Recovery and recrystallisation in mechanically alloyed and annealed, legacy, FeCrAlY ODS alloy precursor powders

K Dawson, A Rao, G J Tatlock and A R Jones
Centre for Materials and Structures, School of Engineering, University of Liverpool, Liverpool, L69 3GH, UK
E-mail: k.dawson@liverpool.ac.uk

Abstract. This study presents findings related to the recrystallisation behaviour in Mechanically Alloyed (MA) and annealed powders of legacy commercial Oxide Dispersion Strengthened (ODS) FeCrAlloy powders PM2000, MA956 and ODM751. Annealing of as-MA ODS alloy powders at temperatures ≥ 800 °C induced primary recrystallisation. The volume fraction (\( V_f \)) recrystallised increased with higher annealing temperatures in the range studied (~800-1050 °C). However, low temperature (650 °C) recovery reduced the subsequent kinetics of recrystallisation in PM2000 alloy. Transmission Electron Microscopy (TEM) analysis of annealed PM2000 and MA956 alloy powders indicates that precipitation of nano-particulate Y-Al-O phases begins at temperatures as low as 650 °C and microstructural changes during annealing of ODS powders involved interactions between nano-particle formation and recovery/recrystallisation processes. High number densities (\( N_V > 10^{23} \text{ m}^{-3} \)) of coherent nano-precipitates were identified in both recovered and recrystallised regions of powder particles. These formed over a range of temperatures used in the consolidation processing of ODS alloys. The orientation relationship between nano-particles and the matrix was identical in both recovered and recrystallised grains, indicating that particles were dissolved at recrystallising interfaces and subsequently reprecipitated. Examination and comparison of as-MA and annealed powder specimens suggests that nuances in the manufacturing of these three, nominally similar, alloys leads to differences in recovery/recrystallisation behaviour, which may influence microstructure and, ultimately, properties in the final product form.

1. Introduction
The production of oxide dispersion strengthened alloys manufactured by mechanical alloying of metallic powders to incorporate powdered yttria was first demonstrated by Benjamin in 1970 [1]. The MA process creates an intimate mixing of constituents typically comprising either blended elemental powders or pre-alloyed metal powders and oxide powders (usually Y₂O₃). The alloy and oxide powders are loaded into milling containers along with milling media (usually steel balls) and during the MA process powders trapped between colliding balls are repeatedly flattening, cold welded, fractured and re-welded. When the MA process is optimised elemental homogenisation can be approached and each MA powder particle should have an identical composition [2]. During the MA process true strains in the region of 9 may be imparted to the powder [3] and high dislocation densities and nano-crystalline structures are produced [4]. Once milled, the MA powders are further processed to produce a consolidated product. During these subsequent steps the powders, which are heavily deformed, undergo thermal degassing treatments, then heating cycles in preparation for densification, typically by extrusion...
or hot isostatic pressing (HIP). In consolidated form the alloys, depending on composition, contain high number densities \((10^{20} \text{ m}^{-3} < N < 10^{24} \text{ m}^{-3})\) of oxide particles and a fine grained but, usually, highly dislocated microstructure.

These materials were designed for use at high temperatures where good creep strength and oxidation resistance are required. The creep performance of this group of alloys can in part be attributed to the dispersion of nano-oxides but is also further enhanced by the generation of high aspect ratio grains formed during secondary recrystallisation annealing treatments which are performed at high homologous temperatures (approximately 0.9 \(T_M\)). Oxidation resistance is afforded by an adherent alumina scale which forms due to the necessary addition of approximately 10 at% aluminium. By making such aluminium additions, the oxide dispersion type and number density is significantly affected. In alloys which do not contain aluminium but are made with additions of yttria and titanium, high number densities \((>10^{23} \text{ m}^{-3})\) of, typically, 2 nm yttrium-titanium oxides precipitate during consolidation. However, in the presence of Al, Ti is displaced from the oxide system and relatively coarse (ca. 20 nm) yttrium-aluminium oxides are formed in number densities ca. \(10^{21} \text{ m}^{-3}\).

