On Nano-Oxide Coarsening Kinetics in the Nanostructured Ferritic Alloy MA957: A Mechanism Based Predictive Model

N.J. Cunningham^{*a}, M.J. Alinger^{a1}, D. Klingensmith^a, Y. Wu^a, and G.R. Odette^a

^a University of California, Santa Barbara, CA 93106, USA

Present Address:

¹ GE Global Research, 1 Research Circle, MB277 Niskayuna, NY 12309, USA

^{*}Corresponding author Nicholas Cunningham njc@nylerrresearch.com

Abstract

Nanostructured ferritic alloys are dispersion strengthened and imbued with remarkable neutron irradiation damage tolerance by an ultrahigh density of nano-oxide precipitates that must remain stable under prolonged high temperature service. Here, previously reported long-time and high-temperature thermal aging data is used to derive a simple, but physically based and quantitatively predictive nano-oxide coarsening model using least square fits to equations representing different underlying mechanisms. A dislocation pipe diffusion model adequately fit the data with a dislocation-detachment climb mechanism providing the best fit. This model is consistent with microstructural observations and recently reported thermo-kinetic nano-oxide nucleation, growth and coarsening simulations that rationalize the underlying physics of coarsening. It is predicted that the nano-oxides will remain fully stable up to 900°C. This remarkable coarsening resistance is due to the extremely low matrix solubility and diffusion rate of Y in equilibrium with $Y_2Ti_2O_7$ that activates lower resistant paths along dislocations.

KEY WORDS: Long term thermal aging; nanostructured ferritic alloy; coarsening; pipe-diffusion; nano-oxides.

1. Introduction

The thermal stability of nanostructured ferritic alloys (NFAs) is critical to their use in advanced fission and future fusion reactors. NFAs are typically 14Cr, 1-3W iron alloys dispersion strengthened by an ultrahigh number (order $5 \times 10^{23}/\text{m}^3$) of stable Y-Ti-O nm-scale oxides (NOs) ≈ 2.5 nm in diameter. The stability of the NOs at expected operating temperatures of up to $\approx 800^\circ\text{C}$ or higher is particularly important since they both strengthen the NFA and stabilize critical dislocation and grain structures [1]. In addition to high strength and creep resistance, the NOs result in remarkable resistance to neutron radiation damage [1-3]. The NOs trap and promote the recombination of excess radiation induced vacancies and self-interstitials, and allow operation at high temperatures above the displacement damage accumulation regime. More importantly, the NOs sequester high concentrations of He in nm-scale interface bubbles, greatly mitigating the otherwise enormously deleterious effect of this insoluble element, which is especially important in fusion applications.

The small NO Y-Ti-O features in MA957, and similar NFAs that are often called (X)YWT, where X is the Cr content, are primarily the complex oxide $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore phase [2-4]. However, in this paper we refer to them simply as NOs, except in the more detailed mechanism discussion Section 5. Since NFA strength and irradiation tolerance depend on the NO mean diameter (d), number density (N) and volume fraction (f), understanding the mechanisms and associated thermodynamics and kinetics of coarsening, as well as developing predictive models, are required to qualify them for nuclear applications.

Thermal aging studies by a number of researchers suggest the NOs in NFAs are extremely stable [5-14]. Atom probe tomography (APT) measurements showed no significant NO coarsening in a 14YWT NFA extruded at 850°C and heat-treated at 1000°C for 1h [5]. Aging alloy MA957 and a similar 12YWT at 1300°C (~0.85 of the melting temperature) for 1 h and 24 h showed only modest coarsening [6,7]. Transmission electron microscopy studies of extracted NOs following 1 h annealing of MA957 at 1200°C found slight coarsening with average particle size increasing from ~2.5 nm to ~3.5 nm [8].

The limits of the NO thermal stability were explored in our previous small angle neutron scattering (SANS) short-to-intermediate-term aging (SITA) study of NFA MA957 for times from 0.33 up to 480 h and temperatures from 1150°C to 1400°C [9,10]. Results show little coarsening at 1150°C, modest and systematic coarsening at 1200°C, and instability at and above 1250°C. A generally similar result was obtained in another SANS and TEM study at aging temperatures from 1050°C to 1400°C at times from 1 to 10 h. Here, coarsening was not observed up to 10 h at 1250°C but was rapid at 1300 and 1400°C [11]. Our previously reported very long-term thermal aging (LTTA) study of MA957 at temperatures from 800°C to 1000°C for times up to 32.4 kh was the first to explore coarsening conditions closer to the expected maximum service temperatures and times. This study found no significant changes in either microhardness or NO size below 900°C, and only modest softening (maximum ~13%±6%) and NO coarsening at 950 and 1000°C [12,13].

