metal atoms in the oxide, according to the following expression:

$$\sigma_0^\phi = \sigma_0 + Ax_{Ti}^\phi \quad \text{Eqn. 5}$$

where x_{Ti}^ϕ is the fraction of all metal atoms that are Ti atoms in the formula unit of oxide phase ϕ . The slope A was determined by interpolation between the bare specific surface energies of Y_2O_3 ($x_{Ti}^\phi=0$) and TiO_2 ($x_{Ti}^\phi=1$) [47]. While this assumption has not been verified for the oxide phases used in the present model, experimental measurements of the interfacial energy between liquid Ni and Ti-bearing YSZ follow a linear relationship in Ti fraction like that of Eqn. 5

reasonably closely [48]. The $x_{Ti}^\phi=0$ intercept of this linear relationship, σ_0^ϕ , is the only adjustable parameter for all the interfacial energy terms.

The second fitting parameter is the O reference state molar free energy $G_{O_2}^{gas}$. This parameter enters into the model in the free energy expressions for Y_2O_3 and TiO_2 in Table 1. In the context of the model, this parameter is equivalent to the reservoir chemical potential of O in solution in the ferrite matrix. Once a value of $G_{O_2}^{gas}$ has been fit, the expression in Table 1 can be used to determine the equivalent partial pressure of O_2 (P_{O_2}), which is often a more convenient and physically intuitive way to describe the oxygen activity.

The model was fit using the experimental data from the alloy MA957 [6, 10-12, 15, 49]. This alloy was chosen because of the availability of data on nanoparticle size and number density for this extensively studied material under multiple aging conditions, thus avoiding complexities associated with fitting to data from alloys with different compositions and processing histories. The σ_0^ϕ and $G_{O_2}^{gas}$ parameters were adjusted to best match SANS measurements of mean Y-Ti-O particle size as function of time during aging of the MA957 base material at temperatures in the range 1223-1573 K [6, 49]. The fitting was done using a simple iterative routine to minimize the sum of the squared residual errors between model calculation and experimental measurements for the longest aging time at each temperature. In order to isolate the dominant growth and coarsening mechanism of nano-oxides in NFAs, the fitting was performed independently for a model scenario that includes only conventional growth and coarsening through bulk lattice diffusion (denoted hereafter the standard model) and for a model that includes both bulk and pipe diffusion mechanisms (denoted the pipe diffusion model). Additional consideration is given to the phase stability during fitting. Specifically, for $G_{O_2}^{gas}$ values below a certain threshold, Ti-

containing oxides are unstable, and Y_2O_3 is the only phase that appears. As the Ti-containing nanoparticles are generally observed in MA957, $G_{O_2}^{gas}$ values below this threshold are not considered. Detailed discussion about the specific values obtained is given in Sec. 3.2.2 and Sec. 3.2.3. Because the primary goal of the model is to describe the long term stability of the nanoprecipitates at elevated temperature, the model was fit to coarsening data only, and is not fit to the kinetics of the initial particle nucleation. The nucleation component of the model was used only to generate an initial particle size distribution that is consistent with experimental data of as-fabricated MA9457, which was then subjected to simulated heat treatment. The parameters used for the nucleation process were therefore chosen based upon convenience and to give the best agreement with experiment, and are not physically related to the best fit parameters for the coarsening process.

3 Results and Discussion

3.1 Predictions of phases and volume fraction at equilibrium

The thermodynamic model described in Sec. 2.1 can be used to make certain predictions about the asymptotic behavior of NFAs, such as the identities and fractions of the phases present at equilibrium. Figure 2 shows a map of the predicted equilibrium precipitate phases at 1273 K in Fe-14Cr- x_Y - x_{Ti} as a function of the O chemical potential in terms of equivalent P_{O_2} and the ratio $x_{Ti}/(x_Y + x_{Ti})$, where the sum $x_Y + x_{Ti}$ was constrained to be equal to 1 at%. Lines corresponding to the equilibrium partial pressures for the reactions $FeO \leftrightarrow Fe + 1/2O_2$, $Cr_2O_3 \leftrightarrow 2Cr + 3/2O_2$, and $TiO \leftrightarrow Ti + O_2$ are shown as well [28, 50]. Over the range of P_{O_2} for which Fe or Cr oxides are stable, the predicted phases are Y_2O_3 , TiO_2 , $Y_2Ti_2O_7$, and Y_2TiO_5 , depending on the Y and Ti alloy composition. Most NFAs occupy the Ti-rich composition range for which the predicted stable phases are TiO_2 and $Y_2Ti_2O_7$, in good qualitative agreement with

many experimental observations [6, 10, 12, 13, 51]. The phase stability behavior is insensitive to the P_{O_2} above the threshold of $P_{O_2} = 10^{-28}$ atm necessary to form Ti containing oxides. Below this limit, only Y_2O_3 appears as a precipitate phase, and all Ti remains in solution. Since this P_{O_2} is well below the stability limit for Cr_2O_3 , it is likely that oxides containing Ti readily form in NFAs under almost any relevant processing or service condition.

The volume fraction of precipitate phase is an alloy property of particular interest in NFAs because, to a first approximation, the contribution of the NFs to the overall strength of the alloy is proportional to the square root of the NFA volume fraction [7]. Figure 3 compares the precipitate volume fraction in a large number of NFAs with varying Ti and Y contents as measured by SANS [2, 8, 12-14, 49, 52-55] with the equilibrium volume fractions of oxide phases predicted by the thermodynamic model for the same alloys, using the given nominal alloy compositions. For cases where it was explicitly stated in the experimental methods that only the Y and Y-Ti oxides are included in the reported volume fractions [2, 12, 13], the predicted values include only these phases as well. In most cases, the predicted volume fractions are slightly above the measured values. The SANS measurements may miss precipitates that are larger than the size range for which the technique has been tuned, as noted by Cunningham et al. [6] to explain the modest drop in precipitate volume fraction during extended aging of the NFA MA957. Considering this possibility and other sources of uncertainty, Fig. 3 demonstrates a reasonably good agreement between the model predictions and experiment. This result suggests that the thermodynamic model adequately captures the trends in both the amount and identities of precipitate phases with Y and Ti alloy content.

Studies to optimize NFA compositions have focused on the effects of O and Ti. For example, Oksiuta et al. [51] examined the precipitate microstructure and the Charpy impact

toughness of an Fe-12Cr-0.2Y- x Ti (at%) NFA, where x varied from 0.1 to 0.6 at%. Figure 4 shows the equilibrium oxide volume fractions predicted by the thermodynamic model for this alloy on the primary axis, and the measured Charpy upper shelf energy on the secondary axis, as functions of Ti content. The thermodynamic model predicts that the Y-Ti oxide volume fraction will plateau at about 0.2 at% Ti, beyond which further additions of this element only increase the volume fraction of TiO₂. This is in qualitative agreement with the observations of Oksiuta et al., who noted significant Ti oxide precipitation in the alloy containing 0.6 at% Ti, but not in the 0.1 or 0.3 at% Ti alloys [51]. A significant drop in Charpy toughness was measured between the 0.3 at% Ti and 0.6 at% Ti alloys, a composition range that corresponds to a significant increase in the predicted volume fraction of TiO₂. Oksiuta et al. attributed this drop in Charpy toughness to the precipitation of a large amount of TiO₂ in the 0.6 at% Ti alloy, which appeared as much larger precipitates often on or near grain boundaries. This result suggests that coarse scale Ti oxide precipitation should be minimized. From the predictions of the thermodynamic model in Figs. 2 and 4, TiO₂ formation can be avoided in alloys with a nominal Ti:Y ratio equal to 1. Cunningham [11] has also studied the effect of the bulk alloy Ti/Y ratio in the range from ≈ 1.6 to 3.5 and showed a small decrease in nanoprecipitate Ti/Y ratio. The corresponding effects on the [Y+Ti]/O ratio, nm-scale oxide sizes, and volume fractions were even weaker. These results are consistent with the predicted thermodynamic effect of higher Ti: the character of the complex Y-T-O oxides nanoprecipitates are not strongly affected, while mass balance considerations indicate that the fraction of Ti-oxides increases.