A recent study \[5\] has shown that during annealing treatments of PM2000 MA powders, at 650 °C, nano-particles approximately 2 nm in diameter are precipitated within a recovered, fine grained, matrix. It was also shown that, during annealing treatments made at higher temperatures (850 °C and 950 °C), the microstructure evolves from the wrought micro-forged structure to a mixed recovered/recrystallised grain structure. It was demonstrated that high number densities of nano-particulates were present in both the recovered grains and recrystallised grains and that an identical orientation relationship existed between the nano-particles and the recovered and recrystallised matrices. In addition, a particle free zone formed in recrystallised grains adjacent to the migrating recrystallising boundary. Based on these findings it was evident that the nano-particles formed during recovery were first dissolved by mobile recrystallising interfaces and then were re-precipitated in the recrystallised grains.

This study builds on our previous work and compares microstructural evolution in annealed, legacy MA precursor powders of ODM751, MA956 and PM2000 ODS alloys.

2. Experimental

The nominal compositions of the three alloy powders studied are presented in Table 1. Powders were annealed for 1 hour over a range of temperatures between 800 °C and 1050 °C. In a separate experiment, powders were first subjected to recovery anneals, for various durations at 650 °C, prior to 1 hour anneals over the temperature range 800 to 1050 °C.

As-MA and annealed powders were mounted in conductive resin and prepared, by standard metallographic techniques, for observations in a scanning electron microscope (SEM). A final polish was performed using a 40 nm colloidal silica suspension; this preparation step enabled backscattered electron channelling contrast images to be recorded. The volume fraction of recrystallised material was measured from electron micrographs using the mean linear line intercept method.

| Table 1. Nominal compositions (wt%) of ODM751, MA956 and PM2000. |
|-------------------------|-----------------|---------|-------|---------|----------|
| Alloy                  | Manufacturer    | Cr  | Al  | Ti   | Mo   | Y_2O_3  | Fe   |
| ODM751                 | Dour Metal S.A. | 16  | 4.5 | 0.6  | 1.5  | 0.5     | Bal  |
| MA956                  | Special Metals Corp. | 20  | 4.5 | 0.4  | _    | 0.5     | Bal  |
| PM2000                 | Plansee GmbH    | 20  | 5.5 | 0.3  | _    | 0.5     | Bal  |

Mechanically alloyed and annealed MA956 and PM2000 powder particles were prepared for TEM/STEM analysis using the method described by Dawson and Tatlock \[6\]. Further specimens were prepared from ODM751, by the FIB lift-out method \[7\], in an FEI Helios 600i FIB instrument. TEM/STEM analysis was performed in a probe-side aberration-corrected JEOL 2100FCs microscope operated at 200kV fitted with an EDAX windowless energy dispersive x-ray spectrometer (EDS).
3. Results

3.1. As-Mechanically Alloyed Powder

By far the most significant differences in as-MA microstructures could be observed between the ODM751 powder (figure 1a) and the MA956 (figure 1b) and PM2000 (figure 1c) powders. The ODM751 powder was inhomogeneous, containing large (<5 μm diameter) aluminium-rich particles, chromium-rich particles and molybdenum rich areas. It is likely that these un-mixed alloy components were present due to a processing route that employed elemental powders mixed with pre-alloyed powders to achieve target alloy compositions [8]. In addition to the heterogeneous distribution of elements, the scale of the as-MA wrought microstructure in ODM751 was not as refined as that displayed in either PM2000 or MA956 powders. Areas as large as 10 μm in diameter composed of micrometre sized grains were not uncommon within ODM751 powder particles. Also apparent was the variation in microstructure and homogeneity of mixing from particle to particle within ODM751 powder; this was, again, far more obvious in ODM751 powder than in either MA956 (figure 1b) or PM2000 (figure 1c).

Figure 1. Backscattered electron images showing the wrought microstructures of as-MA (a) ODM751, (b) MA956 and (c) PM2000

SEM analysis comparing the wrought as-MA microstructures of MA956 and PM2000 powders revealed only subtle differences. Occasional bands of Cr-Al and Fe enriched materials, exhibited as swathes of unmixed alloy, were entrained along the cold welded fold lines of the micro-wrought MA microstructure in the MA956 powder. In addition to the swathe-like structures, which measured micrometres in length, numerous contaminant particles were also seen. The most common particles were titanium carbonitrides (Ti(C,N)), measured in the size range 100 to 500 nm; but silica and alumina particles were also observed. Occasional yttrium-rich particles were also identified but such particles were only a few 10s of nm in diameter. By comparison, PM2000 powder displayed a relatively homogeneous deformed grain structure, revealing grain diameters within the range 20 to 100 nm surrounded by matrix that displayed no definable structure (figure 2a). SEM observations, combined with EDS results, indicated there were fewer contaminant particles such as Ti(C,N) in the PM2000 powder. Figures 2 b and c show different microstructures observed in as-MA ODM751. Many areas displayed well defined grains, often distorted or elongated (figure 2b) whereas highly disordered regions (figure 2c) were similar in appearance to the milled structures of MA956 and PM2000 powders.

