Characterization of the Composition and Structure of Y-Ti-O Rich Precipitates in Nanostructured Ferritic Alloy MA957 by Transmission Electron Microscopy and Atom Probe Tomography -

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SUMMARY

Nano-dispersion strengthened ferrite alloys (NFA) show great promise for structural applications in severe fusion reactor environments. NFA contain an ultra high density of Y-Ti-O enriched nanofeatures (NF) that, along with fine grains and high dislocation densities, provide high tensile, creep and fatigue strength. The NF are remarkably thermally stable and trap He in fine scale bubbles, thereby suppressing fast fracture embrittlement at lower temperatures, void swelling at intermediate temperatures and degradation of creep rupture properties at high temperatures. However, the precise characteristics of various NF are not yet well understood. They appear to range from coherent solute enriched GP-type zones to near stoichiometric complex oxides, such as Y_2TiO_5 and $Y_2Ti_2O_7$. Here we summarize a recent effort to clarify the characteristics of NF for a reference NFA, MA957, based on the application of several complementary micro-analytical characterization techniques. High-resolution transmission electron microscopy (HRTEM)-Fast Fourier Transform (FFT) power spectra diffraction patterns indicate that the larger features (> 10 nm) are primarily Y_2TiO_5. Limited diffraction data show the smaller features (≈5 nm) are not consistent with known oxide phases. Energy dispersive x-ray (EDX) measurements yield average feature compositions of Y/Ti/O ≈ 27/20/53 for both larger and smaller features. In contrast, atom probe tomography data show average solute compositions of Y/Ti/O = 14/41/45 and Y/Ti/O = 20/32/48 for the smaller and larger features, respectively. The APT data also suggest that even the larger particles contain significant quantities of Fe, and to a lesser extent Cr, which are not observed in the EDX measurements.

Introduction and Background

Different micro-analytical characterization techniques yield different conclusions regarding the compositions and structures of the NF in NFA. For example, atom probe tomography (APT) studies show that NF have complex structures composed of Y-Ti-O enriched cores surrounded by Ti-O rich shells, possibly further surrounded by a more diffuse distribution of higher O concentration [1,2]. APT data also indicates that the non-stoichiometric NF have high Ti/Y ratios (typically about 2-4/1) as well as high (Y+Ti)/O ratios greater than 1 (typically 1.25-1.5/1) [1-8]. The APT data, derived from normal reconstruction methods, also generally suggest that the NF contain large quantities of Fe (30-70%). In contrast, most transmission electron microscopy (TEM) studies have typically found complex oxides (Y_2TiO_5 and $Y_2Ti_2O_7$) at feature sizes in the range of about 5 nm and above, nominally with near stoichiometric Ti/Y = 0.5 to 1 and (Y+Ti)/O = 0.57 to 0.6 [9-11].

These differences may be partly due to the fact that there is a range of different NF in NFA. Notably, however, APT data also show that even at sizes greater than 10 nm, the Y-Ti-O features are non-stoichiometric, manifesting a significant O and Y deficits and large Fe excesses. The compositions of the larger features are broadly similar to those found in the smaller NF [12]. Further, the SANS magnetic to nuclear scattering (M/N) ratio measurements of the NF that form at typical extrusion conditions of 1150°C are broadly consistent with a mix of oxides [13]. However, SANS data are not consistent with the very high Ti contents found by APT. Note SANS measurements also suggest that the NF that form during the slow ramp-up of consolidation temperatures contain an even smaller fraction of Ti.

Another confounding factor in interpreting these apparently discordant observations about the NF and larger precipitate phases is that the various characterization studies typically involved different NFA. In order to address this issue, we have organized an informal round robin study of a single NFA, MA957, involving different characterization methods and participating institutions. The techniques include TEM, APT, SANS, x-ray absorption fine structure spectroscopy (XAFS) and positron annihilation spectroscopy (PAS). The institutions include UC Santa Barbara (including SANS studies at the National Institute of Standards and Technology), Oxford University, Los Alamos National Laboratory, Leoben University (Austria), UC Berkeley and Illinois Institute of Technology (working at the Argonne National Laboratory Advanced Photon Source). Here we provide only a brief summary of the status of this ongoing collaboration and details will be presented in a future publication. Here we will focus a comparison of APT and TEM studies at UCSB.

Summary of the Status of the MA 957 Round Robin Collaboration

SANS and TEM studies are being carried out at UCSB and the APT measurements at UCSB, Oxford (E. A. Marquis) and Leoben University (E. Stergar and P. Hosemann) [13]. All the techniques are in relatively good agreement regarding the nominal size (d), number density (N) and volume fraction (f) of the NF. Again details will be provided elsewhere, but all the techniques are consistent with nominal average NF parameters of d ≈ 2.6 nm, N ≈ $7x10^{23}/m^3$ and f ≈ 0.7%. Note individual measurements of the NF characteristics varied by up to a factor of 2 or more, and TEM and APT showed that some regions contained few or no NF.

