CONTROL OF DEFECTS AND MICROSTRUCTURE IN ODS ALLOYS

Gordon J Tatlock
University of Liverpool, Department of Engineering, George Holt Bldg., Ashton Street, Liverpool L69 3GH, UK
E-mail: tatlock@liv.ac.uk; Telephone: + 44 151 794 5367; Fax: +44 151 794 4675

Hameed Al-Badairy[†]
Saudi Aramco, Research and Development Centre, P.O. Box 62, Dhahran 31311, Saudi Arabia
E-mail:hameed.badairy@aramco.com; Telephone: + 966 3 8724066

Chun-Liang Chen
University of Liverpool, Department of Engineering, George Holt Bldg., Ashton Street, Liverpool L69 3GH, UK
E-mail: chen@liv.ac.uk; Telephone: + 44 151 794 5394; Fax: +44 151 794 4675

Andy R Jones
University of Liverpool, 3 Brownlow St., Liverpool L69 3GL, UK
E-mail: andy.jones@liv.ac.uk; Telephone: + 44 151 794 8026; Fax: +44 151 794 8370

ABSTRACT

High-temperature heat exchangers for application in gasifier fuel gas cooling or high efficiency indirectly fired cycles, require development of metal alloys for tubing capable of service at temperatures in excess of 1100^{0}C (~2000^{0}F). And similar, future operational requirements characterize the demands on materials for advanced combustor cans for application in combined cycle gas turbines. Amongst candidate alloys available for high temperature service, commercial FeCrAl-based mechanically alloyed (MA) Oxide Dispersion Strengthened (ODS) materials such as PM2000 (and MA956), have a composition and microstructure designed to impart creep strength and oxidation resistance in components operating at temperatures from ~1050ºC to 1200ºC and above. Despite the potential benefits offered by these FeCrAl-based ODS alloys they currently suffer from a number of performance shortfalls, notably in biaxial creep performance and the performance of joints. In the latter instance, joining techniques that involve fusion techniques can cause agglomeration and loss of the dispersion of fine-scale oxide particles introduced during the mechanical alloying process. This usually leads to disruption in the beneficial grain structures introduced by subsequent secondary recrystallisation annealing, resulting in a substantial reduction in high temperature creep performance in the joint region.

The current work reports studies made on the application of friction stir welding as a solid state technique for autogenous joining of PM2000 ODS alloy sheet; in particular, the influence of the joining process on the initial microstructure of the alloy and the microstructures that developed during subsequent heat treatment. Microstructures throughout the joint region were compared, examining the influence of the friction stir technique on oxide particles and grain structures alike. Separate studies are also reported on the influence of surface finish on the 1100ºC oxidation behaviour of PM2000 alloy sheet and initial results on evolution of microstructure in PM2000 alloy plate hot-spun to produce combustor can geometry components.

INTRODUCTION

The ODS FeCrAl alloys have significant potential for application in components for use in demanding high temperature environments such as power generation plant[1,2,3], where a combination of excellent high temperature creep strength under biaxial loading conditions and oxidation resistance in combustion gases is required[4]. The ODS base alloys can be supplied in various product forms ready for incorporation in components and can be provided with final heat treatments that will generate release condition creep resistant coarse grained microstructures[5] and a protective alpha alumina oxide layer[6]. However incorporation of components in fabricated structures usually involves joining technologies and those which involve fusion techniques generally produce unacceptable, irreversible microstructural change and property degradation in these alloys. Hence, there is considerable interest in finding approaches to the design and fabrication of components in these materials which either involve minimal or zero-fusion joining techniques or, by additional processing, can minimise the number of joints required. Thus, friction stir welding[7], which is a solid state joining technique, offers potential for introducing seam welds in ODS sheet or plate, while established techniques such as metal spinning[8] has the potential to shape a combustor can in one step from ODS alloy plate, obviating the need for any seam welds. The influence of both techniques on ODS alloy parent microstructures is being explored as part of current studies[9, 10] and results are reported in following sections. On a similar theme, of the way processing can influence performance, preliminary results are also presented which indicate the influence that surface finish can have on the oxidation behaviour of PM2000 alloy.

