

Transient liquid phase diffusion bonding and associated recrystallization phenomenon when joining ODS ferritic superalloys

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Oxide dispersion strengthened (ODS) ferritic superalloys attribute their excellent intermediate and high temperature creep resistant properties to the distribution of an inert oxide, Y_2O_3 within highly directional and elongated grains. Careful selection of joining techniques is, therefore, of utmost importance so that the parent metal microstructure is not disrupted and is continuous across the bond line. Transient liquid phase (TLP) bonding is a suitable technique which has been used to join the ferritic superalloys MA957, MA956 and PM2000 using an amorphous foil based on an Fe–B–Si composition. To further minimize disruption to the parent alloy microstructure at the bond line, thin sputter coats based on the Fe–B–Si composition have also been used successfully for TLP bonding. Results have shown a boron-induced secondary recrystallized zone at the bond line in MA957 which acts as a barrier to further grain growth across the bond line on subsequent zone annealing. Differential scanning calorimetry shows that this recrystallization is triggered at $\sim 200^\circ\text{C}$ below the usual recrystallization temperature during heat treatment and occurs only when the metal filler melts and there is a free flux of boron into the base metal. Texture measurements show that the boron-induced recrystallization is of the same nature as the recrystallization produced by heat treatment but possesses a stronger directional $\langle 110 \rangle$ fibre texture. In contrast, grain growth across the bond line could be achieved in TLP bonds produced in MA956. However, a similar heat treatment for PM2000 produced simultaneous but independent secondary recrystallization both at the joint and in the bulk alloy. This difference in behaviour between these two similar alloys is attributed to differences in their thermomechanical processing.

1. Introduction

The use of zirconium-based alloys and austenitic stainless steels for cladding material in fast breeder reactors has remained unchallenged until quite recently. Ferritic stainless steels when exposed to neutron fluxes generally show better resistance to void swelling, high temperature embrittlement and irradiation induced creep compared to the traditionally used cladding materials. However, the relatively poor mechanical strength of the steel at temperatures in excess of 600°C has led to the development of oxide dispersion strengthened (ODS) ferritic alloys [1]. ODS alloys tend to show exceptional creep strength properties and this is attributed to the highly elongated grains (300–600 μm in length) with an aspect ratio typically greater than 10, a stable Y_2O_3 particle dispersion and a strong directional texture.

The application of conventional fusion welding techniques to join these alloys results in a total disruption of this special microstructure and hence a loss in

the high temperature strength properties [2]. The use of transient liquid phase diffusion bonding (TLP), however, offers more promise in maintaining the parent alloy microstructure in the joint region. Briefly, TLP bonding involves using an interlayer which melts at the bonding temperature; with a sufficient hold time at the bonding temperature the interdiffusion of solutes at the liquid filler/parent alloy interface results in isothermal solidification. Since much of the work on joining high-temperature alloys has been based on Ni–Cr superalloys, various nickel-base brazes have been designed to join these materials, but there are at present no commercial iron-base interlayers for use with ferritic superalloys.

Recently work on a novel filler-metal based on the Fe–B–Si system has shown superior microstructural and mechanical properties compared with a commercial nickel-base braze (BNila) when TLP bonding MA957 [3]. The compatibility of the iron foil has been further assessed by TLP bonding

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a commercial ferritic superalloy MA956 and a similar alloy PM2000. A recrystallization phenomenon which is associated with boron diffusion from the liquid filler into the parent metal has also been investigated by means of differential scanning calorimetry and texture measurements.

As an extension of the research, the use of thin sputter coats also based on Fe–B–Si has been studied with the aim of further limiting any disruption to the parent alloy microstructure. Finally, zone annealing and isothermal heat treatments have been used on bonds with the ultimate goal of achieving epitaxial grain growth across the bond line.

2. Experimental procedure

The ferritic ODS alloys MA957 and MA956 and the alloy PM2000 were used in the fine grain condition and hence had not undergone a secondary recrystallization heat treatment. The compositions of the alloys are given in Table I. Both MA956 and PM2000 are similar in composition although PM2000 has a higher Al content. The alloy MA957 is an experimental alloy, the composition of which has been specifically tailored for use as cladding material in fast breeder reactors.