The APT measurements of the average Y, Ti and O solute composition of the small NF less than 5 nm with average Y/Ti/O ≈ 14/41/45 are also very consistent with each other. Measurements of larger features in the range of 5-15 nm are also consistent for the three institutions with average values of Y/Ti/O = 20/32/48. Initial SANS measurements of a French heat of MA957 were consistent with a mix of about 71% $Y_2Ti_2O_7$ and 29% Y_2TiO_5 (or an average Y/Ti/O = 20/17/63) [13] and our more recent unpublished measurements for a US heat of MA957 are consistent with about 55% $YTiO_3$ and 45% Y_2TiO_5 (or an average Y/Ti/O = 22/15/63). The SANS data can only be used to check for the M/N consistency with known phases, and these evaluations are subject to considerable uncertainty, due to factors like use of a Y free alloy as a control and possible incomplete magnetic saturation of the Fe-Cr matrix. Nevertheless, the SANS estimates of Y/Ti > 1 are clearly inconsistent with the much lower values of about 0.34 to 0.63 found in APT studies. The APT, TEM and SANS studies also show the presence of larger oxide and oxynitride features in MA957, like TiO_2 and oxides containing Al, Ti and N, often in complex associated-attached clusters of different phases. As noted previously, the APT generally also suggests that the NF and larger features contain large quantities of Fe and, to a lesser extent, Cr.

Comparison of UCSB APT and TEM Observations

TEM studies in the literature have generally found complex oxides in other NFA that are near stoichiometric compositions, most frequently the pyrochlore phase $Y_2Ti_2O_7$ [9-11]. However, one recent TEM study of MA957 suggested a ratio of Y/Ti < 1 at small NF sizes less than about 10 nm. In order to clarify the structure and composition of the NF and larger features and to make a direct comparison between TEM and APT observations, we have carried out a series of HRTEM lattice imaging observations combined with FFT transform power spectra diffraction patterns to index various features in MA957. We also carried out EDX measurements on these particles. Both bright field and high angle annular dark field (HAADF) where also used to observe the features in MA957 and to characterize their morphology and size distributions. In all cases the particles were extracted from the NFA matrix on thin C replica foils using techniques that will be detailed elsewhere. The TEM was carried out on LaB6 FEA T20 Technai and Titan instruments. The EDX measurements were verified by calibration to bulk oxide phases. Further, HAADF showed that the NF and particles could be extracted down to very small sizes (< 2 nm) and at larger sizes the relatively sharp and sometimes polyhedral particle interfaces indicated that the partial dissolution of any potentially diffuse outer regions of the extracted phases did not occur.

Representative results for a larger particle are illustrated in Figure 1. Figure 1a shows a HRTEM lattice image for a large 30 nm particle and diffraction pattern along with a very similar diffraction pattern from a Crystalkit simulation of orthorhombic Y_2TiO_5. Calculated and measured d-spacings and the corresponding angle between the planes are shown in Table 1. These values are also consistent with Y_2TiO_5, but not with either $Y_2Ti_2O_7$ or $YTiO_3$. A total of 14 particles with sizes greater than 10 nm were indexed in this fashion; a large majority of them were found to be structurally consistent with Y_2TiO_5 oxide. Figure 1b shows another 35 nm particle along with the corresponding EDX spectra yielding a composition of Y/Ti/O = 0.25/0.12/0.63, also consistent with Y_2TiO_5. The particle Y/Ti ratios ranged from ≈ 0.9 to 2.2 (see below), Figure 1c shows a Titan STEM line profile of a ≈ 20 nm particle. Clearly there is no indication of a core-shell type structure, as found in APT studies.