3.2 Modeling of precipitation kinetics in NFAs

While the thermodynamic calculations discussed above can be used to predict the identities and volume fractions of nanoprecipitate phases in equilibrium, the kinetic modeling

approach outlined in Sec. 2.2 must be used to treat the evolution of the precipitates as a function of time, temperature, and alloy composition. This section presents the results of the DFT calculations of the Y-dislocation binding energy, the fitting of the parameters σ_0 and $G_{O_2}^{gas}$, and the predictions of the best-fit kinetic model of nanoprecipitate nucleation, growth and coarsening during thermal aging.

3.2.1 DFT calculations of solute-dislocation binding energies

The binding of the interstitial solutes such as C, N, and O to dislocations in α -Fe has been studied extensively using both experimental [56-60] and theoretical [61-66] approaches. Here, we will first compare the results of the DFT calculations of the dislocation binding energies of these three solutes with results from the literature, to ensure that our simplified approach produces reasonably quantitative values. Table 3 presents the dislocation binding energy values of C, N, and O resulting from the DFT calculations described in Sec. 2.2.4, as well as values determined in previous studies based on a variety of experimental and theoretical approaches. Reasonably good agreement is observed for all three elements. Table 3 also contains the Y-dislocation binding energies calculated for site 1 in Fig. 1a using four different supercell configurations and for sites 2-4 using a single configuration. The strongest binding energy is found for site 1, where all four cell configurations fall within the range of -2.47 and -2.65 eV, indicating that convergence errors with respect to cell size are likely to be on the order of 200 meV. While this is not an insignificant error in absolute terms, it is less than 10% of the magnitude of the overall value and the predicted values should be accurate enough to assess the possible impact of dislocation pipe diffusion on precipitate growth and coarsening. The binding energies calculated for sites 2 and 3 were somewhat weaker than for site 1, but still substantial. Of the sites tested, only site 4 resulted in a repulsive interaction. In the kinetic modeling results

described below, a value of -2.54 eV (-241.2 kJ/mol) was used for the Y-dislocation binding energy, corresponding to the average of the four values determined for site 1. We note that the non-local elasticity theory of Wang [66] predicts a Y binding energy of -1.62 eV. While this is itself a strong attractive interaction in qualitative agreement with the DFT calculations performed here, the lower value demonstrates the need for an atomically resolved method, such as DFT, to capture the full effect of Y-dislocation interactions. Such a strong Y dislocation binding energies are corroborated by significant Y segregation to dislocations observed in the analysis of some APT studies [16].

3.2.2 Calculation of the initial particle size distribution

The kinetic model was first used to simulate the nucleation and growth of the oxide nanoprecipitates from the solid solution, in order to obtain an initial number density and size distribution consistent with SANS measurements for as-consolidated MA957 [10-12]. The base MA957 material exhibits a mean nanoprecipitate radius of 1.35 nm and a density of $9.0 \times 10^{23} \text{ m}^{-3}$ after consolidation at 1338 K [6]. Nucleation and growth of Y-Ti oxide particles were simulated from a starting alloy composition of Fe-14Cr-1Ti-0.14Y at % (corresponding to the nominal composition of MA957) to produce a particle size distribution that was commensurate with these values. A large set of simulations were performed with different values of the parameters σ_0 and $G_{O_2}^{gas}$ (in terms of equivalent P_{O_2}), in order to determine the range of values that produce a nanoprecipitate number density and size distribution consistent with experimental measurements. Figure 5 shows a map of mean particle sizes in σ_0 -- P_{O_2} space after simulated heat treatments of 3 hr at 1338 K. The color at any point on the map indicates the mean precipitate radius produced by the corresponding values of σ_0 and P_{O_2} , according to the figure legend. The dashed line corresponds to the experimentally measured mean particle size. For distributions

that exhibited this value for mean particle size, the calculated number density and volume fractions of the oxide nanoparticles were in the ranges $5.8\text{-}8.8 \times 10^{23} \text{ m}^{-3}$ and 0.6-0.8 %, both in reasonably good agreement with experimental measurements [6]. The dashed line *AB* in Fig. 5 therefore represents a continuous set of values for σ_0 and P_{O_2} that yield an initial particle size distribution that agrees closely with experiment. Values of 2.9 J/m^2 and -415.1 kJ/mol (10^{-19} atm in terms of equivalent P_{O_2} at 1338 K) for σ_0 and $G_{O_2}^{gas}$ were used to generate the initial particle size distribution in the simulated thermal aging studies described below. These values were chosen as they yield close agreement with experimental data, produce nanoprecipitate phases that are in qualitative agreement with experimental observation, and are very close to the best fit parameter values for the standard coarsening model (see Sec. 3.2.3). These values are fit more precisely for the separate cases of coarsening via bulk or dislocation diffusion in Sec. 3.2.3.

The calculated oxide nanoprecipitate volume fractions are shown in Fig. 6, along the trajectory *AB* (dashed line) in Fig. 5, as a function of P_{O_2} . Over most of the range of P_{O_2} values, the $\text{Y}_2\text{Ti}_2\text{O}_7$ phase is the predominant Y-bearing nanoprecipitate phase. For values lower than 10^{-19} atm , the $\text{Y}_2\text{Ti}_2\text{O}_7$ phase begins to disappear in favor of the more Y-rich Y_2TiO_5 and Y_2O_3 phases. By 10^{-26} atm , Y_2O_3 is the only remaining nanoprecipitate phase. This trend toward more Y-rich precipitates in O-poor conditions appears to agree qualitatively with the observations of Cunningham et al. in NFAs containing varying O contents [24]. There are some important differences between the purely thermodynamic predictions and the results of the kinetic calculations in Fig. 6, most notably the absence of the TiO_2 phase in the kinetic model calculations above the limit of TiO_2 stability at this temperature (10^{-25} atm). Evidently, in the kinetic model the driving force for TiO_2 precipitation is not sufficient to overcome the barrier to nucleation over the range of interfacial energy values investigated, even though this phase is

thermodynamically stable in this regime. It is notable that while TiO_2 is observed in MA957 following hot extrusion, a much larger fraction of this element precipitates during long term thermal aging at 1000°C , resulting in a removal of a large excess of Ti from the matrix that is left after the Y-bearing nanoparticles initially form [24]. The suppression of the TiO_2 nucleation observed in the kinetic model is qualitatively consistent with this observation.

Regardless of the phases present, however, the volume fractions in Fig. 6 correspond to a nearly complete depletion of Y from the matrix. The nucleation and growth processes are therefore complete after this initial heat treatment and further evolution of the particle size distribution involves only coarsening and dissolution of existing particles. While little quantitative data are available regarding the kinetics of precipitation in MA957 or other NFAs, these results are qualitatively consistent with the very rapid appearance of the oxide NFs during the initial hot extrusion consolidation treatment of the mechanically alloyed powders [2, 12, 14, 67]. It also should be noted that while still very rapid, oxide NF precipitation is slower at lower consolidation temperatures, manifested in quasi C-curve type behavior [2].