The samples prepared for joining were in the form of discs (diameter 18 mm and thickness 4 mm). The samples bonded for zone annealing were cylinders 20 mm long and 13 mm in diameter. Surface preparation involved grinding to a 1200 grit finish and after degreasing with Inhibisol, the samples were stored in methanol until used for bonding. The iron-base interlayer was used both in the form of a 20 μm thick melt-spun foil and as sputter coats deposited on to the bonding surfaces by r.f. sputtering to give a total coat thickness of 2 μm .

All samples were joined in a vacuum of 4×10^{-2} Pa using pressures of 1.5 and 4 MPa, and bonded at 1190 °C using r.f. induction heating. A rapid heating rate of 9 °C s⁻¹ was used to minimize the premature diffusion of boron out of the interlayer and into the parent alloy. Finally the samples were cooled to room temperature in vacuum on completion of the bonding cycle.

The recrystallization phenomenon induced by the diffusion of boron was investigated using a differential scanning calorimeter (DSC), Netzsch DSC-404/3/413/D. Samples of dimensions 4 × 3 mm were prepared, the metal foil was sandwiched between the two ODS alloy pieces and the “joint assembly” put into platinum crucibles. A DSC trace of temperature difference between the reference and sample versus temperature was recorded. Changes in the microstructure corresponding to the DSC peaks were further confirmed by quenching the sample with argon and then light microscopy used.

Texture measurements were also used to study the nature of recrystallization. A pole figure goniometer with an X-ray source of CoK α and the Bragg angle set at 26° was used to record {110} pole figure from transverse sections taken from three regions: grains recrystallized by high temperature heat treatment, boron-induced recrystallized grains, and grains not

TABLE I Nominal compositions (wt %) of materials used

Materials	Fe	Cr	Al	Ti	Y ₂ O ₃	B	Si
MA957	Balance	14.0	0.06	0.99	0.27	–	–
MA956	Balance	20.0	4.50	0.35	0.52	–	–
PM2000	Balance	20.0	5.50	0.50	0.52	–	–
Fe-foil	78.0	–	–	–	–	13.0	9.0

recrystallized (i.e. in the fine grain condition). Isothermal heat treatments at 1350 °C were used to induce recrystallization in MA956 and PM2000; zone annealing at approximately 1380 °C was used for MA957, in order to promote grain growth across the TLP bonds. Zone annealing was carried out in an atmosphere of argon, and a sample speed of 2.5 mm min⁻¹ was found to be sufficient for homogeneous recrystallization.

3. Results and discussion

3.1. Bonds made using foils and sputter coats

Earlier work on the TLP bonding of MA957 using the iron-base foil, had shown that ferritic joints could be produced with the bond line free from intermetallic precipitates with a hold time of 30 min at the bonding temperature. Shorter bonding times resulted in the formation of borides of iron and chromium along the filler/parent metal interface, and the agglomeration of oxides and Ti-base strengthening precipitates was detected due to parent metal dissolution [4]. However, the most noticeable feature of the bond microstructure was the formation of recrystallized band of grains extending 600 to 2000 μm in length on either side of the joint interface. Similar recrystallization was reported in the TLP bonding of nickel ODS alloys [5] and has been directly associated with the diffusion of boron (present as a melting point depressant in the interlayer). The width of this recrystallized band was seen to increase with increasing hold time at the bonding temperature and unlike previous observations, more than one recrystallization step was recorded (see Fig. 1). In contrast, however, the TLP bonding of both MA956 and PM2000 with the iron-base foil produced ferritic joints which failed to show the boron-induced recrystallized band (see Fig. 2). A continuous hold of 45 min at the bonding temperature failed to remove precipitates formed in the joint region. Laser assisted microprobe mass spectrometric (LAMMS) analysis indicated that these precipitates were borides based on iron and chromium. Unlike the TLP bonds made with MA957, the persistence of these bond line precipitates with increasing hold time indicates that these are stable borides rich in chromium due to the higher chromium content of 20 wt % in MA956 and PM2000. However, these alloys also continued to show a planar interface for up to a 45 min hold. The lack of “melt-back” was attributed to the presence of a surface oxide layer of Al₂O₃ or spinel (Al₂O₃·Cr₂O₃) arising from the high Al and Cr content of these alloys [6]. Work by Nakao and co-workers [7] has shown