While this summary demonstrates that there have been several thermal aging experiments on NFAs, few attempts have been made to quantify and model the NO

coarsening kinetics. Williams suggested that classical Ostwald ripening models can describe NO coarsening at 1200°C in a 14YWT NFA [14]. APT measurements of the average NO radius (r) were fit using a simple lattice diffusion $r = k_1 t^{1/3}$ relation. Here k_1 contains the classical combination of coarsening parameters ($DX_e\gamma$), where γ is the NO interface energy, and X_e and D are the solubility and diffusion coefficient of the rate limiting solute, respectively. However, this model does not properly account for the initial NO size. A detailed cluster dynamics (CD) thermo-kinetic oxide precipitate nucleation, growth and coarsening (NGC) model was recently reported [15], and is consistent with both of our LTТА [13] and SITA [10] databases for NFA MA957. The NGC CD model incorporates thermodynamic and kinetic data, along with first principle calculations for the Y solubility at dislocations. A pipe diffusion mechanism, where the rate limiting species Y dissolves onto and diffuses along, dislocations, was generally consistent with our data sets using reasonable fit parameters. However, this detailed thermo-kinetic treatment is far too complex to be a convenient engineering predictive tool, and largely confronts our aging results, rather than being simply fitted to the entire database, hence, it is quantitatively less accurate.

The goal for this work was to develop a simple, semi-empirical coarsening model that is independent of individual kinetic and thermodynamic parameters and their associated uncertainties, so as to more accurately predict long-term NO stability, while further independently exploring the coarsening mechanisms at play. The model was fit to our entire combined LTТА and SITA aging database [10,13] on MA957 based mainly on SANS measurements of the NO diameter evolution.

2. Materials and the Aging Databases

Alloy MA957 was originally manufactured by INCO in the late 1970s and 1980s, but is no longer commercially available. However, research continued on the remaining stock of MA957, and the alloy has been extensively characterized in many studies, reaching the status of a reference NFA. The alloying and consolidation parameters are proprietary and unknown in specific detail. However, the original patent gives the likely processing route that includes: use of -40 and -80 mesh size powders for all of the metallic alloying elements plus Y_2O_3 ; attritor milling for 24 h at 288 rpm using a 20:1 ball to powder mass ratio; and, extruding the canned powder at 1065°C at a 6:1 ratio [16]. The nominal and measured (method not given) compositions (wt.%) of MA957 from a previous study are shown in Table 1 [17].

Table 1. The nominal and measured composition of MA957.

wt. %	Fe	Cr	Ti	Mo	Y	O	Ni, Al, Mn	Si, C, S, P
Nominal	bal.	14.0	1.0	0.3	0.197	0.053	-	-
Measured*	bal.	13.87	1.05	0.30	0.22	0.22	< 0.15	< 0.05

*Average measured composition from several MA957 heats [17]

As described above, data from our two LTTA and SITA experiments on MA957 were combined in this work. The SITA aging study was for shorter aging times, up to 480 h, at higher temperatures from 1150°C to 1400°C [9,10]. The SITA d versus temperature-time (T-t) database is tabulated in Table A1 in the appendix. The data is also summarized in Figure 1, showing systematic trends of increasing NO diameter minus the initial diameter ($d - d_0$) as a function of T and t. The least square fit slopes of the lines are similar except for the 0.33 h and 480 h times where there is almost no coarsening. Note the SANS data are more uncertain at larger NO sizes due to the emphasis on higher scattering vector (q) regions, thus smaller precipitate sizes. The

LTTA study was for longer times up to 32.4 kh at temperatures from 800°C to 1000°C with the SANS d versus T-t data also summarized in Table A1.

TEM specimens from the 1000°C aging after 21.9 kh were prepared by standard lift-out methods using an FEI Helios focused ion beam instrument equipped with an Omniprobe manipulator. At the final specimen thinning stage the lift-out TEM specimen was cleaned using a low energy beam (2kV, 5.5pA). Bright field TEM images were recorded using an FEI field emission Titan operating at 300KV.

3. Simple Coarsening Models

Precipitate coarsening is driven by the reduction of the total interface energy of the precipitate phase. The coarsening rates are controlled by both thermodynamics and kinetics. Thermodynamics mediates the local equilibrium between the controlling solute concentration in the precipitate and neighboring matrix. The solubility in the matrix at the interface (X_m) is described by the Gibbs-Thomson equation, in its simplest exponential form as,

$$X_m \approx X_e \exp[2\gamma V_m / rRT] . \quad (1a)$$

Again X_e is the equilibrium solubility, γ is the interface energy, while V_m is the molar volume, r is the precipitate radius while R and T are the gas constant and absolute temperature, respectively. For small values of $2\gamma V_m / rRT$ the solubility can be linearly approximated as

$$X_m \approx X_e [1 + 2\gamma V_m / rRT]. \quad (1b)$$

Thus $X_m > X_e$ increases with decreasing r , and coarsening occurs by the flow of solutes from smaller dissolving precipitates to larger growing precipitates. The average precipitate size and size distribution increases with time and is classically

described by the Lifshitz-Slyozov-Wagner (LSW) theory of coarsening of a self-similar size distributions [18,19]. Note such coarsening is often called Ostwald Ripening.

