1.4 Inter-Laboratory Atom Probe Tomography Characterization Study of the Nanofeatures and the Bulk and Matrix Compositions of US MA957

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OBJECTIVE

The objective of this work was to carry out an inter-laboratory comparison of the nano-features (NF) and bulk and matrix compositions of a reference nano-structured ferritic alloy (NFA) characterized by atom probe tomography (APT) at four institutions. The reference NFA was an as-extruded heat of US MA957.

SUMMARY

APT studies were carried out at the University of California Santa Barbara (UCSB), University of Leoben (UL) in Austria, Oxford University (OU) in England and University of Rouen (UR) in France. The tools used at UCSB, OU and LU were all Cameca (previously Imago) HR3000X-HR Local Electrode Atom Probes (LEAPs), while the fourth instrument at Rouen was a Camaca Laser Assisted Wide Angle Tomographic Atom Probe (LAWATAP). The measurements reported by the various APT groups are in remarkable agreement with one another. The bulk average compositions (at.%) for Fe, Cr, Ti, Y and O are: 83.6±0.39, 14.8±0.46, 0.771±0.059, 0.064±0.022 and 0.273±0.031, respectively. The corresponding matrix Fe, Cr, Ti, Y and O are, respectively: 84.1±0.283, 14.7±0.212, 0.636±0.021, 0.017±0.001 and 0.109±0.020. The average NF compositions, based only on their Y, Ti and O contents (at.%), are 13.9±0.92 Y, 41.6±3.34 Ti and 45.4±4.77 O, respectively. The corresponding average NF number density (N) and average diameter (<d>) are: $5.1\pm1.06\times10^{23}/m^3$ and 2.72±0.56 nm, respectively.

PROGRESS AND STATUS

Experimental Methods

Data was collected using a range of experimental conditions. Similarities and differences in the various APT methods are briefly summarized here, but will be discussed in much greater detail in future publications. The compositions of the matrix and overall bulk were evaluated, along with the composition, number density (N) and diameters of the NF; the mean diameter is reported here, <d>. Not all of these measurements are available from all the participating institutions at this time, so this should be considered to be a preliminary report. The data analysis is continuing along with some additional APT measurements. In total, volume equivalent to ≈ 500×10^6 atoms were probed in this study.

Samples at UCSB were prepared by either electropolishing or using an FEI Helios 600 focused ion beam (FIB) instrument, while all samples prepared RU and LU were electropolished. LEAP measurements at all three institutions were performed in voltage or laser mode with a 200 to 250 kHz pulse rate and 0.5 to 1% target evaporation ratio. The analysis conditions at UCSB ranged from 0.05 to 0.5 nJ laser pulse energy, temperatures between 33 and 70 K and a 20 to 25% pulse fraction. All the samples at LU were run in laser pulsing mode at energies between 0.1

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and 0.3 nJ and temperature between 33 and 58 K. At Oxford samples were run in either voltage mode (25°K and 15%) or in laser pulsing, typically at 40-50°K and 0.4 nJ to minimize the Fe^*/Fe^{2+} ratio. LAWATAP measurements at UR used a laser pulse rate of 100 kHz, at a laser power of either 0.14 or 0.19 nJ at 50 K. In the later case, the laser energies were set to get a laser pulse equivalent to a voltage pulse fraction of 20%. It should be noted that the laser spot size is larger in the LAWATAP, hence the corresponding energy density is significantly lower than in the laser LEAP measurements.

The LEAP data were analyzed using the IVAS software package, while the LAWATAP results were analyzed with the GRM 3D Data Software developed by the Group of the Physics of Materials (GPM) at UR. In all the IVAS reconstructions, the NFs were identified and their compositions were determined using the maximum separation distance method for the solute ions of interest, Y, Ti and O, including their ionic forms like TiO and YO [1]. All these solute ions in a cluster were used to determine the radius of gyration (l_g), which is related to an estimated physical spherical radius as $r_{sphere} = 1.29l_g$ [2,3]. At OU the clusters were identified using the TIO and YO molecular species. Cluster compositions were measured with a $L= d_{max}$ and $e = d_{max}/2$. The cluster compositions were calculated after removing all of the Fe atoms and other elements proportionately to the matrix composition. At UR cluster atoms were identified by using a grid to divide the analyzed volume into small cubes, first calculating the concentration of solutes in each cube, and then assigning a concentration value to each ion using linear interpolation based on its proximity to the center of the surrounding cube volumes. Atoms at concentrations greater than a specified limit were considered to be in the cluster. The NF number density was calculated using the total number of ranged atoms in the measured volume. NFs on the edge of the volume were counted as one-half.

The mass spectrum for MA957 has many overlapping and interfering peaks. In order to obtain better estimates of composition, where possible the natural isotope abundance and the ion counts in the most isolated peaks were used to establish the contributions from the same element with overlapping peaks. Large post-peak tails, especially from Fe^{+2} isotopes, overlap the peaks for Y^{+3} and some TiO^{+2}. The numbers of ions in these smaller peaks were found by subtracting off the post peak Fe^{+2} tail.

