

Reduction in Defect Content of ODS Alloys

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Abstract

Oxide dispersion strengthened (ODS) alloys prepared by mechanical alloying (MA) and subsequent consolidation are of increasing interest for potential application in components for use in power generation and furnace applications. After MA, canned alloy powders are usually subjected to a series of heat treatments. These heat treatments, particularly those at higher temperatures, last long enough, many hours in some cases, for significant changes to occur within the powder charge or consolidated material. Such changes may be beneficial, such as the degassing of the powder in the can or the secondary recrystallisation of the consolidated alloy. However, this is not always the case and this work involves investigation of the microstructural evolution and tendency for oxidation of the alloys ODS-Fe₃Al and PM2000 during heat treatment. Where the effects of high temperature annealing are found to be deleterious to alloy properties, routes are suggested whereby detrimental effects may be kept to a minimum; how oxidation may be inhibited, how alloy powder properties affect oxidation behaviour and how incidental microstructural changes may be controlled during annealing processes.

Introduction

Alumina-forming ferritic steels with oxide dispersion strengthening (ODS) represent an important alloy group for high temperature applications. They offer the potential for high temperature strength and creep resistance by virtue of their dispersion strengthening and form a stable, compact α -alumina scale providing excellent high-temperature oxidation resistance. This is combined with the use of cost-effective iron as the main alloy constituent. Not surprisingly, the bulk of the research that has been devoted to the development of these alloys has concentrated on the improvement of mechanical and corrosion properties. However, with the potential for increasingly demanding end applications, further research has become necessary to fine tune these alloys to further enhance performance and reliability. In the ODS-Fe₃Al developmental alloys, fundamental research on quality and performance issues is now being conducted concurrent with processing developments [1,2,3].

This work is part of an ongoing microstructural investigation into a prototype ODS-Fe₃Al alloy for use in the power generation industry. Compared to the ODS-FeCrAl alloys, the prototype ODS-Fe₃Al alloy studied here has inherently superior sulphidation and carburisation resistance and, potentially, may have longer oxidation-limited lifetime.[4] However, the microstructure of the consolidated ODS-Fe₃Al is not yet sufficiently homogeneous and reproducibly defect free for service. Defect categories have included fine grained regions within the desirable, coarse secondary recrystallised microstructure, large concentrations of Al_x(O,N)_y particles, intrusions and dispersoid-free regions within the alloy. The origin of these problems has been traced to various preconsolidation processes within the alloy production route.[1,2,3]

A favoured production route for these alloys is mechanical alloying (MA) whereby the alloy is produced in powder form and subsequently consolidated by means of hot extrusion or HIP. Prior to consolidation, the powder

undergoes high temperature anneal processes, typically comprising a degassing process at $\approx 600^{\circ}\text{C}$, a preconsolidation high temperature ‘soak’ at $\approx 1000^{\circ}\text{C}$ and, after consolidation, recrystallisation annealing at temperatures around 1300°C . These annealing processes are at high enough temperatures and last long enough for significant oxidation and microstructural change to occur in some alloys. In particular, oxidation of ODS- Fe_3Al powder during processing prior to consolidation has led to the entrainment of particulate oxide in the consolidated material. This interferes with the crucial secondary recrystallisation process.[5] Once such problems have been identified, modifications to alloy processing can be conceived and tested. In the following, the origins and influence of some of the processing quality issues noted above are investigated and methods suggested by which some of these phenomena may be controlled or ameliorated.

Effect of process modifications on powder oxidation

As-MA PM2000 powder was compacted in a cylindrical die ($\text{Ø}10\text{mm} \times 6\text{mm}$) by simple uniaxial compression to a pressure of 635 MPa. To simulate canning, the powder, still contained in its die, was annealed at 1000°C for 1 hour under a vacuum of 10^{-3} mbar. After annealing, the compressive strength of the resulting powder was measured.