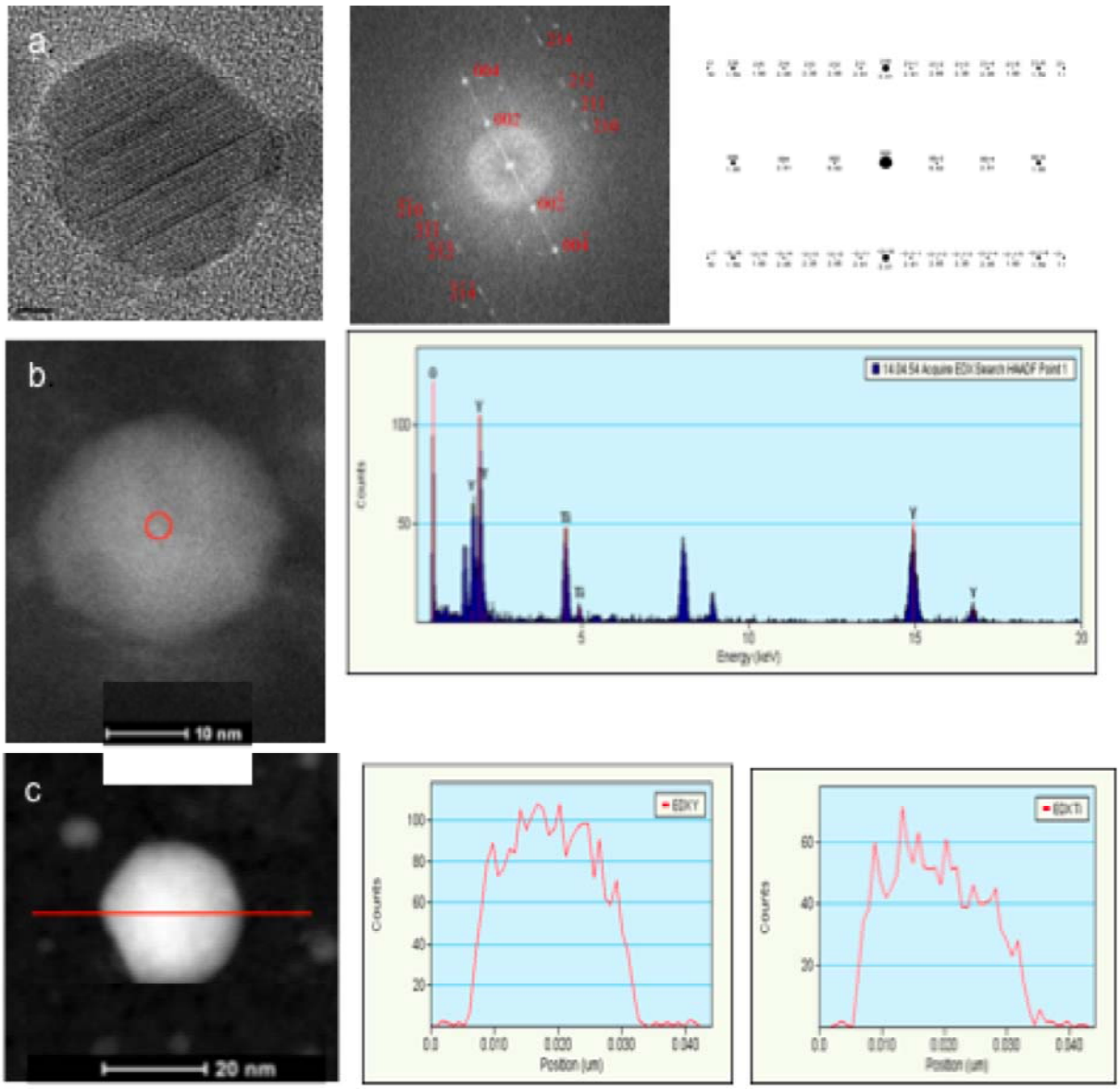

Figure 1 a) A HRTEM image of a large feature and the corresponding derived and simulated diffraction patterns that are consistent with orthorhombic Y2TiO5; b) EDX spectra from a large feature indicating a compositions of Y/Ti/O = 25/12/63 consistent with Y_2TiO_5; c) STEM Ti and Y composition profiles for a large feature that do not show Ti enrichment in an outer shell.

Table 1 Measured and nominal Y_2TiO_5 d-spacings and the corresponding inter-planar angles for the large particle indexed in Figure 1

System	d1 (002)	d2 (210)	interplanar angle
Measured	5.52	3.15	89.8 °
Nominal Y_2TiO_5	5.625	3.21	90.0°

Figure 2a shows the corresponding FFT power spectra for a smaller ≈ 5nm particle that index two d spacings of 3.1Å and 3.0Å with an inter-planar angle of about 73.5°. These values are not consistent with cubic $Y_2Ti_2O_7$, orthorhombic $YTiO_3$ or either hexagonal or orthorhombic Y_2TiO_5. However, indexing was usually more difficult in the smaller feature size range, and it was generally not possible to extract two d-spacings and an inter-planar-angle for low index particle orientations. Figure 2b shows the EDX spectrum for a smaller ≈ 5 nm particle yielding Y/Ti/O = 14/15/71. Figure 2c shows the measured Y/Ti ratios are scattered, ranging from less than 1 to more than 2 and averaging ≈ 1.5. The Y/Ti ratio is not strongly affected by the particle size.