It is important to emphasize that the initial oxide nanoprecipitate characteristics are not highly sensitive to the fit parameters, since the decomposition is so highly driven by the very large non-equilibrium free energy of the initial highly supersaturated solid solution. A wide range of parameters will yield a high density of stable nanoprecipitates between 1-3 nm in diameter. The most significant result is that approximately 0.8 volume % of oxide nanoprecipitates that are primarily composed of $\text{Y}_2\text{Ti}_2\text{O}_7$ quickly form for most values of P_{O_2} . Following nucleation and initial growth the particle size distribution is in a state of over-nucleation, in which the concentration of Y remaining in the matrix is near zero and the associated coarsening rates are negligible for short times. The initial particle size distribution is

therefore virtually stationary on the timescale of initial alloy processing. We next consider the evolution of the particle size distribution under very high-temperature or long-time thermal aging conditions, during which measurable coarsening does occur

3.2.3 Model fitting to particle size evolution under long-term thermal aging

In order to identify the most likely coarsening mechanism in this alloy, a particle size distribution described by values of 1.32 nm, $8.8 \times 10^{23} \text{ m}^{-3}$, and 0.8 % for mean radius, number density, and volume fraction, respectively, was subjected to simulated long term thermal aging heat treatments. This particle size distribution consisted almost entirely of $\text{Y}_2\text{Ti}_2\text{O}_7$ particles, in good qualitative agreement with experimental observation of this alloy [12].

The best-fit values of the interfacial energies in the standard and pipe diffusion models are shown in Fig. 7a using the form of Eqn. 5, along with the bare surface energies of Y_2O_3 and TiO_2 , as well as the liquid Fe-solid TiO_2 interfacial energy [47]. The best-fit values for the standard model are quite high, and are near the highest range reported even for incoherent planar interfaces [68], while the values for the pipe diffusion model are closer to the experimental surface energies of Y_2O_3 and TiO_2 and the interfacial energy of TiO_2 with liquid Fe [47]. The best-fit O chemical potentials for the standard (dashed line) and pipe diffusion (solid line) models are plotted in Fig. 7b, in terms of equivalent P_{O_2} as a function of temperature. For comparison, and to provide context, the curves corresponding to O chemical potential for which the reactions $2\text{Cr} + 3/2 \text{O}_2 \leftrightarrow \text{Cr}_2\text{O}_3$ and $\text{Ti} + \text{O}_2 \leftrightarrow \text{TiO}_2$ are in equilibrium are included as well (dotted lines). The best fit chemical potential for the pipe diffusion model is quite low, but is just above the equilibrium curve for Cr/ Cr_2O_3 , which is certainly physically plausible. However, the best-fit curve for the standard model is well below the Cr/ Cr_2O_3 equilibrium curve. It is more difficult to justify this value physically, because Cr_2O_3 is often observed among the oxide scales

in NFAs. It should be reemphasized here that while some intuitive arguments can be offered regarding the coexistence of the Cr and Fe oxide phases with the Y-Ti nano oxides and what this implies for the chemical potential of O in NFAs, measured matrix O concentrations generally far exceed the solubility of O in equilibrium with these phases. It is therefore clear that the simplified thermodynamic equilibrium framework utilized in this work does not reflect all of the physical aspects of the internal O environment in NFAs. For instance, strong binding of O to matrix defects such as dislocations or vacancies is not included in the model developed here, and could significantly enhance the apparent solubility of O in the ferrite matrix. However, the O residing in these bound states is not free to participate in the formation of the oxide nanoprecipitates, and therefore it would be erroneous to include it in the reservoir of available O. Generally speaking, the causes and possible implications of the unexpectedly high measured O content in NFAs remain unexplained, and should be further explored.

The change in the mean precipitate radius in MA957 as a function of aging time is shown in Fig. 8, including both of the best-fit model cases and the measured data [6, 49]. The best-fit pipe diffusion model (solid lines) shows reasonably good agreement with the experimental data, especially for longer aging times. In contrast, the best-fit standard model (dashed lines) predicts little coarsening even at high temperature. The failure of the best-fit standard model to reproduce the experimental coarsening behavior is due predominantly to the low solubility of Y in the ferrite matrix. To increase this solubility, and thereby increase the coarsening rate in the standard model, a much lower O reservoir chemical potential would have to be applied. However, it is evident from Fig. 7b that the O chemical potential used in the standard model is just above the value corresponding to Ti/TiO₂ equilibrium, and as demonstrated in Figs. 2 and 6, below this threshold Y₂O₃ becomes the only stable oxide phase.

Therefore, the O reservoir chemical potential parameter in the standard model cannot be decreased any further, if the correct precipitate phases are to be retained. In contrast, the effective Y solubility in the pipe diffusion model is enhanced by strong Y-dislocation binding. This leads to reasonable coarsening rates while allowing the O chemical potential to remain within the range of stability for the Ti-bearing oxide phases.

Note that the coarsening rates in both models are monotonically increasing with the product of the Y diffusion coefficient, Y solubility, and the Gibbs-Thompson effect as mediated by the oxide interfacial energy. Therefore, in principle it would be possible to construct a standard model that matched the experimentally measured coarsening rates by assigning a much higher diffusion coefficient to Y atoms and thereby compensate for the very low Y solubility. However, the effective heats of Y solution in the standard and pipe models differ by an amount equal to the Y dislocation binding energy of -241.2 kJ/mol. As the activation energy of Y matrix diffusion is only 218.1 kJ/mol, it is clear that no physically reasonable value of the Y diffusion coefficient can make up for the gulf between the Y solubilities in the standard and pipe diffusion models. Thus, there does not seem to be any combination of interfacial energies and O chemical potential values for which the standard model can reproduce both the correct nanoprecipitate phases and coarsening rates that match experimental observations, these features can only be self-consistently reproduced by the pipe diffusion model. This result is in agreement with the conclusions of Cunningham et al [6, 11], who observed that no physically plausible mechanism could seem to account for the nanoprecipitate coarsening measured in MA957 that did not include the effects of dislocation pipe diffusion.

Cunningham et al. [6] modeled coarsening kinetics using the simplified expressions summarized by Ardell [69]. Cunningham notes that the change in mean precipitate radius during

aging is best described by a linear relationship with time raised to the power 1/5, characteristic of coarsening via pipe diffusion. Furthermore Cunningham noted that the product of the interface energy, matrix solubility, and matrix diffusion coefficient, which governs coarsening via bulk diffusion, is many orders of magnitude too low to account for observed coarsening rates. The increased solubility and higher diffusion coefficient of Y on dislocations rationalizes these experimental observations. Cunningham et al. [6] also report TEM observations of a high degree of oxide NF-dislocation association under long-term thermal aging conditions, which corroborates the importance of dislocation diffusion in oxide nanoprecipitate coarsening. This association can arise through a simple mechanism of dislocation climb and pinning by the nanoprecipitates during aging [11].

3.3 Predictions of the fitted model for long term thermal stability and alloy design

The best-fit pipe diffusion model captures many the significant features of the oxide NF size distribution evolution in the NFA MA957 during thermal aging over a wide range of aging conditions, and can therefore be used to make predictions for conditions that have not been explored experimentally. This section presents such predictions over timespans relevant to nuclear power applications. The effects of Ti alloy content on initial nanoprecipitate phase and mean size are examined as well. Figure 9 illustrates the model predicted change in mean nanoprecipitate radius in MA957 after aging for 50 and 80 years as a function of aging temperature. Very little coarsening is predicted over these time spans in the temperature range most of interest for NFA applications (1000-1100 K). While this is an encouraging prediction, it does not account for the role that irradiation may play on nanoprecipitate size evolution, though studies have to date generally indicated that the oxide nanoprecipitates in NFAs are resistant to direct irradiation-induced dissolution [70, 71]. Note that the potential effects of irradiation on

coarsening via dislocation pipe diffusion are presently unknown and should be considered in future modeling efforts.