The NOs are predominantly located in the matrix, not on grain boundaries; and it is the matrix NOs that primarily provide the outstanding functionality of NFA. The solute diffusion coefficient and the corresponding diffusion path control the matrix NO coarsening kinetics, which we will describe here as have a $t^{1/p}$ time scaling. For clarity we give two simplified examples. Assuming Eq. 1b, coarsening by a lattice diffusion path, occurs at a rate dr/dt proportional to $2\gamma V_m/r^2 RT$. Thus time integration leads to $p = 3$. For pipe diffusion along dislocations $p = 5$. The higher value of $p = 5$ is due to the higher dimensionality in the pipe diffusion case, since the dr/dt is also scales with the area of the dislocation core (πr_c^2). More generally, and considering the possibility of interface mobility controlled kinetics, p varies from 1 to 5; but as we will later show, $p = 6$ is also a possibility. More detailed and rigorous treatments can be found in [18,19] and the classic publication by Ardell [20]. Note the Ardell paper appears to deal with a grain boundary coarsening path, but it actually also treats this as a process of diffusion along one to n dislocation pipes.

These reduced-order, linearized models can be represented by simple, yet still physically rich, equations that are convenient for fitting the coarsening data. Thus we use a coarsening expression with the general form,

$$[d(t)^p - d_o^p] = K_p(T)t, \quad (2a)$$

or equivalently,

$$[d(t)^p - d_o^p]^{1/p} = [K_p(T)t]^{1/p} \quad (2b)$$

Equation 2 for the coarsened NO diameter $[d(t)]$ reflects integrating the effect of the average instantaneous feature size on the corresponding radial growth rate, starting at the initial, pre-aging diameter, d_0 . The $K_p(T)$ rate coefficient contains the combination of material properties controlling the rate of coarsening and is exponentially dependent on temperature. The other material properties include the Y diffusion coefficient (D_Y), solubility (X_Y), γ and length scales that describe the length scale dimensionality of $K_p(T)$. The coarsening progresses with a $1/p$ power of time (t) dependence, where the p is specific to the coarsening mechanism in play. For example, Speight showed a one-fourth ($p = 4$) coarsening dependence for precipitates on high angle grain boundaries [21]. Ardell derived the one-fifth ($p = 5$) dependence for diffusion on one to multiple (n) dislocations (for large n , low angle grain boundaries) and refined the coarsening model to account for the precipitate volume fraction dependence [20].

Another mechanism was proposed by Vengrenovich et al. [22] for coarsening by $t^{1/6}$ kinetics ($p = 6$) assuming that previously pinned dislocations detach from growing precipitates and climb to add additional pipes that intersect the remaining features. More generally the detachment stress is controlled by the dislocation size dependent obstacle pinning strength, or their spacing (λ), adding the extra unit of length-scale dimensionality to the single dislocation pipe diffusion $p = 5$ case. In the following sections we apply Equation 2 to the combined MA957 aging database to derive a predictive best-fit coarsening model.

4. Database Least Squares Fitting

The combined aging database was analyzed in three ways. The first approach was to use Equation 2b to non-linear least square fit (LSF) the p and $K(T)$ terms to the individual data sets at each temperature. As shown in Table 2, the fitted p is highly scattered, ranging from ≈ 1.4 (at 950°C) to 10.7 (1300°C). The fitted p averaged $\approx 6.2 \pm 2.9$. Note that these fit values reflect the assumption that a given p represents data at all aging times, but this may not always be the case.

Table 2. The fitted p for individual temperature data sets.

T_a °C	1400	1350	1300	1250	1225	1200	1175	1150	1000	950
p	8.1 ± 2.3	9.4 ± 2.9	10.7 ± 2.9	6.8 ± 0.8	7.5 ± 0.7	5.2 ± 0.4	2.6 ± 0.3	3.0 ± 2.2	7.7 ± 14.5	1.4

A second approach was to LSF to all the data simultaneously, replacing the $k(T)$ term with a common $k_o \exp(-Q_o/RT)$.

$$[d(t)^p - d_o^p]^{1/p} = [k_o \exp(-Q_o/RT)t]^{1/p} \quad (3)$$

The Q_o represents the exponential temperature dependence of the DX_e term. The fitting yielded $k_o = 7.3 \times 10^{29} \text{ nm}^p/\text{h}$, $p = 6.26 \pm 0.5$ and $Q_o = 764 \pm 46 \text{ kJ/mole}$. The corresponding standard deviation of the predicted versus measured d was $\approx \pm 0.63 \text{ nm}$. The fit values are summarized in Table 4. A corresponding plot of $[d(t)^{6.26} - d_o^{6.26}]^{1/6.26}$ versus $t^{1/6.26}$ for all the temperatures is shown in Figure 2a. Note plotting the increase in d with $t^{1/p}$ shows deviations from the fitted model on an appropriate physical length scale.