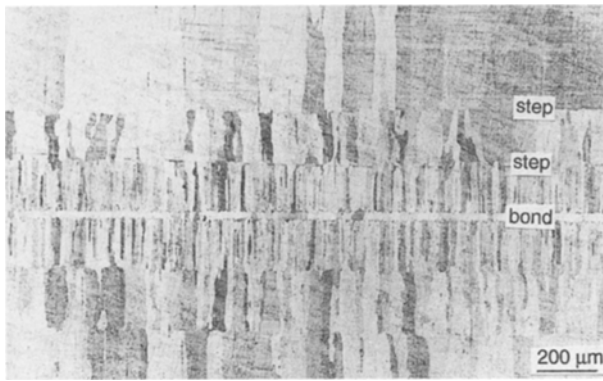


Figure 1 Joint microstructure showing boron-induced recrystallization (“step-like” grain morphology) when bonding MA957 at 1190 °C, 1.5 MPa, 30 min.



Figure 2 Joint microstructures produced on bonding (a) MA956 and (b) PM2000 at 1190 °C, 4 MPa, 30 min using the iron foil (2605 S2).

that the presence of a thin oxide layer can have a significant affect on the kinetics of parent metal dissolution. It is possible that this layer could also act as a barrier and hence restrict the free diffusion of boron from the liquid filler into the parent metal. However, considering the high concentration of boron (13 wt %) in the foil and the small atomic size of boron (0.046 nm), some recrystallization due to boron diffusion would be expected. Instead the absence of recrystallization could be related to the presence of bond line precipitates in MA956 and PM2000. Because the precipitates are borides the total flux of boron will be considerably reduced as much of the boron is “tied up” in these precipitates.

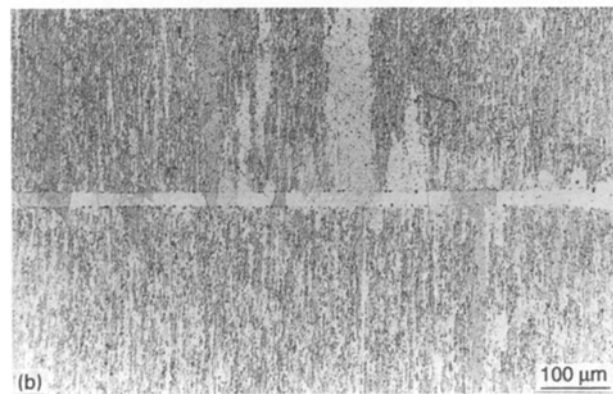
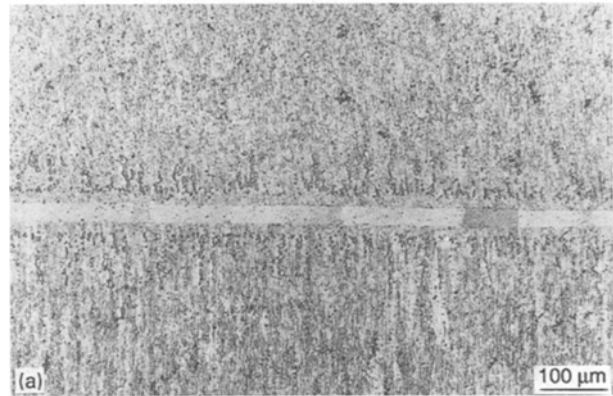


Figure 3 Joint microstructures produced using a 2 μm sputter coat at 1190 °C, 4 MPa, 10 min with (a) MA957 and (b) MA956.

Fabricating TLP bonds with MA957 and MA956 using thin sputter coats as interlayers produced joints similar in microstructure. These joints were free from precipitates, pores and excessive agglomerations, and in general, no secondary recrystallization was observed (Fig. 3). The reduction in parent metal dissolution and hence agglomeration of the precipitate strengthening phase in MA957 was probably due to the lower total volume of boron present in the thin sputter coats compared with that in the foils; the ratio of Fe:B:Si in the sputtered coatings was kept constant and similar to that of the foils. This lower volume of boron could also be responsible for the absence of the recrystallized bands of grains at the joint.