In a further trial, as-MA ODS- Fe_3Al and PM2000 were both compacted and annealed as above, but with the inclusion of two hydrogen purges of the vacuum system prior to evacuation to 10^{-3} mbar. Due to significant shrinkage during sintering, the resulting pellets were severely cracked and compressive strengths were estimated from hardness measurements taken from the pellet fragments.

The effects of hydrogen purging on ODS- Fe_3Al and PM2000 powder charges and the effect of cold compaction of ODS- Fe_3Al powder prior to annealing on powder oxidation and subsequent sintering efficiency have already been reported.[3] Figure 1 shows these data alongside the new data on the effects of cold compaction of PM2000 powder and the effect of combining hydrogen purging with cold compaction for both ODS- Fe_3Al and PM2000.

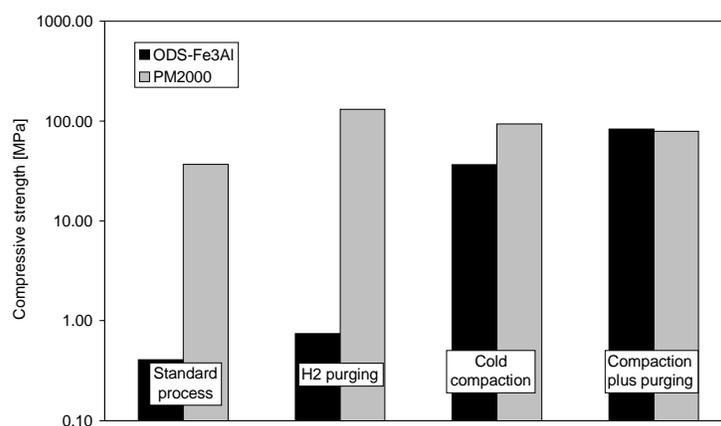


Figure 1 The effect of process modifications on the sintered strength of ODS- Fe_3Al and PM2000 powders.

It can be seen that cold compaction of the alloy powder prior to annealing produced a dramatic improvement in sintered strength. Whereas hydrogen purging alone produced the largest enhancement in sintered strength in PM2000 powder, cold compaction increased sintered strength in ODS- Fe_3Al powder by a factor of 89 as opposed to the factor of ~ 3 increase seen with PM2000 powder. It is believed that this is due to more rapid oxidation in ODS- Fe_3Al powder than PM2000 and, therefore, that the most effective way to reduce oxidation during consolidation is to minimise the powder free surface area by use of processes such as cold compaction.[3,6]

The two techniques can be seen to be highly effective but in an alloy specific way. It could have been expected, therefore, that the combination of the two techniques would not yield significant further improvements on the application of the individual techniques. In the case of PM2000 powder, this was indeed the case, with no obvious additional benefit (within experimental error) gained by combining purging and compaction. However, a further improvement in sinter strength was possible for the ODS-Fe₃Al alloy: a sintered pellet produced by a combination of hydrogen purging and cold compaction had a compressive strength a factor 203 times higher than that produced by straightforward vacuum annealing. The ODS-Fe₃Al pellet was, in fact, of similar strength to a similarly processed PM2000 pellet whereas after straightforward annealing, the PM2000 pellet was a factor of 90 times stronger. It would appear that a combination of cold compaction and hydrogen purging can significantly reduce the oxidation of densely packed ODS-Fe₃Al during annealing.

Variation of oxidation behaviour between different batches of ODS-Fe₃Al powder.

It has previously been reported that aluminium depleted regions (ADRs) exist within some batches of as-MA ODS-Fe₃Al powder and the size and concentration of these regions varies between powder variants.[2,3] The greatest differences in ADR content were between ODS-Fe₃Al variants PMWY2 and PMWY3. The oxidation behaviour of these powders has been studied.

Samples of each powder were annealed at 1200°C for 24 hours. In order to accelerate oxidation, the powders were oxidized at atmospheric pressure rather than at the 10⁻³ mbar characteristic of processing atmospheres. After oxidation, the powders were examined by means of SEM and EDS.