It has been widely reported that adding Ti to Y-based NFAs refines the mean size of the oxide NFs; however, the mechanism behind this effect is currently unknown. In Fig. 10, the predicted mean Y bearing nano-oxide radius in a Fe-14Cr-0.14Y- x Ti (at%) alloy after 3 hours at 1338 K is plotted as a function of Ti alloy content along with the corresponding oxide phase volume fractions. The model predicts a reduction in mean oxide nano-oxide size with increasing Ti alloy content, in qualitative agreement with numerous experimental observations [2, 9, 72, 73]. This reduction in size also corresponds to a gradual change in the dominant oxide phase, from Y_2O_3 to Y_2TiO_5 and finally to $Y_2Ti_2O_7$. In the present model, the promotion of the complex Y-Ti oxide phases over Y_2O_3 results in a smaller mean particle size due to the following mechanisms: (i) the phases Y_2TiO_5 and $Y_2Ti_2O_7$ have moderately stronger driving forces for precipitation than Y_2O_3 , (ii) the presence of both Ti and Y monomers provides more opportunities for nucleation of the Y-Ti-O phases to occur, and (iii) the Ti-containing oxide phases have a lower interfacial energy than Y_2O_3 within the fitting and assumptions of our model, thus increasing the nucleation rate. Taken together, these mechanisms result in a higher number of smaller oxide NFs. It should be noted that the same qualitative behavior is observed even if the interfacial energies of all three Y-bearing oxides are assumed to be equal, though the magnitude of the refinement is reduced. According to the model predictions, most of the particle size refinement of Ti is achieved by around 0.16 at% Ti, or slightly greater than a Ti:Y ratio of 1.

4 Conclusions

A framework has been developed for studying the thermodynamic and kinetic aspects of oxide precipitation in NFAs. This framework draws upon available thermodynamic and kinetic

data, first principles-based Y-dislocation interaction energetics, and a rate theory cluster dynamics-based description of precipitation kinetics. The framework is used to explore nucleation, growth and coarsening mechanisms including phase stability and nanoprecipitate evolution as functions of alloy composition. While a number of approximations were adopted in assembling this framework, with reasonable physical parameter values the resulting model adequately captures many phenomena observed during nanoprecipitate evolution in NFAs. However, significant fitting to experimental data was employed to evaluate two key parameters: the specific oxide-matrix interfacial energy and the reservoir O chemical potential. Furthermore, the Y dislocation diffusion coefficient was treated highly approximately. This model should therefore be regarded as being semi-empirical.

The principal conclusions derived from the model are as follows

- The precipitate volume fractions and phase identities predicted by the equilibrium thermodynamic model are in reasonably good agreement with many experimental observations. This result provides additional evidence that the O-rich nanoprecipitates in most NFAs are primarily equilibrium Y-Ti oxide phases.
- DFT calculations of the higher solubility of Y on dislocations combined with fitted interfacial energy and reservoir O potential parameters provide a good fit to coarsening data in the NFA MA957, supporting the conclusion that dislocation pipe diffusion is the dominant coarsening mechanism. This corroborates the conclusions of Cunningham et al. [6] based upon simplified analysis of coarsening data.
- The extrapolations of the best-fit model indicate that little coarsening of the nanoprecipitates in the NFA MA957 should be expected over timespans of 50-80 years at operating temperatures relevant to nuclear power applications. This is in agreement with

Cunningham et al. who predicted the precipitates would be thermally stable up to about 1123 K [6, 11].

- The particle refining benefit of small additions of Ti is predicted to be due to the increased opportunity and driving force for nucleation of Y-Ti oxides over Y_2O_3 . The majority of this beneficial effect is achieved for nominal alloy compositions with Ti:Y ratio slightly greater than 1. Thus this framework also provides important guidance to alloy design efforts as well as experiments tailored to testing the model predictions.

The model also provides significant mechanistic insights into nanoprecipitate behavior in NFAs. The thermodynamic component of the model yields strong driving forces for the precipitation of Y-Ti oxides that result in very rapid nucleation, even assuming rather high interfacial energies of 1-2 J/m². In addition to the large formation enthalpy of the oxide phases, these large driving forces arise in part from the very low solubility of Y in the Fe-Cr matrix. This low solubility prohibits coarsening through Ostwald ripening and consequently the nm-scale precipitates remain quite stable after the rapid nucleation period. In fact, under standard assumptions of precipitation theory significant coarsening of the nanoprecipitates does not seem possible at all, and some additional mechanism such as pipe diffusion must be invoked to reproduce the rates observed experimentally. The best-fit pipe diffusion model yields an effective activation energy for coarsening of 603 kJ/mol, comparable but slightly lower than the value of 673 kJ/mol determined by Cunningham et al [6]. Given that the activation energy of Y diffusion in the dislocation (D_Y^D) is estimated to be only 109 kJ/mol, it is evident that the coarsening rate is dominated by Y solubility.

This research can serve as a foundation for future modeling efforts of NFA processing and ageing. Furthermore, the current framework may be improved and expanded in a number of

ways. Further study on interfacial energetics, Y-dislocation interactions and diffusion, and nanoparticle nucleation pathways would all lead to important model refinements. Additionally, the present model deals only with thermal effects on the nanoprecipitate distribution, and the long-term impact of irradiation on the nanoprecipitates remains a particularly significant open question.

Appendix 1

A1.1 Basic formalism and equations

In the kinetic theory of Slezov, the ensemble of precipitates of a given phase in the system is described by the size distribution function $f^\phi(n, t)$, which specifies the concentration of precipitates or clusters of phase ϕ containing n constituent structural units at time t . In the present model we assume that the O atoms diffuse at a much higher rate than the metal atoms, and consequently the growth of the oxide precipitates is controlled kinetically by the aggregation of Y and Ti monomers. Therefore, for the purposes of describing the growth kinetics, the constituent structural units are taken to be integer numbers of Y and Ti atoms in proportions that match the Y:Ti ratios of the four oxide phases considered for precipitation. Specifically, these are

$$\begin{aligned}
 n^{203} &= 1Y \\
 n^{227} &= 1Y + 1Ti \\
 n^{215} &= 2Y + 1Ti \\
 n^{012} &= 1Ti
 \end{aligned}
 \tag{Eqn. A1}$$

O is not included as a part of the constituent structural units because it is assumed that O arrives at the cluster nearly instantaneously on the timescale of Y and Ti diffusion, so the kinetics of O diffusion is not included explicitly in the model equations. The expressions for the volume and

the free energy per structural unit of the oxide phases are defined assuming O joins the oxide precipitates in the correct stoichiometric proportions instantaneously from the background reservoir of O.

The evolution of the function $f^\phi(n, t)$ for each oxide phase ϕ is described by the following partial differential equation:

$$\frac{\partial f^\phi(n, t)}{\partial t} = -\frac{\partial J^\phi(n, t)}{\partial n} \quad \text{Eqn. A2}$$

where $J^\phi(n, t)$ is the flux in cluster size space. Because $f^\phi(n, t)$ is discrete in cluster size n , in practice Eqn. A2 may be recast as a set of ordinary differential equations as:

$$\frac{df_n^\phi(t)}{dt} = J_{n-1}^\phi - J_n^\phi \quad \text{Eqn. A3}$$

where $f_n^\phi(t)$ is the concentration of clusters of phase ϕ and size n and J_n^ϕ is the flux of clusters of phase ϕ between sizes n and $n + 1$. These fluxes are expressed as

$$J_n^\phi = w_n^\phi \left\{ f_n^\phi(t) - f_{n+1}^\phi(t) \exp \left[\frac{\Delta G^\phi(n+1) - \Delta G^\phi(n)}{RT} \right] \right\} \quad \text{Eqn. A4}$$

The term w_n^ϕ is the rate at which a cluster of size n incorporates a constituent structural unit from the matrix phase and grows to size $n + 1$. Under the assumptions that the clusters are spherical and grow by three dimensional monomer diffusion from the matrix phase to the surface of the cluster, the rates w_n^ϕ can be written as

$$w_n^\phi = 4\pi \frac{a_p^\phi}{\omega_p^\phi} D_{eff}^\phi n^{1/3} \quad \text{Eqn. A5}$$

where a_p^ϕ is the characteristic length of a constituent structural unit in phase ϕ . This parameter is equal to the radius of a sphere with volume equal to the volume per structural unit of phase

ω_p^ϕ :

$$a_p^\phi = \left[\frac{3\omega_p^\phi}{4\pi} \right]^{1/3} \quad \text{Eqn. A6}$$

D_{eff}^ϕ represents an effective diffusion coefficient that controls the precipitate growth kinetics of phase ϕ . This parameter is defined according to

$$\frac{1}{D_{eff}^\phi} = \sum_i \frac{(v_i^\phi)^2}{x_i D_i} \quad \text{Eqn. A7}$$

with $i = \text{Y, Ti}$. x_i and D_i are the mole fraction and diffusion coefficient of species i in the matrix phase, respectively. Under the assumption that the Y:Ti ratio of precipitates of a given phase is constant for all precipitate sizes, the parameter v_i^ϕ is equal to the number of atoms of species i per constituent structural unit of precipitate phase ϕ , as summarized in Eqn. A1.

