7.1 ON NANOFEATURE COARSENING KINETICS IN MA957: FITTED LATTICE AND DISLOCATION PIPE DIFFUSION MODELS

— N. J. Cunningham, M. J. Alinger, G. R. Odette, and D. Klingensmith (University of California, Santa Barbara)

OBJECTIVES

The objective of this work is to derive a coarsening model for the nanofeatures in nanostructured ferritic alloys.

SUMMARY

The development of advanced structural and functional materials with unprecedented properties that are enabled by a controlled distribution of nanoscale features (NF) presents enormous opportunities and challenges. One significant challenge is to develop an understanding of and control over the stability of the NF under far from equilibrium, interface dominated, high temperature conditions. Indeed, in the context of the classical near equilibrium materials theory, stable NF might seem an oxymoron. Here we explore the long-term thermal stability of a class of potentially transformational alloys for high temperature energy applications, that we call nanostructured ferritic alloys (NFA). Ultra high densities of Y-Ti-O NF endow NFA with outstanding strength and irradiation tolerance. We have previously reported the results of long-term thermal aging (LTTA) studies of NF and NFA between 800ºC and 1000ºC for times up to 32.4 kh using a toolkit of characterization techniques [1-3]. The NFA are stable at 900°C and below, while experiencing slow, but systematic NF coarsening at 950 and 1000°C, that is accompanied by small reductions in strength and modest grain growth. In the present work we use our experimental observations and data in the literature to derive a quantitative semi-empirical NF coarsening model for aging between 950 and 1300°C. The model predicts negligible coarsening rates below 900°C.

PROGRESS AND STATUS

Background

NFA 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 NF and the balance of the NFA microstructures. We have previously reported on LTTA studies of NFA MA957. Here we describe the development of a quantitative, semi-empirical model of the coarsening kinetics of the NF based on the LTTA results and other data from the literature.

Analysis Methods

The NF coarsening data analyzed in this work includes:

- LTTA up to 31.2 kh at 950 and 1000°C in MA957 (this study).
- Short to intermediate times up to 480 h at 1200 and 1250ºC in MA957 taken from the work of Alinger et al. [4].

- Short time up to 24 h at 1300°C for MA957 from Miller et al. [5].
- Short to intermediate time up to 100 h at 1200°C for a 14YWT NFA from Williams et al. [6].

These data were analyzed using classical coarsening models as summarized by Ardell [7]. The models can generally be represented by

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

Here d_o and d are the average initial and coarsened NF diameters and k_p is a material property-temperature dependent rate coefficient. The values of p and parameters in k_p depend on the coarsening mechanism. The power p varies from 2, for interface controlled coarsening, to 5 for a dislocation pipe diffusion mechanism. The p for lattice diffusion controlled coarsening is 3. Using this model, non-linear least square fits (LSF) were used to estimate, p, the rate coefficients, k_p or k_{po} (see below), and the activation energy, Q_p. One approach was the fit all the data simultaneously as

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

to determine p, k_{op} and Q_p. Here R is the universal gas constant and T is the aging temperature in °K. Another method used data set at each temperature to individually determine p and $k_p(T)$. The latter approach yielded a range of p values. In order to establish a unified model the third approach was to fit $k_p(T)$ with fixed values of p = 3 and 5. Then $\ln[k_p]$ vs. 1/T data were then used to fit Q_p.

RESULTS

The data analyzed is shown in Table 1. A high degree of scatter is present in the 1000ºC and 950ºC LTTA data, but it can be reasonably represented by the model with either p=3 or p=5, as shown in Figure 1. Further details on the materials and aging conditions are given in the references [1-6]. Table 1 indicates the technique [small angle neutron scattering (SANS) or atom probe tomography (APT)] used to measure changes in d as a function of time and temperature for the NFA MA957 and a model 14YWT NFA.

Table 1. Analyzed aging data.

Anneal Time (h)	Diameter (nm)	LSF
Miller 1300ºC (MA957 – APT)		
0	2.4	$p_{unconst}$ = 2.7
1	3.4	k_3 = 3.15
24	9.2	k_5 = 4.52
Alinger 1250ºC (MA957 – SANS)		
0	2.64	$p_{unconst}$ = 6.8±0.8
0.33	3.18	k_3 = 1.74±0.17
1	3.58	k_5 = 3.31±0.16
3	5.30	
9	6.30	
27	6.44	
81	7.44	
243	9.18	
Alinger 1200ºC (MA957 – SANS)		
0	2.64	$p_{unconst}$ = 5.2±0.4
3	3.26	k_3 = 1.06±0.07
9	3.68	k_5 = 2.21±0.03
27	4.32	
81	5.12	
243	6.86	
480	7.44	
Williams 1200ºC (14YWT – APT)		
0	5.0	$p_{unconst}$ = 19.3±4.3
1	5.44	k_3 = 1.46±0.27
4	5.70	k_5 = 2.95±0.33
24	5.94	
100	6.8	
Cunningham 1000ºC (MA957 – SANS)		
0	2.68	$p_{unconst}$ = 7.7±14.5
3000	3.26	k_3 = 0.103±0.015
4000	2.82	k_5 = 0.440±0.043
8000	2.82	
11000	3.47	
19500	3.87	
21900	2.94	
Cunningham 950ºC (MA957 – SANS)		
0	2.68	No fit but
3000	2.73	$p_{unconst}$ < 2
6600	2.64	k_3 = 0.054±0.018
9600	2.65	k_5 = 0.235±0.088
17700	2.85	
31200	3.46	