As anticipated, after annealing for 24 hours at 1200°C, both PMWY2 and PMWY3 powders exhibited alumina surface layers. However, on the PMWY2 powder, discontinuities in the alumina scale were present in the form of areas of iron oxide. This is shown in Figure 2 where an area of iron oxide can be seen in both the secondary and backscattered electron images together with EDS spectra from the iron oxide and the surrounding alumina scale.

Further samples of powder were cyclically oxidized at 1200°C with 24 hour cycles in ambient laboratory air. After each cycle, the samples were weighed and their masses plotted against time in order to monitor the progression of oxidation.

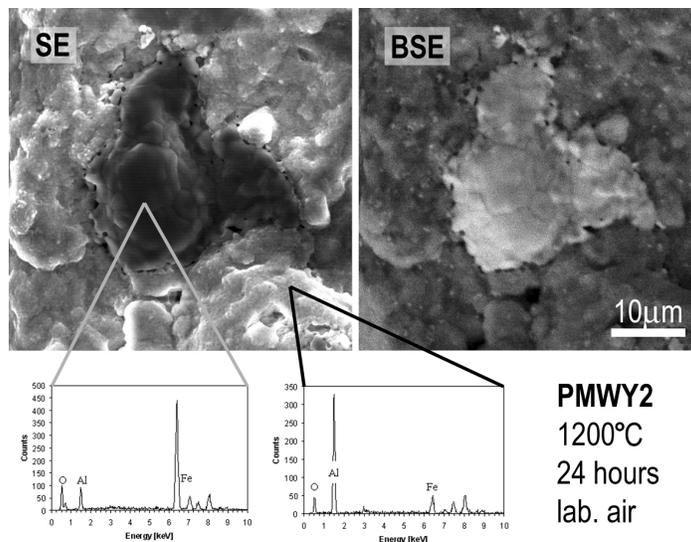


Figure 2 Iron oxide region found within the alumina scale on an oxidized PMWY2 ODS-Fe₃Al powder particle.

The mass gain data collected during cyclic oxidation of the powders can be seen in Figure 3. Both powders show an initial rapid increase in mass and then the mass increase slows to a steady level, slightly higher in powder PMWY2. After 120 hours, the mass increase of the PMWY2 powder accelerated. This increased rate coincided with the formation of regions of a black oxide on increasing numbers of the PMWY2 particles. Powder PMWY3 did not show such an increase in mass gain rate until after 250 hours and, even then, the mass gain rate was not as high as that seen in PMWY2. Again, the rate increase coincided with the formation of a black oxide.

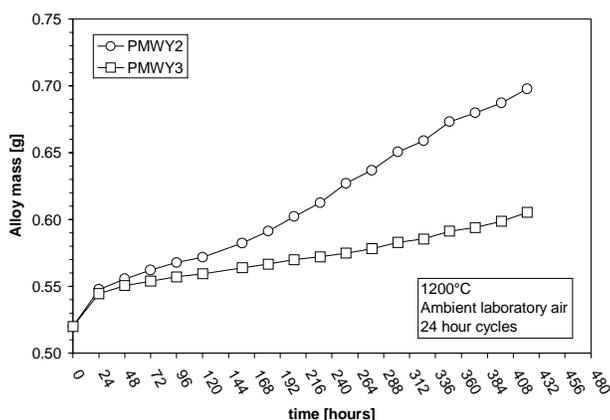


Figure 3 Mass gain of powders PMWY2 and PMWY3 during cyclic oxidation.