The term $\Delta G^\phi(n)$ is the change in free energy corresponding to the formation of a cluster of phase ϕ containing n structural units from the constituent atoms in solution in the matrix phase. This parameter is defined as

$$\Delta G^\phi(n) = n \left(g_p^\phi - \sum_i v_i^\phi \mu_i \right) + \sigma^\phi(n). \quad \text{Eqn. A8}$$

Here, g_p^ϕ is the free energy per structural unit of the precipitate phase, μ_i is the chemical potential of species i in the matrix phase, and $\sigma^\phi(n)$ is the interfacial energy of a cluster of phase ϕ and size n . To evaluate $\sigma^\phi(n)$, we assume the clusters are spherical and have a

constant specific interfacial energy. Because the Y and Ti contents in NFAs are fairly dilute (typically 1 at% or less), the chemical potentials can be expressed to good approximation as

$$\mu_i = \mu_i^0(T) + RT \ln(x_i) \quad \text{Eqn. A9}$$

In terms of the thermodynamic parameters used to describe the solid solution phase, the term $\mu_i^0(T)$ is computed by the following expression:

$$\mu_i^0(T) = {}^0G_i^\alpha + x_{Fe} \sum_j {}^{(j)}L_{Fei}^\alpha x_{Fe}^j + x_{Cr} \sum_j {}^{(j)}L_{Cri}^\alpha x_{Cr}^j \quad \text{Eqn. A10}$$

The free energy per structural unit g_p^ϕ is defined as the molar free energy of the precipitate phase as computed in Table 1 normalized by the moles of structural units per mole of oxide.

When numerically integrating the set of ordinary differential equations defined by Eqn. A3, the following set of initial and boundary conditions are applied:

$$\begin{aligned} f_n^\phi(0) \Big|_{n>1} &= 0 \\ f_1^\phi(t) &= \prod_i x_i^{\nu_i^\phi} \\ x_i(0) &= x_i^0 \\ x_i(t) &= x_i(0) - \sum_\phi \left[\nu_i^\phi \sum_{n=1}^{n_{\max}} n f_n^\phi(t) \right] \\ \frac{df_n^\phi(t)}{dt} \Big|_{n \geq n_{\max}} &= 0 \end{aligned} \quad \text{Eqn. A11}$$

where x_i^0 is the initial alloy concentration of species i , and $n_{\max}$ is the maximum cluster size considered. In this study, $n_{\max}$ was set to 10,000 structural units, which corresponds to precipitates of about 10 nm in diameter.

A1.2 Formal considerations for the dislocation pipe diffusion mechanism

In order to incorporate precipitate growth and especially coarsening via dislocation diffusion into this model, some modifications to the basic equations are necessary. Conceptually, this model assumes that each oxide precipitate or cluster is intersected by some number of dislocations, and that these dislocations act as pipes through which monomers diffuse to join or leave the clusters. Therefore, the coefficients w_n^ϕ must be rederived assuming a pipe diffusion mechanism, rather than normal three dimensional bulk diffusion. In performing this derivation, we follow the approach of Clouet et al. [74]. We assume that diffusion to the surface of a given cluster of size n with radius r_n occurs through N^D dislocation pipes of cross sectional area A^D , each intersecting the cluster normal to the surface. By the approach of Clouet et al., the concentration profile within each pipe is described by

$$x_i(r) = x_i^\infty \frac{r - r_n}{r} \quad \text{Eqn. A12}$$

where x_i^∞ is the average concentration of species i far from the cluster surface and r is the radial distance from the center of the cluster along the axis of the pipe. The rate $w_{i,n}^\phi$ for species i is then computed by integrating the flux through the particle surface. For a dislocation diffusion mechanism, this yields

$$w_{i,n}^{\phi_D} = \frac{N^D A^D x_i^\infty D_i^D}{\omega_p^\phi r_n} \quad \text{Eqn. A13}$$

where D_i^D is the dislocation diffusion coefficient of species i . In this study, we assume N^D is equal to 2 (corresponding to one dislocation completely intersecting each precipitate) and A^D is equal to the area of a circle with radius given by the lattice parameter of α -Fe. Ardell [69] has derived a similar expression for precipitate coarsening rate by a pipe diffusion mechanism that

explicitly includes both the absorption and emission components of the mobile particle flux through the precipitate surface, whereas here the rate coefficients $w_{i,n}^\phi$ indirectly account for the particle emission by the detailed balance formulation in Eqn. A4.

In the present model, it is assumed that clusters of each phase can nucleate, grow and coarsen through both normal bulk diffusion and dislocation diffusion simultaneously. In practice, this is implemented by distinguishing between clusters of the oxide phases residing in the undefected matrix phase, designated ϕ , and those residing on dislocations, designated ϕ_D . The kinetics of the former are described using Eqn. A3, while the later are described using the following equation, which allows for both normal bulk diffusion and pipe diffusion effects to occur simultaneously:

$$\frac{df_n^{\phi_D}(t)}{dt} = [J_{n-1}^{\phi_D} + I_{n-1}^{\phi_D}] - [J_n^{\phi_D} + I_n^{\phi_D}] \quad \text{Eqn. A14}$$

where the terms $J_n^{\phi_D}$ and $I_n^{\phi_D}$ are the fluxes of clusters of species ϕ_D through normal bulk diffusion and dislocation diffusion, respectively. The dislocation diffusion fluxes are defined by

$$I_n^{\phi_D} = w_n^{\phi_D} \left\{ f_n^{\phi_D}(t) - f_{n+1}^{\phi_D}(t) \exp \left[\frac{\Delta G^{\phi_D}(n+1) - \Delta G^{\phi_D}(n)}{RT} \right] \right\} \quad \text{Eqn. A15}$$

When evaluating the dislocation diffusion fluxes, it is assumed that only the Y atoms interact strongly with the dislocations. This assumption is based on the following observations: First, some APT measurements indicate that Y segregation to dislocations is much stronger in NFAs than Ti segregation [16]. Second, Y is much less soluble in Fe than Ti [75, 76] but is strongly bound to dislocations (see below). Therefore, the growth and coarsening rates of Y-Ti oxide nanoprecipitates are most likely rate-limited by Y diffusion and solubility, respectively [6]. The mechanism of Ti aggregation can be treated by assuming local equilibrium and thus will not

have a large impact on the aggregate kinetics. Under this assumption, the effective coefficients of aggregation $w_n^{\phi_D}$ for the dislocation diffusion fluxes are expressed by

$$\begin{aligned}\frac{1}{w_n^{\phi_D}} &= \frac{(v_{Ti}^{\phi_D})^2}{w_{Ti,n}^{\phi}} + \frac{(v_Y^{\phi_D})^2}{w_{Y,n}^{\phi_D}}, \\ w_{Ti,n}^{\phi} &= 4\pi \frac{a_p^{\phi}}{\omega_p^{\phi}} x_{Ti} D_{Ti} n^{1/3}, \\ w_{Y,n}^{\phi_D} &= \frac{N^D A^D x_Y^D D_Y^D}{\omega_p^{\phi} r_n x_{tot}^D}\end{aligned}\tag{Eqn. A16}$$

where D_Y^D is the diffusion coefficient of Y in the dislocation pipe and x_Y^D is the mole fraction of Y atoms on dislocation sites. The term x_{tot}^D is the total fraction of dislocation sites in the system, which is assumed to be equal to the volume fraction of dislocation pipes, defined by

$$x_{tot}^D = \rho^D A^D \tag{Eqn. A17}$$

where ρ^D is the dislocation density. The free energy differences $\Delta G^{\phi_D}(n)$ are defined using Eqn. A8, except that the chemical potential of Y is now evaluated for a Y atom in the dislocation core, defined approximately as:

$$\mu_Y^D = \mu_Y^0(T) + \Delta E_Y^D + RT \ln \left[\frac{x_Y^D}{x_{tot}^D} \right] \tag{Eqn. A18}$$

where ΔE_Y^D is the energy of a Y atom in a dislocation core relative to the energy of a Y atom in bulk, undefected Fe.

