1.2 Further Atom Probe Tomography Studies of Nanostructured Ferritic Alloy MA957 in Three Conditions

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Objective

The objective of this work is to characterize the size distributions, number densities, microstructural associations, compositions, structures and thermal stability of the Y-Ti-O nanofeatures (NFs) in ferritic nanostructured alloys (NFA).

Summary

We report on atom probe tomography (APT) studies on nano-structured ferritic alloys (NFAs) that contain an ultrahigh density of nm-scale Y-Ti-O nanofeatures (NFs). A local electrode atom probe (LEAP) was used to characterize the NFs in both as-extruded bar (US) and thick walled tube (French) heats of MA957. APT was also carried out on the US MA957 following long-term thermal aging (LTTA) at 1000ºC for 19 kh. The as-extruded US MA957 was found to contain ≈ 3.2×10^{23} NFs/m^3 with an average diameter of ≈ 2.4 nm. The French MA957 tubing contained an average of 6.1×10^{23} NFs/m^3 with an average diameter of ≈ 2.8 nm. The average Y/Ti/O ratio of ≈ 13/47/40 was similar in both heats. The NFs coarsen under 1000°C LTTA, with average number densities and diameters decreasing to 7×10^{22} NFs/m^3 and increasing to ≈ 2.8 nm, respectively. The NF composition in the aged condition is relatively unchanged with only a slight increase in the Y/Ti ratio.

Introduction and Background

Nano-structured ferritic alloys (NFA) have high tensile and creep strength permitting operation up to 800°C, manifest remarkable resistance to radiation damage and can manage a high concentration of He [1]. These outstanding properties derive from an ultrahigh density of Ti-Y-O enriched nano-features (NF) that provide dispersion strengthening, help stabilize dislocation and fine grain structures, reduce excess concentrations of displacement defects and trap He in fine bubbles [1]. Here we further characterize the NF in NFA MA957 in various conditions.

Material and Methods

The following report describes atom probe tomography (APT) data acquired from three conditions of the alloy MA957. This new data is compared to and combined with APT data previously reported on the same materials. The base MA957 is as-extruded 1150°C, 25mm diameter round bar acquired from Pacific Northwest National Laboratory and referred to as US-MA957. A 9 mm thick, 65 mm outer diameter tube fabricated by center drilling the bar of base material followed by hot extrusion is referred to as Fr-MA957. This heat was acquired from CEA Saclay in France via Oak Ridge National Laboratory. The third variation is the US-MA57 after long-term thermal aging (LTTA) at 1000°C for 19kh. This sample was wrapped in high Cr stainless steel foil during aging to reduce the loss of this element. Approximately two millimeters of the sample surface was removed to avoid the effect of near surface effects.

APT was performed using an Imago Local-Electrode Atom Probe (LEAP) 3000X HR. Samples are prepared by either electropolishing or micromachining using an FEI Helios 600 focused ion beam (FIB). Electropolished samples were made from ~0.5x0.5x20 mm bars using the two stage process described by Miller [2]. FIB sample preparation used the trench method described by Thompson [3]. Each sharpened tip is cleaned to remove Ga damage first using a 5 KeV and then a final 2 KeV beam at 28 pA. The LEAP samples were examined in voltage or laser mode with 200kHz laser or voltage pulse repetition rate, 0.5% or 1% evaporation rate, and a 34 K to 60 K temperature range. In the voltage mode the pulse fraction was either 20 or 25% while in laser mode green (λ = 532 nm) laser pulse energies varied from 0.13 nJ to 0.15 nJ. The Imago Interactive Visualization and Analysis Software (IVAS) package was used for reconstruction and analysis of the LEAP data. The average number densities of the NF are weighted with the total atoms collected, and the NF size and composition averages are weighted based on NF count.

Results

US-MA957

Eight US-MA957 runs carried out in the UCSB LEAP were reported previously [4]. The corresponding results for 2 additional FIBed needles are presented here. The new measurements of the NF sizes (d) and compositions are generally similar to the previous results.

