Karl Dawson^{a*}, Sarah J. Haigh^b, Gordon J. Tatlock^a and Andy R. Jones^a

a. Centre for Materials and Structures, School of Engineering, University of Liverpool, L69 3GH, UK

b. School of Materials, Materials Science Centre, University of Manchester, M13 9PL, UK

* k.dawson@liverpool.ac.uk

Abstract

The early stages of nano-particulate formation in mechanically alloyed and annealed, precursor powders used to manufacture the legacy commercial oxide dispersion strengthened alloy PM2000, formerly produced by Plansee GmbH, have been investigated. Powders were analysed in both the as-mechanically-alloyed condition and after annealing over the temperature range 923 K to 1423 K.

The nucleation and growth of coherent nano-particles in the partially recovered, fine grained, ferritic matrix of powders annealed at temperatures as low as 923 K has been confirmed. Powders annealed for 1 hour at temperatures of 1123 K and 1223K were partially recrystallised and contained high number densities ($N_V > 10^{23} \text{ m}^{-3}$) of coherent 2nm yttrium-aluminium-oxygen rich nano-particles.

The identification of particle free zones in recrystallised grains, adjacent to recrystallising interfaces, plus the identical orientation relationships between nano-particles and the matrices in both unrecrystallised and recrystallised grains, indicates that the Y-Al-O nano-particles, first formed in fine grained regions, are dissolved during recrystallisation and re-precipitated subsequently in recrystallised grains.

1. Introduction

Aluminium containing ferritic Oxide Dispersion Strengthened (ODS) FeCrAlY alloys were initially developed for application as coarse grained variants in high temperature environments due to their excellent creep strength and oxidation resistance [1-3]. In more recent times ODS materials that are capable of forming protective α -alumina scales have attracted increasing interest for applications in future nuclear installations due to their resistance to corrosion in super-critical water [4] and liquid metal environments [5, 6].

Conventionally, ODS alloys have fallen into one of two groups, based on their intended application. Those designed for use in nuclear environments typically contain between 9 and 14wt.% Cr and are characterised by the formation of high number densities ($N_V > 10^{23} \text{ m}^{-3}$) of 1 to 5 nm diameter yttrium-titanium oxides [7-9]. Alloys designed for

application at high homologous temperatures generally have greater concentrations of Cr (16 – 20 wt.%) and incorporate aluminium (typically ~5 wt.%) in order that a protective alumina scale can be formed. However, ODS alloys which contain aluminium, in general, form yttrium-aluminium oxides which are larger (10 – 30nm) [10-12] and fewer in number (10^{20} to 10^{21} m⁻³) [11, 12] than those found in nuclear alloys containing yttrium and titanium and *no* aluminium. A variety of yttrium aluminium oxides have been identified in FeCrAlY ODS alloys: tetragonal Y₃Al₅O₁₂ (YAT) [10]; perovskite structured YAlO₃ (YAP) [13-15]; hexagonal oxide (YAH) [15]; cubic yttrium aluminium garnet (YAG) [14]; and monoclinic Y₄Al₂O₉ (YAM) [16]. These Y-Al containing alloys also tend to contain low number densities of relatively coarse alumina and titanium carbonitride particles [10].

To date, the majority of published work on the characterisation of particle formation in ODS alloys has focused on fully consolidated materials. Ferritic ODS alloy powders have been consolidated at temperatures as low as 1123 K [17] and it has been shown that resulting oxide particle dispersions are influenced by consolidation temperature [17-19]. However, less is known about behaviour at lower temperatures; or about microstructural change in the unconsolidated powders. A number of reports exist which detail the evolution of oxides, from the initial stages of particle formation, in mechanically alloyed powders annealed at 1073 K [17, 20-22] but these studies were all performed on powders which did not contain aluminium and there remains a lack of published work detailing early stage, low temperature precipitation behaviour in FeCrAlY ODS alloy powders.

The study of oxide particle formation at low temperatures in ODS alloys is pertinent as degassing procedures are typically performed in the temperature range 523 K to 688 K [7, 23-26], although degassing has also been performed at higher temperatures of 873 K and above [27, 28], while consolidation of gas atomization reaction synthesized ODS alloy precursor powders has been performed at temperatures as low as 973 K [25].

To address this knowledge gap in this technologically crucial class of alloys, we present in this work a study carried out on legacy, commercial ODS alloy PM2000 powders, produced by Plansee GmbH, in the as-Mechanically Alloyed (MA) condition and annealed within the temperature range 923 K to 1423 K. The findings provide an insight into the evolution of alloy microstructure and the formation of particle dispersions over the temperature range used in the commercial manufacture of ODS alloys. The current study presents an opportunity to assess microstructural evolution and precipitation events in MA ODS powders in response to isothermal heat treatments. The temperature range examined is typical of that encountered during thermal degassing and high temperature soaks that are applied prior to extrusion. A number of previously unreported findings are presented which may influence future manufacturing routes chosen to optimise microstructure and properties in this class of ODS alloys.

2. Experimental

Mechanically alloyed precursor powders of ODS alloy PM2000 used in this study were purchased from Plansee GmbH in 2007. The chemical composition (wt.%) of these PM2000 precursor powders is presented in Table 1, from measurements made in 2010. The concentration of Fe, Cr, Al, Ti and Y was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), carbon was measured by the combustion method and oxygen by Inert Gas Fusion (IGF) analysis. Chemical analysis of recent (2014) extrusions, produced from the same batch of powders, indicate negligible changes in composition.

Table 1. Chemical composition (wt.%) of the PM2000 powder.

Fe	Cr	Al	Ti	Y	O	C	N	others
74.41	18.88	5.43	0.47	3940wppm	2313wppm	40wppm	80wppm	bal.

The microstructures of powders in the as-MA condition and after 5 different heat treatments were investigated. Annealing schedules lasting for 1 hour were applied to separate batches of powder at temperatures of 1123 K, 1223 K, and 1423K. A small amount of powder was also annealed for 5 hours at 923 K and a fraction of this powder received a further heat treatment for 1 hour at 1123 K.

