

ON THE PRECIPITATION KINETICS, THERMAL STABILITY AND STRENGTHENING MECHANISMS OF NANOMETER SCALE Y-Ti-O CLUSTERS IN NANOSTRUCTURED FERRITIC ALLOYS—M. J. Alinger and G. R. Odette (University of California, Santa Barbara)

OBJECTIVE

The objective of this study was to explore the factors that control the formation and stability of Y-Ti-O nanoclusters (NCs) in nanostructured ferritic alloys (NFAs).

SUMMARY

A systematic matrix of annealing times and temperatures were used to assess the kinetics of NC precipitation in Fe-14Cr powders mechanically alloyed (MA) with Ti and Y_2O_3 (U14YWT). The MA dissolves the Y, O, and Ti as supersaturated solutes that subsequently precipitate during hot powder consolidation, or annealing, in the form of nm-scale solute clusters (NCs). The NCs evolve extremely rapidly due to high diffusion rates and excess vacancies produced by MA. The non-equilibrium kinetics of NC evolution is nucleation controlled, with the number density (N) scaling with an effective activation energy of $\approx 53 \pm 15$ kJ/mole. The stability of the NCs during high-temperature annealing of MA957 was also characterized. The NCs coarsen and transform to nearer-to-equilibrium oxide phases at radii ≥ 3.5 nm, with a high effective activation energy of ≈ 880 kJ/mole and a time dependence characteristic of a dislocation pipe diffusion mechanism, with $r(t) - r(0) \propto t^{1/5}$. The effect of the micro-nanostructure on the alloy strength was assessed by microhardness measurements. The NCs can be sheared by dislocations and have an obstacle strength (α) that increases with r (nm) as $\alpha \approx 0.37 \log(r/2b)$ (≈ 0.1 to 0.5).

PROGRESS AND STATUS

Introduction

The objective of this work is to develop a fundamental understanding of the kinetics of NC nucleation, growth, coarsening and transformations, as well as their strengthening contributions, to provide a basis for tailoring NFA microstructures to specific applications; and to predict their thermal stability during extended, high temperature service.

Experimental Procedure

Materials, Annealing Conditions, and Characterization Methods

NC precipitation kinetics were studied using milled and annealed U14YWT powders described in a previous report [1]. Note the NCs that form in the annealed powders are similar to those observed in hot consolidated alloys that experience the same time-temperature history. The powder anneals were performed using two different heat-up rates: a ramp anneal (RA) to mimic HIP consolidation; and an isothermal anneal (IA) with very rapid heating and cooling to observe short time processes. The annealing was carried out at selected combinations of times (t) and temperatures (T) that ranged from 1/3 to 81 h and 600 to 1150°C, respectively. Due to the relatively large supply of available material, thermal aging treatments were carried out on MA957 to evaluate the stability of the NCs at selected t-T combinations that ranged from 1/3 to 480 h and 1150 to 1400°C. Small angle neutron scattering (SANS) was used to characterize the NCs in both cases, and Vickers microhardness was used to measure the strength of consolidated alloys and annealed MA 957. Additional details can be found in the dissertation of the lead author [2].

Results

NC Formation and Growth

Figure 1 shows an example of the NC evolution at 1000°C as a function t for both RA and IA powders, in terms of the NC radius (r), volume fraction (f), number density (N), and magnetic to nuclear scattering ratio (M/N). The formation of Y-Ti-O rich NCs is very rapid (almost time-independent) at all T . This is believed to be due to the high diffusion rates at higher T and large super-saturations of excess vacancies produced by MA at lower T . Figure 2 shows a corresponding example of the T -dependence of the NC parameters at $t = 1/3$ h. The NC N , f , and M/N decrease and the r increases with higher T . The NC N , f , and M/N are also higher for the RA compared to the IA powders, since the alloys spend considerable time at lower temperatures in the former case. These results suggest that the kinetics of non-equilibrium NC precipitation are primarily nucleation-controlled.