EXPERIMENTAL

The PM2000 alloy used in the current work was supplied free issue in several product forms and conditions by Siemens Industrial Turbomachinery Ltd. Alloy sheet (as-rolled) nominally 2mm in thickness was supplied direct by Siemens in the as-friction stir welded condition, where subcontract joining (50mm/min threaded tool speed) had been performed by TWI. Combustor cans, manufactured on subcontract elsewhere, by hot metal spinning of nominally 10mm thick PM2000 flat alloy plate, were also supplied by Siemens for metallurgical examination.
Separately, samples of 2mm thick PM2000 alloy sheet subject to high temperature annealing (2000h/1100ºC) in simulated combustion gases were supplied for metallographic examination by Cranfield University, UK.
Standard metallographic techniques reported elsewhere[9] were used to prepare samples for imaging using low voltage Scanning Electron Microscopy (SEM) channelling contrast, Electron BackScatter Diffraction (EBSD) analysis and Transmission Electron Microscopy (TEM) examination.

RESULTS AND DISCUSSION

FRICTION STIR WELDING

A typical SEM channelling contrast image of a transverse section through 2mm thick friction stir welded PM2000 sheet in the welded and secondary recrystallised (SR) annealed (1h/1380ºC) condition is shown in Fig.1.

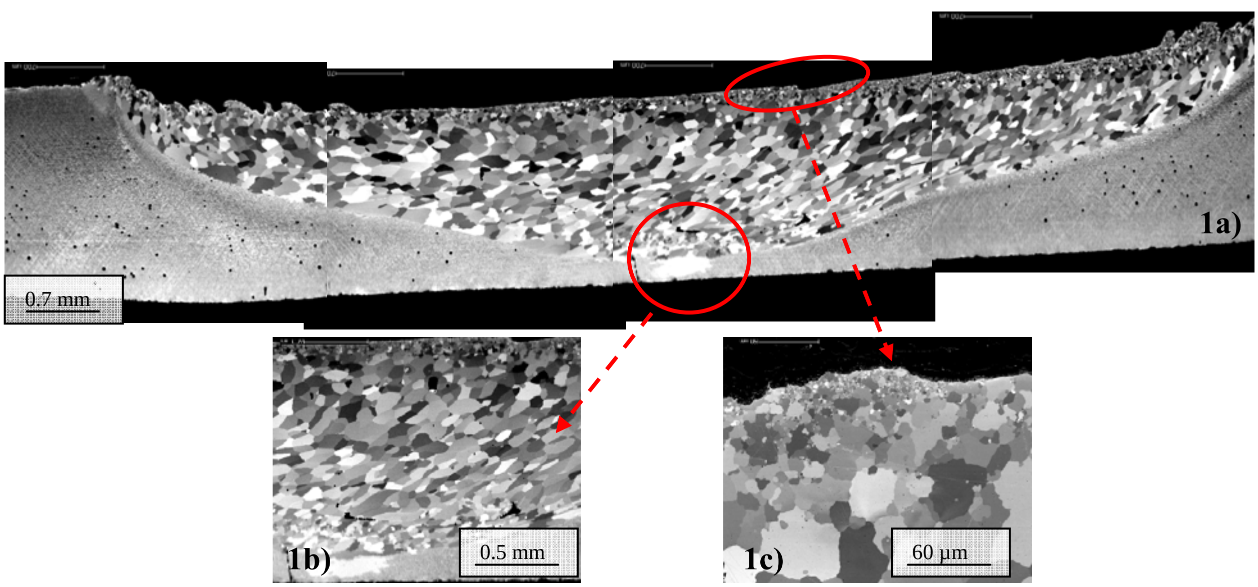

Figure 1. a) Channelling contrast image of SR friction stir weld in PM2000, showing the weld and HAZ. b) a large recrystallised grain grown into parent plate in the weld root c) fine grained region on weld cap.

The image reveals a large, relatively equiaxed grain structure in the weld itself, a Heat Affected Zone (HAZ), and parent plate that has remained in a fine-grained condition despite receiving the standard (1h/1380ºC) release SR anneal for these materials. Also, there is some evidence of an apparent tendency for 'layering' of grain structures in the weld nugget itself, consistent with the cylindrical sheets of material that are extruded during each rotation of the threaded tool which deposits material from the 'front' to the back' of the weld during the friction stir joining process. The large recrystallised grain seen in the root of the weld (Fig. 1b) has grown into parent sheet outside the weld zone, suggestion that the pattern of deformation in the weld root region enabled progress of secondary recrystallisation beyond the weld zone itself. In contrast, in the rest of the parent sheet, there appears to have been no further secondary recrystallisation, either by independent nucleation in the PM2000 sheet, or by intrusion of growing grains nucleated originally in the weld zone. Recrystallisation at the surface of the friction stir weld tended to be characterised by a layer of much finer grains (Fig. 1c). It is thought this could have arisen due to the cooling rate at the weld surface during joining, prior to the recrystallisation anneal. It is also worth noting that despite the fact that the parent material did not undergo secondary recrystallisation during post weld annealing, there is clear evidence (Fig. 1a) of the sort of porosity that evolves in these materials after high temperature annealing. It is suspected that the reason the PM2000 sheet failed to undergo secondary recrystallisation was that it was supplied in a processed condition which had allowed some recovery, thereby reducing the remaining level of stored energy below that which would enable nucleation of secondary recrystallisation to occur.