The formation of similar alumina scales over the majority of powder particles from both of the powder variants studied would be expected as the alloys are of practically the same composition. This is what was observed in the powders oxidised in this work although the presence of substantial islands of iron oxide within the alumina scale formed on variant PMWY2 suggests that the ADRs in this variant may affect oxidation behaviour. The ADRs represent areas of the alloy depleted not only in the aluminium necessary for the formation of a protective alumina scale, but also depleted in yttria-based compounds essential for good oxide adhesion as well as alloy strength.[7] It is postulated, therefore, that the iron oxide islands are associated with ADRs that intersect the particle surface. The reduced level of aluminium in such particles would hinder alumina formation and would promote the formation of iron and possibly chromium oxides, particularly in the early stages of oxidation before diffusion induces chemical homogeneity. The lack of yttria in ADRs would also contribute to earlier, local decohesion of protective scale and accelerate the tendency towards breakaway oxidation. This effect would be more obvious in longer-term oxidation than the 24 hour oxidation illustrated in Figure 2, and may be responsible for the early breakaway oxidation of variant PMWY2 seen in the mass gain data in Figure 3. Here, not only would the aluminium reservoir be decreased by the presence of ADRs, but the adhesion and homogeneity of the protective scale could be compromised by areas lacking in yttria dispersoid, resulting in an oxidation lifetime only half that of PMWY3. Onset of breakaway oxidation could be seen to be quite gradual compared to mass gain data typical of single coupons of ODS alloys. This is attributed to the fact that a broad population of particles was oxidised in the same crucible during the experiment. Each particle behaved slightly differently and the onset of breakaway oxidation was distributed over a period of time as a cumulative effect of individual powder particles going into breakaway one by one.

The effect of powder particle size distribution on canned powder oxidation

As-MA ODS-Fe₃Al and PM2000 powders were sieved to prepare size fractions >425µm and <75µm. These fractions, together with un-sieved as-MA powders were separately, but simultaneously annealed at 1000°C for 1 hour under 10⁻³ mbar in an open ceramic boat. After annealing, the powders were carefully studied using SEM and EDS in cross-section and plan view and the degree of oxidation measured in each case.

After annealing, powder particles of all types and sizes had formed a surface oxide scale, at least on the outermost particles in the annealing crucible. The thicknesses of the scales were measured from cross-sectioned powder particles, but showed no obvious trends associating oxide thickness with particle size. This is shown in Table 1. As seen before, unsieved ODS-Fe₃Al forms a thicker oxide scale than unsieved PM2000.[3] However, without the benefit of these previous results, it would be difficult to conclude from Table 1 that such a trend exists.

Table 1 Measurement of oxide thicknesses from different alloys and powder particle sizes.

	PMWY2 oxide thickness [μm]	PMWY3 oxide thickness [μm]	PM2000 oxide thickness [μm]
Large fraction	0.68	1.06	0.73
Unsieved	0.72	-	0.53
Small fraction	0.67	-	0.71

The powder particle size ought not to have a significant effect on the thickness of oxide scale that forms over a period as short as 1 hour, such as used in this study. The only parameter that is influenced by particle size is the aluminium reservoir available for the formation of protective alumina scale. Smaller particles would therefore be expected to go into breakaway oxidation sooner than larger particles but over a much greater period of time than covered in this work.[8]

Although particle size does not appear to have an effect on oxide scale formation, the range of particle sizes within a particular powder appears to affect the distribution of oxidised particles through the depth of a sample of annealed powder. It was found that unsieved powders, with a wide range of particle sizes formed a ‘crust’ of oxidised particles at the surface of the sample. This crust could be up to 1mm thick on some samples and appeared to protect the powder on the interior of the sample from extensive oxidation. The difference in oxidation levels in the ‘crust’ and interior can be seen in Figures 4a and 4b.

In powders that had been sieved and therefore covered a narrow range of particles sizes, the degree of oxidation was uniform throughout the powder sample, with significant thicknesses of oxide forming on all particles.