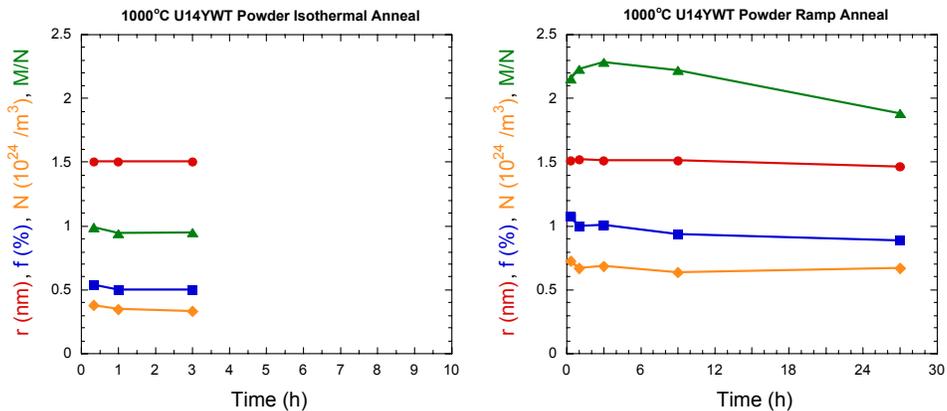


Fig. 1. An example of the NC evolution at 1000°C in annealed powders as a function t .

If the NC atomic solute densities are ≈ 1.1 to 1.2 times higher than the matrix Fe-Cr phase, the M/N ratio which is a measure of the composition of the NCs, is generally consistent with data from 3D atom probe tomography (APT) studies reported by Miller et al. [3], as well as limited measurements we have made on the consolidated UCSB model alloy U14YWT. These atom densities, and the observed solute (Y+Ti) to O ratios, that are >1 , are inconsistent with the properties of known equilibrium oxide phases. The increases in the M/N indicate that the NCs lose Ti (and Y?) and gain Fe with decreasing T . The RA T - t history, and effectively lower T , also increases the apparent Fe content (higher M/N) of the NC compared to the IA treatment.

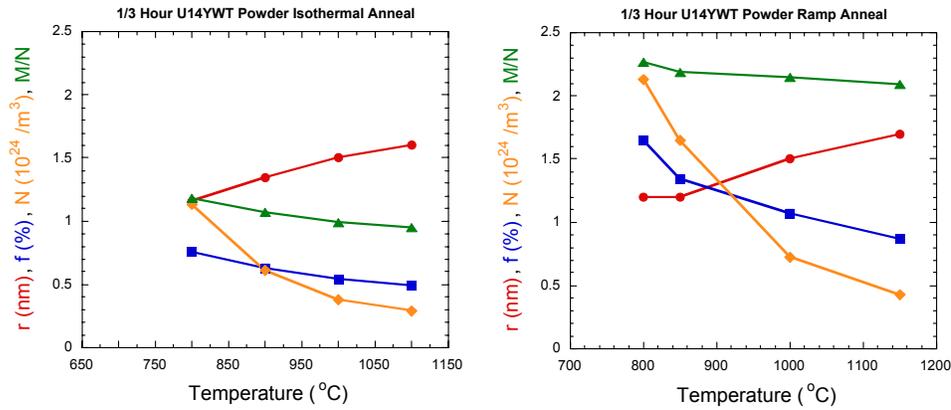


Fig. 2. An example of the NC evolution at 1/3 h as a function T.

The non-equilibrium kinetics of NC evolution is nucleation controlled, with the number density (N) scaling with an effective activation energy of $\approx 53 \pm 15$ kJ/mole as shown in Fig. 3.