The effects of a wider range of annealing treatments on the hardness of PM2000 powder and a comparison with recrystallised PM2000 tube annealed at 1653 K was also made. Hardness measurements were recorded using a Matsuzawa Seiki micro-indentation tester, model DMH-2, using a 50g load and dwell time of 10 seconds.

Most PM2000 powder particles were prepared for transmission electron microscopy (TEM) analysis by a novel electropolishing technique. Electropolishing was adopted as the preferred specimen preparation technique in cases where nano-particle analysis was critical; hence Focussed Ion Beam (FIB) induced artefacts could be avoided. Briefly, pre-thinned powder particles, only a few microns in thickness, were suspended from gold TEM support grids; particles were secured by platinum deposition. The grid and particle assemblies were then electropolished in a 5% vol. perchloric acid 95%vol. methanol electrolyte at 223 K for durations of approximately 6 seconds. Specimens of as-milled, 923 K annealed and 1423 K annealed powders were prepared using an FEI Helios 600i FIB instrument. Primary cutting and thinning steps were performed using a Ga ion beam operated with an acceleration voltage of 30kV and followed by a final low energy (2 kV) polish.

Secondary electron imaging and Electron BackScatter Diffraction (EBSD) analysis were performed in the FEI FIB instrument using an EDAX EBSD system.

Scanning Transmission Electron Microscopy (STEM) and TEM was performed using a probe side aberration corrected JEOL 2100FC_s fitted with a windowless EDAX energy dispersive x-ray detector and a Gatan Quantum GIF spectroscopy and imaging system. Energy Dispersive x-ray Spectroscopy (EDS) maps were recorded using a probe side aberration corrected FEI Titan G2 80-200 STEM, equipped with ChemiSTEM™ technology, operated at 200kV. The thickness of TEM specimens was measured using a number of techniques including the contamination spot separation method, as described by Williams and Carter [29], Electron Energy Loss Spectroscopy (EELS) energy filtered TEM thickness maps and STEM-EELS absolute thickness maps. The accuracy of the contamination spot separation method and EELS measurements are expected to be $\pm 50\text{nm}$ [30] and $\pm 20\%$ [31], respectively.

3. Results

3.1. Ferritic Microstructures

Thin lamella TEM specimens, sectioned by FIB from as-milled PM2000 powder particles revealed evidence of the folding and welding procedure associated with mechanical alloying. The microstructure observed in SEM images (Fig. 1a) contained very fine stringers of particles, some identified as aluminium oxide, which delineated a number of the fold lines in the micro-wrought MA structure. In general, the alumina particles were only a few tens of nanometres in diameter but single particles as large as 200nm were also measured. Transmission electron microscopy revealed a distorted ferritic microstructure consisting of elongated grains (lamellae), often only 10nm or so in width and with lengths exceeding 300nm (Fig. 1b).

Fig 1. (a) SEM secondary electron image showing aluminium oxide particles in a FIB sectioned as-MA PM2000 powder particle and (b) TEM image of the distorted ferritic MA microstructure.

After annealing at 923 K for 5 hours, a significant fraction of the microstructural distortion observed in as-milled powders was removed by the recovery process. The modified ferritic microstructure displayed elongated features characteristic of the deformation history. These lamellae-like structures were composed of small grains/sub-grains which contained residual free dislocations. A separate EBSD study [Dawson et al., to be published] also showed that most of the fine grained regions contained low angle boundaries, consistent with the recovery process. Grain diameters measured in the polygonized substructure were within the range of 30 to 300nm.

Fig. 2. EBSD Image Quality map of a PM2000 powder particle after a heat treatment of 5 hours at 923 K, followed by 1 hour 1123 K, revealing recrystallised grains and areas consisting of un-resolved fine grains (dark regions).

After annealing at higher temperatures (e.g. 1123 K, or powders first annealed for 5 hours at 923 K followed by 1 hour at 1123 K), cross sectioned powders revealed bimodal grain structures comprising large (typically 2 to 10µm) recrystallised grains together with regions that retained a fine grained structure similar to that observed in powders annealed for 5 hours at 923 K. Fig. 2 shows an EBSD image quality map displaying a bimodal, unrecrystallised-recrystallised, grain structure in a cross-sectioned powder particle which had been annealed at 923 K for 5 hours followed by a further 1 hour at 1123 K. Cross-sectioned powder particles which had been annealed at 1223 K for 1 hour also displayed bimodal grain structures, comprising pockets of sub-300nm grains and dislocation substructures distributed amongst larger, recrystallised grains (Fig. 3). The pockets of fine grained material were less pervasive than in powders annealed at lower temperatures.

Fig. 3. BF STEM showing the mixed recrystallised-unrecrystallised ferritic microstructure in PM2000 powder annealed for 1 hour at 1223 K (electropolished specimen).

PM2000 powders annealed for 1 hour at 1423 K displayed a predominantly recrystallised ferritic matrix containing grains as large as 10 μ m in diameter. However, small, isolated, residual pockets of fine, unrecrystallised grains, which contained many dislocations, were observed at boundaries between large recrystallised grains.

3.2. *Precipitation*

Other than fine stringers of alumina, no identifiable second phase particles were observed in as-MA PM2000 and selected area diffraction experiments did not reveal any evidence of crystalline yttria.

TEM analysis of PM2000 powders annealed for 5 hours at 923 K revealed a distribution of very fine intragranular particles 1 to 5 nm in diameter (Figs. 4a and 4b). The particles, which had a mean diameter of only 1.8 ± 0.7 nm, showed good image contrast in grains oriented close to low index zone axes but were not visible in grains where there was a lack of diffraction contrast; hence it was not clear whether or not precipitation was completely homogeneous. Previous experience has shown that successful imaging of similar particles in other ODS alloys can be particularly sensitive to imaging parameters, in particular, crystal orientation.

Fig. 4. (a) and (b) TEM images showing intragranular nano-particles in PM2000 powder annealed for 5 hours at 923 K ((a) FIB and (b) electropolished specimens).

