Comparison of atom probe tomography and transmission electron microscopy analysis of oxide dispersion strengthened steels

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Abstract. Oxide dispersion strengthened steels owe part of their high temperature stability to the nano-scale oxides they contain. These yttrium-titanium oxides are notoriously difficult to characterise since they are embedded in a magnetic-ferritic matrix and often <10 nm across. This study uses correlated transmission electron microscopy and atom probe tomography on the same material to explore the kind of information that can be gained on the character of the oxide particles.

The influence of chromium in these alloys is of interest, therefore two model ODS steels Fe-(14Cr)-0.2Ti-0.3Y_2O_3 are compared. TEM is shown to accurately measure the size of the oxide particles and atom probe tomography is necessary to observe the smallest sub-1.5 nm particles. Larger Y_2Ti_3O_7 and Y_2TiO_5 structured particles were identified by high-resolution transmission electron microscopy, but the smallest oxides remain difficult to index. Chemical data from energy-filtered TEM agreed qualitatively with the atom probe findings. It was found that the majority of the oxide particles exhibit an unoxidised chromium shell which may be responsible for reducing the ultimate size of the oxide particles.

1. Introduction & Background
Ferritic oxide dispersion strengthened (ODS) steels are being considered as structural materials for fission and fusion reactors due to their low activation, high temperature stability and radiation resistance [1]. The 1–10 nm yttrium-titanium rich oxides that hinder dislocation motion at high temperature also harmlessly recombine radiation defects and trap inert gases away from grain boundaries [2]. Understanding the particle character is critical because the size distribution and dispersion influence the mechanical properties [3] and their chemical nature determines their thermal and radiation stability [4].

Many methods have been used to study these nano-scale oxides [5, 6, 7] but only transmission electron microscopy (TEM) and atom probe tomography (APT) provide sufficiently spatially resolved chemical and structural information to distinguish the smaller oxides from larger oxides located at the surface, grain boundaries and in the bulk.

The methodology of this study includes both TEM and APT of the same specimens to give a more convincing and complete characterisation of the same volume of material. The focus of the TEM examination was the spatial distribution, size and the structure of the oxides. With atomistic sensitivity and sub-nanometer resolution, APT was used to study the chemistry of individual oxide particles and their chromium content.
Part of the uncertainty relating to the identity of the oxides undoubtedly comes from the many different alloy compositions and processing routes used to produce different ODS alloys. In this study, the alloys have identical processing history and a systematic variation in chemistry to determine the influence of chromium on the oxide particles. Chromium is a key component of structural steels, providing enhanced strength and corrosion resistance. The model ODS steels are nominally Fe-0.2Ti-0.3Y2O3 and Fe-14Cr-0.2Ti-0.3Y2O3 (all wt%) and are produced by the Indira Gandhi Centre for Atomic Research (India).

Titanium has been attributed to having a strong refining influence on the oxides [8] but the effect of chromium has been less fully investigated. Chromium rich shells around the Y-Ti-oxides have been observed by TEM [9] and APT [10]. By comparing model alloys with and without a chromium addition the effect of chromium can be evaluated.

2. Materials & Methods
A pre-alloyed powder containing Fe-(14Cr)-0.2 Ti was mechanically alloyed with 0.3 Y2O3 powder (all in wt%) using a horizontal high-energy Simoloyer attritor mill. Milling under an argon atmosphere took 4 hrs using a ball-to-powder ratio of 10:1. Consolidation was achieved using hot extrusion at 1050 °C and 1150 °C for the Cr-free and Cr containing alloys respectively.

Bulk material were cut to 0.5x0.5x20 mm and electropolished into needles using perchloric acid by standard methods [11]. TEM samples were also prepared using a FIB lift-out technique.

200 keV TEM observations were made using a Philips CM20 and a JEOL 2200MCO FEG TEM fitted with a monochromator, two spherical aberration (Cs) correctors and an Ω-filter. The largest (120 µm) condenser aperture was used and the beam was focused to give an an image with a diameter slightly bigger than the CCD to maximise intensity. The convergence and objective aperture half-angles were 6 mrad and 20 mrad, respectively. Low-loss energy-filtered series collected from the 10–80 eV energy-loss range included the Y N2,3 (26 eV), Cr M2,3 (42 eV) and Fe M2,3 (54 eV) edges. Steps of 1 eV, using a 2 eV slit and 6 s acquisition time per image were used and images were hardware binned by 4 to 1024×1024 pixels. The EFTEM series were processed after acquisition using multivariate statistical analysis (MSA) in order to reduce statistical noise, as described elsewhere [9].

Atom probe analyses were performed using a LEAP-3000X HR microscope. During analysis, samples were maintained at 50 K and a 532 nm wavelength laser with a pulse width of 10 ps, repetition rate of 200 kHz, pulse energy of 0.3 nJ and spot size of less than 10 µm were used to promote field evaporation. Oxide clusters in the data were identified using the method of maximum separation of Y, YO, TiO and O ions. A maximum separation of core ions of 0.7–1.1 nm was used with a Nmin between 8–15. The concentration line profiles were calculated in MATLAB for every cluster in the data scaled to each cluster’s size. In this way profiles of large and small clusters can be combined on the same plot. Previously, representative clusters had to be chosen for analysis but using this method all the clusters can be investigated.