A third approach was to fix p at nominal values for a specified coarsening mechanism and LSF $K_p = [k_o \exp(-Q_o/RT)]^{1/p}$, again at each aging temperature. The fits for $p = 3$ (lattice diffusion) and 5 (dislocation pipe diffusion) are shown in Figure

2b and c, and the corresponding K_p fit values for $p = 3$ and 5 are summarized in Table 3. In the case of the lowest temperature 950°C data, the standard error in K_p are $\pm 33\%$ and $\pm 37\%$ for $p = 3$ and 5, respectively. The corresponding standard error for the K_p using the 1000°C data are $\approx \pm 14\%$ and 10% for $p = 3$ and 5, respectively. A power of $p = 5$ provided the best fit for the majority of the 10 temperatures. The standard errors for fitted K_p for all the other higher-temperature, shorter-term aging SITA data averaged $\pm 12\%$ and $\pm 7\%$ for $p = 3$ and 5, respectively.

Table 3. $k_{03 \text{ or } 5}$ fitting parameter values for assumed $p = 3$ or 5 coarsening.

°C	1400	1350	1300	1250	1225	1200	1175	1150	1000	950
K_3	6.89 ± 0.64	4.40 ± 0.71	3.34 ± 0.56	1.74 ± 0.17	1.46 ± 0.27	1.06 ± 0.07	1.19 ± 0.19	1.06 ± 0.07	0.103 ± 0.015	0.054 ± 0.018
K_5	8.86 ± 0.64	6.37 ± 0.44	4.87 ± 0.35	3.31 ± 0.16	2.38 ± 0.14	2.21 ± 0.03	2.21 ± 0.03	1.60 ± 0.16	0.440 ± 0.043	0.235 ± 0.088

Figure 3 cross plots $\ln(K) = \ln\{[k_{op}\exp(-Q_{op}/RT)]^{1/p}\}$ versus $1/T$ for $p = 3$ and 5 to derive the corresponding activation energy, Q_{op} . Here the LSF line slope m is equal to $[Q_{op}/R \cdot p]$. Thus Q_{op} is given by the product $R \cdot p \cdot m$. For $p = 5$, $Q_{o5} \approx 673 \pm 12$ and for $p = 3$, $Q_{op} \approx 554 \pm 11$ kJ/mole. The overall predicted versus measured SD of $[d - d_0]$ were 1.07 and 0.67 nm for $p = 3$ and 5, respectively. Table 4 summarizes these results. The dashed line in Figure 3 is fit only to the high temperature data at $> 1000^\circ\text{C}$ but extrapolates very well to lower temperature data at 1000 and 950°C. APT data from aging studies by Miller [6] on MA957 and Williams [14] on another 14YWT NFA are also shown for comparison, as the blue triangle and diamond, respectively.

Table 4. Fit Q_p , $k_{p(o)}$ and standard deviation (SD) of the measured versus predicted d.

	LSF $p = 6.26$	Fixed $p=3$	Fixed $p=5$
Q_p (kJ/mole)	764 ± 46	554 ± 11	673 ± 12
k_{p0} (nm ^p /h)	7.3×10^{29}	6.0×10^{19}	4.4×10^{25}
SD $d_{\text{meas.}} - d_{\text{predicted}}$ (nm)	0.63	1.07	0.67

The results of these LSF exercises can be summarized as follows.

- There is large scatter in the fitted p values for individual data sets. This is likely associated with a combination of experimental scatter in the coarsening data itself, inadequacies in the simplified models used in the fits, and the strong covariance between the individual p and Q_p .
- The p fits to the overall database and the average of the fitted p were $\approx 6.26 \pm 0.5$ and 6.2 ± 2.9 , which are larger than values for lattice and pipe diffusion coarsening models, and more consistent with a pipe diffusion-dislocation detachment model [22].
- The overall predicted minus measured $d(t,T)$ standard deviations for a fixed $p = 5$ was relatively small at ≈ 0.6 nm.
- The corresponding standard deviation for a fixed $p = 3$ for lattice diffusion is significantly larger than for $p = 5$ and can be rejected on a statistical basis
- Fits to the coarsening data to evaluate effective activation for coarsening, Q_p , are excellent in all cases.