High resolution TEM images of FIB prepared specimens (e.g. Fig.4a) revealed nano-particle distributions similar to those observed in electropolished specimens (Fig. 4b). Cube shaped particles were identified which were faceted parallel to the $\{200\}_{\alpha}$ (α = ferrite matrix) planes with occasional faceting of the cube corners parallel to $\{011\}_{\alpha}$ planes. Although under appropriate imaging conditions these features displayed strong image contrast against surrounding matrix, it was not possible to differentiate their crystal structure from the lattice of the ferrite matrix. In addition to the very fine intragranular particles, slightly larger (3 to 6nm diameter) grain boundary particles were also observed.

SEM images of FIB prepared surfaces revealed alumina stringers that were much the same as those observed in the as-MA material. However, these particles were now observed along grain boundaries rather than appearing along fold lines, and may well have contributed to arrest of grain boundary migration.

Powders annealed for 1 hour at 1123 K were analysed in the TEM; BF-STEM and HAADF-STEM images revealed distributions of fine nano-particles in both the fine grained material (Fig. 5a) and recrystallised grains (Fig. 5b).

Fig. 5. (a) HAADF-STEM image showing nano-particles in a fine grained region and (b) a BF-STEM image of nano-particles in a recrystallised grain oriented on the [111] zone (electropolished specimen of powder annealed for 1 hour at 1123 K).

The size distribution of intragranular nano-particles measured in both fine grained and recrystallised regions were similar; however, grain boundary particles were marginally coarser than intragranular particles, hence a greater number of marginally coarser particles were observed in the fine grained material where grain boundary area per unit volume was substantially higher. As a result, the local mean particle diameter was 2.5nm in fine grained regions; slightly coarser than the mean particle diameter of 2.1 ± 0.7 nm measured in the recrystallised grains.

The nano-particle number density measured in recrystallised grains, in powder annealed for 1 hour at 1123 K, was $N_V \approx 8 \times 10^{23} \text{m}^{-3}$. The nano-particle number density in fine grained material could not be determined accurately but appeared similar to that in recrystallised grains.

It is worth noting that although the number density of large particles (>10 nm in diameter) was low (N_V ca. $10^{19} - 10^{20} \text{m}^{-3}$) in comparison to that of nano-particles, their contribution to total particle volume fraction might not be insignificant and their distribution would particularly affect grain boundary migration.

Fig. 6. (a) HAADF image and (b-d) EDS elemental maps showing yttrium aluminium rich particles in a fine grained region of a PM2000 powder particle annealed 1 hour at 1123 K (electropolished specimen).

Fig. 7. (a) HAADF image and (b-d) EDS elemental maps showing yttrium aluminium containing nano-particles in a recrystallised ferrite grain in a PM2000 powder particle annealed 1 hour at 1123 K (electropolished specimen).

Contrast observed in HAADF STEM images suggested that the nano-particles had a lower average atomic weight than the ferrite matrix (Figs. 6a and 7a). High resolution EDS mapping confirmed that the nano-sized particles, which dominated precipitation in both fine and recrystallised grains, were enriched in yttrium and aluminium (Figs. 6 and 7). A slight enhancement in oxygen signal (not shown) was also associated with the nano-particles; hence it is very likely that the nano-scale features are yttrium aluminium oxides or their precursors. Chromium and iron concentrations were depleted in the localities of the oxides and titanium concentrations were at background levels.

Electropolished TEM specimens, prepared from powder particles annealed for 1 hour at 1223 K, provided good thin areas of recrystallised grains and fine grained regions as well as recrystallising interfaces. A dispersion of nano-particles with $N_v \approx 5.1 \times 10^{23} \text{ m}^{-3}$ and mean particle diameter of $2.3 \pm 0.8 \text{ nm}$, was measured in the recrystallised grains. A slightly lower precipitate number density of $1.7 \times 10^{23} \text{ m}^{-3}$ was determined in fine grained material.

Precipitation in both the fine grains (Fig. 8a) and recrystallised grains (Fig. 8b) displayed widespread common orientation relationships (OR) with the local ferrite matrix. Yttrium-aluminium rich nano-particles were pervasive throughout all regions; particles as small as 3nm were identified as Y-Al-O in both recrystallised grains and fine grained regions and relatively coarse spherical particles, such as those shown in Fig. 8a shared similar compositions to the much smaller nano-particles.

Coherent particles showing Ashby-Brown strain contrast lobes [32] were observed in fine grains under the appropriate imaging conditions (Fig. 8a). A high number density of sub-5nm particles were observed, which displayed a common

orientation relationship with the surrounding ferrite. The nano-particles did not appear to exhibit preferred nucleation sites, such as dislocations or grain boundaries, but were distributed homogeneously in intragranular material. In recrystallised grains, small (1.8 to 5nm) cube shaped Y-Al-O nano-particles displayed major facets parallel to $\{200\}_\alpha$ planes (Fig. 8b). Similar cube shaped nano-particles displaying an identical registry with the ferrite matrix were ubiquitous across the entirety of single, large ($>2\mu\text{m}$ diameter), recrystallised grains.

Fig. 8. BF-STEM images of PM2000 annealed for 1 hour at 1223 K showing (a) coherent yttrium aluminium oxides in an unrecrystallised fine grain and (b) cube shaped Y-Al-O particles in a recrystallised grain on a $\langle 100 \rangle$ zone axis (electropolished specimen).

Fig. 9. PM2000 powder annealed for 1 hour at 1223 K (a) BF (b) HAADF STEM images of a chamfered cube Y-Al-O particle in recrystallised $[100]$ ferrite and (c) EDS line scan through the particle shown in a&b (electropolished specimen).