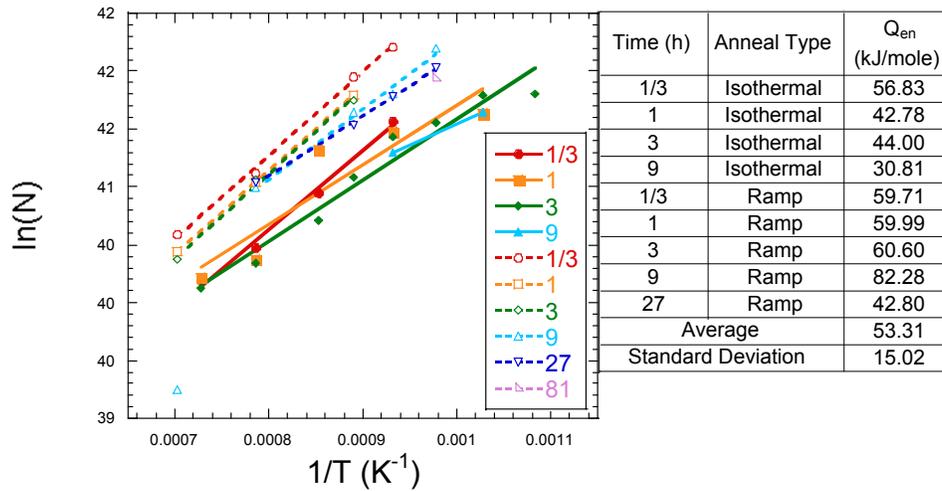


Fig. 3. $\ln[N]$ (N in units of NCs/m³) versus $1/T$ (in units of $1/^\circ\text{K}$). The $N(T)$ can be described by a simple time-independent rapid nucleation model, with an effective activation energy of $\approx 53 \pm 15$ kJ/ mole.

NC Thermal Stability in MA957

As shown in Fig. 4a and b, the NCs in the MA957 alloy extruded at 1150°C are very stable and initially coarsen by a dislocation pipe diffusion mechanism as $r = r_o[k_c t + 1]^{1/5}$, where r_o is the as-processed NC radius and $k_c = k_{c0}\exp(-Q_c/RT)$ is a temperature-dependent rate constant.

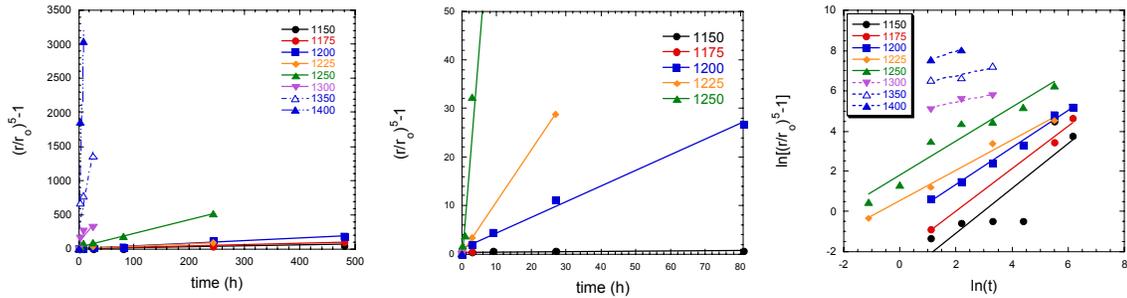


Fig. 4. Plots of $(r/r_o)^5 - 1$ versus annealing time a) all T versus all t ; b) for all T versus short t prior to transformation to nearer-to-equilibrium oxide phases; and c) $\ln[(r/r_o)^5 - 1]$ versus $\ln(t)$ data and fits to evaluate the p -dependence of $r = r_o[k_c t + 1]^p$, yielding $p \approx 1/5$ for the shorter t data with $r < 3.5$ nm (solid lines).

The NCs transform to nearer-to-equilibrium oxide phases at $r \gtrsim 3.5$ nm. Analysis of the data T -dependence of the NC ($r < 3.5$ nm) coarsening data a number of different ways, including as shown in Fig. 5, yields an average effective activation energy of $Q_c \approx 880 \pm 125$ kJ/mole, and $k_{c0} \approx 2.95 \times 10^{27}$ /s. The very high value of Q_c is believed to be associated with the combination of low solubility of Y in ferrite (with large atomic size differences) and the high strength of Y-Ti-O bonds. As shown in Fig. 6, extrapolating the model to lower service temperatures predicts that the NCs will resist coarsening, for example, up to $t > 10^5$ h at 1000°C.