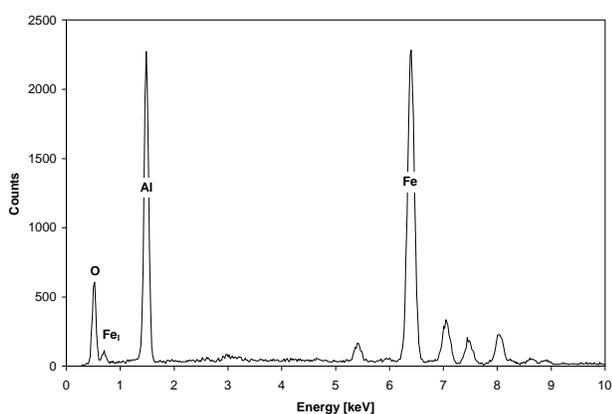


Figure 4a
EDS spectrum from the oxidised powder ‘crust’.

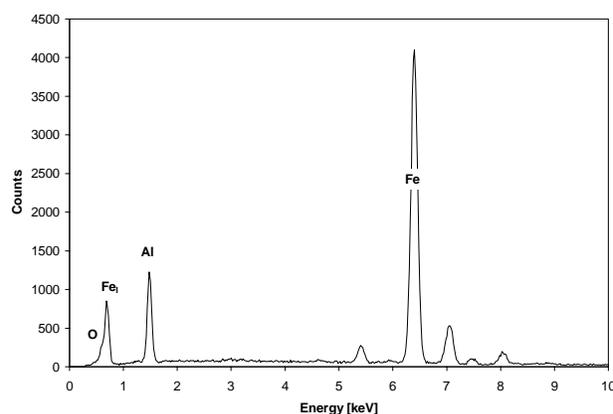


Figure 4b
EDS spectrum from the innermost, protected powder.

The formation of the 'crust' on unsieved powders is attributed to the higher effective tap density possible using powder with a wide range of particles sizes, where smaller particles can pack into interstices between larger powder particles, and so on. Interstices remaining at the onset of annealing are further narrowed by a combination of oxide scale formation and sintering, thus forming a solid crust. This 'crust' was seen to be sufficiently dense to afford shielding from oxidation to further, unoxidized powder deeper within the sample. In sieved powder samples with a narrow range of particle sizes, such thorough packing was not possible and uniform oxidation took place through the whole sample.

Evolution of the microstructure of PM2000 powder during annealing

The evolution of the microstructure of PM2000 powder was studied in detail using samples annealed at 619, 773 and 876°C, and in the as-MA condition. This was a continuation of earlier studies to understand and benchmark microstructural change occurring in annealed powders prior to consolidation. Channelling contrast images were produced using a FEG-SEM. Microhardness testing of powder annealed at temperatures between 25 and 900°C revealed that with increasing temperature, after initial softening at 550°C, there was an increase in hardness between 600°C and 750°C before a final softening at temperatures above 780°C, see Figure 5. [1,6]

The temperatures used in pre-consolidation annealing are sufficiently high for significant microstructural change to take place in as-MA powder particles. Figures 6a-d show the changes in microstructure that occur in PM2000 powder annealed for 1 hour at different temperatures.

An as-MA powder particle is shown in Fig. 6. The highly mechanically deformed state of this powder results in a bright, featureless channelling contrast image. After annealing at 619°C for 1 hour (Figure 6b), large recrystallised grains can be seen surrounded by a microstructure that appears mottled and on a scale just below the resolution limit of the microscope. After annealing at 773°C for 1 hour (Figure 6c), the fine microstructure has coarsened, and annealing at 876°C for 1 hour results in a microstructure comprising only large, recrystallised grains several microns in diameter.