3.2. DSC and texture measurements

DSC analysis performed on MA957 in the fine grain condition shows that the alloy recrystallized in the range 1380–1430 °C, as shown in the trace in Fig. 4. The DSC in Fig. 5 trace taken from a TLP joint, was found to show three exothermic and one endothermic peak. The first exothermic peak (A) is at 1145 °C followed by another (B) at 1160 °C and (C) at 1180 °C. The endothermic peak (D) occurs at about 1220 °C. By quenching the samples using argon gas, changes in microstructure at these temperatures were confirmed. The micrographs in Fig. 6(a) show that the exothermic peaks A–C correspond to the formation of boride precipitates, but that the foil had not completely melted. However, the micrograph in Fig. 6(b) shows the quenched microstructure from 1220 °C (i.e. peak

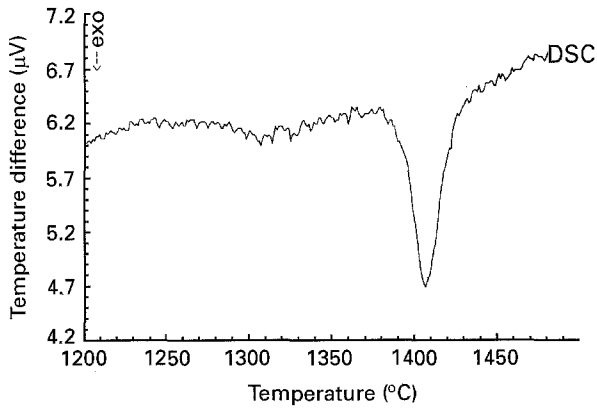


Figure 4 DSC trace showing the recrystallization temperature range (1380 to 1430 °C) for MA957.

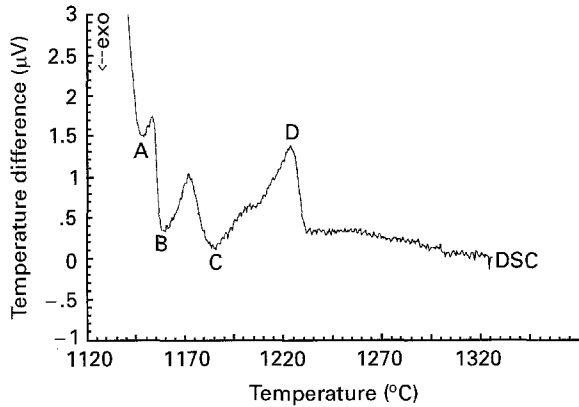


Figure 5 DSC trace obtained from a TLP bond made using the iron-base foil to join MA957.

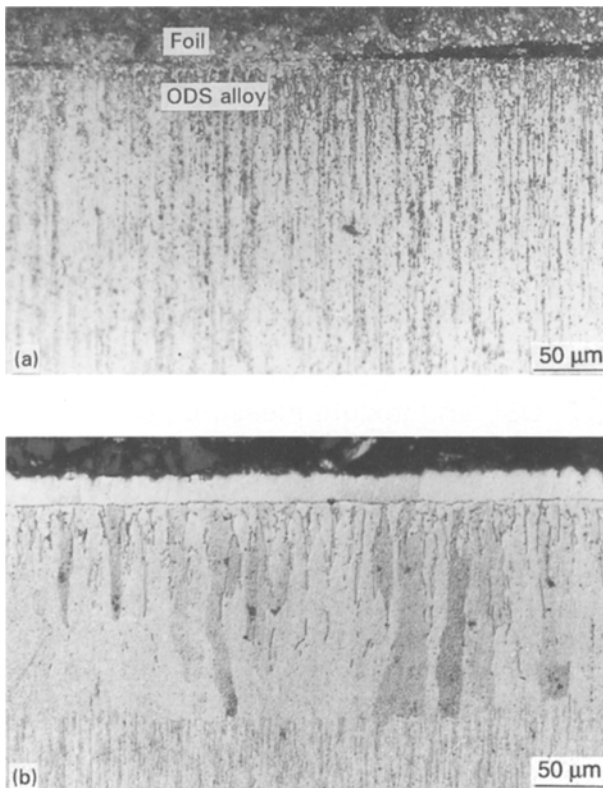


Figure 6 Light micrographs showing the quenched microstructures of MA957 corresponding to (a) points A-C; (b) point D on the DSC trace in Fig. 5.