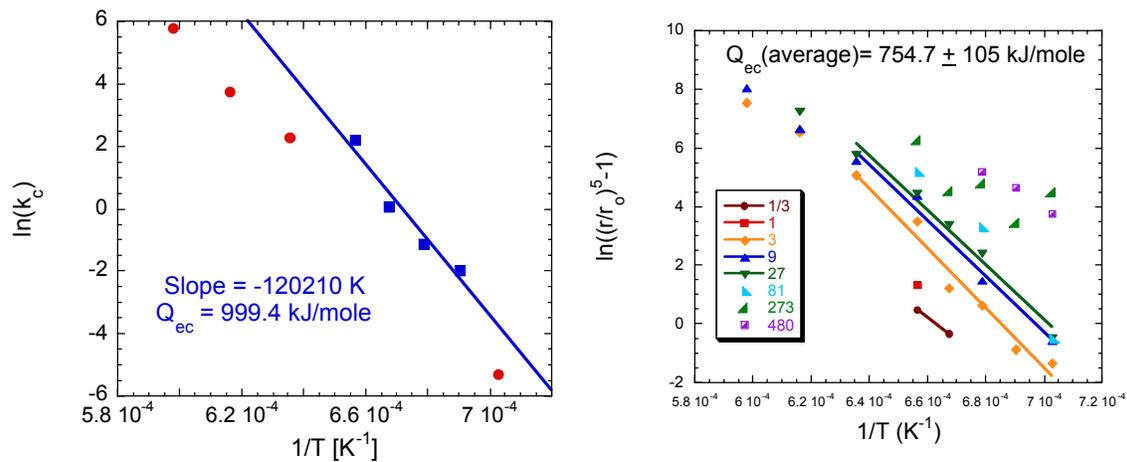


Fig. 5. Effective coarsening activation energy, Q_{ec} , of a) 999.4 kJ/mole from a plot of $\ln(k_c(T))$ versus $1/T$ and b) 754.7 kJ/mole from a plot of least squares fit of $\ln((r/r_o)^5 - 1)$ vs. t_a against $1/T$.

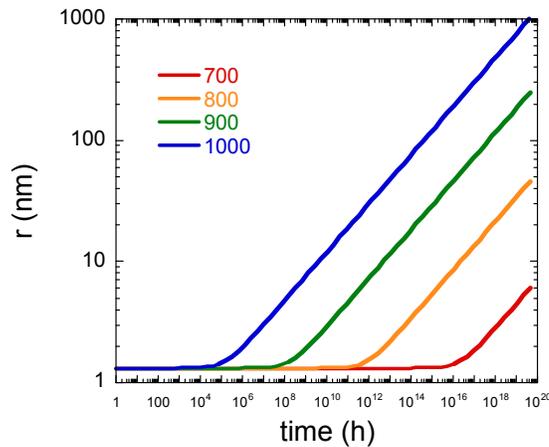


Fig. 6. The predicted r as a function of time for various temperatures.

NFA Strengthening Contributions

The total yield stress (σ_y) of NFAs includes ‘baseline’ (σ_b) contributions from the lattice resistance of ‘impure’ unalloyed Fe, polycrystalline grains or nanograins, substitutional alloy solutes and dislocations, as well as hardening due to NCs that act as dispersed barriers to dislocation slip. The baseline strength depends on the alloy composition and heat treatment history and ranges from $\sigma_b \approx 600$ to 950 MPa. Assuming the NCs contribution to σ_y is given by $\sigma_o = \sigma_y - \sigma_b$, the obstacle strength α can be estimated as, $\alpha(r) = \lambda\sigma_o/[2.45Gb]$, where $\lambda(=1.81r/\sqrt{f}-1.63r)$ is the NC spacing on the slip plane, G is the shear modulus, and b is the Burger’s vector. Here r , f , and, hence, λ , are determined from the SANS measurements.