Throughout the evolution of the functions $f_n^{\phi}(t)$ and $f_n^{\phi_D}(t)$, the monomer concentrations x_{Ti} , x_Y , and x_Y^D must be tracked explicitly. This is accomplished with the following set of equations:

$$\begin{aligned}
\frac{dx_{Ti}}{dt} &= - \left[\sum_{\phi} \nu_{Ti}^{\phi} \sum_{n=1}^{n_{Max}} n \frac{df_n^{\phi}(t)}{dt} + \sum_{\phi_D} \nu_{Ti}^{\phi_D} \sum_{n=1}^{n_{Max}} n \frac{df_n^{\phi_D}(t)}{dt} \right] \\
\frac{dx_Y}{dt} &= - \left[\sum_{\phi} \nu_Y^{\phi} \sum_{n=1}^{n_{Max}} n [J_{n-1}^{\phi} - J_n^{\phi}] + \sum_{\phi_D} \nu_Y^{\phi_D} \sum_{n=1}^{n_{Max}} n [J_{n-1}^{\phi_D} - J_n^{\phi_D}] \right] - K_{YD} \\
\frac{dx_Y^D}{dt} &= - \sum_{\phi_D} \nu_Y^{\phi_D} \sum_{n=1}^{n_{Max}} n [I_{n-1}^{\phi_D} - I_n^{\phi_D}] + K_{YD}
\end{aligned} \tag{Eqn. A19}$$

The term K_{YD} is the net rate at which Y atoms enter dislocation pipes. This rate may be cast in the formalism of Slezov as flux in the form of Eqn. A4, describing the reaction of Y atoms on the lattice with dislocation sites to form Y bound to dislocations. The resulting expression is

$$K_{YD} = 4\pi D_Y \frac{a_m^{Fe}}{\omega_m^{Fe}} \left[x_Y (x_{tot}^D - x_Y^D) - x_Y^D \exp \left[\frac{\Delta E_Y^D}{RT} \right] \right] \tag{Eqn. A20}$$

where a_m^{Fe} and ω_m^{Fe} are the atomic radius and volume of Fe, respectively. The conditions defined in Eqn. A11 still apply, with the following modifications for the monomer concentrations:

$$\begin{aligned}
x_Y(0) &= x_Y^0 (1 - x_{tot}^D) \\
x_Y^D(0) &= x_Y^0 x_{tot}^D
\end{aligned} \tag{Eqn. A21}$$

Acknowledgements

Research from L. Barnard was conducted under appointment to the Rickover Graduate Fellowship Program. Financial support for D. Morgan and for equipment and travel for L. Barnard was provided by the DOE Nuclear Engineering University Program (NEUP), initially under Grant Number 10-888 and then under NSF DMR-Award 110564. This work benefitted

from the use of the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575.

Bibliography

- [1]M.K. Miller, C.M. Parish, Q. Li, Mater Sci Tech-Lond, 29, (2013), 1174-1178
- [2]G.R. Odette, M.J. Alinger, B.D. Wirth, Annual Review of Materials Research, 38, (2008), 471-503
- [3]G.R. Odette, D.T. Hoelzer, Jom-Us, 62, (2010), 84-92
- [4]S. Ukai, M. Fujiwara, Journal of Nuclear Materials, 307, (2002), 749-757
- [5]S.J. Zinkle, J.T. Busby, Materials Today, 12, (2009), 12-19
- [6]N. Cunningham, G.R. Odette, Acta Materialia, (submitted 2013),
- [7]J.H. Kim, T.S. Byun, D.T. Hoelzer, C.H. Park, J.T. Yeom, J.K. Hong, Mat Sci Eng a-Struct, 559, (2013), 111-118
- [8]P. Miao, G.R. Odette, T. Yamamoto, M. Alinger, D. Klingensmith, Journal of Nuclear Materials, 377, (2008), 59-64
- [9]J. Ribis, Y. de Carlan, Acta Materialia, 60, (2012), 238-252
- [10]Y. Wu, E.M. Haney, N.J. Cunningham, G.R. Odette, Acta Materialia, 60, (2012), 3456-3468
- [11]N. Cunningham, Study of structure, composition, and stability of Y-Ti-O nm-scale features in nano-structured ferritic alloys, in: Mechanical Engineering and Materials Science, University of California Santa Barbara, Santa Barbara, CA, 2012.
- [12]M.J. Alinger, G.R. Odette, D.T. Hoelzer, Acta Materialia, 57, (2009), 392-406
- [13]M. Ohnuma, J. Suzuki, S. Ohtsuka, Acta Materialia, 57, (2009), 5571-5581
- [14]S.W. Kim, T. Shobu, S. Ohtsuka, T. Kaito, M. Inoue, M. Ohnuma, Materials Transactions, 50, (2009), 917-921
- [15]S. Yamashita, S. Ohtsuka, N. Akasaka, S. Ukai, S. Ohnuki, Phil Mag Lett, 84, (2004), 525-529
- [16]M.K. Miller, E.A. Kenik, K.F. Russell, L. Heatherly, D.T. Hoelzer, P.J. Maziasz, Mat Sci Eng a-Struct, 353, (2003), 140-145
- [17]M.K. Miller, K.F. Russell, D.T. Hoelzer, Journal of Nuclear Materials, 351, (2006), 261-268
- [18]M.K. Miller, D.T. Hoelzer, E.A. Kenik, K.F. Russell, Journal of Nuclear Materials, 329, (2004), 338-341
- [19]E.A. Marquis, Appl Phys Lett, 93, (2008),