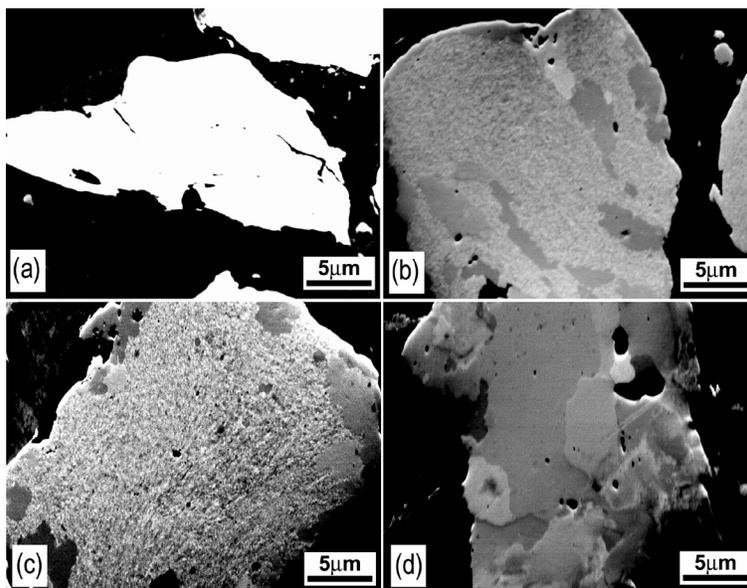


Figure 6
Microstructural changes in PM2000 powder from the a) as-MA condition when it is annealed for 1 hour at b) 619°C, b) 773°C and d) 876°C

Figure 6 shows that recrystallisation appears to proceed at different rates across a single particle and illustrates the inhomogeneous nature of the MA process. The fine microstructures generated initially on annealing may be formed by advanced recovery processes such as subgrain coalescence or by primary recrystallisation to an ultrafine grain size. The formation of this fine microstructure coincides with the fairly rapid initial softening of the powder. A similarly rapid decrease in hardness occurs as the coarse recrystallised microstructure develops above 780°C. These reductions in hardness are separated by an intermediate hardness increase that is tentatively attributed to solution hardening by substitutional species accompanying homogenisation of the mechanically alloyed composition. [9]

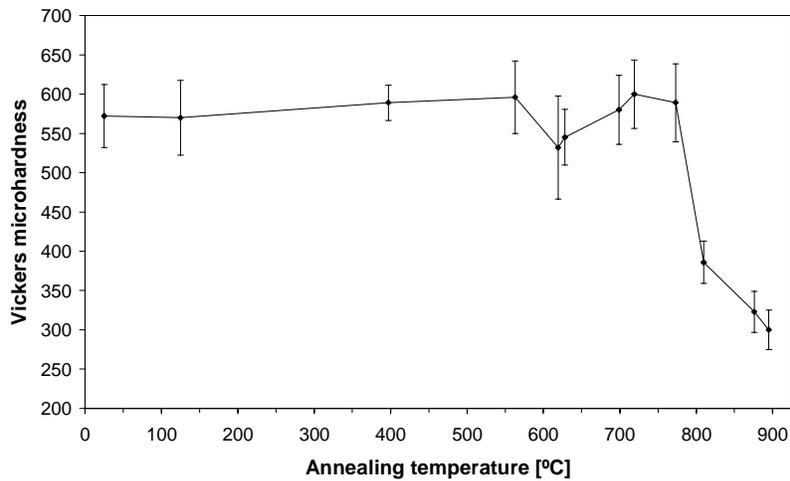


Figure 5
Changes in the microhardness of PM2000 particles with 1 hour annealing temperature. [6]

Formation and prevention of undesirable acicular precipitates in ODS-Fe₃Al

The formation of acicular precipitates in secondary recrystallised ODS-Fe₃Al was studied by electron diffraction in the TEM in samples produced by altering the cooling rate after secondary recrystallisation annealing. Samples that were heated for 1 hour at 1275°C in order to effect secondary recrystallisation were then either furnace cooled or air-cooled.