In the same $[100]\alpha$ oriented grain as shown in Fig.8b, slightly larger particles ($>5\text{nm}$) adopted a truncated rhombic dodecahedron morphology (chamfered cube) with minor facets parallel to $\{110\}\alpha$ planes (Figs. 9a and 9b). Faceting parallel to $\{110\}\alpha$ planes became increasingly apparent in larger particles. Fig. 9c shows an EDS line scan across a cube shaped yttrium-aluminium particle located in recrystallised material; Fe is omitted from the plot. The EDS element profile reveals a reduced Cr concentration in the vicinity of the oxide feature which is clearly enriched in yttrium and oxygen. Less clear is the aluminium content of the precipitate; however, as there is no detectable drop in aluminium signal associated with the particle it is possible that it contains some aluminium.

Nano-particle distributions in the vicinity of many recrystallising interfaces, observed in powders annealed at 1123 K, 1223 K and 1423K, exhibited Particle Free Zones (PFZ) in the recrystallised grains directly behind the advancing interface; these features were frequent but not pervasive. The PFZs were seen most clearly where the recrystallising interface lay virtually parallel to the electron beam with the recrystallised grain oriented close to a low index zone axis (Fig. 10). Within the PFZs, which extended 20 to 50 nm into recrystallised grains, only larger, spherical yttrium aluminium oxides were observed; hence these regions could more accurately be referred to as nano-particle free zones.

Fig. 10. BF STEM image showing a particle free zone in a recrystallised ferrite grain behind an advancing recrystallisation front in PM2000 powder annealed for 1 hour at 1223 K (electropolished specimen).

Analysis of moiré fringes displayed by large (ca. 10nm) spherical particles in these regions indicated that those close to one another sometimes shared similar spatial orientations, although no simple orientation relationship was observed with the recrystallised grain in which they were located. This could suggest that such particles may have had an

orientation relationship with a single unrecrystallised grain that was replaced by a matrix with new orientation during the recrystallisation process.

Powder specimens which were annealed for 1 hour at 1423 K, revealed a dispersion of oxides distributed homogeneously throughout recrystallised grains and residual fine grained regions. It was evident that fine grained material had retained high number densities of dislocations induced by the MA process. Images of recrystallised grains revealed a particle number density of $1.1 \times 10^{23} \text{ m}^{-3}$ within the 3 to 12 nm diameter size range with mean diameter of $5 \pm 1.2 \text{ nm}$. The larger particles, i.e. those approaching 10 nm in diameter, appeared almost spherical at low magnification (Fig. 11). However, on close examination, these oxides often displayed facets parallel to $\{200\}_{\alpha}$ planes. Smaller precipitates, in the 3 to 6 nm size range, were also faceted but retained a more angular morphology than their larger counterparts. The frequent observation of moiré fringes observed in images recorded throughout the study of the powders annealed at 1423 K indicated that many oxides in recrystallised grains shared common spatial orientations but no simple OR with adjacent ferrite.

Fig. 11. TEM image of PM2000 powder annealed for 1 hour at 1423 K (FIB specimen).

The combined results of nano-particle number density and size distribution measurements, as a function of isothermal heat treatment, are presented in Fig. 12. Number density values were only calculated for 1 hour heat treatments at 1123 K, 1223 K and 1423 K. In each case, foil thickness was measured by a different method, hence different values are expected due to the relatively low accuracy of the contamination separation method and EELS thickness mapping.

This accuracy limitation meant it was not appropriate to compute and compare oxide volume fractions. Particle size analysis data is presented, for convenience, in Table 2, where N represents the number of particles measured.

Fig. 12. Nano-particle number density versus size distribution plot for annealed PM2000 powders.

These data show that mean nano-particle size increased from 2.1 nm to 5 nm as the temperature of the 1 hour anneal was increased from 1123 K to 1423 K while number densities decreased from $8 \times 10^{23} \text{ m}^{-3}$ at 1123 K to $1.1 \times 10^{23} \text{ m}^{-3}$ at 1423 K. It is evident that oxide particles remain dimensionally stable, retaining a mean diameter of approximately 2nm, in powders annealed for short durations in the temperature range 923 K to 1223 K but coarsen noticeably during annealing at 1423 K.

Table 2. Nano-particle size distribution data for PM2000 powders annealed over the temperature range of 923 K to 1423 K (particles with diameters > 10 nm were not considered in this analysis).

Annealing temperature (K)	Duration (hours)	* N_v (m^{-3})	Mean dia. (nm)	std. dev. (nm)	N
923	5	—	1.8	0.7	170
1123	1	8×10^{23}	2.1	0.7	369
1223	1	5.1×10^{23}	2.3	0.8	267
1423	1	1.1×10^{23}	5	1.2	236

* N_v determined from measurements in recrystallised grains.

3.3. Crystal Structure of Nano-Particles

In general, PM2000 powders annealed at temperatures ≤ 1223 K contained high number densities of sub-5nm Y-Al-O particles which exhibited ‘dark’ contrast compared to the surrounding ferrite matrix in HAADF-STEM, BF-STEM (Fig. 8) and BF TEM (Fig. 13a) images.

Fig. 13. BF TEM images of faceted nano-particles in PM2000 annealed for 1 hour at 1123 K in (a) fine grained [001] ferrite and (b) recrystallised [100] oriented ferrite, both display faceting parallel to the $\{002\}_\alpha$ planes (electropolished specimen).