Figure 7 shows that $\alpha(r)$ is the same for MA 957 and the UCSB model alloys and increases linearly as $\alpha \approx \log[r/2b]$. Thus the NC and small oxides act as weak to moderately strong ($\alpha \approx 0.1$ to 0.5) obstacles that can be sheared by dislocations.

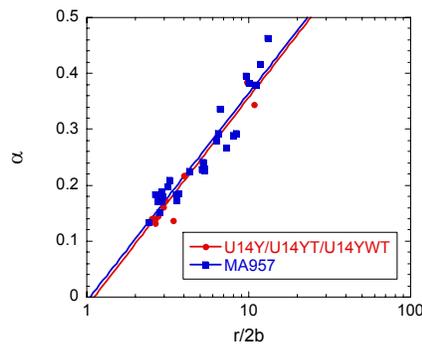


Fig. 7. Plot of α versus $\log(r/2b)$ for the U14 alloys containing Y or Ti and Y and the annealed MA957.

As shown in Fig. 8, for a given volume fraction, f , of NC obstacles, the peak hardening occurs at $r \approx 1.4$ nm, with a maximum value of σ_o/\sqrt{f} of about 7600 MPa. The $\log(r/2b)$ size scaling is consistent with a

modulus interaction mechanism. This mechanism has been modeled by Russell and Brown [2] for nm-scale coherent Cu precipitates. The peak strength of the NC is more than 2 times that for Cu clusters.

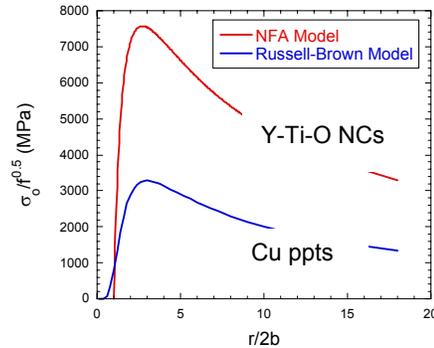


Fig. 8. The predicted σ_0/\sqrt{f} ($f = 0.01$) versus $r/2b$ for NCs and for the Russell-Brown model, showing the peak hardening occurs $r/2b \approx 1.4$ nm.

Future Work

Future work will focus on the following items:

1. Better identification of the character of the NCs using a variety of techniques, including additional ATP studies, as well as transmission electron microscopy and positron annihilation spectroscopy.
2. Extension of the NC thermal stability studies to lower temperatures and longer times.
3. Comprehensive characterization of the coupled evolutions of the NC, dislocation and nano-grain structures during processing and thermal service.
4. Assessment of alternative alloys and processing paths.
5. Evaluating and hopefully resolving of the issue of inhomogeneous microstructures and NC distributions in the UCSB model alloys.
6. Characterization of the constitutive and fracture toughness properties of NFAs and their relation to the overall microstructure.
7. Modeling the thermo-kinetics of micro-nanostructural evolutions in NFAs as well as the structure-property relations.

Acknowledgements

The authors gratefully acknowledge the supply of Fe-14Cr powders provided by and many helpful discussions with Dr. D. Hoelzer of ORNL. We also thank Doug Klingensmith (UCSB) for his contributions to the SANS experiments and Professor Brian Wirth (UC Berkeley) for his help in analysis of the SANS data. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing facilities used in this work. This research was supported by DOE Office of Fusion Energy Science (Grant # DE-FG03-94ER54275) and the INERI DOE Office of Nuclear Energy through a subcontract with ORNL (Grant # 400014112).

References

- [1] M. J. Alinger, G. R. Odette, and D. T. Hoelzer, Fusion Materials Semiannual Progress Report DOE/ER 0310/35 (December 2003) 129–134.
- [2] M. J. Alinger, On the Formation and Stability of Nanometer Scale Precipitates in Ferritic Alloys During Processing and High Temperature Service, dissertation submitted in partial fulfillment of Ph.D. degree in Materials from the University of California, Santa Barbara (September 2004).
- [3] M. K. Miller et al., Mater. Sci. Engr. A V353 (2003) 140–145.
- [4] K. C. Russell and L. M. Brown, Acta Metall. V20 (1972) 969.