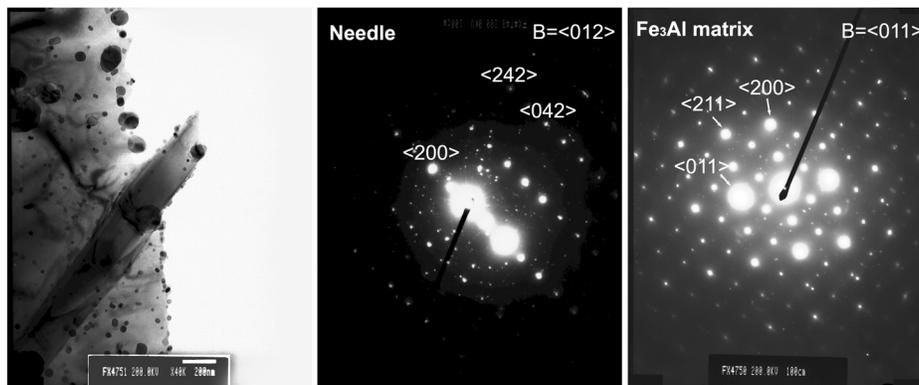


Figure 7 A TEM micrograph of an acicular precipitate (needle) in consolidated ODS-Fe₃Al together with electron diffraction patterns from the needle and from the bulk alloy matrix.

The presence of acicular precipitates has already been reported.[1,5] They have been identified as having a similar composition to the bulk alloy but with slightly higher chromium and carbon levels, and preliminary analyses suggested they had an ordered DO_3 structure.[3]

It has been observed that these aciculae only form within the alloy on extremely slow cooling (furnace cooling). Samples that were air-cooled did not contain any trace of the aciculae.

The electron diffraction data shown in Figure 7 confirms that the aciculae have an f.c.c. structure, as found in the superlattice of the DO_3 structure, in contrast to the b.c.c. B2 structure of the bulk alloy. It had been suggested that the aciculae might be carbides with the $L1_2$ ordered f.c.c. structure.[5] This appears not to be the case, as at carbon concentrations high enough for carbide formation to occur, precipitation of graphite also occurs on cooling, even at high cooling rates. At low carbon concentrations, as are found in these aciculae by EDS analysis, only the intermetallic phases exist.[10] Given the similarity in composition between the aciculae and the bulk alloy, the aciculae would appear to be the product of a phase change from B2 FeAl to DO_3 Fe₃Al. Such a phase change would be expected to occur at 400-500°C as the consolidated alloy cools from the secondary recrystallisation temperature (1275°C). However at these temperatures diffusion rates are so low that aciculae of the size observed (~10µm in length) would take hours to form. Therefore with all but the slowest cooling rates, there would be insufficient time for significant precipitation. This agrees with what is seen in practice, where furnace-cooled ODS-Fe₃Al contained aciculae but air-cooled samples contained no trace of them. Since the aciculae appear to be a lower temperature phase rather than refractory carbides, it would appear unlikely that they would be present at anticipated heat exchanger service temperatures (1100°C) to affect creep performance.

Conclusions

Oxidation of ODS-Fe₃Al and PM2000 powders during high temperature annealing processes may be reduced by hydrogen purging of the canned powders, cold compaction of the powders or a combination of these two techniques prior to consolidation.

The presence of aluminium depleted regions (ADRs) within powder particles leads to the formation of iron oxide inhomogeneities in the protective alumina scale after short term oxidation, and reduces oxidation lifetime by 50% in long term cyclic oxidation of powders.

Powder particle size has no effect on short-term oxidation behaviour. However, a large range of particle sizes in a powder sample can lead to close packing of the powder particles and the formation of a 'crust' on the surface that substantially protects powder within the sample from further oxidation.

During annealing at temperatures similar to those used in powder production, recovery and recrystallisation processes have been observed in PM2000 powder. These processes cause softening of the powder while a process of dissolution of inhomogeneities causes a solution hardening effect.

Potentially harmful acicular precipitates have been identified in consolidated ODS-Fe₃Al. They form by the precipitation of the DO_3 Fe₃Al phase during cooling at temperatures around 400-500°C. Only at very slow cooling rates can these aciculae form and their formation is completely inhibited when samples of the alloy are air-cooled.

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