EBSD was used to investigate the grain orientation and the grain boundary geometries in the weld samples. Figure 2a shows an orientation map of the friction stir weld region after secondary recrystallisation, which demonstrates

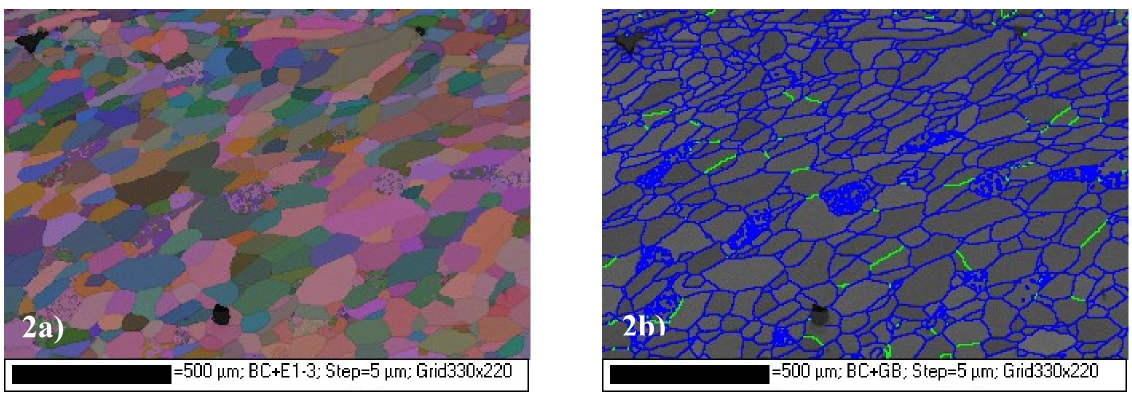

Figure 2: a) EBSD grain orientation (colour map) and b) grain boundary angle maps (blue = high angle (>10^0) boundary; green = low angle boundary) from the FSW region.

that grains were oriented randomly in this region. Overall there was no evidence of any preferred orientation in the secondary recrystallised grain structures that formed in the weld zone after annealing (1h/1380ºC). Fig. 2b shows the grain boundary misorientation map for the same region as shown in Fig. 2a. High angle grain boundaries (defined here as those with a misorientation >10 degrees) are highlighted in blue and can be seen to comprise the majority of boundaries in the weld after recrystallization. Similar EBSD analysis of regions away from the weld zone in annealed sheet suggested that the majority of the microstructure comprised elongated grains which consisted of numerous sub-grains with an irregular morphology, confirming that in the non-FSW region of the PM2000 sheet only recovery had taken place.

TEM observations provided further details of the grain structures, deformation behaviour, and particle size distributions in the various sample regions (FSW and non-FSW regions, before and after the recrystallisation treatment). Figure 3a shows the microstructure of the non-FSW region before recrystallisation treatment. It reveals a fine grain/sub-grain structure elongated and aligned with the working direction in the plane of the sheet and containing large numbers of fine-scale Yttrium Aluminium Garnet (YAG) particles. The material is in a fine grained condition characteristic of the microstructure in these alloys following consolidation and working, and contains a high density of sub-grain boundaries and a residual density of free dislocations within the sub-grain interiors. Additionally, the fine YAG particles tended to be aligned along the grain boundaries in the working direction in the plane of the sheet. There was also clear evidence of Zener pinning of dislocations at particles in the microstructure. Figure 3b shows the microstructure of the non-FSW region after the secondary recrystallisation anneal. The elongated sub-grain structures remained and, together with the particles, showed slight evidence of coarsening, while the residual dislocation density within the sub-grains was reduced by recovery processes.