Table 1 shows the average APT composition for all sample runs and the bulk chemistry of MA957 measured in another study [5]. Including the new datasets, the average size of the NF is <d> = 2.4 nm. The overall number densities (N) of NFs varied from ≈ 0.7 to $7.1 \times 10^{23}/m^3$, averaging $3.2 \times 10^{23}/m^3$. The N for the new measurements is higher than the overall average, ranging from ≈ 3.8 to $7.1 \times 10^{23}/m^3$. This large variability reflects the heterogeneous distribution of the NFs, from the nanometer to micron length scales, as well as the small APT volumes analyzed. The overall average nominal Y/Ti/O ratio of the US-MA957 is 14.4/45.6/39.9. The average N and <d> are shown in Table 2.

Figure 1 shows a subset of the data from one of the newly analyzed samples. This sample contained the highest N for any of the US-MA957 runs. No grain boundaries were observed and all the NFs were relatively small (d < 4 nm). The previous samples with lower N typically contained larger (some >10nm diameter) precipitates that were not uniformly present through the sample and were probably associated with grain boundaries.

Table 1. Bulk composition of US MA957

At%	Bulk Chemistry	APT US-MA957
Fe	82.97	83.29
Cr	14.32	14.76
Ti	**1.123**	**0.868**
Mo	0.170	0.144
Y	**0.128**	**0.084**
O	**0.786**	**0.365**
Ni	0.089	0.157
Al	0.183	0.042
Mn	0.065	0.098
Si	0.059	0.066
C	0.073	0.008
Cu	0.009	0.008
B	-	0.023
Co	-	0.049
V	-	0.054
Nb	-	0.005

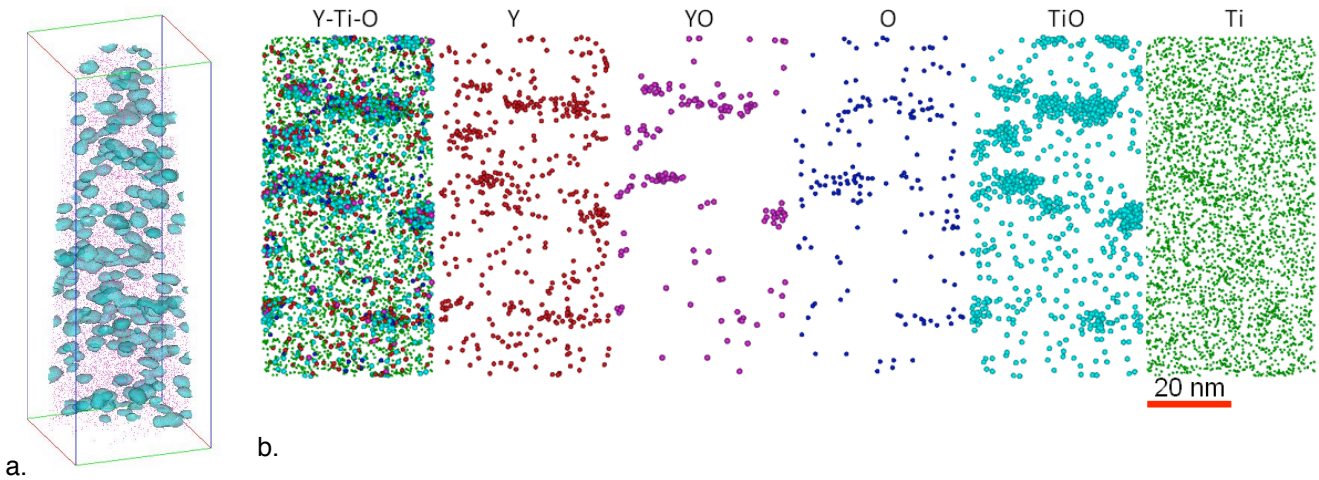

Figure 1. a) 3% Y-Ti-O isoconcentration surfaces in MA957 sample with high number density of NFs; b) 20x20 x40 nm^3 volumes of Y, Ti, and O ions in data set.

A small sample run of approximately 1.5 million ions contained a grain boundary near the edge of the data set. Atom maps of Cr overlaid with specific ions are shown in Figure 2 for this sample. Many solute ions segregate to the grain boundaries including Cr, Ti, Mo, B, and P.