- [20]C.A. Williams, G.D.W. Smith, E.A. Marquis, Scripta Materialia, 67, (2012), 108-111
- [21]C.A. Williams, G.D.W. Smith, E.A. Marquis, Ultramicroscopy, 125, (2013), 10-17
- [22]C.A. Williams, P. Unifantowicz, N. Baluc, G.D.W. Smith, E.A. Marquis, Acta Materialia, 61, (2013), 2219-2235
- [23]L. Barnard, G.R. Odette, I. Szlufarska, D. Morgan, Acta Materialia, 60, (2012), 935-947
- [24]N.J. Cunningham, Y. Wu, A. Etienne, E.M. Haney, G.R. Odette, E. Stergar, D.T. Hoelzer, Y.D. Kim, B.D. Wirth, S.A. Maloy, Journal of Nuclear Materials, 444, (2014), 35-38
- [25]W.P. Gong, D.J. Li, Z.S. Chen, F. Zheng, Y. Liu, Y. Du, B.Y. Huang, Calphad, 33, (2009), 624-627
- [26]A. De Bremaecker, Journal of Nuclear Materials, 428, (2012), 13-30
- [27]S. Ukai, S. Ohtsuka, Energy Materials, 2, (2007), 26-35
- [28]R. Luoma, *A Thermodynamic Analysis of the System Fe-Cr-Ni-C-O*, “The” Finnish academies of technology., 2002.
- [29]V.V. Slezov, Kinetics of first order phase transitions, in, Wiley-VCH, Weinheim, 2009, pp. 1 online resource (xiv, 415 p.).
- [30]V.V. Slezov, J. Schmelzer, Phys Rev E, 65, (2002),
- [31]P. Klugkist, C. Herzig, Physica status solidi, 148, (1995), 413-421
- [32]D. Murali, B.K. Panigrahi, M.C. Valsakumar, C.S. Sundar, Journal of Nuclear Materials, 419, (2011), 208-212
- [33]G.R. Love, Acta Metall Mater, 12, (1964), 731-737
- [34]K.M. Miller, K.W. Ingle, A.G. Crocker, Acta Metall Mater, 29, (1981), 1599-1606
- [35]Y. Mishin, C. Herzig, Mat Sci Eng a-Struct, 260, (1999), 55-71
- [36]R.C. Picu, D. Zhang, Acta Materialia, 52, (2004), 161-171
- [37]S.H. Song, X.M. Chen, L.Q. Weng, Mat Sci Eng a-Struct, 528, (2011), 7196-7199
- [38]A.C. Hindmarsh, P.N. Brown, K.E. Grant, S.L. Lee, R. Serban, D.E. Shumaker, C.S. Woodward, Acm T Math Software, 31, (2005), 363-396
- [39]P. Franciosi, Acta Metall Mater, 31, (1983), 1331-1342
- [40]P.C. Gehlen, Rosenfie.Ar, G.T. Hahn, J Appl Phys, 39, (1968), 5246-&
- [41]G. Kresse, Thesis, in, Technische University at Wien, 1993.
- [42]G. Kresse, J. Furthmuller, Physical Review B, 54, (1996), 11169-11186
- [43]G. Kresse, J. Furthmuller, Computational Materials Science, 6, (1996), 15-50
- [44]G. Kresse, J. Hafner, Physical Review B, 47, (1993), 558-561
- [45]J.P. Perdew, K. Burke, M. Ernzerhof, Physical Review Letters, 77, (1996), 3865-3868
- [46]P.E. Blochl, Phys. Rev. B, 50, (1994), 953
- [47]G. Triantafyllou, G.N. Angelopoulos, P. Nikolopoulos, Journal of Materials Science, 45, (2010), 2015-2022
- [48]X. Mantzouris, N. Zouvelou, D. Skarmoutsos, P. Nikolopoulos, F. Tietz, Journal of Materials Science, 40, (2005), 2471-2475
- [49]M. Alinger, Thesis, in, University of California Santa Barbara, 2004.
- [50]M. Cancarevic, M. Zinkevich, F. Aldinger, Calphad, 31, (2007), 330-342
- [51]Z. Oksiuta, N. Baluc, Advanced Materials Research, 59, (2009), -
- [52]C. Heintze, M. Hernández-Mayoral, A. Ulbricht, F. Bergner, A. Shariq, T. Weissgärber, H. Frielinghaus, Journal of Nuclear Materials, 428, (2012), 139-146
- [53]P. Olier, J. Malaplate, M.H. Mathon, D. Nunes, D. Hamon, L. Toulbi, Y. de Carlan, L. Chaffron, Journal of Nuclear Materials, 428, (2012), 40-46
- [54]Z. Száraz, G. Török, V. Kršjak, P. Hähner, Journal of Nuclear Materials, 435, (2013), 56-62

- [55]S.Y. Zhong, J. Ribis, V. Klosek, Y. de Carlan, N. Lochet, V. Ji, M.H. Mathon, *Journal of Nuclear Materials*, 428, (2012), 154-159
- [56]V.G. Gavriluk, N.P. Kushnareva, V.G. Prokopenko, *Fiz Met Metalloved+*, 42, (1976), 1288-1293
- [57]B. Henderson, *Defects in crystalline solids*, Edward Arnold, London,, 1972.
- [58]K. Kamber, D. Keefer, C. Wert, *Acta Metall Mater*, 9, (1961), 403-414
- [59]D.P. Petarra, D.N. Beshers, *Acta Metall Mater*, 15, (1967), 791-&
- [60]W.R. Thomas, G.M. Leak, *Proc. Phys. Soc. B*, 68, (1955), 1001-1007
- [61]E. Clouet, S. Garruchet, H. Nguyen, M. Perez, C.S. Becquart, *Acta Materialia*, 56, (2008), 3450-3460
- [62]A.W. Cochardt, G. Schoek, H. Wiedersich, *Acta Metall Mater*, 3, (1955), 533-537
- [63]J.T.M. De Hosson, *Solid State Communications*, 17, (1975),
- [64]Y.Q. Feng, C.Y. Wang, *J Alloy Compd*, 312, (2000), 219-227
- [65]K. Tapasa, Y.N. Osetsky, D.J. Bacon, *Acta Materialia*, 55, (2007), 93-104
- [66]R. Wang, *J Phys D Appl Phys*, 23, (1990), 263-265
- [67]M. Brocq, B. Radiguet, S. Poissonnet, F. Cuvilly, P. Pareige, F. Legendre, *Journal of Nuclear Materials*, 409, (2011), 80-85
- [68]J.M. Howe, *Interfaces in materials : atomic structure, thermodynamics and kinetics of solid-vapor, solid-liquid and solid-solid interfaces*, Wiley, New York, 1997.
- [69]A.J. Ardell, *Acta Metall Mater*, 20, (1972), 601-&
- [70]A.G. Certain, K.G. Field, T.R. Allen, M.K. Miller, J. Bentley, J.T. Busby, *Journal of Nuclear Materials*, 407, (2010), 2-9
- [71]M.L. Lescoat, J. Ribis, A. Gentils, O. Kaïtasov, Y. de Carlan, A. Legris, *Journal of Nuclear Materials*, 428, (2012), 176-182
- [72]P. Dou, A. Kimura, R. Kasada, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe, *Journal of Nuclear Materials*, 442, (2013), S95-S100
- [73]P. He, M. Klimenkov, R. Lindau, A. Möslang, *Journal of Nuclear Materials*, 428, (2012), 131-138
- [74]E. Clouet, A. Barbu, L. Lae, G. Martin, *Acta Materialia*, 53, (2005), 2313-2325
- [75]H. Bo, J. Wang, L. Duarte, C. Leinenbach, L.B. Liu, H.S. Liu, Z.P. Jin, *T Nonferr Metal Soc*, 22, (2012), 2204-2211
- [76]Z. Du, W. Zhang, Y. Zhuang, *Rare metals*, 16, (1996), 52-58
- [77]D. Djurovic, M. Zinkevich, F. Aldinger, *Calphad*, 31, (2007), 560-566
- [78]A.T. Dinsdale, *Calphad*, 15, (1991), 317-425
- [79]G. Ghosh, *J Phase Equilib*, 23, (2002), 310-328
- [80]B. Hasek, Thesis: Thermodynamoc modeling and first-principles calculations of the Cr-Hf-Y ternary system, in: *Materials Science and Engineering*, The Pennsylvania State University, 2010.
- [81]Y. Jiang, J.R. Smith, G.R. Odette, *Acta Materialia*, 58, (2010), 1536-1543
- [82]X. Li, M.W. Finnis, J. He, R.K. Behera, S.R. Phillpot, S.B. Sinnott, E.C. Dickey, *Acta Materialia*, 57, (2009), 5882-5891
- [83]M.G. Paton, E.N. Maslen, *Acta Crystallographica*, 19, (1965), 307-&

Captions:

Figure 1: Figure 1a (left): Atomistic model of [100](010) dislocation. The colors different {001} planes. For binding energy calculations, Y is inserted into substitutional sites 1-4, and C/N/O is inserted into interstitial site 5. b (right): Schematic illustration of the 4 dislocation array in the simulation supercell used to calculate dislocation binding energies when viewed along the [001] direction. The solid and dashed lines correspond to the planes composed of the light and dark atoms in the atomistic model of Fig. 1a, respectively.

