8.3 Nanofeature-Dislocation Associations and a Fitted Long Term Thermal Aging Pipe Diffusion Model for MA957 — Y. Wu, N. J. Cunningham, G. R. Odette and D. Klingensmith (University of California - Santa Barbara)

OBJECTIVES

The objective of this work is to determine and model the high-temperature nanofeature coarsening mechanism in nanostructured ferritic alloys.

SUMMARY

Nanostructured ferritic alloys (NFAs) have applications in advanced fission and fusion reactors and are strengthened by a high number density of Y-Ti-O nanofeatures (NFs) that are very stable up to 1000ºC [1]. Previously reported long and short-term aging studies from between 800ºC and 1400ºC on NFA MA957 for times up to 32.4 kh were used to develop a coarsening model in the form:

$$[d(t)^p - d_o^p] = [k_p(T)t] \quad (1)$$

Here t is the aging time and d is the average NF diameter starting at d_o. Simple models predict p ranging from 2 to 5, depending on the operative coarsening mechanism. Our data is most consistent with a pipe diffusion mechanism (p=5) [2]. However, a least square fit of all the data gives a higher p values of 6.26, possibly suggesting that combinations of complex phenomena operate during aging; for example, rather than random pipe diffusion processes, coarsening and other stages of NF evolution may involve highly correlated multispecies mechanisms.

In this short report we present TEM data for 1000ºC aging to 21.9 kh that provides strong support for pipe diffusion coarsening (p = 5), since most of the NFs are associated with dislocations. Additional aging studies at intermediate temperatures (1075ºC to 1200ºC) and times (<10 kh) are underway to help more accurately identify the coarsening mechanisms and kinetics.

BACKGROUND

NFAs have a unique combination of high temperature strength and radiation damage tolerance. These important attributes are primarily due to an ultrahigh density of oxide NF with average diameters in the range of 2-3 nm. Thus a critical issue is the high temperature long-term thermal and radiation stability of the NFs and the balance of the NFA microstructures. We have previously reported long-term thermal aging (LTTA) studies of NFA MA957 to derive fits by semi-empirical models of the coarsening kinetics [2]. All fitted models predicted that the NFs are stable up to 900ºC for long times (>10^5 h). The data are most consistent with a pipe diffusion mechanism (p = 5), although the best statistical fit yields p = 6.26. Here we propose a new coarsening concept that yields a p = 6.

STATUS AND PROGRESS

Equation 1 can be expressed as:

$$[d(t)^p - d_o^p] = k_{po}[\exp(-Q_p/RT)]t \quad (2)$$

This equation was non-linear least square fit (LSF) to all the data between 950 and 1400°C simultaneously. Here, Q_p is the activation energy for coarsening, R is the universal gas constant, T is the aging temperature, and k_{po}, p, (and Q_p) are fitting parameters. Alternately, Equation 1 was fit at individual aging temperatures with imposed model based p values of 3 (lattice diffusion) and 5 (pipe diffusion) to derive corresponding $k_{3/5}(T)$. Plots of $\ln[k_{3/5}]$ versus 1/T were fit to obtain the corresponding $Q_{3/5}$. The fitting results, reported previously, are summarized in Table 1 [2].The simultaneous data fitting yielded a p = 6.26 and a corresponding Q_p = 764±46 kJ/mole, with a standard deviation (SD) in the predicted versus measured [d - d_o] of 0.63 nm. Fixing p gave the overall predicted versus measured [d - d_o] SD of 1.07 and 0.67 nm for p = 3 and 5, respectively. The difference between the two fixed order kinetics models is statistically significant and sufficient to eliminate the p = 3 case. However, the differences in the fits p = 5 and 6.26 models are not statistically significant, and both strongly support a pipe diffusion related mechanism. For p = 5, Q_5 = 673±12 kJ/mole.

Table 1. Fit Q_p ,k_p and SD of the measured versus predicted [d - d_o] for various p.