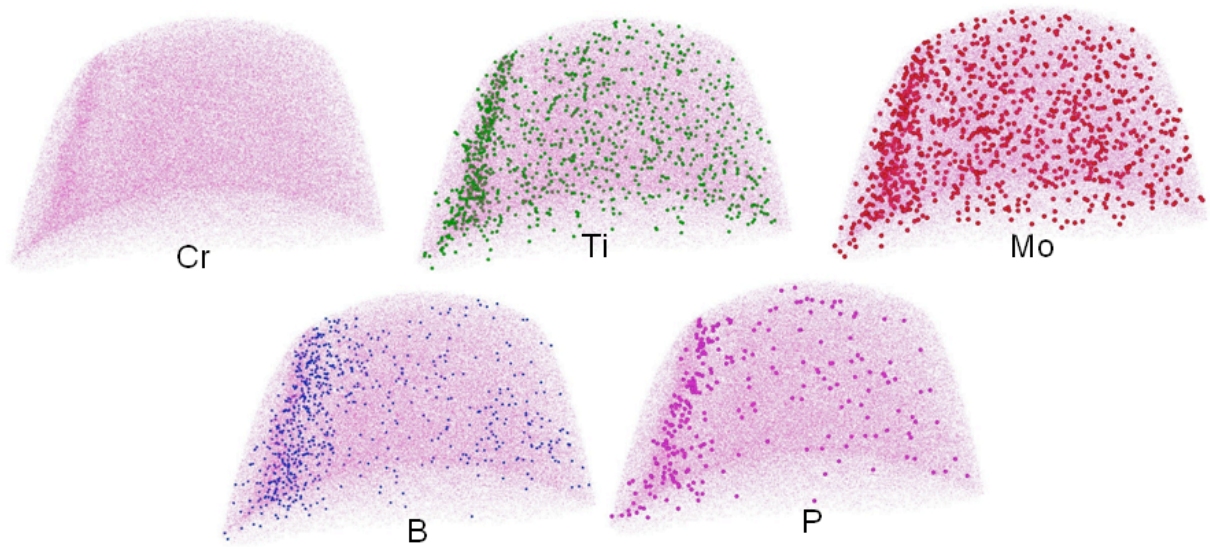

Figure 2. a) Atom maps of MA957 showing segregation to the grain boundary.

Fr-MA957

Two new Fr-MA957 samples were prepared by electropolishing and run in either laser mode or voltage mode with four and five million ions detected, respectively. In a previous report only one Fr-MA957 data set was available for comparison with the US-MA957 [4]. Figure 3 shows Y-Ti-O isoconcentration surfaces for a subset of the voltage mode run where only small NFs were observed. The laser mode run consisted mostly of small NFs, but a

large, Ti-rich, precipitate was also observed on the edge of the dataset. The Y/Ti/O ratio for an observed fraction of the larger precipitate was 1.1/32.6/66.3.

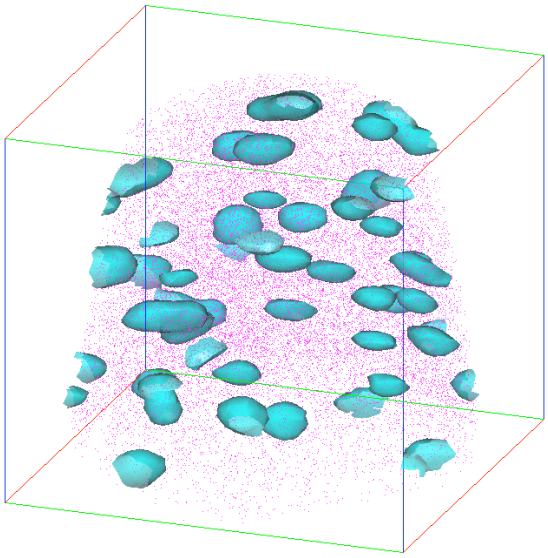

Figure 3. Atom map of Fr-MA957 with 3.5% Y-Ti-O isoconcentration surfaces.

Combining all Fr-MA957 sample data to date gives a number density range from N = 3.1 to 7.8×10^{23} m^{-3}, with an overall average for the Fr-MA957 of 6.1×10^{23} m^{-3}. The previous Fr-MA957 run had slightly larger NFs with <d> ~ 3.1 nm compared to the newer data sets with <d> between 2.0 and 2.4 nm, and with an overall average of 2.4 nm. The overall average Y/Ti/O ratio for the Fr-MA957 is 12.5/47.0/40.4. The compositions were similar between the previous and new voltage run, but the laser run with the large Ti-rich phase had a Y/Ti/O ratio of 16.1/37.5/46.3, excluding the Ti-rich phase. The overall average number density and diameter for the Fr-MA957 is given in Table 2.