There is a significant gap in the aging data between 1000 and 1150°C that could be filled in the future to better discriminate between the $p = 5$ and ≈ 6 models. However, more precise model selection is confounded by the strong covariance between p and Q_p . That is, fixing p at 5 and 6 results in predicting similar d because of the covariant changes in the corresponding simultaneously fitted Q_p . Thus reliably discriminating between the $p = 5$ and 6 models would require very long aging times. For example, aging at 1100°C would require aging ≈ 200 kh to reach an

approximately 20% difference in NO size between the predicted d of 11.8 nm for $p = 5$ and 9.4 nm for $p = 6$. Given the insensitivity of the predicted d to the value of p in the range of roughly 5 to 6, we believe the $p = 5$, pipe diffusion model is adequate for practical engineering prediction purposes, especially since it can easily be physically parameterized. The numerical $p = 5$ expression is given in Equation A1 in the appendix.

To further illustrate this point, Figure 4a shows the predictions of the three models at 150,000 h as a function of temperature up to 1000°C for $d_0 = 2.68$ nm. Using $p = 3$ predicts a faster coarsening rate compared to the $p = 5$ or 6.3 models. However, the difference in d between $p = 5$ and 6.3 at 1000°C is only ≈ 0.5 nm, or less than 12%. In all cases it is clear that the NO coarsening rates are negligible below $\approx 950^\circ\text{C}$. Figure 4b plots the time needed to double d_0 as a function of $1/T$ for the $p = 5$ model.

For perspective, the $p = 5$ model predicts that at 1000°C a 2.68 nm NO would double in size at $\approx 10^5$ h while at 800°C this would take $> 10^8$ h. The aged d data can be used along with the size dependent obstacle strengthening contribution model, derived by Alinger, to predict the reduction in strength associated with NO coarsening [1]. Of course, the NOs contribute only one component of the NFA strength, which is also provided by dislocations and grain boundaries. Aging at 1000°C for 19.5 kh resulted in no observable changes in the dislocation structure and grain size [13]. The precipitate strength contribution model is proportional to $\approx \kappa\sqrt{f}/d$ where κ is an effective dislocation obstacle strength factor [8,23,24]. The Hall-Petch contribution is given by $k/\sqrt{d_g}$ where d_g is the grain diameter [13]. Using the nominal

SANS data for f and d , and recent estimates of $k = 12500$ MPa-nm and an unaged yield stress of $\sigma_y = 850$ MPa for MA957 [1,23], the reductions in strength are predicted to be ≈ 20 and 12% (averaging 16%) for 19.5 and 21 kh at 1000°C, respectively; this compares favorably to the corresponding observed values of 13% and 7% (averaging 10%). Given the uncertainties in the measurements and simplicity of the models, the agreement is reasonable. Further, at 19.5 kh the corresponding predicted strength reductions are 12 and 18% (averaging 15%) for the TEM and APT data, respectively.

Additional characterization of grain growth and dislocation recovery kinetics (if any) would be needed to develop an overall model for the evolution of NFA strength as a function of aging time and temperature. However, this is beyond the scope of this paper. Our major conclusion is that softening is likely to be negligible at service temperatures up to 850°C even for very long service times.

5. Coarsening Mechanisms

As shown elsewhere, the NOs in MA957 are primarily the pyrochlore $Y_2Ti_2O_7$ complex oxide [2-4]. Thus for near-equilibrium conditions, the matrix solubility of Y, X_{Ym} , would be controlled by this phase and the matrix Ti and O activities [15]. Assuming Ti is in equilibrium with the metallic phase, the critical solute activity controlling X_{Ym} is the O partial pressure, P_{O_2} . The predicted matrix solubility, $X_{Ym} \approx 4.7 \times 10^{-29}$ at 1000°C, is clearly the rate controlling mechanism [15]. The low Y solubility is due to the very high stability of the $Y_2Ti_2O_7$ phase and the high solution enthalpy for Y. Assuming lattice diffusion controlled kinetics ($p = 3$), the classical NO coarsening rate is given by [20]

$$\{[d(t)^3 - d_o^3]/t\}^{1/3} \approx K_3 \approx [7\gamma V_m D_{Ym} X_{Ym} / RT]^{1/3} \text{ nm/h}^{1/3} \quad (4)$$

Here, the experimental estimate of D_{Ym} is the matrix diffusion coefficient of Y in ferrite ($\approx 9 \times 10^{-16} \text{ m}^2/\text{s}$ at 1000°C) [15], γ is the NO-matrix interface energy ($\approx 1.2 \text{ J/m}^2$) from [15] and V_m is the ferrite molar volume ($\approx 7 \times 10^{-6} \text{ m}^3/\text{mole}$). Equation 4 yields a predicted coarsening rate $[d(t)^3 - d_o^3]/t^{1/3} \approx 10^{-7} \text{ nm/h}^{1/3}$ compared to the measured value of $1.1 \times 10^{-3} \text{ nm/h}^{1/3}$. Thus the $[7\gamma V D_m X_m / RT]$ term would have to be 1.33×10^{12} times larger to explain the observed coarsening rate.