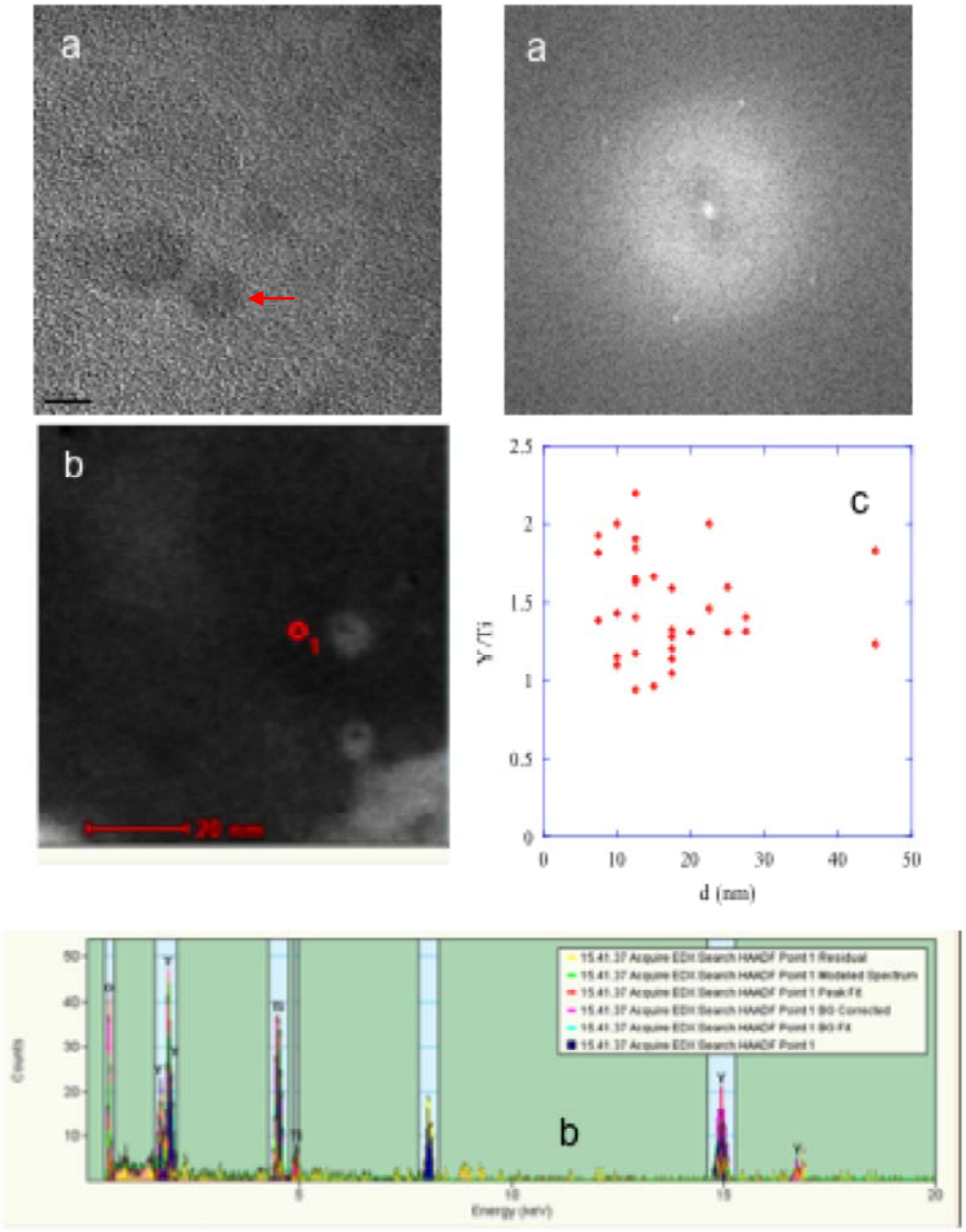

Figure 2 a) A HRTEM lattice image of a small feature and corresponding diffraction pattern; b) the EDX spectrum for a small feature with Y/Ti/O = 14/15/71; c) the observed Y/Ti ratio as a function of average ±2.5 nm binned feature sizes.

Figure 3a summarizes the average composition estimates derived from the various techniques along with the oxide compositions. There is reasonable overall agreement but the APT Y/Ti are not consistent with the results of the other techniques, or the known complex oxide phases. Figure 3b shows a representative HAADF micrograph of the NF and larger features along with the corresponding size distribution. This figure emphasizes that the observation of oxides that are primarily Y_2TiO_5 phases was for features larger than 10 nm and that the oxide-like but typically non-stoichiometric Y/Ti ratio, averaging 1.4, was observed for features generally larger than 5 nm. However, the NF at sizes less than 5 nm have only been probed by SANS and APT techniques with differences that remain to be resolved.