Results

Table 1 summarizes the bulk composition measurements for the key matrix and solute elements Fe, Cr, Ti, Y, O and Mo. The numbers for the various labs are the un-weighted averages of the individual APT measurements that collectively result in the total of the number of ions collected that are also shown in the Table. The overall averages of the different labs are: 83.6±0.39 Fe, 14.8±0.46 Cr, 0.771±0.059 Ti, 0.064±0.022 Y, 0.273±0.032 O, and 0.158±0.016 Mo. The standard deviations (SD) are relatively small in all cases. Table 2 summarizes the matrix compositions, defined, as the solute atoms not included in the NF clusters. The averages are 84.1±0.283 Fe, 14.7±0.212 Cr, 0.636±0.021 Ti, 0.017±0.001 Y, 0.109±0.020 O and 0.143±0.017 Mo. The matrix composition SD are again all relatively small.

Table 1. APT bulk average compositions of MA957 (at%).

Lab	Fe	Cr	Ti	Y	O	Mo	10^6 ions
UCSB	83.4	14.8	0.831	0.054	0.296	0.143	57.1
Rouen	83.3	15.2	0.771	0.049	0.287	0.155	32.6
Leoben	84.0	14.3	0.713	0.089	0.236	0.174	70.0
Av	83.6	14.8	0.771	0.064	0.273	0.158	-
SD	0.39	0.46	0.059	0.022	0.032	0.016	-

Table 2. APT matrix average compositions of MA957 (at%).

Lab	Fe	Cr	Ti	Y	O	Mo	10^6 ions
UCSB	84.0	14.8	0.651	0.017	0.092	0.108	9.7
Rouen	83.9	15.0	0.636	0.015	0.123	0.162	32.6
Oxford	84.4	14.5	0.622	0.019	0.114	0.160	TBD
Av	84.1	14.7	0.636	0.017	0.109	0.143	-
SD	0.283	0.212	0.021	0.001	0.020	0.037	-

Based on standard analysis the NF nominally contains large quantities of matrix Fe and Cr. For reasons that will be discussed in detail in future publications, and which are also the subject of a growing literature [for example see 4,5] the large quantities of NF Fe and, at least to a significant extent Cr, are believed to be artifacts of the APT method. These artifacts are primarily associated with so-called trajectory aberrations that artificially insert matrix ions into the NF volume in the case of features that have a lower evaporation potential than the bulk ferrite phase [6,7]. Thus we focus here on the Y, Ti and O ions that are the ingredients of the complex oxides like $Y_2Ti_2O_7$ that are known to form the core of NF in NFA [6]. The average NF compositions for the various labs are shown in Table 3. The overall average solute values are: 13.9±0.81 Y, 41.9±3.19 Ti and 44.2±4.65 O. Thus the compositions of the NF are also very similar in all cases. The corresponding average Y/Ti ratio is 0.33 and the average (Y+TI)/O ratio is 1.24. Notably these values are inconsistent with known Y-Ti-O complex oxides, like cubic pyrochlore $Y_2Ti_2O_7$ and orthorhombic Y_2TiO_5.

Table 4 shows that the various APT measurements NF N and <d> are also in reasonably good agreement with one another. The overall averages are N = $5.1\pm1.06\times10^{23}/m^3$ and <d> = 2.72±0.56 nm. The only apparent systematic difference is that the <d> is significantly larger in the case of the LAWATAP (RU) results, with <d> =3.36 nm, compared to the average of 2.38 for the LEAP measurements at UCSB and LU.

Table 3. APT NF Y-Ti-O solute compositions (%).

Lab	Y	Ti	0	10^6 at
UCSB	14.4	45.6	39.9	57.1
Rouen	14.3	40.7	45.0	32.6
Leoben	14.4	44.0	42.0	65
Oxford	12.5	37.3	52.2	NA
Aver	13.9	41.9	44.8	-
SD	0.81	3.19	4.65	-

Table 4. APT NF number densities (N) and average diameters (<d>).

Lab	N ($10^{23}/m^3$)	<d> (nm)	# Clust
UCSB	3.9	1.18	805
Rouen	6.6	1.68	404
Leoben	5.7	1.21	823
Oxford	4.4	-	TBD
Aver	5.1	1.36	
SD	1.06	0.28	-

ANALYSIS AND DISCUSSION

A detailed analysis and interpretation of these results will be presented in a future publication. However, it is useful to briefly examine the implications of these observations. First, APT measurements clearly can be very precise, and overall do not seem to be highly dependent on the individual laboratory where they are carried out. However, being precise does not necessarily translate to being accurate if the technique implicitly shares common limitations, anomalies and artifacts. For example it is now established by TEM, in the size range where the two techniques overlap, that the NF in MA957 consist of the pyrochlore $Y_2Ti_2O_7$ complex oxide, with a Y/Ti ratio ≈ 1, rather than the 0.33 observed in APT [6]. The (Ti+Y)/O ratio is harder to establish with TEM but is lower for $Y_2Ti_2O_7$ at ≈ 0.57 than observed by APT at ≈ 1.24. Discussion of the limitations that might lead to these apparent discrepancies are beyond the scope of this short report. However, we will further analyze the results to probe possible explanations of APT observations and to gain additional insight.