Assuming Henry's law behavior, the X_{Ym} is equivalent to an effective solution energy for Y near $1000^\circ\text{C} \approx 698 \text{ kJ/mole}$. Adding a calculated Y matrix diffusion activation energy of 218 kJ/mole [15] to this value results in an overall activation energy for matrix NO coarsening of $\approx 916 \text{ kJ/mole}$, which is 1.6 times higher than for the $p = 3$ model fit of 555 kJ/mole found in this study. Clearly the lattice Y dissolution-diffusion mechanism is not consistent with experiment.

The data is better fit by a dislocation pipe diffusion mechanism ($p = 5$). The TEM micrographs in Figure 5a and b for the 1000°C and 21.9 kh aged condition show most of the NOs are associated with dislocations. Neglecting the volume fraction effects, classical NO coarsening by dislocation pipe diffusion [20] is given by,

$$\{[d(t)^5 - d_o^5]/t\}^{1/5} = K_5 = \{32A\gamma V D_{Yd} X_{Yd} / RT\}^{1/5} \quad (5)$$

Here, A is the cross section area for pipe diffusion (taken as $\approx 4b^2 \approx 2.5 \times 10^{-19} \text{ m}^2$). Coarsening on dislocations is consistent with a much higher value of $D_Y X_Y$. The binding energy of Y to dislocations was determined by first principal calculations to be $\approx 241.2 \text{ kJ/mole}$ [15]. Further, assuming that the Y diffusion activation energy at

dislocations is reduced by a typical factor of 2, to ≈ 109 kJ/mole, and ignoring differences in the pre-exponential factor, the dislocation $D_{Yd}X_{Yd}$ term is $\approx 5.4 \times 10^{14}$ times higher than the corresponding matrix $D_{Ym}X_{Ym}$. The absolute coarsening rate is predicted to be ≈ 0.054 nm/h^{1/5}, much closer to the measured value of 0.085 nm/h^{1/5}. Using the parameters given above, the nominal value of the $\{32A\gamma VD_{Yd}X_{Yd}/RT\}$ term for the $p = 5$ model is only ≈ 10.3 lower. This is considered to be very good agreement, and the $p = 5$ pipe diffusion model is clearly far superior to the $p = 3$ lattice diffusion model. Based on the assumption the net activation energy for $D_{Yd}X_{Yd}$ can be approximated as $698-250 = 448$ kJ/mole and that for pipe diffusion the activation energy is 109 kJ/mole, the overall activation energy for $D_{Yd}X_{Yd}$ is ≈ 557 kJ/mole, or about a factor of ≈ 0.82 lower than the fitted value. Note the free energy difference driving coarsening of $\approx 4\gamma V_m/d$ is enormously smaller by comparison, at only ≈ 12.9 kJ/mole.

The $p = 5$ results can be compared to the detailed thermo-kinetic model reported in reference [15]. Note, the more complex physical model was fit only to the longest time coarsening data, and generally over predicts d at shorter time, corresponding to a higher effective p . However, fits to the temperature dependence predicted by the model yield an effective activation energy of 694 kJ/mole, which is very close to the experimental value of 673 ± 12 kJ/mole for the $p = 5$ model.

While the $p = 5$ model is far superior to that for $p = 3$, the overall kinetics are slightly better fit by a $p \approx 6$ time scaling. Although we do not propose a quantitative model, it is noted that $p \approx 6$ kinetics is rationalized by a mechanism that also considers dislocation climb. We hypothesize that climb provides a larger number of

intersections between the NOs and the dislocation pipes. As the NOs coarsen, the threshold σ_c stress for Nabarro-Herring climb would decrease with increasing d and decreasing N roughly in proportion to the precipitate spacing λ , as $\sigma_c \propto 1/\lambda$. This concept leads to a higher p and is similar to the theory proposed by Vengrenovich et al. who show that coarsening by pipe-diffusion along dislocations that are able to detach from precipitates and climb as the stress fields are reduced around growing precipitates also yields $p = 6$ [22].