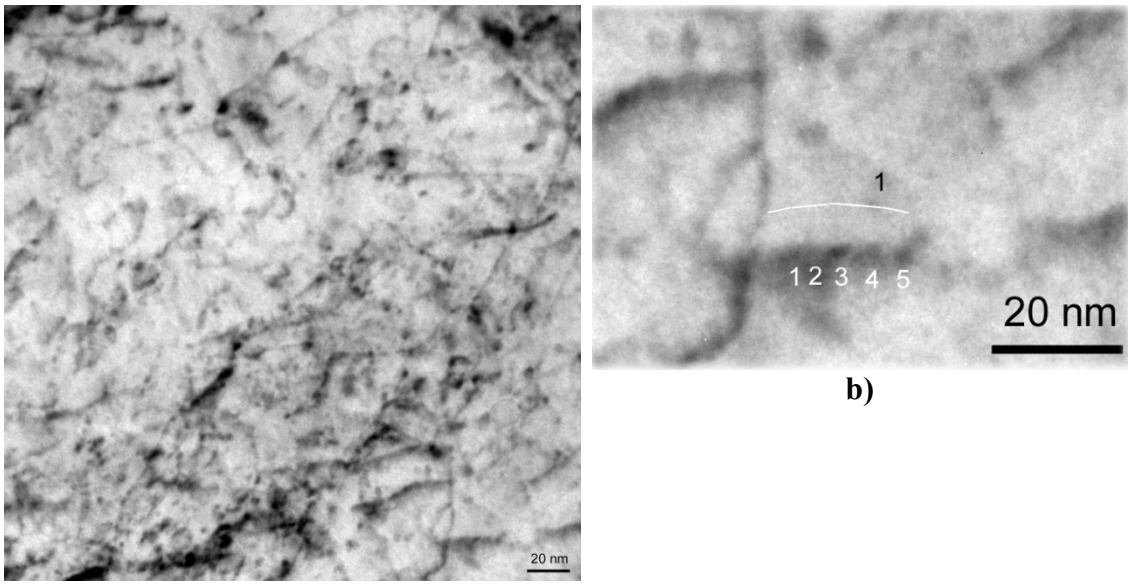
Order of Aging Kinetics	p = 6.26	p=3	p=5
Q_p (kJ/mole)	764±46	554±11	673±12
k_p or k_{po} $(nm/h)^p$	$7.3x10^{29}$	$6.0x10^{19}$	$4.4x10^{25}$
Pred. vs. meas. SD [d - d_o] nm	0.63	1.07	0.67

We can further analyze the results as follows. As shown elsewhere, the NFs in MA957 are primarily a pyroclore-type $Y_2Ti_2O_7$ complex oxide [3]. Thus for near-equilibrium conditions, the matrix solubility of Y, X_y, would be controlled by this phase and the matrix Ti and O activities. Assuming O is in equilibrium with Cr-oxide and Ti is in equilibrium with a metallic reference state, $X_m \approx 10^{-25}$ [4]; that is, the solubility of Y is extremely low. Indeed this is the case under almost any set of plausible thermodynamic assumptions. Thus Y dissolution from the $Y_2Ti_2O_7$ oxide is expected to be the rate controlling mechanism. For purposes of comparison, assuming lattice diffusion controlled kinetics (p = 3), the NF coarsening rate is given by

$$[d(t)^3 - d_o^3]/t] = k_3 \approx [7\gamma V D_y X_y/RT]\ [nm/h] \qquad (3)$$

D_y is the matrix diffusion coefficient, γ is the NF-matrix interface energy, and V is the molar volume, taken as that for Fe. At 1000°C, D_y is experimentally estimated to be ≈ $8x10^{-16}$ m^2/s. Taking nominal values of γ = 2 J/m^2, V = $7x10^{-6}$ m^3/mole and $X_y = 10^{-25}$, yields a predicted coarsening rate of $[d(t)^3 - d_o^3]/t]^{1/3} \approx 1.4x10^{-6}$ $nm/h^{1/3}$, compared to the measured value of $1.1x10^{-3}$ $nm/h^{1/3}$. A first principles diffusion model predicts $D_y = 9x10^{-16}$ at 1000°C with an activation energy of Q_{md} ≈ 218 kJ/mole [5]. The $X_y = 10^{-25}$ represents an effective Y dissolution energy of Q_{ys} ≈ 609 kJ/mole. Thus the overall activation energy for matrix diffusion NF coarsening is ≈ 827 kJ/mole, which is substantially higher than for the p = 3 model fit of 555 kJ/mole. Clearly the lattice Y dissolution-diffusion mechanism is not consistent with the observed NF coarsening rates.