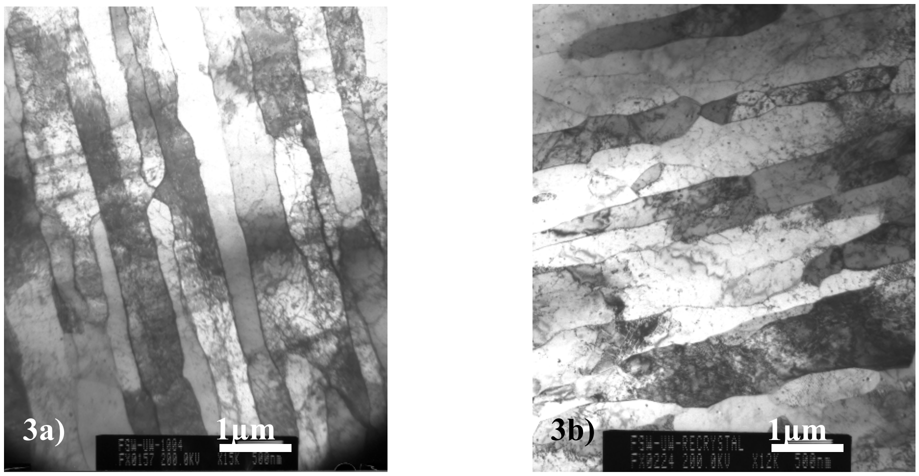

Figure 3: TEM micrographs of the non-FSW region a) before and b) after the SR (1h/1380ºC) anneal

On the other hand, Fig. 4a shows the microstructure of the FSW region before the recrystallisation treatment. A fine, equiaxed grain/sub-grain structure exists with a relatively low dislocation density present within sub-grain interiors. It was noted that the YAG particle array had been re-distributed into a more random arrangement in the matrix, with

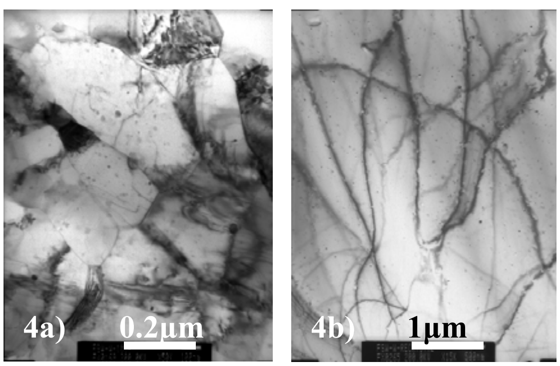

Figure 4: TEM micrographs of the FSW region a) before and b) after the SR (1h/1380ºC) anneal

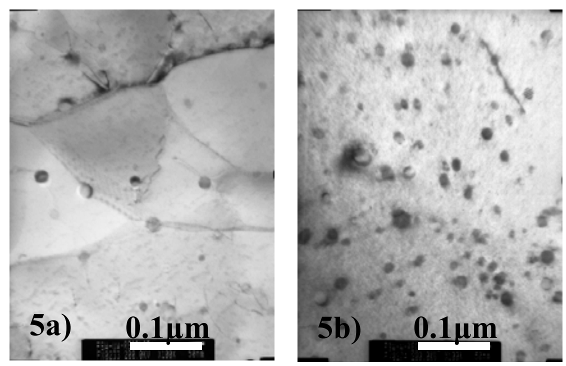

Figure 5: YAG particles in a) non-FSW and b) FSW regions following an SR (1h/1380ºC) anneal

no significant evidence for any remaining alignment of YAG particles or of aligned, coincident grain boundaries. This suggests that the FSW process had had significant effect on the particle distribution in the PM2000 and that the temperature rise accompanying the process had also led to significant re-arrangement of the dislocation/sub-grain structures. The microstructure of the FSW region after recrystallisation is shown in Fig. 4b. Unlike the parent sheet, the FSW region was, essentially, dislocation free, having undergone recrystallisation to a relatively coarse grain size, confirming that FSW imparted sufficient additional stored energy as well as microstructural change to enable nucleation of SR in the weld region. In addition, Figs 5a and 5b show that the size distribution of the YAG particles remains similar in the weld zone to that in the parent PM2000 sheet after SR, with perhaps a slight coarsening in both regions compared to the as-received condition.