High resolution TEM images of these ‘dark’ features were recorded in fine ferrite grains oriented on $[111]_\alpha$, $[110]_\alpha$ and $[100]_\alpha$ zone axes. In addition, BF-STEM and atomic resolution HAADF STEM images were recorded of recrystallised grains oriented on $[100]_\alpha$ and $[111]_\alpha$ zone axes. Of the many tens of images, in which the matrix displayed well resolved lattice fringes, or atomic columns in the case of HAADF STEM images, only a very small fraction of precipitates displayed any crystalline features that could be differentiated from the body centred cubic (BCC) ferrite lattice of the surrounding matrix. From the many HAADF images recorded of ferrite on low index ferrite zone axes there were no instances in which atomic columns of sub-5nm diameter precipitates could be differentiated from those of the matrix. In addition to the dark features, a number of bright, well defined, semi-coherent chamfered cube shaped nano-particles were observed. These particles were seen in both fine grains oriented close to a $\langle 100 \rangle$ zone axis (Fig. 4a) and $\langle 100 \rangle$ oriented recrystallised grains (Fig. 13b); the bright nano-particles were observed in powders annealed at 923 K and 1123 K. Analysis of their crystal structures indicated possible cube on cube (FCC oxide) or $[100]_\alpha/[100]_{ox}$ and $(011)_\alpha/(002)_{ox}$ (BCC oxide) orientation relationships. The features, which measured ≈ 2 nm in diameter presented interplanar spacings of approximately $2.90\text{\AA}$ parallel to $\{002\}_\alpha$ planes, i.e. approximately twice the spacing of $\{002\}_\alpha$ atomic planes. Close analysis of high resolution TEM images in the immediate vicinity of these nano-features revealed strong deviation of the $\{110\}_\alpha$ lattice planes due to coherency strains (Fig. 13b), suggesting these are real features of the alloy, not surface contamination. Although the bright precipitates shared morphological similarities to the omnipresent dark particles, it was not possible to determine if they were the same phase and the bright nano-particles were not typical of the majority of nano-features imaged.

However, due to similarities in shape, size and identical growth habits these findings are included in an effort to help determine possible structures of the ubiquitous nano-particles.

In powders annealed at 1423 K, numerous oxide particles exhibited well defined lattice fringes and many displayed crystal structures consistent with monoclinic yttrium aluminium oxide, $\text{Y}_4\text{Al}_2\text{O}_9$, (YAM) (Fig. 14). Although the YAM crystal structure provided the only satisfactory solution for an oxide type typical of that previously identified in PM2000 alloy, more definitive chemical analysis is required to improve confidence in phase assignment. No evidence was found of particles with crystal structures in agreement with mixed Y-Al-O oxides of the type YAG, YAH, YAP or YAT.

Fig. 14. (a) HRTEM image of a semicoherent precipitate, consistent with the YAM structure, in PM2000 annealed at 1423 K and (b) the corresponding Fourier transform indexed for the YAM [102] zone axis (FIB specimen).

3.4. Micro-indentation Hardness Measurements

Fig. 15. Micro-indentation hardness measurements on PM2000 powder after a range of annealing treatments compared to measurements from a recrystallised PM2000 tube.

The results of micro-indentation hardness measurements performed on as-milled and annealed PM2000 powders are presented in Fig. 15. The mean hardness values decreased with increasing temperature and also with time at temperature. Powders that had been heat treated for 1 hour at 1323 K and 1423 K displayed hardness levels similar to consolidated PM2000 tube which had been extruded and heat treated for 1 hour at 1653 K (Fig. 15). The error bars shown in Fig. 15 display the spread of hardness values about the mean hardness but do not include errors in measurement. A significant degree of scatter in hardness values was observed and this might be attributed to variations in sample thickness and to the cracks, voids and pores introduced during mechanical alloying. However, the greater scatter measured in powders annealed at 1123 K and 1223 K was also related to the bimodal unrecrystallised-recrystallised microstructure observed after these annealing regimes. Although nano-particle number density measurements suggest that the contribution of Orowan stress to room temperature strength should be comparable in both fine grains and recrystallised grains, it is likely that the Hall-Petch strengthening mechanism and dislocation substructures would lead to a greater hardness in the fine grained material. As such, hardness values in as-milled and 923 K annealed powders with homogenous microstructure would have reflected entirely fine grained microstructures, hence the higher hardness values observed. Powders annealed at 1323 K and 1423 K displayed microstructures dominated by recrystallised grains and the hardness in these powders was comparably low. Micro-indentation measurements made on powder annealed at either 1123 K or 1223 K would have sampled either fine grained regions, recrystallised grains or a mixture of both, hence exhibited the greater variations in hardness values observed.

4. Discussion

Compelling evidence has been presented which shows that yttrium-aluminium-oxygen rich nano-particles, approximately 2 nm in diameter, are formed in as-MA PM2000 ODS alloy powders annealed subsequently at temperatures as low as 923 K. This appears to be the first confirmed report of nano-particle formation at such low temperatures in a FeCrAlY ODS alloy and builds on previous reports [17, 20-22] that identified particle formation over the temperature range 1073 K to 1173 K in Fe 14wt.% Cr, Y_2O_3 , Y_2O_3 -Ti and Y_2O_3 -W-Ti ODS material. Moreover, it is the first report that widespread Y-Al-rich nano-particulate (<5 nm) formation can be induced in annealed, legacy commercial alloy PM2000. Furthermore, the identification in this work of nano-particle formation

after 5 hours at temperatures as low as 923 K is significant, as similar temperatures have been used for degassing treatments [33] in FeCrAlY ODS alloy powder processing; hence nano-particulate precipitation and any influence of such particles on recovery and subsequent recrystallisation behaviour begins at this early stage.

High number densities of yttrium-aluminium-oxygen nano-particles, with mean diameters of approximately 2 to 2.5 nm, have been identified in mechanically alloyed PM2000 powders annealed over the temperature range 923 K to 1223 K. A particle number density of $8 \times 10^{23} \text{ m}^{-3}$ was measured in powders annealed for 1 hour at 1123 K dropping to $5 \times 10^{23} \text{ m}^{-3}$ after annealing for 1 hour at 1223 K. The particle size data contrasts with mean oxide particle diameters reported for consolidated PM2000 alloy which are typically of the order of 16 to 30 nm [11, 12, 34, 35]. The particle size distribution and number density data reported in PM2000 powder in the present work is more refined than class-leading nano-particulate data reported for consolidated Hf and Zr-modified FeCrAlY ODS alloys [36] and FeCrAlY ODS material extruded at 1323 K [15].