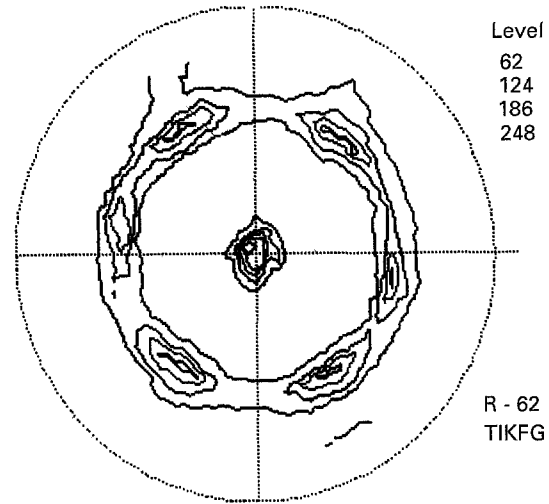


Figure 7 $\{110\}$ pole figure for MA957 in the fine grain state.

D on the DSC trace in Fig. 5). The foil not only had melted, but boron-induced recrystallization was also apparent in the parent metal. This shows that recrystallization is triggered only when the foil melts, and seems to be associated with a free flux of boron out of the liquid filler. However, the melting temperature of the foil appears to have increased from about 1165 °C to about 1220 °C. This is not entirely surprising if we consider that some boron is lost by solid-state diffusion during heating; the loss of boron is greater when a slower heating rate is used as in this case (typically 40 °C min⁻¹).

Texture measurements were undertaken to determine the nature of the boron-induced recrystallized grains and hence to establish if this phenomenon was the same recrystallization observed during high temperature heat treatments. This is significant since experiments have shown that the effect of solute diffusion in some metal systems has been observed to markedly alter the crystal orientation by changing the kinetics in certain orientations e.g. 0.5 at% Mn in single crystal aluminium [8] giving rise to a preferred orientation. In Fig. 7, the stereographic projection for the fine grain condition indicates a strong $\langle 110 \rangle$ fibre texture. Measurements show that the grain orientations consist of three major components; $\{110\}\langle 001 \rangle$, $\{110\}\langle 110 \rangle$, and $\{001\}\langle 111 \rangle$. This mixture of components is not surprising since the alloy has undergone hot extrusion during the thermomechanical processing stage in manufacture and it is generally known that deformation in a b.c.c. metal has a tendency to lead to $\langle 110 \rangle$ fibre texture and sheet rolling textures $\{112\}\langle 110 \rangle$ to $\{100\}\langle 011 \rangle$ [9]. The heat-treated recrystallized bulk sample, however, shows a much weaker $\langle 110 \rangle$ fibre texture (see Fig. 8). This is surprising as recrystallization in other ferritic alloys (MA956) tends to produce a much stronger texture [10]. However, the grain orientations show two dominant components, $\{110\}\langle 110 \rangle$ and $\{110\}\langle 111 \rangle$ which were also present in the fine grain condition. The stereographic projection obtained from the boron-induced recrystallized grains is shown in Fig. 9. In this case, there is a strong $\langle 110 \rangle$ fibre

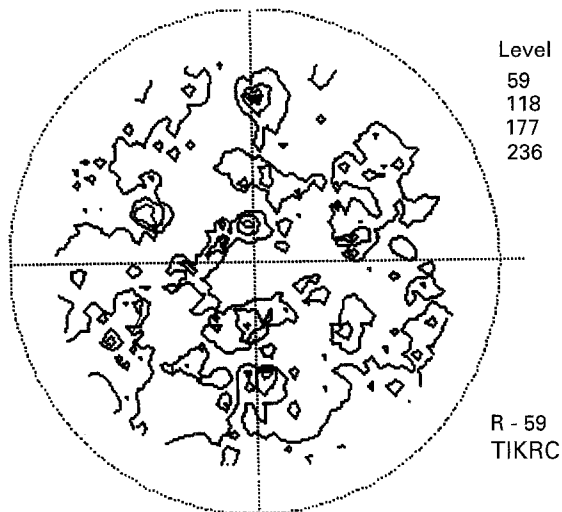


Figure 8 $\{110\}$ pole figure for MA957 in the recrystallized state after heat treatment.