EFFECTS OF SURFACE ROUGHNESS ON OXIDATION OF PM2000

The microstructures of three PM2000 sheet samples with three different surface roughness conditions (A5-as received (Ra (mean roughness) of 4.8µm, Rt (maximum roughness) of 45.3µm), G5-coarse ground (Ra of 4.7µm, Rt of 24.9µm) and D5-fine ground (Ra of 0.4µm, Rt of 4.4µm) were investigated after cyclic oxidation in combustion gases for 2000hours at 1100ºC. Figure 5a shows the SEM image of the oxide scale layer in the as-received sample. The oxide scale grew over the irregular geometry of the parent metal surface. Numerous cracks, fractures, voids, and spallation were found. This implies that large stresses are generated by the oxidation process. These are growth stresses, which arise due to the finite size of specimens and the resultant curvature, and thermal stresses, which arise from differential thermal expansion or contraction between the matrix and scale. A columnar grain structure was observed in the oxide scale. Figure 5b shows a micrograph of the oxide scale layer on the coarse ground specimen. Oxide spallation of the scale was clear on both sides of the specimen, particularly on the uneven surface regions, where large stresses could be generated. However, the microstructure of the scale showed fewer cracks, fractures and voids and, in general, the scale grew relatively evenly over the matrix. In contrast, the oxide scale on the fine ground specimen was tightly adherent and had a fine microstructure, as shown in Fig. 5c. An extremely uniform scale without cracks, fractures and voids was found to have grown over the flat surface of the matrix, with a columnar grain structure clearly visible in the scale. Overall, the morphologies of the oxide scales were found to be strongly affected by the parent alloy surface quality, with increased roughness leading to increasing levels of defects (cracks, fracture, and spallation). However, the thickness of the oxide scale was found to be largely independent of surface quality, except where spallation had occurred.

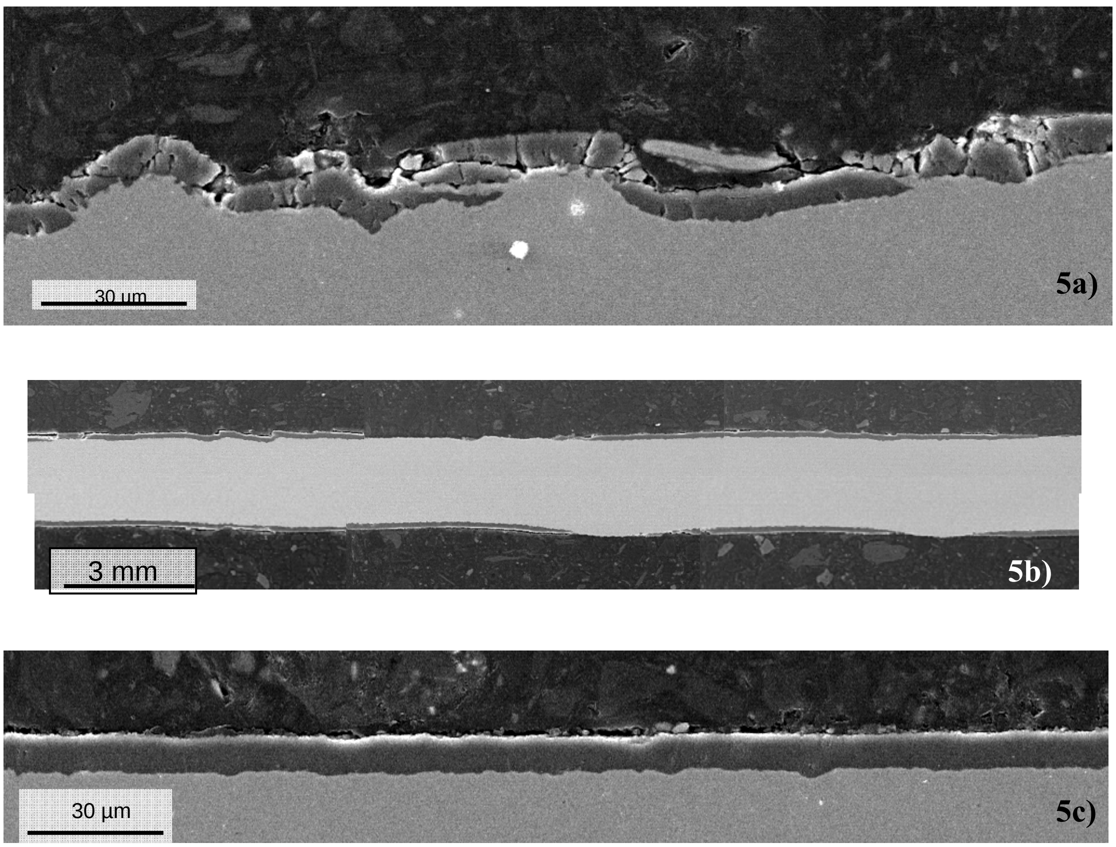

Figure 5: SEM images of oxide scale on a) as-received b) coarse ground and c) fine ground PM2000 alloy sheet subject to cyclic oxidation in combustion gases for 2000hours at 1100ºC.