PM2000 powders annealed at temperatures $\leq 1223 \text{ K}$ contained nano-particle distributions which exhibited no lattice contrast that enabled identification of their crystal structure. In most instances the lattice sites in the nano-particles could not be differentiated from that of the surrounding ferrite and particles appeared only as dark features faceted parallel to low index matrix planes. It was clear from TEM analysis that the dominant nano-particle distributions were Y-Al-O rich; but a satisfactory correlation with known Y-Al-O structures, common to FeCrAlY ODS alloys, could not be determined. Y-Al-O features, in many ways, were similar to the Y-Ti-Cr-O nano-clusters observed in 14CrYWT ODS alloy, as described by Brandes et al. [37]. Interestingly, although the composition of the nano-particles obviously differs between PM2000 and 14CrYWT, their morphologies and growth habits appear, in many ways, identical. Hence, one possible explanation for an inability to identify a distinct structure for the Y-Al-O nano-particles is that they are a highly-defective, non-equilibrium phase in which the solute atoms occupy the lattice sites of the BCC ferritic matrix, as described by Hoelzer et al. [38].

PM2000 powder particles annealed for 1 hour at 1123 K were found to be partially recrystallised with a microstructure comprising large (1-10 μm) recrystallised grains and partially recovered fine grained (typically 50-300 nm) regions. Recrystallised grains contained very low dislocation densities; in contrast, high number densities of dislocations were retained in the fine grained regions. Both recrystallised and recovered regions contained distributions of nano-particles. This strongly suggests that recrystallisation took place through material in which high number densities of nano-particles had already formed. In a separate experiment, PM2000 powders initially annealed for 5 hours at 923 K, where widespread precipitation of nano-particles in a fine grained recovered structure was confirmed, were

subsequently annealed for 1 hour at 1123 K, where primary recrystallisation took place in the presence of the particle distribution ($N_v \sim 10^{23} \text{m}^{-3}$) established at 923 K; this confirmed that recrystallisation can take place in PM2000 powder containing high number densities of nano-particles.

Furthermore, crystallographic orientation relationships and growth habits between the nano-particle distributions and the parent ferrite matrix were observed in both unrecrystallised (fine grains) and recrystallised grains. Since an orientation relationship and growth habit existed before and subsequent to recrystallisation, this implies either that the nano-particle distributions rotated as a whole, as described by Koch [39] or, as is more likely, dissolved during recrystallisation and re-precipitated subsequently. Such phenomena have been reported previously, not in ferritic ODS alloys, but in different alloy systems [40-42].

It seems likely that, in the present system, particles established in fine grained regions were dissolved due to the passage of a mobile recrystallisation front. However, it is not clear if precipitate instabilities were caused by an increase in interface energy due to loss of coherency with the matrix or as a result of fluctuations in alloy composition in the vicinity of grain boundaries as was observed in the present study and has also been reported by Bouchard [40] in Ti-Y₂O₃ systems. The ensuing precipitate dissolution produces a supersaturated matrix from which nucleation and growth of new coherent nano-particles with an OR with the recrystallised grains commences.

Similar observations have been described by Porter and Ralph in their study of γ' dissolution and re-precipitation in nickel superalloys [42] and by Naka et al. [43], who investigated dissolution and reprecipitation of Y₂O₃ precipitates at the recrystallisation front in titanium ODS alloys. Both Porter [42] and Naka [43] reported coherent precipitation with identical orientation relationships on either side of the recrystallisation front in the Ni- γ' and Ti-Y₂O₃ systems respectively.

Re-precipitation behind recrystallising interfaces is usually characterised by the presence of a PFZ due to the kinetics of nucleation and growth of new particles behind the recrystallisation front. This was observed on numerous occasions in the present study. In some instances, however, PFZs were not observed. The absence of a PFZ may, occasionally, have been an observational effect due to boundaries presented at an inclined angle to the incident electron beam.

However, where this was not the case it is possible that locally reduced kinetics of recrystallisation and rates of boundary migration may have allowed the necessary time for nucleation and growth of new nano-particulate particles immediately behind a recrystallising interface without a clear PFZ emerging. This explanation seems plausible since Laurent-Brocq et al. [22] demonstrated that nucleation of oxides in ferritic ODS alloys was complete within the first 5

minutes of annealing at 1073 K and continued exposure for a further 55 minutes did not result in any significant coarsening.

In PM2000 powders annealed at 1423 K, nano-particles coarsened to a mean diameter of approximately 5 nm and the number density dropped to $1.1 \times 10^{23} \text{ m}^{-3}$. In addition, although the larger oxides had become spheroidised but remained stable within the size range of 3 to 12 nm, many of the particles displayed moiré fringes which indicated they shared a common orientation in the matrix. Although these figures are extraordinary in terms of particle size and number density in consolidated PM2000 material, it appears that nano-particles in aluminium containing ferritic ODS alloys are not as resilient to coarsening as the Y-Ti oxide nano-clusters that form in alloys such as 12CrYWT and MA957. Studies have shown that Y-Ti-O nano-particles can remain stable for short durations at temperatures as high as 1573 K [44, 45]. However, these differences could relate to development of different oxide phases in the Y-Ti-O and Y-Al-O systems. Oxides analysed in ODS alloys which precipitate Y-Ti-O and Y_2O_3 , before and after heat treatments, have well defined crystal structures which have been identified as $\text{Y}_2\text{Ti}_2\text{O}_7$ [9, 46-48] and Y_2O_3 [47]. It has been demonstrated that these oxides retain some coherence with the ferrite matrix which influences coarsening behaviour [47]; this contrasts with extruded PM2000 in which oxides have no orientation relationship with the matrix. It is probable that the loss of coherence of oxides in PM2000, at a temperature between 1223 K and 1423 K, contributes to their subsequent coarsening. It is also likely that Y-Ti-O nano-clusters, which precipitate at temperatures in the region of 1073 K to 1123 K in nuclear-type ODS alloys [17, 20-22], are dissolved and re-precipitated during repeated dynamic recrystallisation occurring during high temperature, high strain rate processing [49-51] such as extrusion, hence coherent nano-particulates which have well defined orientation relationships are retained and pervasive in these consolidated alloys [46, 47]. Interestingly, the work of Dou et al. [15, 18], which investigated the effects of extrusion temperature on the microstructure and properties of FeCrAlY ODS alloy, showed large numbers of coherent YAH oxides, which shared common orientations in the matrix of material extruded at 1323 K.