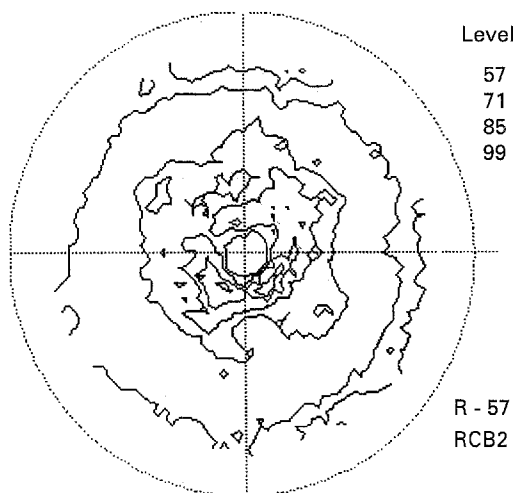


Figure 9 $\{110\}$ pole figure for boron-induced recrystallized grains in MA957.

texture and the crystal planes and orientations which dominate are again $\{110\}\langle 110 \rangle$ and $\{110\}\langle 111 \rangle$. This, therefore, suggests that boron diffusion triggers the same basic recrystallization phenomenon as occurs during higher temperature heat treatment, and that boron diffusion does not alter the crystal orientations during the growth selection process. The presence of boron noticeably enhances the $\langle 110 \rangle$ fibre texture compared to that produced after high temperature heat treatment. This implies that the presence of boron does give some advantages over conventional heat treatments as a means of inducing recrystallization in ODS alloys; not only can recrystallization be induced at much lower temperatures but a stronger directional texture is possible.

3.3. Recrystallizing heat treatments

3.3.1. Zone annealing bonds made with MA957

The main purpose of joining the ODS alloys in their fine grain condition was to subsequently use recrystallizing heat treatments to encourage grain growth

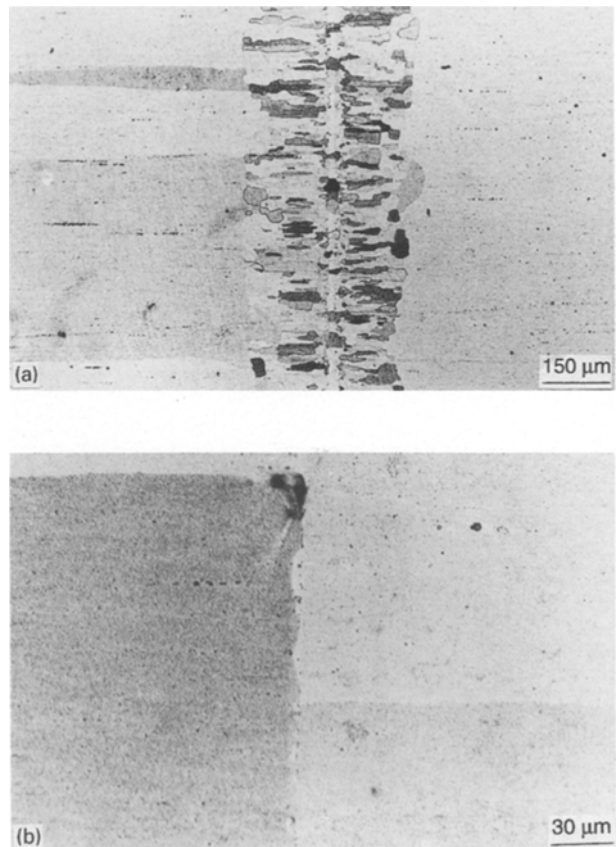


Figure 10 Micrographs showing the effect of zone annealing TLP bonds made using MA957 with (a) iron-base foil and (b) sputter coat.

across the bond line, with the aim of removing the planar interface. Isothermal heat treatments failed to recrystallize the ODS alloy MA957 within an acceptable length of time and therefore, zone annealing with a moving r.f. induction coil was used as a method of inducing grain growth across the bond line.