For comparison, Fig. 6 shows results from Cranfield University[11] of change in mass in annealed specimens of the three different surface finishes. It illustrates that mass change in the as-received specimen exhibits a significant drop after 1000 hours; however, the curves of the coarse and fine ground specimens increase with exposure times. This is likely to have been due to numerous instances of spallation during the early stages of exposure, followed by re-oxidation and subsequent re-spallation, leading to overall loss of mass on the samples with the as-received finish. Analysis of the microstructure shows evidence of re-oxidation, as illustrated, for example, in Figure 5a. On the other hand, there is no evidence to show that re-oxidation took place on the coarse and fine ground specimens. The fine

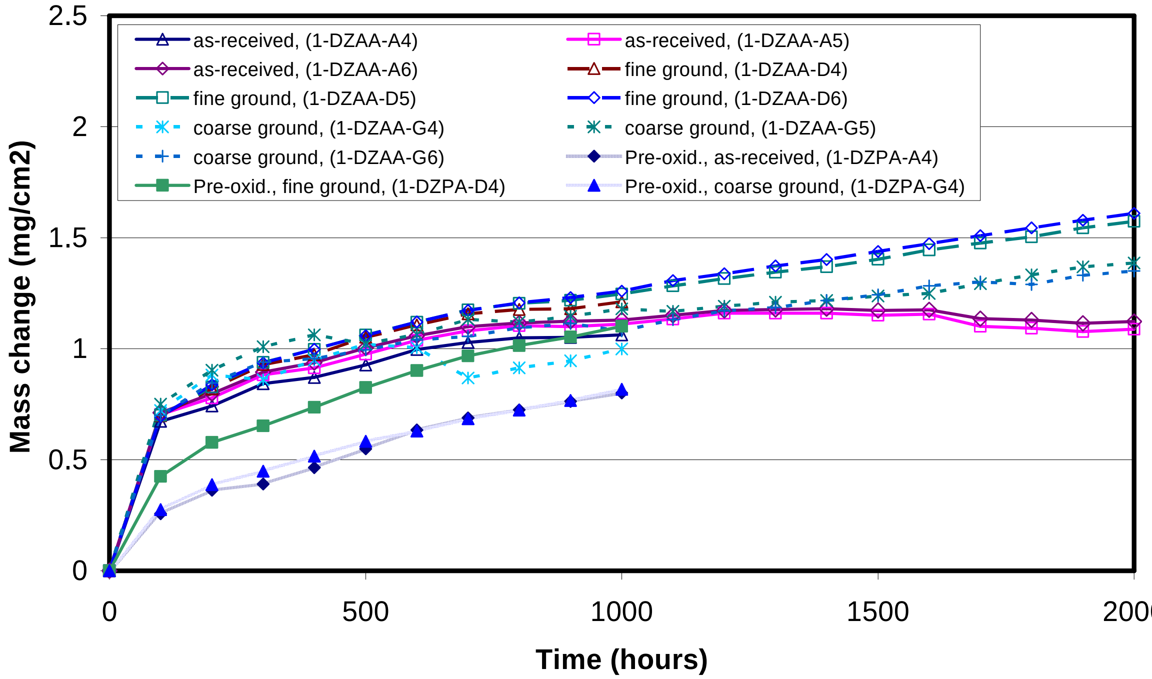

Figure 6: 'Isothermal' exposure of P2000 in combustion gas at 1100°C showing the effects of surface finish and pre-oxidation.[11]

ground specimens exhibited larger change (gain) in net mass than the coarse ground PM2000 samples, due to the occurrence of limited oxide scale spallation on the annealed, course ground sample.

HOT SPUN PM2000 COMBUSTOR CANS

Figure 7a is a transverse section which shows the microstructure near the inner surface of an SR PM2000 can produced from a 10mm thick alloy precursor plate by hot spinning (gas burner preheat). Large grains and numerous small voids were observed in this region (Fig 7b). While no evidence was found for large grains near the outer surface of the hot spun can, a thin layer of smaller recrystallised grains was observed, Fig. 7c. This suggests that the complex pattern of deformation introduced during the hot spinning process leads to significant heterogeneities in recrystallisation behaviour across the thickness of the can wall. This microstructural variability is consistent with the sort of deformation complexities that would be anticipated as a result of shape change introduced using, essentially, a single-sided industrial working process. These results are similar in terms of the level of microstructural change,