The simultaneous fit of all the data yielded p = 5.55±0.49 and Q_p = 673±41 kJ/mole. The predicted d minus measured d standard deviation is ≈ ±0.5 nm. However, this fit is dominated by the higher temperature data. The unconstrained fit to the individual data sets yielded p values ranging from < 2 to 19.3, as given in Table 1. At 1300ºC (Miller) p ≈ 2.7, but this fit is for only two data points; the p for the 950°C (Cunningham) is < 2, but this data is highly scattered, since the changes in d are small. The other p values

were all > 5, averaging 6.63. After constraining p to values ≤ 6, the fit of p for the other 3 datasets, including at 1000°C, averaged 5.8 in reasonable agreement with the p = 5 pipe diffusion mechanism. Again, these results are summarized in Table 1. Fits of k_p to the individual datasets for fixed p = 3 and 5 yielded Q_3 and Q_5 values and standard errors of 551±10.5 and 665±12.8 kJ/mole, respectively. The corresponding k_{po} are also found from these fits and used to predict coarsening d values for any aging time and temperature condition. The estimated Q values and standard deviations for the predicted minus measured d for each analysis is summarized in Table 2.

Table 2. Fit Q values with standard error and measured d – predicted d standard deviation (SD).

	Non-linear LSF	**p = 3**	**p = 5**
Activation Energy (kJ/mole)	Q_p = 673±41	Q_3 = 551±10.5	Q_5 = 665±12.8
SD of $d_{meas.}$ - $d_{predicted}$ (nm)	SD = 0.51	SD = 0.83	SD = 0.51

Figure 1 shows the $[d^p - d_o^p]^{1/p} = kt^{1/p}$ fits for p = 3 (1a) and 5 (1b). For the 950ºC data the standard error in the slope, k, is in excess of 30% for both p values. The 1000ºC data has a standard error of ≈14% for p = 3 and 10% for p = 5. The Alinger 1200ºC data is best represented with p = 5 with a standard error of 1.5%. The Williams 1200ºC data is less well represented by the model, but the best fit occurs with p = 5. The Alinger 1250ºC data is also best represented by p = 5 with a standard error of 4.7% compared with 9.8% for p = 3. As stated above the Miller 1300ºC is best represented by p = 3, but this fit only includes two data points.

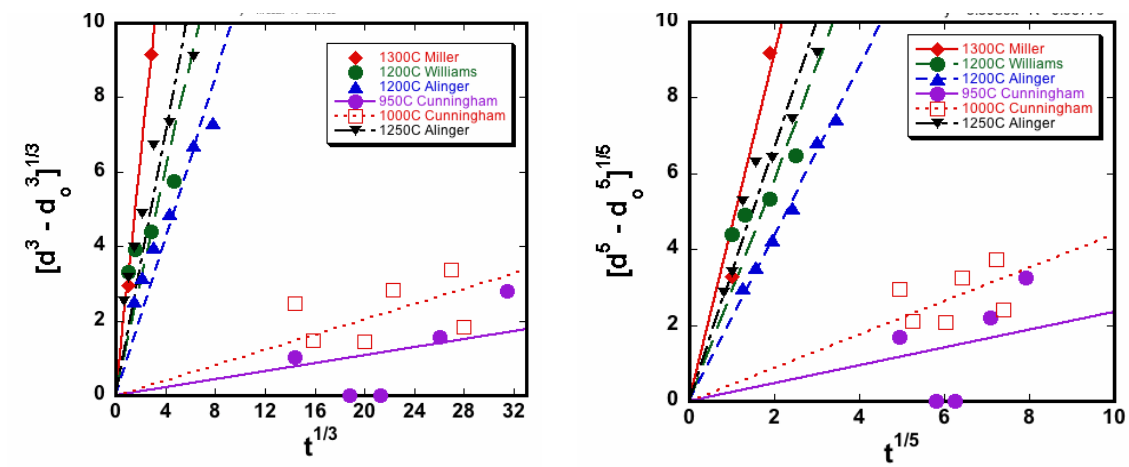

Figure 1. $[d^p - d_o^p]^{1/p} = kt^{1/p}$ fits for a) p = 3 and b) p = 5.

Figure 2 shows the corresponding ln(k) vs 1/T plots that were fit to derive Q_p, which is given by R*p*m, where m is the slope of the LSF and R is the gas constant. For p = 5 the Q_5 ≈ 665 kJ/mole with the overall NF coarsening rate in MA957 for p = 5 can be expressed as

$$d(t,T) = [2.4\text{x}10^{25}\exp(-665{,}000/RT)t + d_o^5]^{1/5} \text{ (nm)}$$

For p =3 the $Q_5 \approx 551$ kJ/mole

$$d(t,T) = [5.0\text{x}10^{19}\exp(-551{,}000/RT)t + d_o^3]^{1/3} \text{ (nm)}$$

Note the Williams data was not used in the $\ln[k_p(T)]$ vs. 1/T fits, but is shown for comparison.