Transmission electron microscopy studies, which included large area selected area diffraction analysis, did not reveal evidence of unmixed yttria in as-MA PM2000; all patterns were consistent with the BCC ferrite structure.
3.2. Evolution of recovered and annealed microstructures

The annealing of MA956 and ODM751 alloy powders, at 950 °C for 1 hour, produced both general recrystallisation and bands of finer recrystallised grains (figures 3a and 3b). PM2000 powders, on the other hand, annealed under identical conditions, showed a propensity to form large recrystallised grains whilst retaining areas of fine-grained recovered alloy (figure 3c). It was evident that each of the nominally similar legacy commercial ODS alloy powders studied exhibited a specific pattern of recrystallisation behaviour with differences apparent in both the morphology of microstructural evolution and process kinetics.

In the annealed condition, ODM751 displayed regions of recovered fine grained material and areas which had recrystallised. Calculating the volume fraction of recrystallised material in ODM751 proved difficult as there was an overlap in the grain size distributions of the two regions. TEM analysis of 850 °C annealed ODM751 powder also revealed occasional small diameter recrystallised grains within fine grained recovered regions.

In addition to difficulties associated with differentiation between fine recrystallised and recovered ODM751 grain structures, large areas of coarse grained material were apparent in the as-MA powder. Moreover, considerable variations in the $V_f$ of coarse and fine-grained material were observed from one particle to another. This is consistent with the inhomogeneous nature of the as-MA ODM751 powders. Fine grained regions contained greater concentrations of sub-μm particles, a large proportion of which were sub 100 nm oxides, than were observed in recrystallised areas. Broad sweep EDS line-scans recorded across these un-recrystallised swathes and the findings of EDS point analyses suggest that many of the particles located in the recovered grains were Y and Al oxides.
Due to limited supply of raw materials, measurements of recrystallised volume fractions in the MA956 were limited to 2 annealing temperatures. However, preliminary results suggest that the recrystallisation kinetics of MA956 powders were similar to those displayed by PM2000 (figure 4a). In contrast, annealing for 1 hour at 850 °C did not induce measurable recrystallisation in the ODM 751 powder. After annealing at 950 °C and 1050 °C recrystallisation was observed in ODM751 but the volume fraction measured was low compared to both MA956 and PM2000 alloy powders (figure 4a).

In a separate experiment, PM2000 powders were subjected to recovery anneals at 650 °C for 2 or 5 hours before the application of a second, 1 hour, heat treatment performed at higher temperatures. Although the kinetics of recrystallisation were reduced as a result of a 5 hour anneal at 650 °C prior to a 1 hour anneal at 850 °C, the effects became less noticeable when higher temperature recrystallisation treatments were performed. The duration of the recovery anneal also influenced recrystallisation kinetics e.g. a 2 hour anneal at 650 °C prior to a 1 hour anneal at 850 °C had little effect on the recrystallised volume fraction of powder (figure 4b).

TEM/STEM analysis of 850 °C and 950 °C annealed MA956 powders enabled examination of the mixed recrystallised and recovered microstructures in greater detail. Fine-grained material contained high number densities of dislocations and grains were often elongated; a legacy of the ‘micro-forging’ action of the MA process. Recrystallised grains, in contrast, contained negligible numbers of dislocations, but groups/stringers of particles which were aligned parallel to neighbouring elongated fine grains were observed (figure 5a); again, this was assumed to be carried over from the MA process.

In addition to the aforementioned aligned and relatively coarse particles, high number densities (>10^{23} m^{-3}) of cube shaped nano-particles precipitated homogeneously in both fine grained and recrystallised regions of annealed MA956 (figure 5b). The nano-particles, which were enriched in yttrium, aluminium and oxygen, displayed identical growth habits, i.e. facets parallel to the ferrite \{200\} planes, to nano-particles which have been identified in PM2000 powders with similar annealing histories [5]. The same orientation relationship displayed by nano-particles and the ferrite matrices in annealed PM2000 powders were observed in both recrystallised and recovered grains of MA956 alloy powder.
The number densities and size distributions of precipitates measured in both recovered and recrystallised grains in annealed MA956 powder could not be differentiated; hence volume fractions of nano-particles in these two regions could be considered essentially equal. However, slight differences were recorded in precipitate populations measured between MA956 and PM2000. The mean diameter of nano-particles measured in powders annealed for 1h at 950 °C were 2.3 nm (±0.8 nm) and 3.3 nm (±1.6 nm) in PM2000 and MA956, respectively; and the particle number density was greater in the PM2000 alloy powders (figure 5c).