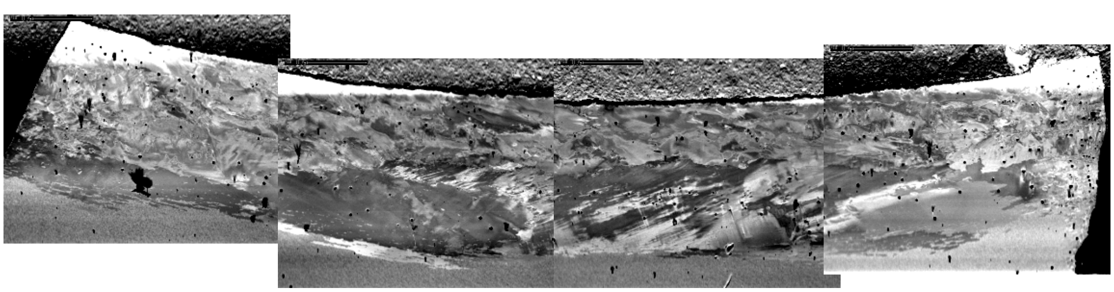

Figure 7a: SEM image showing the microstructure of a transverse section through a PM2000 spun can near the inner wall (10mm thickness).

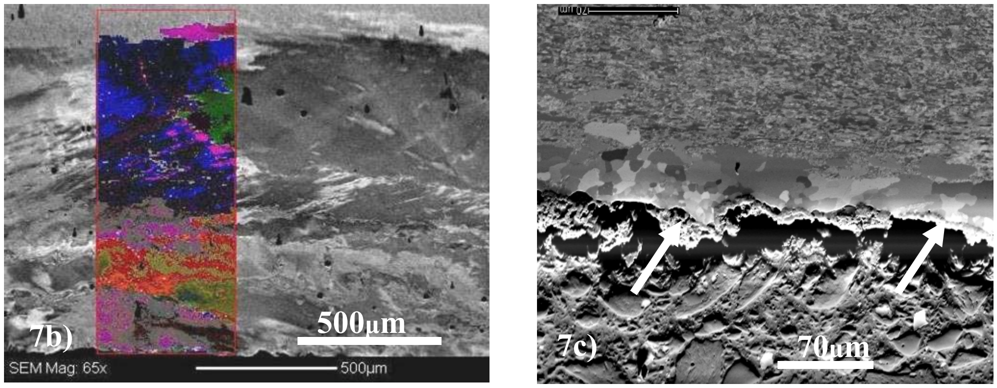

Figure 7 continued: b) EBSD detail from Fig 7a illustrating local grain structures c) fine grained regions adjacent to the outer wall regions (arrowed) of the spun can.

following deformation and recrystallisation, to those seen in PM2000 subject to industrial flow forming, another complex industrial deformation process.[4, 5]

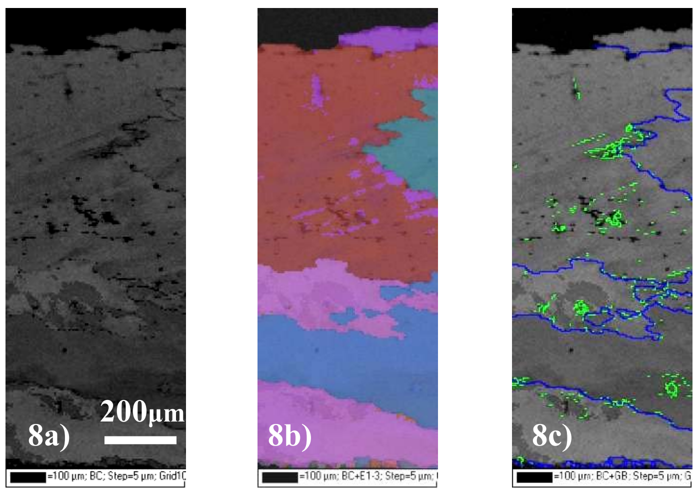

Figure 8: a) SEM image of microstructure near spun can inner wall b) corresponding EBSD image showing grain orientation contrast c) EBSD of same area showing high angle (>10^0, blue), and low angle (<10^0, green) boundaries

EBSD data showing grain orientation and grain boundary misorientation in the region near the spun can inner wall are shown in Fig. 8 and confirm the presence of large recrystallised grains with high angle grain boundaries, together with the presence of a small number of low angle grain boundaries. The results (Fig. 8b) provided no indication of any strong texture effects in this region.