Zone annealing failed to grow grains across TLP bonds made using MA957, either with foils or sputter coated interlayers (see Fig. 10). However, the reasons for failure were different for the two types of interlayers used. The failure in the case of foils was due to the formation, during bonding, of the boron-induced recrystallized band of grains on either side of the bond. Although recrystallized grains were produced by zone annealing along the length of the sample the growing front was unable to “engulf” the prematurely recrystallized grains that had already formed at the bond interface due to the diffusion of boron. The failure to absorb these grains into the growing front was probably due to the boron-induced grains having lost the driving force necessary for further grain boundary migration. When sputter coat interlayers were used, the absence of the recrystallized band of grains allowed complete grain growth up to the filler/parent alloy interface on the zone annealing side. However, independent recrystallization seems to have been triggered at the opposite bond interface as the hot zone approached the joint region. Therefore, although grain growth was seen on both sides of the bond region, secondary recrystallized grains failed to cross the bond interfaces in MA957.

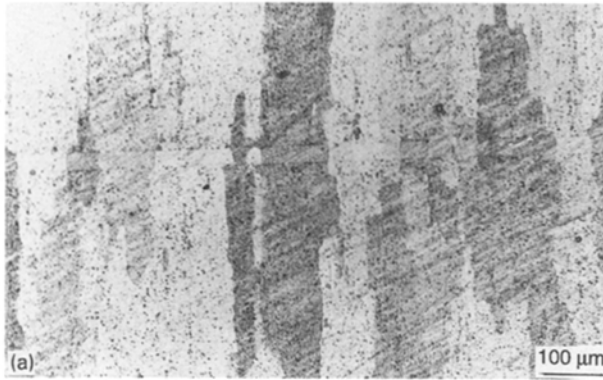


Figure 11 Micrographs showing the effect of isothermal heat treatment (at 1350 °C for 30 min) on TLP bonds made using MA956 with (a) foil interlayer and (b) sputter coat.

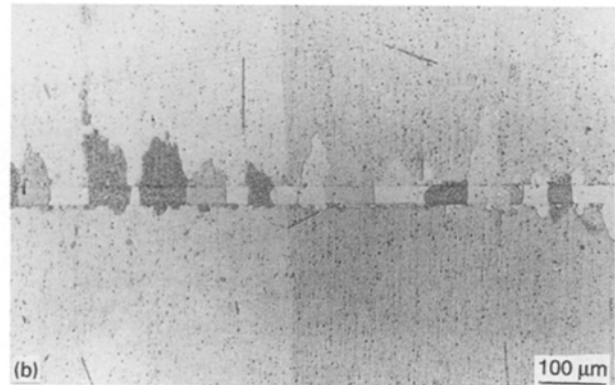
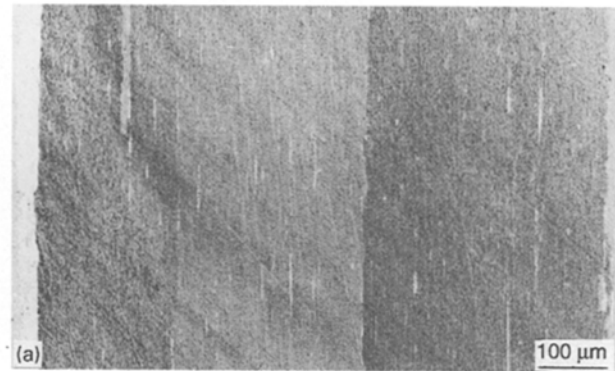


Figure 12 Micrographs showing the effect of isothermal heat treatment (at 1350 °C for 30 min) on (a) MA956-bulk alloy and (b) PM2000-TLP bond.

3.3.2. Isothermal heat treatments

Recrystallizing isothermal heat treatments carried out with TLP bonds made with MA956 were successful with both foils and sputter coats (see Fig. 11). Recrystallization in MA956 resulted in complete, uninterrupted grain growth across the bond interface. Examination of the bonds showed that the widths of the recrystallized grains in the parent metal were similar to those of the grains within the braze microstructure, and also that the grain boundaries of the recrystallized parent metal microstructure were coincident with those of the braze microstructure. When unbonded MA956 was heat treated under identical conditions, recrystallized grains with widths three times greater than those seen for grains in the bonded samples were produced (see Fig. 12(a)). These observations imply that recrystallization in the bonded samples must have nucleated at the filler/parent metal interface, (thus determining the parent metal grain widths), and then continued outwards in both directions through the bulk of the alloy.