The tremendous resistance to oxide coarsening in MA957 may suggest the need for new ways of thinking about far from equilibrium material states, where classical near equilibrium concepts no longer directly apply. In this particular example, the Fe-Y-Ti-O system was pushed very far from equilibrium during mechanical alloying that forces Y into solution prior to precipitation during high temperature powder consolidation. In order to coarsen, the Y must somehow *re-dissolve*, which is the rate controlling process due to its very low solubility in Fe. The dissolution rate is very slow since the activation energies remain high, while the thermal driving free energy is very low. Dissolution rates may also be decreased by non-equilibrium oxygen activities that drive the $2\text{Ti} + 2\text{Y} + 7\text{O} \rightarrow \text{Y}_2\text{Ti}_2\text{O}_7$ reaction in the forward oxidation direction. Apparently, dislocations provide a slow, but finite, solubility-diffusion path. However, the resulting kinetics remains highly frustrated, providing an unprecedented degree of effective NO precipitate stability. The NO-ferrite matrix system is effectively trapped, and almost frozen, in a metastable state up to very high service temperatures, even for nm-scale features.

6. Summary and Conclusions

The LTТА results from our previous study for temperatures up to 1000°C [13] were combined with our SITA data reported by Alinger [9,10] for aging MA957 at higher temperatures from 1150°C to 1400°C and shorter times from 0.33 to 480 h. The model equations were fit to the data three different ways. First, individual fits to each temperature data showed large scatter, but averaging the fitting parameter values gave a $p = 6.2 \pm 2.9$, which is most consistent with a dislocation detachment-climb pipe diffusion mechanism. Fitting all the data simultaneously gave a similar $p = 6.28 \pm 0.5$ and an activation energy of 764 ± 46 kJ/mole. Equations holding the p values fixed for lattice diffusion ($p = 3$) or pipe diffusion ($p = 5$) were used to determine the activation energy and coarsening pre-exponential coefficients. The $p = 3$ model can be rejected on both a statistical and mechanistic basis. The $p = 5$ model is consistent with microstructural observations of dislocation-NO associations during aging, and mechanistic assessments of the predicted coarsening rates. The covariance between the value of p and Q_p reduces the sensitivity of the predicted d to the specific value selected. Thus the $p = 5$ model is sufficiently robust for practical purposes. Both $p = 5$ and ≈ 6 models indicates that the NOs will remain effectively fully stable for temperatures up to 900°C.

The remarkable coarsening resistance is due to the low solubility of Y in equilibrium with NO $Y_2Ti_2O_7$ precipitates, which is the rate-controlling step. Indeed, it appears that sufficient solubility and diffusion rates occur only on dislocations, leading to a pipe diffusion mechanism.

One final caveat is in order. The MA957 characterized in this study was most likely extruded at $\approx 1065^\circ\text{C}$. Thus future work will be directed at the effects of lower consolidation temperature on the NO and NFA stability.

Acknowledgments

This work was primarily supported by the DOE Office of Fusion Energy (DE-FG03-94ER54275). We also acknowledge the support of the National Institute of Standards and Technology, US Department of Commerce, in providing the neutron research facilities (NIST Center for Neutron Research) used in this work.

Appendix

Table A1. NO d (nm) in alloy MA957 as a function of aging time and temperature determined by SANS measurements [9,10,13]

T($^\circ\text{C}$)		T($^\circ\text{C}$)		T($^\circ\text{C}$)								
950		1000			1150	1175	1200	1225	1250	1300	1350	1400
t (h)	d (nm)	t (h)	d (nm)	t (h)	d (nm)							
3000	2.73	3000	3.26	0.33	-	-	-	2.92	3.18	-	-	-
6600	2.64	4000	2.82	3	2.76	2.82	3.26	3.54	5.30	7.26	9.68	11.86
9600	2.65	8000	2.82	9	2.88	-	3.68	-	6.30	8.00	9.96	13.08
17700	2.85	11000	3.47	27	2.90	-	4.32	5.18	6.44	8.32	11.14	-
31200	3.46	19500	3.87	81	2.90	-	5.12	-	7.44	-	-	-
		21900	2.94	243	6.46	5.28	6.86	6.50	9.18	-	-	-
				480	5.58	6.68	7.44	-	-	-	-	-

$d_0 = 2.64$ nm for $T > 1000^\circ\text{C}$ and 2.68 nm for $T = 950$ and 1000°C

In absolute terms the $p = 5$ coarsening equation for MA957 is given by

$$\begin{aligned}
 d(T,t) &= [k_{50} \exp(-Q_{50}/RT)t - d_0^p]^{1/p} \\
 &= [4.4 \times 10^{25} \text{ nm}^5/\text{h} \cdot \exp(-673 \text{ kJ/mol}/(8.314 \text{ JK}^{-1}\text{mol}^{-1} \cdot T))t - d_0^5]^{1/5} \quad (\text{A1})
 \end{aligned}$$