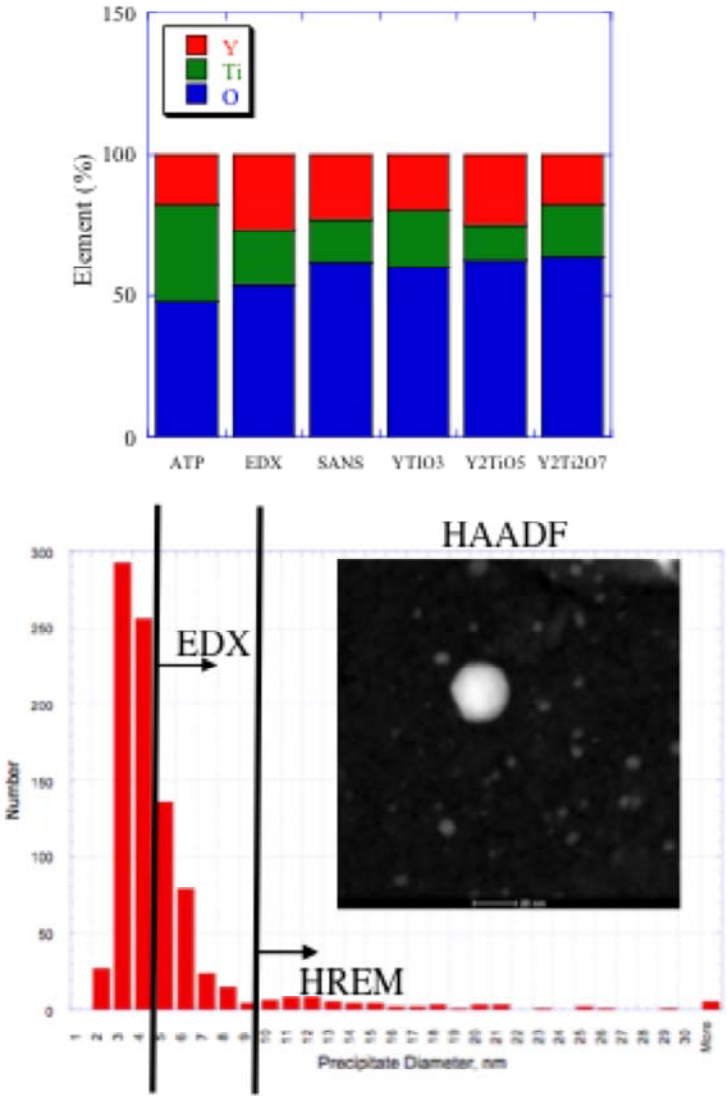

Figure 3 a) Summary of the small feature (NF) composition measured by different techniques compared to those for complex oxides; b) a typical HAADF image of the NF and a larger feature and the corresponding size distribution.

Discussion and Conclusions

First we note that our results are not consistent with the findings of a similar study by Sakasegawa et al [14]. These researchers reported pyrochlore $Y_2Ti_2O_7$ oxides, rather than Y_2TiO_5, and found that the Y/Ti ratio is 0.5 or

less for small NF below about 10 nm. The corresponding compositions measured at larger sizes were 1 to 1.5, slightly below that found in this study.

A major objective of this work was to *directly* compare compositions measured by TEM EDX and APT in larger features. We believe these results clearly show that APT compositions reflect some significant artifacts. First the large quantities of Fe, and to a lesser extent Cr, observed by APT are not supported by the EDX measurements. This conclusion can be qualitatively understood in terms of ion trajectory aberrations in the APT field evaporation process that mixes surrounding matrix atoms with the solutes that are actually in the features [15]. The low Y/Ti and O/(Ti + Y) ratios in APT are also anomalous. Presumably this is also the case for the smaller NF as well. Possible reasons for these APT anomalies are under investigation.

Future Work

The APT, work described above is preliminary and represents ongoing research, including the round robin collaboration on MA957. Current work on MA957 at UCSB includes: a) X-ray diffraction measurements on bulk extractions; b) indexing of the interfaces of both extracted and embedded particles; c) use of energy filtered TEM (EFTEM) to image and characterize the compositions of extracted particles; d) additional PAS and XAFS studies. It is also hoped that TEM energy electron loss spectroscopy (EELS) and anomalous small angle X-ray scattering measurements at the APS will be carried out in the future.

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