Analysis of PM2000 powder annealed at 1423 K revealed that not all regions of recrystallised material contained coherent nano-particles and spherical randomly oriented oxides could be seen. This contrasts with the analysis of material annealed at lower temperatures where orientation relationships were pervasive. It may be the case that randomly oriented oxides exceeded a critical diameter, so were not dissolved during recrystallisation remaining stable during the passage of recrystallisation fronts; hence retained their original spatial orientation.

Although following annealing at 1423 K, Y-Al containing nano-particles in the powders had coarsened considerably, the particle number density ($1.1 \times 10^{23} \text{ m}^{-3}$) remained more than an order of magnitude greater than values reported in the literature ($\sim 4 \times 10^{21} \text{ m}^{-3}$) for consolidated PM2000 alloy [11, 12]. These results indicate the magnitude of particle coarsening induced by the typical consolidation processes used for these alloys.

5. Conclusions

The present study has reported on the microstructural changes that occur in mechanically alloyed legacy, commercial PM2000 ODS alloy powders subjected to annealing in the temperature range (923 K-1423 K), typically used in the consolidation (degassing, extrusion etc) of commercial ferritic ODS alloys. The findings indicate that, under optimised conditions, it might be possible to produce ferritic ODS alloys containing ca.5wt.% aluminium that exhibit true nano-particle ($\sim 2 \text{ nm}$) size dispersions. It has been shown that nano-particles form and interact with recrystallisation occurring in individual PM2000 powder particles at temperatures much lower than those typically used in consolidation processing, which may have implications for optimum conditions chosen for processing ODS materials.

In summary, conclusions include:

- It is possible to form yttrium-aluminium-oxygen rich nano-particles of $\sim 2 \text{ nm}$ mean diameter and N_v as high as $\sim 8 \times 10^{23} \text{ m}^{-3}$ in as-MA PM2000 alloy powders annealed for short periods (1-5 hours) in the temperature range 923 K-1223 K.
- As-MA PM2000 alloy powders annealed at temperatures $\geq 1123 \text{ K}$, for durations of 1 hour or longer, underwent partial recrystallisation. The resultant microstructure comprised a mixture of large (typically 2-10 μm) recrystallised grains and recovered fine grained (30-300 nm) regions. Both fine grained and recrystallised regions contained dispersions ($N_v > 10^{23} \text{ m}^{-3}$) of $\sim 2 \text{ nm}$ diameter nano-particles. It was established that recrystallisation occurs in the presence of these Y-Al-O nano-particles.
- During recrystallisation nano-particles first formed in fine grained, unrecrystallised material dissolve at recrystallising interfaces then re-precipitate in recrystallised grains with an orientation relationship and growth habits identical to those displayed by nano-particles in the unrecrystallised grains; hence an orientation relationship exists between the nano-particles and the matrix on both sides of the recrystallisation front. Clear evidence has been found of PFZs in recrystallised grains behind individual migrating recrystallising interfaces.
- The majority of Y-Al-O nano-particles observed in powders annealed at temperatures $< 1223 \text{ K}$ appeared as dark faceted features which did not display lattice contrast that could be differentiated from the ferrite matrix;

hence the crystal structure of nano-particles formed at low temperatures in PM2000 powder has yet to be determined. The crystal structures of oxides observed in powder annealed at 1423 K could, in many cases, be assigned as monoclinic yttrium aluminium oxide (YAM).

- After a 1 hour anneal at 1423 K nano-particles with a mean diameter of 5 ± 1.2 nm and N_v of $1.1 \times 10^{23} \text{ m}^{-3}$ were retained in the PM2000 powder particles, contrasting with oxide particle diameters in the range 16-30 nm reported elsewhere to be prevalent in fully consolidated PM2000.
- After annealing for 1 hour at 1423 K PM2000 powder particles were predominantly recrystallised with a grain size typically in the range 2-10 μm ; however, some fine grained (30-300 nm), unrecrystallised regions persisted, located mainly in isolated pockets at the interface between recrystallised grains.

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References

- [1] A. Czyrska-Filemonowicz, B. Dubiel, Journal of Materials Processing Technology. 64 (1997) 53-64.
- [2] P. Lours, J. Alexis, G. Bernhart, Journal of Materials Science Letters. 17 (1998) 1089-1093.
- [3] S. Dryepondt, A. Rouaix-Vande Put, B. A. Pint, Oxidation of Metals. (2013) 1-12.
- [4] J. H. Lee, R. Kasada, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe, Journal of Nuclear Materials. 417 (2011) 1225-1228.
- [5] A. Kimura, R. Kasada, N. Iwata, H. Kishimoto, C. H. Zhang, J. Isselin, P. Dou, J. H. Lee, N. Muthukumar, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, T. F. Abe, Journal of Nuclear Materials. 417 (2011) 176-179.
- [6] S. Ukai, Oxide Dispersion Strengthened Steels, in: Comprehensive Nuclear Materials, Elsevier, Oxford, (2012) 241-271.
- [7] S. Ukai, M. Harada, H. Okada, M. Inoue, S. Nomura, S. Shikakura, K. Asabe, T. Nishida, M. Fujiwara, Journal of Nuclear Materials. 204 (1993) 65-73.