4. Discussion

The microstructures of and chemical distributions measured in as-MA ODM751, MA956 and PM2000 powders differed significantly. This suggests that the mechanical alloying processes and procedures adopted by the three manufacturers produced results which could be ranked in the following order: PM2000 powders appeared homogeneous, hence best mixed. MA956 powders were similar to PM2000 but Ti(C,N) and unmixed swathes of material revealed that slightly less homogeneous alloying had been achieved in the MA956 powder. In contrast, ODM751 powders appeared to be less thoroughly blended, with significant variations observed from one particle to another. It is likely that large particle-free, recrystallized grains that have been observed in consolidated ODM751 [9] may be the consequence of incorporation of such inhomogeneously milled powders. The coarse particles and poor distributions in ODM751 reported by Foxman et al. [10], were likely to have been caused by the incomplete dissolution of yttria, during the MA process, which has been observed in the present study. However, it is interesting to note that consolidated ODM751 offers superior creep strength to MA956 and matches the performance of PM2000 [8, 11, 12]. A possible explanation has been attributed to the addition of molybdenum made to ODM751[3] but it would be of significant interest to determine what level of inhomogeneities can be tolerated after the MA process whilst retaining acceptable levels of alloy performance.

SEM analysis of the wrought as-MA microstructures in MA956 and PM2000 powders revealed subtle differences in their deformation structures. A greater grain size distribution observed in the MA956 powder indicated a less complete/homogeneous mixing had been achieved during MA; as such, one might assume greater heterogeneities in stored energy would exist and play a role in the recrystallisation behaviour of these powders. In addition, more obvious differences included the numerous Ti(C,N) particles and occasional swathes of Cr-Al and Fe-enriched material observed in MA956; these too would be expected to affect the local kinetics of recrystallisation.

After annealing as-MA powders for 1 hour at 950 °C, elemental distributions within the FeCrAl and FeCrAlMo matrices were homogenised. However, Ti(C,N) particles were identified in MA956 and swathes of alloy showing enhanced aluminium-yttrium concentrations, probably in the form of oxides.
were observed in ODM751. This indicates that intermediate temperature annealing treatments are capable of homogenising some elemental distributions but fail to dissolve more stable compounds.

The recrystallisation kinetics of ODM751 were slower than those of either PM2000 or MA956 at temperatures between 850-1050 °C. The difference in recrystallisation behaviour probably involved a combination of factors, including: a lower overall level of stored energy, as evidenced from analysis of the as-MA powders; and relatively coarse oxide particles left in more highly deformed areas of ODM751 as a result of failure to drive ytrria into solution during MA.

All powders that were annealed at 950 °C showed some evidence of recrystallisation; yet their microstructures differed greatly. PM2000 powders displayed a bimodal grain size distribution comprising fine recovered and large recrystallised grains. The grain size distribution in recovered regions was narrow, with recovered grains easily distinguished from the much larger recrystallised grains. MA956 powders, in the same condition, displayed a similar recovered grain size distribution but the size range of recrystallised grains was broader than in PM2000 powder. ODM751 powders annealed for 1 hour at 950 °C were also partially recrystallised but the microstructure was significantly different to the PM2000 and MA956 powders. Recrystallised grains were smaller than those observed in the Plansee and Special Metals powders and it was sometimes difficult to easily differentiate between recrystallised and recovered regions. However, concentrations of larger oxide particles, present due to incomplete MA, were a constant and clear signature in recovered regions.

As first demonstrated in PM2000 alloy powder [5], this study shows that recrystallisation in MA956 powder progresses by passage of recrystallizing interfaces through material in which high number densities of nano-particles have already precipitated. In addition, the existence of an identical orientation relationship between nano-particles and matrix in both regions suggests that these particles dissolve during recrystallisation and re-precipitate behind the recrystallising interface.