3. Results & Discussion
The particle radii were measured using diffraction contrast (Fig. 1a), Fresnel imaging and EFTEM (Fig. 1b) techniques. All of these gave consistent results and the size distributions are shown in figure 2b. The TEM imaging of electropolished atom probe needles leads to a bias in counting medium sized particles as they are more obvious in the thicker shank of the tip (leftmost Fig.1a), but very large particles are physically too large to exist in the end of the tip. EFTEM provides a wider field of view but is limited to thin regions (< 100 nm). The APT data is in the form of a point cloud and the particles exist as more diffuse clusters. It is common to report the radius of gyration (Rg) of these clusters to compare their size. Trajectory aberrations can influence the lateral dimensions of the particles and oxygen spreading can increase their size perpendicular to the analysis direction, Z. But the size along Z is relatively unchanged in spite of these aberrations [12], therefore only the component of Rg along Z is reported. The Rg is much smaller than the radius measured by TEM as shown in the size distributions in figure 2b. Because
only 37% of the atoms are detected in the LEAP some reduction of size is expected, especially for the smaller clusters. The extent of the clusters (in Z) was measured to be 3 times $R_{gc}$ and may therefore give a more representative size measurement. In the Fe-14Cr alloy, the number density of particles as measured by TEM was 3.0–4.4x10^{22} per m^{3} but ten times greater than this when measured by APT (Fig.2b), suggesting that the APT is indeed more sensitive to the numerous smaller oxide particles.

Faceted particle edges parallel to \{110\}_{\text{matrix}} were observed when viewing down [002]_{\text{matrix}}. No structural determination was possible for the <2 nm particles, but larger particles were structurally consistent with the bulk structures of Y_{2}Ti_{2}O_{7} and Y_{2}TiO_{5}. The composition of the oxides from APT in both alloys shows a range of Y:Ti ratios consistent with either bulk stoichiometry but the oxygen content is only 50–60 at%. Fe is present in the clusters because of trajectory aberrations [12]. Fe & Cr are not expected in the oxide core by energetic considerations [13] and Fe has not been found in extracted particles [5].

In the Fe-14Cr alloy, a Cr-rich shell was apparent using EFTEM in >10 nm particles and in most clusters observed using APT. As shown in figure 2a the Cr ions have a shell-like profile (11.5 at% in the bulk) but the CrO ions take a profile similar to the O and FeO ions. We do not believe that there is either oxidised Fe or Cr in the particles, but that oxygen atoms originating from the particles combine with Fe or Cr from the matrix and evaporate as FeO or CrO molecular species. Similarly partially-oxidised Cr-rich shells have been reported in similar alloys [10].

The addition of Cr to the alloy reduces the average size and distribution of sizes of the Y-Ti oxides (Fig. 2b). The addition of Cr could increase the rate of nucleation of the Y-Ti oxides or reduce the rate of coarsening in order that the average size is reduced even with the increased consolidation temperature. The smallest clusters contain fewer than 100 atoms making the evaluation of shell size uncertain. For the larger clusters, the shell size increases with cluster radius. Quantification of the size of the Cr-shell will help to clarify the mechanism of its formation. This shell should not be ignored as it reduces the oxide-metal surface energy, could increase thermal stability and has implications for the response of the oxide particles to radiation.
Figure 2. (a) Average line profiles along the analysis direction from atom probe (Cr-free = 200 and Cr-alloy = 500 clusters total). Each line profile was normalised to the size of the oxide clusters so that different sized clusters could be compared on one plot. Core ions=YO+Y+TiO.
(b) Size distributions of oxide clusters in the same alloys measured by TEM and APT ($R_{gc}$).

4. Conclusions
TEM and APT have been used to characterise model ODS steels and investigate the oxides present in detail. For larger particles diffraction contrast was suitable to determine their size and EFTEM imaging of the $Y_{N2,3}$ edge showed yttrium rich oxides as small as 1.5 nm in diameter. The smallest most numerous (<1.5 nm) oxides were only visible using atom probe tomography but the size measurement by APT requires careful calibration of the reconstructed data and analysis to reduce the influence of trajectory aberrations. Low-loss EFTEM images showed Y-rich particles with a Cr-rich shell and the bulk oxides $Y_2Ti_2O_7$ and $Y_2TiO_5$ were identified by structural measurements. Y-Ti-oxide clusters in the APT data had compositions consistent with these two bulk oxides but were oxygen deficient. From the profile of the CrO ions collected by APT, it is more likely the Cr shell is metallic or only partially oxidised. The influence of the Cr on the oxides is to reduce their average size and increase their number density.

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