Figure 2: Equilibrium phases predicted by the thermodynamic model as a function of O partial pressure P_{O_2} and nominal fractions of Ti and Y in the alloy Fe-14Cr- x_Y - x_{Ti} at 1273 K. Dotted lines correspond to the equilibrium partial pressures for the reactions $FeO \leftrightarrow Fe + 1/2O_2$, $Cr_2O_3 \leftrightarrow 2Cr + 3/2O_2$, and $TiO \leftrightarrow Ti + O_2$.

Figure 3: Comparison of measured precipitate volume fractions for alloys of different compositions (citations in text) with the equilibrium oxide volume fractions predicted by the thermodynamic model.

Figure 4: Predicted equilibrium oxide fraction (left axis) and measured Charpy upper shelf impact energy measured by Oksiuta et al. [51] (right axis) as a function of Ti alloy content in an Fe-12Cr-0.2Y- x Ti (at%) NFA.

Figure 5: Map of calculated mean oxide nanoparticle sizes as in σ_0 -- P_{O_2} space after simulated heat treatment of the MA957 solid solution at 1338 K for 3 hours. The dashed line corresponds to measured mean particle size in the MA957 material prior to aging. No data was collected for the gray region, as the interfacial energies in this region are too high for nucleation to occur

Figure 6: Volume fractions of calculated nanoparticle distributions along the trajectory AB in Fig. 5.

Figure 7a (left): Best fit values for the interfacial energies used in the kinetic precipitation model, using the form of Eqn. 5. b (right): Best fit values of the O chemical potential, in terms of equivalent P_{O_2} . Curves corresponding to equilibrium values of P_{O_2} for the reactions $2Cr + 3/2 O_2 \leftrightarrow Cr_2O_3$ and $Ti + O_2 \leftrightarrow TiO_2$ are included for reference.

Figure 8: Mean $Y_2Ti_2O_7$ precipitate radius in alloy MA957 as a function of time during thermal aging. Data points represent experimental measurements [6, 49] while the curves represent the calculations of the best fit models. The colors of the solid and dashed lines correspond to the colors of the markers for the matching heat treatment.

Figure 9: Predictions from the best fit pipe diffusion model of the change in mean $Y_2Ti_2O_7$ precipitate radius in alloy MA957 after 50 and 80 years as a function of aging temperature.

Figure 10: Model predictions from the best fit pipe diffusion model of the Y and Y-Ti oxide mean precipitate radius and volume fractions after heat treatment for 3 hours at 1338 K as a function of Ti content in an Fe-14Cr-0.14Y-xTi alloy. A dashed line indicates an alloy composition of 0.14 Ti, giving a Y:Ti ratio of 1:1.

Table 1: CALPHAD parameters used in the thermodynamic and kinetic models. All parameters have units J/mol.

Table 2: Physical quantities and parameters used in the kinetic precipitation model.

Table 3: Solute-dislocation binding energies resulting from DFT calculations of this study as well as other theoretical methods and experimental measurements from the literature.

Table 1:

Model	Expression	Source
Y ₂ O ₃ (bixbyite)	$G^{203} = -1976462 + 731.6512T - 121.881T \ln T - 0.00506T^2 + 1090000T^{-1} - 13000000T^{-2} - \frac{3}{2}G_{O_2}^{gas}(T, P_{O_2})$	[77]
TiO ₂ (rutile)	$G^{012} = -976986.6 + 484.74037T - 77.76175T \ln T + 1683920T^{-1} - 67156800T^{-2} - G_{O_2}^{gas}(T, P_{O_2})$	[50]
Y ₂ Ti ₂ O ₇ (pyrochlore)	$G^{227} = G^{203} + 2G^{012} - 65569.9 - 37.19T$	[25]
Y ₂ TiO ₅ (orthorhombic)	$G^{215} = G^{203} + G^{012} - 31976.9 - 21.3T$	[25]
Y (α)	${}^0G_Y^\alpha = -1297.798 + 134.528352T - 27.3038477T \ln T - 0.541758 \times 10^{-3}T^2 - 0.305012 \times 10^{-6}T^3$	[78]
Ti (α)	${}^0G_{Ti}^\alpha = 6667.385 + 105.366379T - 22.3771T \ln T + 1.21707 \times 10^{-3}T^2 - 0.84534 \times 10^{-6}T^3 - 2002750T^{-1}$	[78]
O ₂ (gas)	$\frac{1}{2}G_{O_2}^{gas} = -6568.763 + 12.659879T - 16.8138T \ln T - 0.595797 \times 10^{-3}T^2 + 0.006781 \times 10^{-6}T^3 + 4383200T^{-1} + RT \ln P_{O_2}$	[78]
Solid Solution (α)	${}^{(0)}L_{FeY}^\alpha = 100000$	[75, 76, 79, 80]
	${}^{(0)}L_{CrY}^\alpha = 300000$	
	${}^{(1)}L_{CrY}^\alpha = 230000$	
	${}^{(0)}L_{FeTi}^\alpha = -69241.924 + 25.246T + 0.0001T^2 + 120000T^{-1}$	
	${}^{(1)}L_{FeTi}^\alpha = 5018.986 - 4.992T$	
	${}^{(2)}L_{FeTi}^\alpha = 23023.241 - 13.110T$	
	${}^{(0)}L_{CrTi}^\alpha = -2247.87 + 9.14144T$	
	${}^{(1)}L_{CrTi}^\alpha = 198.73$	

Table 2:

Parameter	Description	Value	Source
ω_p^ϕ	Volume per structural unit of the precipitate phase ϕ (m ³)	Y ₂ O ₃ : 3.9×10 ⁻²⁹ Y ₂ Ti ₂ O ₇ : 6.6×10 ⁻²⁹ Y ₂ TiO ₅ : 1.1×10 ⁻²⁸ TiO ₂ : 3.1×10 ⁻²⁹ Fe: 1.2×10 ⁻²⁹	[88-90]
D_i^0	Pre-exponential factor for diffusion coefficient of species i (m ² /sec)	Ti: 0.21 Y: 8.0×10 ⁻⁷ Y (dislocation): 8.0×10 ⁻⁷	[38, 39]
Q_i	Activation energy for diffusion coefficient of species i (kJ/mol)	Ti: 293.2 Y: 218.1 Y (dislocation): 109.0	[38, 39, 46-50]
σ_0	Intercept of specific interfacial energy expression Eqn. 28 (J/m ²)	Pipe diffusion model: 1.70 Standard model: 2.57	Best model fits
A	Slope of specific interfacial energy expression Eqn. 28 (J/m ²)	-1.2	Interpolation of data from [60, 61]
μ_o	Background O chemical potential (kJ/mol)	Pipe diffusion model: -415.1 Standard model: -474.4	Best model fits
ΔE_Y^D	Y-Dislocation binding energy (kJ/mol)	-241.2	DFT calculation in this work

Table 3

Element	Binding energy (eV)	Method	Source
C	-0.66-0.75, -0.70 mean	Empirical potential	[61, 63, 65]
	-0.50-0.75, -0.62 mean	Elasticity theory	[62, 66]
	-0.45-0.75, 0.57 mean	Experiment	[56-58]
	-0.67	DFT calculation	This study
N	-0.40-0.80, -0.56 mean	Experiment	[59, 60]
	-0.35	DFT calculation	This study
O	-1.0	Elasticity theory	[66]
	-0.90	DFT calculation	This study
	Y Binding energy (eV)	Y occupation site	Supercell size
Y	-2.62	1	6×6×3
	-2.47	1	6×6×4
	-2.46	1	6×8×3
	-2.61	1	8×6×3
	-2.11	2	8×6×3
	-2.17	3	8×6×3
	0.29	4	8×6×3