- [8] S. Yamashita, S. Ohtsuka, N. Akasaka, S. Ukai, S. Ohnuki, *Philosophical Magazine Letters*. 84 (2004) 525-529.
- [9] G. R. Odette, *JOM*. 66 (2014) 2427-2441.
- [10] B. Dubiel, M. Wróbel, P. J. Ennis, A. Czyrska-Filemonowicz, *Scripta Materialia*. 37 (1997) 1215-1220.
- [11] J. H. Schneibel, M. Heilmaier, W. Blum, G. Hasemann, T. Shanmugasundaram, *Acta Materialia*. 59 (2011) 1300-1308.
- [12] A. Wasilkowska, M. Bartsch, U. Messerschmidt, R. Herzog, A. Czyrska-Filemonowicz, *Journal of Materials Processing Technology*. 133 (2003) 218-224.
- [13] C. H. Zhang, A. Kimura, R. Kasada, J. Jang, H. Kishimoto, Y. T. Yang, *Journal of Nuclear Materials*. 417 (2011) 221-224.
- [14] M. Klimiankou, R. Lindau, A. Möslang, J. Schröder, *Powder Metallurgy*. 48 (2005) 277-287.
- [15] P. Dou, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe, *Acta Materialia*. 59 (2011) 992-1002.
- [16] L. L. Hsiung, M. J. Fluss, A. Kimura, *Materials Letters*. 64 (2010) 1782-1785.
- [17] M. J. Alinger, G. R. Odette, D. T. Hoelzer, *Acta Materialia*. 57 (2009) 392-406.
- [18] P. Dou, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe, *Journal of Nuclear Materials*. 417 (2011) 166-170.
- [19] M. J. Alinger, G. R. Odette, D. T. Hoelzer, *Journal of Nuclear Materials*. 329-333 (2004) 382-386.
- [20] H. Zhang, M. J. Gorley, K. B. Chong, M. E. Fitzpatrick, S. G. Roberts, P. S. Grant, *Journal of Alloys and Compounds*. 582 (2014) 769-773.
- [21] C. A. Williams, P. Unifantowicz, N. Baluc, G. D. W. Smith, E. A. Marquis, *Acta Materialia*. 61 (2013) 2219-2235.
- [22] M. Laurent-Brocq, F. Legendre, M. H. Mathon, A. Mascaro, S. Poissonnet, B. Radiguet, P. Pareige, M. Loyer, O. Leseigneur, *Acta Materialia*. 60 (2012) 7150-7159.
- [23] J. H. Kim, T. S. Byun, D. T. Hoelzer, *Journal of Nuclear Materials*. 407 (2010) 143-150.
- [24] N. J. Cunningham, A. Etienne, G. R. Odette, E. Stergar, Y. Wu, B. D. Wirth, *Materials Research Society*. 1298 (2011) 3-8.
- [25] J. R. Rieken, I. E. Anderson, M. J. Kramer, G. R. Odette, E. Stergar, E. Haney, *Journal of Nuclear Materials*. 428 (2012) 65-75.
- [26] P. He, M. Klimenkov, R. Lindau, A. Möslang, *Journal of Nuclear Materials*. 428 (2012) 131-138.

- [27] Z. Oksiuta, N. Baluc, *Journal of Nuclear Materials*. 386–388 (2009) 426-429.
- [28] A. R. Jones, J. Ritherdon, *Materials at High Temperatures*. 16 (1999) 181-188.
- [29] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy*, in: vol 3, Springer US, Boston, 2009.
- [30] D. A. Rae, V. D. Scott, G. Love, *Errors in Foil Thickness Measurement Using Contamination Spot Method*, Metals Society, London, 1981, p. 57 - 62.
- [31] K. Iakoubovskii, K. Mitsuishi, Y. Nakayama, K. Furuya, *Microscopy Research and Technique*. 71 (2008) 626-631.
- [32] M. F. Ashby, L. M. Brown, *Philosophical Magazine*. 8 (1963) 1083.
- [33] J. Ritherdon, A. R. Jones, I. G. Wright, *Powder Metallurgy*. 46 (2003) 319-323.
- [34] K. Dawson, S. Cater, G. J. Tatlock, C. Stanhope, *Materials Science and Technology*. 30 (2014) 1685-1690.
- [35] J. C. Walker, K. M. Berggreen, A. R. Jones, C. J. Sutcliffe, *Advanced Engineering Materials*. 11 (2009) 541-546.
- [36] C. Z. Yu, H. Oka, N. Hashimoto, S. Ohnuki, *Journal of Nuclear Materials*. 417 (2011) 286-288.
- [37] M. C. Brandes, L. Kovarik, M. K. Miller, M. J. Mills, *Journal of Materials Science*. 47 (2012) 3913-3923.
- [38] D. T. Hoelzer, J. Bentley, M. A. Sokolov, M. K. Miller, G. R. Odette, M. J. Alinger, *Journal of Nuclear Materials*. 367-370 (2007) 166-172.
- [39] E. F. Koch, K. T. Aust, *Acta Metallurgica*. 15 (1967) 405-409.
- [40] E. Bouchaud, J. P. Bouchaud, S. Naka, G. Lapasset, H. Octor, *Acta Metallurgica et Materialia*. 40 (1992) 3451-3458.
- [41] S. Naka, M. Marty, H. Octor, *Journal of Materials Science*. 22 (1987) 887-895.
- [42] A. Porter, B. Ralph, *Journal of Materials Science*. 16 (1981) 707-713.
- [43] S. Naka, H. Octor, E. Bouchaud, T. Khan, *Scripta Metallurgica*. 23 (1989) 501-505.
- [44] M. K. Miller, D. T. Hoelzer, E. A. Kenik, K. F. Russell, *Journal of Nuclear Materials*. 329-333 (2004) 338-341.
- [45] M. K. Miller, D. T. Hoelzer, E. A. Kenik, K. F. Russell, *Intermetallics*. 13 (2005) 387-392.
- [46] K. Dawson, G. J. Tatlock, *Journal of Nuclear Materials*. 444 (2014) 252-260.
- [47] J. Ribis, Y. de Carlan, *Acta Materialia*. 60 (2012) 238-252.
- [48] Y. Wu, E. M. Haney, N. J. Cunningham, G. R. Odette, *Acta Materialia*. 60 (2012) 3456-3468.
- [49] S.-I. Kim, Y.-C. Yoo, *Materials Science and Engineering. A* 311 (2001) 108-113.

[50] M. Ghanzani Shaban, B. Eghbali, *Materials Science and Technology*. 27 (2011) 1802-1808.

[51] S. Venugopal, S. L. Mannan, Y. V. R. K. Prasad, *Materials Science and Technology*. 9 (1993) 899-906.