Figure 3 shows the predictions of these models for 50,000 to 150,000 h as a function of temperature. The prediction is based on a d_o = 2.68 nm. The model using p = 3 gives higher coarsening rates compared to p = 5, and is a more conservative value. However, the data is significantly more consistent with a p = 5 value. In either case it is clear that the NF coarsening rates are negligible below 900°C.

DISCUSSION AND FUTURE STUDIES

The results reported here is only one part of a larger effort to understand the thermal stability of NFA. Other aspects of this research include developing models of strength and other property changes in NFA under LTTA conditions, including the effects of evolutions in the balance of grain, dislocation and precipitate microstructures. In addition, experimental and modeling studies are being carried out to better understand the detailed (and complex) physics of NF coarsening and the evolution in NFA under far from equilibrium conditions.

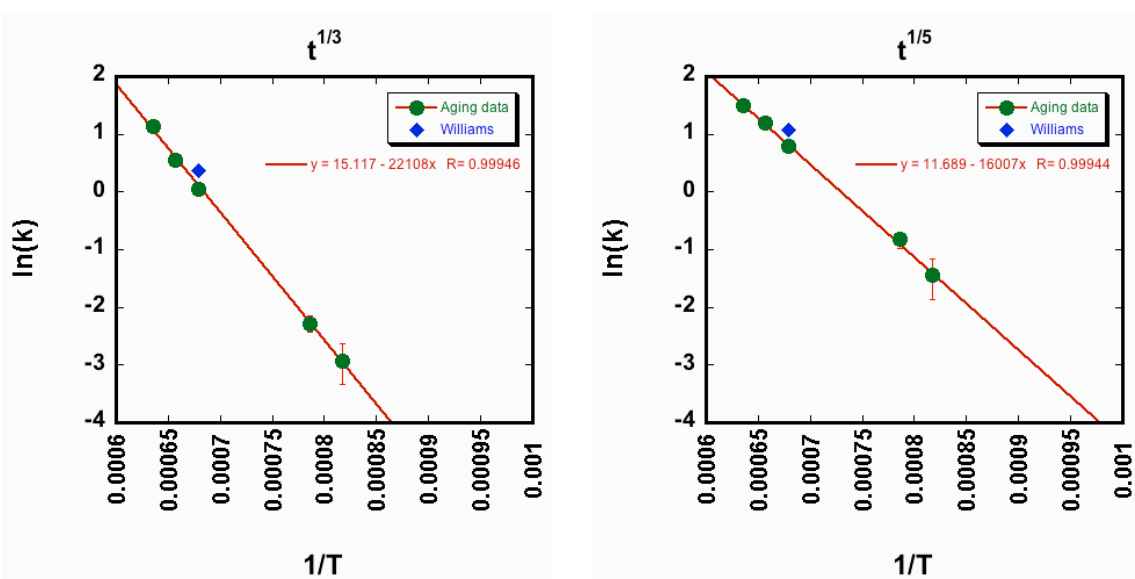

Figure 2. ln(k) vs 1/T plots for a) p = 3 and b) p = 5.

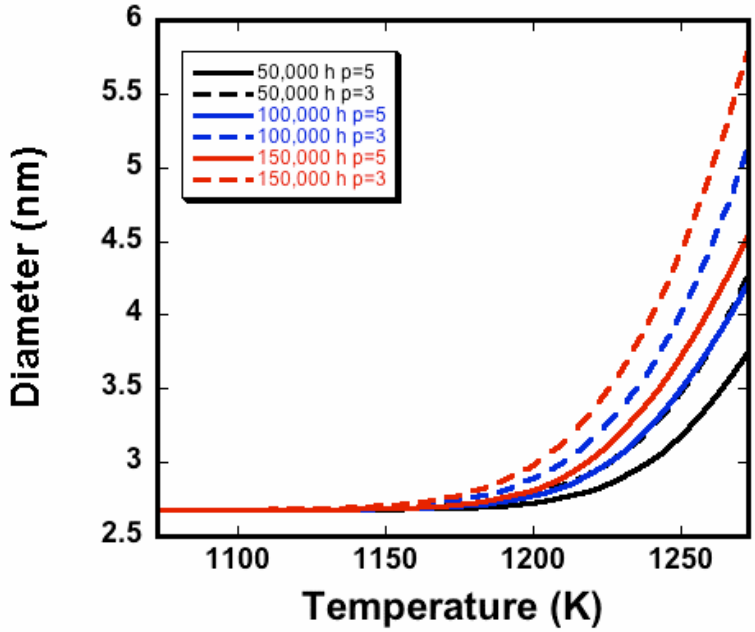

Figure 3. Predicted coarsening based on p = 3 and p = 5 models.

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