The data is better fit by a dislocation pipe diffusion model (p = 5), which is also qualitatively consistent with a much higher value of the product of the Y diffusion coefficient and solubility at a dislocation, D_dX_d. The TEM micrographs in Figure 1a and b for 1000°C-21.9 kh aged MA957 provide strong support for the dominant role of dislocations in coarsening, since most of the NFs are seen to be associated with dislocations.



a) **b)**

Figure 1. TEM micrographs showing high concentration of NF on dislocations.

In the case of NF coarsening by dislocation pipe diffusion,

$$[d(t)^5 - d_o^5]/t]^{1/5} = k_5^{1/5} = [C_o A\gamma V D_{yd} X_{yd}/RT]^{1/5} \quad (4)$$

Here, C_o (≈ 0.1) is the product of a constant times a factor that depends of the volume fraction of the coarsening feature and A (≈ $4b^2$, where b is the Burger's vector) is the cross section area for pipe diffusion [6]. The measured activation energy of 673 kJ/mole can be used to estimate the $D_{yd}X_{yd}$ product at dislocations using a nominal pre-exponential D_{od} of 10^{-6} m^2/s, $D_{yd}X_{yd} \approx 10^{-6}\exp(-673{,}000/RT)$ or 2.4×10^{-34} m^2/s at 1000°C. The resulting predicted coarsening rate of 1.65×10^{-3} $nm/h^{1/5}$ is 51.5 times lower compared to the measured rate of 0.085 $nm/h.^{1/5}$ Note that the ratio of the fitted pipe diffusion to the estimated matrix coarsening activation energies 673/827 kJ/mole ≈ 0.81 is not unreasonable, and might be expected to be even lower. However, even a rollup of upper bound uncertainties in the temperature insensitive parameters $C_oA\gamma VD_{od}$ in Eq. 4, is probably not sufficient to quantitatively account for the difference between the predicted and measured coarsening rates. But the simple p = 5 pipe diffusion model is certainly qualitatively better than that for p = 3. Figure 4 plots the predicted time needed to double d_o, t_2, as a function of temperature evaluated as:

$$t_2 = 31 d_o^5/k_5(T) \quad (5)$$

Here the $k_5(T)$ are the fit values so these results demonstrate the excellent fit by the model over a wide range of temperature.

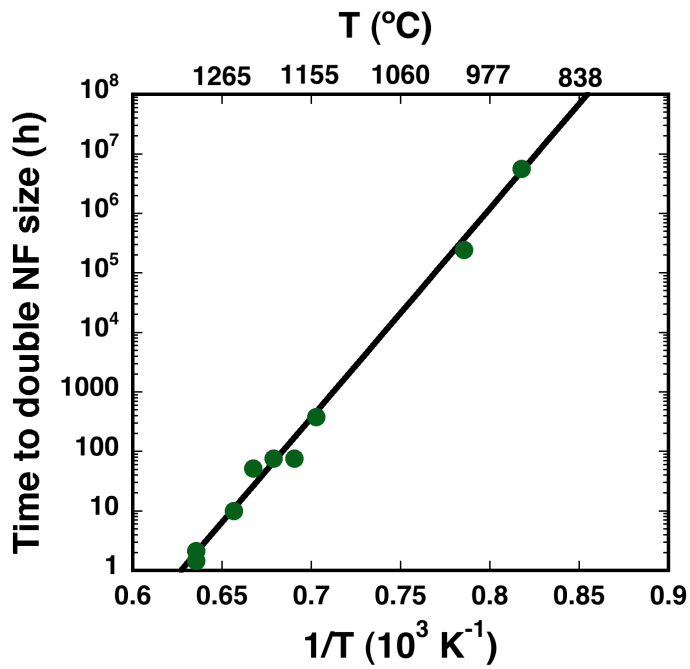


Figure 4. Predicted times to double d_o as a function of T based on the P = 5 pipe diffusion model.