Table 5 shows the nominal overall chemical composition of the MA957 along with the average APT bulk and matrix compositions. The bulk compositions of Y, Ti, O and C are significantly lower than the nominal alloy chemistry. This may be due to the sequestering of these elements in a low number density of coarse phases, such that the probability of encountering them in APT study is very low. Alternatively, the APT may undercount some of these elements. Table 5 also shows the difference between the APT bulk and matrix compositions. The differences are small except in the case of Y, Ti and O, consistent with the fact that these elements are associated with the phase separated NF. The fraction of these solutes that are presumably associated with the NF is 0.23, 0.75 and 0.61 of the bulk composition for Ti, Y and O, respectively. Table 6 summarizes the estimated NF solute contents based on the atomic fraction differences (%), consisting of 0.143 Ti, 0.049 Y and 0.17 O, respectively. Table 7 summarizes various estimates of the NF volume fraction (f_{nf}) in various ways. In the first case, the f_{nf} is estimated to simply be the sum of the Y, Ti and O differences between the bulk and matrix, which is f_{nf} ≈ 0.36%. In the

second case it is assumed that the Y, Ti and O reside in a stoichiometric $Y_2Ti_2O_7$ oxides with a density of 4.98 g/cm^3, based on the Y estimated to be in the NF, giving $f_{nf} \approx 0.28\%$. The two other estimates of f_{nf} are based on the Ti and O NF $Y_2Ti_2O_7$ contents, resulting in $f_{nf} \approx 0.81$ and 0.16%, respectively. These estimates of f_{nf} are somewhat lower than SANS measurements with $f_{nf} \approx 0.92 \pm 0.08$, except for the estimate based on Ti. Table 8 compares the estimated NF Y/Ti and (Y+Ti)/O ratios based on both direct evaluations of the clusters and the solute atomic balance estimates. The agreement is remarkably good, although the two evaluations are not completely independent of one other.

Table 5. Averages solute location and differences including some trace elements (%).

Loc	Fe	Cr	Ti	Y	O	Mo	Mn	Si	C	Al
Chem	83	14.3	1.12	0.128	0.79	0.17	0.065	0.059	0.073	0.183
Bulk	83.6	14.8	0.779	0.065	0.281	0.157	0.066	0.069	0.006	0.038
Matr	84.1	14.7	0.636	0.017	0.109	0.143	0.057	0.076	0.005	0.022
Diff	-0.50	0.031	0.143	0.049	0.172	0.014	0.009	-0.006	0.001	0.016
Dif/Av	-0.01	0.00	0.18	0.75	0.61	0.09	0.14	-0.09	0.17	0.42

Table 6. Y, Ti, O solute balances estimates of f_{nf} (%).

Location/Solute	Ti	Y	O
Bulk	0.779	0.065	0.281
Matrix	0.636	0.017	0.109
Estimated in NF	0.143	0.049	0.172

Table 7. Solute balance estimates of NF volume fractions (f_{nf}) and solute ratios.

f_{nf}(%), Y/Ti, (Y+Ti)/O	
f_{nf} from Y+Ti+O	0.36
f_{nf} from $Y_2Ti_2O_7$ and Y	0.28
f_{nf} from $Y_2Ti_2O_7$ and Ti	0.81
f_{nf} from $Y_2Ti_2O_7$ and O	0.16

Table 8. Comparison of NF Y/Ti and (Y+Ti)/O ratios from APT evaluations (DE) of the clusters and atomic mass balance estimates (MB).

Ratios	Clusters	Atomic Balances
Y/Ti	0.33	0.34
(Y+Ti)/O	1.24	1.12

CONCLUSIONS

An inter-laboratory round robin APT study of the bulk, matrix and NF compositions of a US heat of MA957 showed that the results found by the four participants are generally in excellent agreement with one another. The agreement is also good for the number densities of the NF. There is a more significant difference in the LAWATAP evaluation of the average NF diameter, which is significantly larger than observed in the LEAP measurements. This difference could come from the tools used for the data analysis. Some LEAP data will be analyzed with the GPM 3D Software to clarify this point. Solute atom fraction based estimates of the NF volume fractions are reasonable but somewhat lower than the estimates based on SANS. However, direct APT evaluation of the NF composition is in good agreement with indirect estimates based on the differences between bulk and matrix Y, Ti and O contents. Both indicate an Y/Ti ratio of ≈ 0.33±0.01 and a (Y+Ti)/O ≈ 1.18±0.06.

FUTURE WORK

The data analysis will be completed and a few additional measurements will be carried as needed. A paper on these results will be prepared for journal publication. This paper will be expanded to discuss APT issues, anomalies and artifacts.

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