Before heat treatment, the TLP bonds made with PM2000 using foils had similar joint microstructures to those of MA956. However, on isothermal heat treatment of bonds made with foils, two independent regions of recrystallization were observed (Fig. 12(b)). Small grains seem to have grown right across the bond line yet they remain confined to the joint region and do not extend substantially into the parent metal. Initially this recrystallization was considered to be similar to the boron-induced recrystallization

observed in MA957 (during bonding). However, a characteristic feature of boron-induced recrystallization is that the grain growth occurs quite evenly on both sides of the joint and grain growth is initiated at the bond line but does not cross it. In PM2000 the recrystallized grains appear to grow into the parent metal more on one side of the bond than on the other side. In addition, these grains appear to have crossed the bond line. Accordingly, it would seem that recrystallization in PM2000 has been “triggered” at the filler/parent metal interface, just as in MA956 but grain growth has been inhibited from spreading throughout the alloy. This could only be possible if there was simultaneous, competing grain growth elsewhere in the alloy. In fact, observations indicated in Fig. 12(b), that recrystallization had occurred in the bulk of the alloy producing grains several orders of magnitude larger than those observed at the bond. These large grains failed to cross the bond and stopped on either side of the joint interfaces (meeting up with the smaller grains formed at the bond line). The initiation site for this second recrystallization may have been at the specimen surface.

These apparent differences in recrystallization behaviour on heat treatment between essentially similar ferritic alloys can be attributed only to differences in prior thermomechanical processing. Although precise information on the manufacturing process could not be obtained (because of confidentiality) work by Baloch [11] using zone annealing and isothermal heat treatments to investigate recrystallization in

ODS alloys, reported significant differences in recrystallization behaviour between MA956 and MA957. These differences were attributed not only to deformation applied to the alloys (and thus to stored energy) but also to the degree of oxide particle alignment in the rolling direction. Greater particle alignment was noticed in MA956 than in MA957 and this was found to strongly influence the shape of the recrystallized grains (highly directional columnar grains were produced in MA956 compared to the more equiaxed grains developed in MA957).

It appears, therefore, that the observed differences during the TLP bonding of MA957, MA956 and PM2000 is not attributed to changes during the bonding process but to the inherent differences in these alloys due to the mechanical alloying process.

4. Conclusions

An iron-base foil containing the melting point depressants boron and silicon has been used successfully as a TLP interlayer for joining the ferritic superalloys MA956, PM2000 and MA957. The diffusion of boron from the interlayer into the parent metal results in secondary recrystallization on either side of the joint interface when bonding MA957. DSC analysis shows that recrystallization at the joint is triggered when the interlayer melts and there is a free flux of boron from the liquid filler into the parent metal. This boron-induced grain growth occurs at a temperature, approximately 200 °C below the recrystallization temperature. Texture measurements show that the boron-induced grains are essentially of the same orientation as those observed after high temperature recrystallization but tend to possess a stronger $\langle 110 \rangle$ fibre texture. These recrystallized grains act as a barrier to grain growth across the bond line on subsequent zone annealing of TLP bonds made using MA957.

The absence of premature recrystallization due to boron at the joint interface when bonding MA956 allows grain growth and parent metal microstructure to develop across the joint region after isothermal heat treatments at the recrystallization temperature. Similar heat treatments, however, failed to produce undisrupted grain growth across bonds made using PM2000, and instead resulted in simultaneous recrystallization both at the bond interface and in the parent metal. The difference in recrystallization behaviour in nominally similar ferritic alloys were attributed to

differences introduced during the mechanical alloying stage of manufacture.

Preliminary work shows that sputter coats based on Fe-B-Si can be deposited using r.f. sputtering techniques. Thin sputter coats can be used as TLP interlayers with the advantage of reducing the boron-induced recrystallization at the joint and reducing excessive parent metal dissolution, particularly when bonding the alloy MA957.

Acknowledgements

The authors wish to thank Dr R. E. Somekh for providing the sputter coated samples and Mr R. Sweeney at the Department of Materials, Imperial College for texture measurements. Financial support from the Engineering Research Council and AEA Technology (Risley) is also gratefully acknowledged.

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Received 21 March

and accepted 11 April 1995