CONCLUSIONS

The microstructures developed in friction stir welds in PM2000 sheet and in can spun from PM2000 plate have been examined and an assessment made of the influence of surface finish on the morphology of oxidation in the same alloy. Conclusions of this work are:

(i) friction stir welding appears to hold promise as a technique for solid state joining of ODS materials such as alloy PM2000 in sheet or plate form;

(ii) there appears to be no loss or coarsening of the distribution of YAG particles in the friction stir weld zone. In fact, the joining process homogenizes the spatial distribution of oxide particles in the weld, removing stringers present in parent sheet and encouraging subsequent formation of equiaxed secondary recrystallised grain structures;

(iii) parent sheet in friction stir weld samples resisted secondary recrystallisation on annealing (1h/1180^{0}C) following joining, suggesting the alloy had been subject to an earlier recovery anneal; however, there was some evidence of growth of recrystallised grains across the weld interface, suggesting that, in the right samples, it might be possible to achieve more extensive recrystallisation through the joint and, therefore, improved final properties;

(iv) Surface finish affects the degree of oxide spallation and, hence, mass change that occurs during high temperature oxidation of PM2000 alloy in combustion gases. Fine ground samples provide the most adherent oxide scale;

(v) Recrystallisation in samples of PM2000 alloy processed from plate into can by metal spinning produces microstructures which vary across the wall of the can. This behaviour is very similar to the sort of recrystallisation observed in flow formed PM2000 and reflects the complex patterns of deformation that arise in these industrial processing methods.

ACKNOWLEDGEMENTS

The authors are grateful for funding from the Advanced Research Materials (ARM) Programme, U.S. Department of Energy, Office of Fossil Energy under contract DE-AC05-96OR22464 managed by U.T.–Battelle, LLC. The authors also acknowledge Siemens Industrial Turbomachinery Ltd., UK and Cranfield University, UK who supplied the friction stir welded PM2000 alloy sheet and spun can, and PM2000 alloy oxidation samples, respectively. The authors also appreciate the access to facilities and support of Professor D.J.Prior and Mr D Atkinson in the SEM-EBSD studies.

REFERENCES

1. J.S. Benjamin, '*Dispersion strengthened superalloys by Mechanical Alloying'*, Metall. Trans., vol. 1, 2943–51, 1970.
2. J. Ritherdon, A. R. Jones, U. Müller, and I. G. Wright, *'Improving the high-temperature performance in ODS alloys for application in advanced power plant,'* 927-938 in Parsons 2003: Engineering Issues in Turbine Machinery, Power Plant and Renewables, Eds. A. Strang, et al., for the Institute of Materials, Minerals, and Mining, 2003.
3. I.G. Wright, B.A. Pint, and Z.P. Lu, *'Overview of ODS alloy development,'* Presented at the 19th Annual Conference on Fossil Energy Materials, Knoxville, Tennessee, May 9th-11th, 2005.
4. F Starr, A R White and B Kazimierzak, *Proc. Conf. 'Materials for Advanced Power Engineering'*, Liege, Eds Coutsouradis et al., Kluwer, Academic Pub.,1393, 1994
5. R. Timmins and E. Arzt *`Diffusion creep in a coarse grained ODS superalloy. under transverse loading'*, Scripta Metall., 22, 1353-1356, 1988.
6. W. J. Quadakkers, *'Growth mechanisms of oxide scales on ODS alloys in the temperature range 1000-1100°C'* Werkstoffe und Korrosion 41, 659-668, 1990
7. W. M. Thomas, D. G. Staines, I. M. Norris, R. Frias, *'Friction Stir Welding – Tools and Developments'*, Doc IIW-1639-03, Welding in the World, Vol. 47, n° 11/12, 10-17, 2003
8. E. Quigley and J. Monaghan**,** ***'****Metal forming: an analysis of spinning processes'*, Journal of Materials Processing Technology, 103(1), 114-119, 2000.
9. J. Ritherdon and A.R. Jones, *'Reduction in Defect Content in ODS Alloys'* Proc. 19th Annual Conf. on Fossil Energy Materials, Knoxville, Tennessee, May 9-11, 2005, Eds. Judkins et al., ORNL, 2005.
10. A.R.Jones , Ö. Selsil and S. E. Burns 'Reduction in Defect Content in ODS Alloys, Proc.20th Annual Conf. on Fossil Energy Materials, June 12-14 2006, Ed. R.R. Judkins, Oak Ridge National Laboratory, Tennessee, USA, 39, 2006
11. N.J.Simms and J.E.Oakey, Cranfield University, UK, private communication.