REFERENCES

1. G.R. Odette, M.J. Alinger, and B.D. Wirth, *Annual Review of Materials Research*, Vol. 38, 2008, 472.
2. Y. Wu, E.M. Haney, N.J. Cunningham, G.R. Odette, *Acta Mater.* 60, 2012, 3456-3468.
3. J. Ribis and Y. de Carlan, *Acta Mater.*, 60, 2012, 238-252.
4. G.R. Odette, *J. of Mater.*, 66, 2014, 2427-2441.
5. M.K. Miller, K.F. Russell and D.T. Hoelzer, *J. Nucl. Mater.*, 351, 2006, 261-268.
6. M.K. Miller, D.T. Hoelzer, E.A. Kenik and K.F. Russell, *J. Nucl. Mater.*, 329, 2004, 338-341.
7. M.K. Miller, D.T. Hoelzer, E.A. Kenik and K.F. Russell, *Intermetallics*, 329, 2005, 387-392.
8. H. Sakasegawa, F. Legendre, L. Boulanger, L. Chaffron, T. Cozzika, J. Malaplate, J. Henry, Y. de Carlan and M. Brocq, *Mater. Res. Soc. Symp. Proc.* Vol 1125, 2009.
9. M.J. Alinger, *On the Formation and Stability of Nanometer Scale Precipitates in Ferritic Alloys during Processing and High Temperature Service*, Thesis (PhD), University of California Santa Barbara, 2004
10. M.J. Alinger, G.R. Odette, and D.T. Hoelzer, *J. Nucl. Mater.*, 329-333, 2004, 382-386.
11. S.Y. Zhong, J. Ribis, V. Klosek, Y. de Carlan, N. Locket, V. Ji, and M.H. Mathon, *J. Nucl. Mater.*, 428, 2012, 154-159.
12. P. Miao, G.R. Odette, T. Yamamoto, M. Alinger, and D. Klingensmith, *J. Nucl. Mater.*, 377, 2008, 59-64.
13. N. Cunningham, Y. Wu, D. Klingensmith, and G.R. Odette, *Mater. Sci. and Engr. A*, 613, 2014, 296-305.
14. C.A. Williams, G.D.W. Smith, E.A. Marquis, *Scripta Mater.*, 67, 2012, 108-111.
15. L. Barnard, N. Cunningham, G.R. Odette, I. Szlufarska, and D. Morgan, *Acta Mater.*, 91, 2015, 340-354.
16. J.J. Fisher, U.S. Patent No. 4,075,010, 1978.
17. H.L. Hamilton, D.S. Gelles, R.J. Lobsinger, G.D. Johnson, W.F. Brown, M.M. Paxton, R.J. Puigh, C.R. Eiholzer, C. Martinez, and M.A. Blotter, Technical Report PNL-13168, 1991
18. I.M. Lifshitz and V.V. Slyzov, *J. Phys. Chem. Solids*, 19, 1961, 35.
19. C. Z. Wagner, *Electrochem*, 65, 1961, 581.
20. A.J. Ardell, *Acta Metall.*, 20, 1972, 601-609.

21. M.V. Speight, *Acta Metall. Trans.*, 20, 1972, 61.
22. R.D. Vengrenovich, Y.V. Gudyma, and S.V. Yarema, *Scripta Mater.*, 46, 2002, 363-367.
23. N. Cunningham, Y. Wu, A. Etienne, E.M. Haney, G.R. Odette, E. Stergar, D.T. Hoelzer, Y.D. Kim, B.D. Wirth, and S.A. Maloy, *J. Nucl. Mater.*, 444, 2014, 35-38.
24. J. W. Martin, *Micromechanisms in Particle Hardened Alloys*, Cambridge Press (1980)

Figure(s)

Figure 1. Coarsening trends in our SITA database [9,10].

Figure 2. $[d^p - d_o^p]^{1/p} = [Kt]^{1/p}$ fits, where K is variously defined as: a) $k_o \exp(-Q_o/RT)$; $[k_{o3} \exp(-Q_{o3}/RT)]^{1/3}$; and, c) $[k_{o5} \exp(-Q_{o5}/RT)]^{1/5}$.

Figure 3. $\ln(K)$ vs $1/T$ plots for a) $p = 3$ and b) $p = 5$.

Figure 4. a) Comparison between the predicted coarsening ($d_0=2.7$ nm) vs. aging temperature for 150 kh aging time for $p = 3, 5$, and 6.26 ; b) time to double NO size based on $p = 5$.

a)

b)

Figure 5. TEM micrographs showing high concentration of NO on dislocations a) at low magnification and b) at high magnification showing single NO (1 black) in matrix and multiple NO (1-5 white) lined up on a dislocation.