Recrystallisation in such heavily precipitated material probably occurs due to a combination of the high residual stored energy from MA, despite recovery, together with the dissolution of particles at recrystallising interfaces. Although clear evidence of precipitate free zones adjacent to recrystallising interfaces was not observed in MA956 powders, it has been observed in PM2000 powders [5] and in other ODS alloy systems [13]. As such, dissolving precipitates might not exercise full Zener pinning on grain boundaries but exert a lesser force associated with solute drag. In contrast, larger precipitates pin recrystallising interfaces, with clear evidence observed of bowing boundaries pinned by 10 nm oxides. This explanation is consistent with evidence presented here, where recrystallisation commences in the presence of 2 to 3 nm particles, which can be dissolved by migrating boundaries, yet recrystallisation was suppressed in ODM751 in regions of relatively coarse oxide particles.

5. Conclusions
The microstructure of as-MA ODM751 powder differs significantly from those of as-MA MA956 and PM2000. ODM751 powders were incompletely homogenised by mechanical alloying; this could be due to factors which might include the adoption of a different processing route, process time, or use of pre-alloyed or elemental powders as the initial feedstock.

Annealing at 950 °C induced partial recrystallisation in all as-MA powders. High number densities of Y-Al-O nano-particles were identified in both PM2000 and MA956 powders.

Under the same annealing conditions, the V_f recrystallised differs between the three alloy powders studied; but in all cases, once recrystallisation initiated, V_f increased with annealing temperature.

The recrystallisation kinetics in MA PM2000 powder were reduced by the application of an initial 650 °C recovery annealing treatment. The change in kinetics was sensitive to the duration of recovery anneal and the temperature of the subsequent recrystallisation treatment.

Acknowledgements
We are pleased to acknowledge the financial support of this work through the Advanced Research Materials (ARM) Programme, U.S. Department of Energy, Office of Fossil Energy, managed by U.T.-
Batelle, LLC, and the Engineering and Physical Sciences Research Council – Materials for Fusion and Fission Power – grant EP/H018921/1.

We would also like to express our gratitude to both Special Metals and Bohumil Kazimierzak (Dour Metal s.r.o.) for providing the mechanically alloyed MA956 and ODM751 powders respectively.

References
[1] Benjamin J S 1970 Metall. Trans. 1 pp 2943-2951
[2] Laurent-Brocq M, Legendre F, Mathon M H, Mascaro A, Poissonnet S, Radiguet B, Pareige P, Loyer M and Leseigneur O 2012 Acta Mater. 60 pp 7150-7159
[3] Bhadeshia H K D H 1997 Mater. Sci. Eng. A 223 pp 64-77
[4] Suryanarayana C 2001 Prog. Mater. Sci. 46 pp 1-184
[5] Dawson K, Haigh S J, Tatlock G J and Jones A R 2015 J. Nucl. Mater. 464 pp 200-209
[6] Dawson K, Tatlock G J 2015 Micron 74 pp 54-58
[7] Giannuzzi L A, Kempshall B W, Schwarz S M, Lomness J K, Prenitzer B I and Stevie F A 2005 FIB Lift-Out Specimen Preparation Techniques: Introduction to Focused Ion Beams, Eds. Giannuzzi L A and Stevie FA (Springer US) pp 201-228
[8] Kazimierzak B, Prignon M, Lecomte-Mertens C and Coutsouradis D 1990 Fe Base ODS Alloys with Improved Mechanical Strength: Proc. Int. Symp. High Temperature Materials for Power Engineering (Liege) pp 131-142
[9] Jaeger D M and Jones A R 1994 Dispersoid Distributions in Fe-based ODS alloys made by Mechanical Alloying: Proc. Int. Symp. Materials for Advanced Power Engineering (Liege) p 1507
[10] Foxman Z, Sobol O, Pinkas M, Landau A, Hähner P, Krsjak V and Meshi L 2012 Metallogr. Microstruct. Anal. 1 pp 158-164
[11] Kazimierzak B, Prignon M, Lecomte-Mertens C and Coutsouradis D 1990 Anti-Corros Method M 37 pp 4-9
[12] Hurst R and Hähner P 2010 Materials qualification testing for next generation nuclear reactors: Proc. Int. Symp. Baltica VIII: Life Management and Maintenance for Power Plants, (Helsinki) pp 324-350
[13] Naka S, Octor H, Bouchaud E and Khan T 1989 Scripta Metall. 23 pp 501-505