The best empirical fit to the coarsening data was p = 6.26, with an activation energy of 764 kJ/mole. Conceptually this dimensionality could be associated with a p ≈ 6 model that involves pipe diffusion combined with detachment and climb of dislocations, which then intersect a new set of previously isolated NFs. It is postulated that the increase in p from 5 to ≈ 6 could be associated with a detachment stress controlled by NF spacing on a dislocation line, Λ, and a non-dimensional factor h, relating Λ to the detachment mechanism. The resulting kinetics can be dimensionally represented by

$$[d(t)^6 - d_o^6]/t]^{1/6} = k_6^{1/6} = [C_o A \gamma V \eta \Lambda D_d X_d / RT]^{1/6} \quad (6)$$

Additional TEM studies would be needed to test and parameterize p = 6 model. However, it is not clear that this would lead to full quantitative agreement as the actual coarsening mechanisms are likely to be even more complex. For example, rather than random pipe diffusion processes, coarsening and other stages of NF evolution may involve highly correlated multispecies mechanisms.

The failure of simple models to predict quantitatively the observed coarsening rates may suggest the need for new ways of thinking about far from equilibrium material states, where classical near equilibrium concepts no longer apply. In this case the pre-precipitated NFA-NF system has been pushed to the ultrahigh free energy state by what can be considered the mechanical work of alloying. The free energy reduction during the initial precipitation is also very large, so that the system is effectively trapped and *almost* frozen in a metastable state. However, the free energy still decreases slowly by complex processes that do not normally operate for near-equilibrium conditions.

FUTURE WORK

LTTA studies are under way that will be used to observe coarsening at intermediate time and temperature spanning the previous studies. Table 2 show predicted average NF d after aging at 1075ºC and 1200ºC for up to 4000 h for different p values. The aged alloys will be examined after 500, 1000, 2000, and 4000 h using SANS, TEM, and APT. The 1075ºC aging will add valuable data points between the previous long term thermal aging at and below 1000ºC and the shorter term aging above 1200ºC. A careful examination of medium term aging at 1200ºC should reveal the coarsening mechanism at play. Note, significant differences between the p values are not apparent until after 1000 h.

Table 2. Predicted d after 500, 1000, 2000, and 4000 h at 1075 and 1200°C for p = 3, 5, and 6.26.

d_o = 2.68 nm	d (nm) at 1075/1200°C			
t (h)	500	1000	2000	4000
p = 3	3.57/8.98	4.15/11.27	4.98/14.16	6.12/17.83
p = 5	3.71/7.98	4.18/9.09	4.7410.44	5.42/11.99
p = 6.26	3.70/7.47	4.09/8.35	4.54/9.33	5.06/10.42

REFERENCES

1. G. R. Odette, M. J. Alinger, and B. D. Wirth, *Annu. Rev. Mater. Res.* **38** (2008) 472.
2. N. J. Cunningham, M. J. Alinger, G. R. Odette, and D. Klingensmith, "On Nanofeature Coarsening Kinetics in MA957: Fitted Lattice and Dislocation Pipe Diffusion Models," Fusion Materials Semiannual Progress Report for period ending June 30, 2012, 116-121, DOE-ER-0313/52.
3. Y. Wu, E. M. Haney, N. J. Cunningham, and G. R. Odette, *Acta Mater.* **60** (2012) 3456-3468.
4. L. Barnard and D. Morgan, Personal communication.
5. D. Murali, B. K. Panigrahi, M. C. Valsakumar, and C. S. Sundar, *J. Nucl. Mater.* **419** (2011) 208-212.
6. A. J. Ardell, *Acta Metall.* **20** (1972) 601-609.