US-MA957 LTTA

It has been previously found that NFs are unaffected by long-term thermal aging up to 900ºC. At 950ºC slight coarsening occurs, while at 1000ºC more significant coarsening is observed. The grain sizes, however, remain relatively unchanged as shown in Figure 4. Here the grain structure of the as-extruded US heat of MA957 and LTTA MA957 perpendicular to the extrusion direction are compared. The as-extruded MA957 has a uniform, fine grain structure with aspect ratio about 5:1. This structure is largely unchanged after 19 kh at 1000ºC aging. Higher magnification still shows the presence of small precipitates in the MA957 after LTTA.

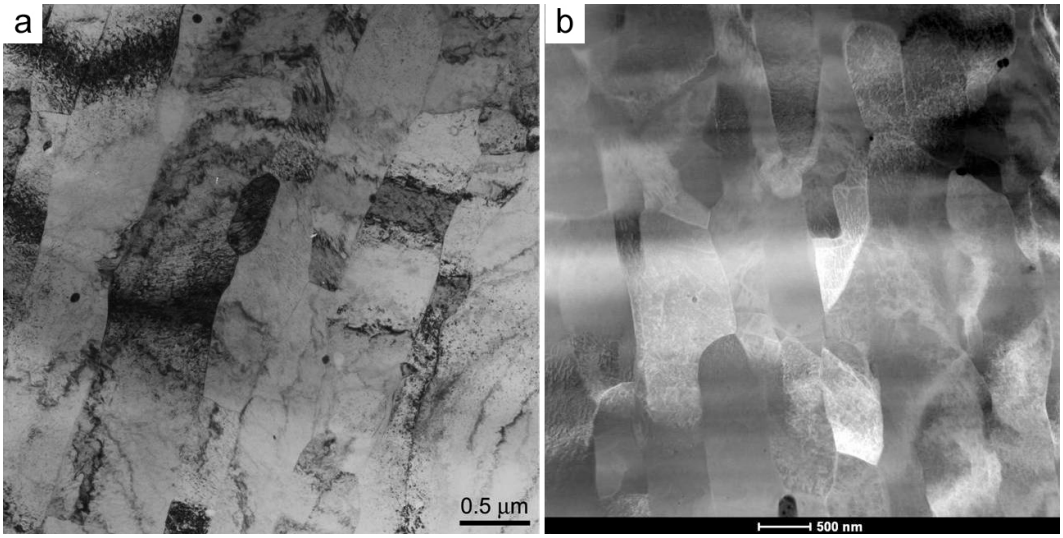

Figure 4. TEM micrographs perpendicular to extrusion direction a) As-received MA957 using bright field imagine, b) STEM imaging of 1000ºC, 19 kh aged MA957.

Table 2. MA957 NF size and number density comparison (add compositions)

NF Parameter	US-MA957	Fr-MA957	LTTA US-MA957
Average diameter <d> (nm)	2.4	2.8	2.8
Number density N (10^{23} m^{-3})	3.2	6.1	0.7

The previous APT revealed a decrease in the number density and a slight increase in the NF size for the 1000ºC LTTA sample. In addition, the total Ti content of the MA957 was reduced from nominal levels of ≈ 1.1 to 0.22 at%. Most of the residual Ti was found to be associated with the precipitates, while the balance was missing from the matrix. However, the composition of the NFs is only modestly affected, with a slight decrease in Ti level. One APT sample contained a grain boundary along its entire length. The Cr, B, Mo, and P segregation to the boundary was similar to the un-aged MA957; no Ti segregation was observed. The Cr content of the bulk sample was found to be ≈ 18 at% which is significantly higher than the ~14.8 at% observed in the un-aged MA957. This increase in Cr is not understood. Additional APT measurements performed on the 1000ºC LTTA confirmed the previous measurement of ≈18 at% Cr. They also showed a lower number of larger NF. The overall average Y/Ti/O ratio for all MA957 LTTA samples is 17.7/34.2/48.1. The Y/Ti ratio is higher than the un-aged material. The size and number density is compared to the US-MA957 and the Fr-MA957 APT results in Table 2 below.

References

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