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Transient liquid-phase bonding of ferritic oxide dispersion strengthened superalloy MA957 using a conventional nickel braze and a novel iron-base foil

T. I. KHAN, E. R. WALLACH
Department of Material Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ UK

It has been shown that an iron foil based on the Fe–B–Si system is a suitable material for use as a high-temperature interlayer for transient liquid-phase (TLP) bonding of ferritic oxide dispersion strengthened alloys. TLP bonding produced ferritic joints, free from intermetallic precipitates and identical in composition to that of the parent metal. In contrast, however, TLP bonding using the nickel-base foil, BNi1a, resulted in an austenitic bond region stabilized by the high nickel concentration. Furthermore, the retention of the melting point depressants, particularly silicon, at the centre of the joints resulted in the bond solidifying with the formation of silicide–boride precipitates both at the bond centre and at the braze/parent metal interface. High-temperature heat treatments failed to remove the γ-Fe phase and the precipitates, and their presence detrimentally affected the mechanical properties of the joint. The formation of intermetallic precipitates at the braze centre has been attributed to the initial high concentration of chromium present in the BNi1a brazing foil. Preliminary mechanical tests showed that bond strengths of joints made using the iron-base foil were superior to those obtained using the commercial nickel braze. When the iron-base foil was used, bond strengths both at room temperature and at the service temperature (700 °C) were near parent metal strengths. However, at room temperature, failure was observed to occur away from the bond interface, whilst at elevated temperatures, joints failed along the bond interface; this was attributed to the effects of melt-back phenomenon characteristic in TLP bonding.

1. Introduction

Transient liquid-phase (TLP) joining is a process which involves melting an insert filler metal between the two surfaces to be joined; the joint is then held at the bonding temperature for a sufficient length of time to allow the melting point depressants to diffuse out of the liquid insert and into the parent alloy, resulting in an isothermally solidified bond. The solidified bond should consist of a primary solid solution with a composition similar to that of the parent metal and free from precipitates.

One of the most important considerations for producing a "good" joint will be its final composition which will depend on the interlayer used. Much of the work on TLP joining of oxide dispersion strengthened (ODS) alloys has been primarily concerned with the nickel-base ODS alloys and used the commercial high-temperature brazing materials which were designed to suit nickel-base superalloys. More recently, there has been increased interest in ferritic ODS superalloys because of their excellent oxidation and corrosion resistance, but there are no corresponding high-temperature ferrous brazing alloys. An attempt has been made to develop an iron-base brazing foil [1] using mainly manganese as a melting-point depressant. The intention was to reduce the level of boron in the brazement hence avoiding the formation of precipitates such as chromium borides; however, the use of this foil to join the ferritic ODS alloy MA956 [2] failed to produce joints free of these embrittling precipitates.

Certain brazing foils are produced by a process of melt spinning and one advantage of this process is that extremely thin foils (25–50 μm) are produced. The commonly used melting-point depressants boron, silicon and phosphorus are an essential part of the melt-spinning process and hence are also an advantage in TLP bonding because they can rapidly diffuse out of the liquid filler during bonding. The loss of melting point depressants from the filler raises the melting temperature of the subsequent joint to a level similar to that of the parent metal. Currently, soft ferrous magnets are being produced in the form of foils 20 μm thick by the melt-spinning process, for applications in transformer cores. As the composition of these foils is also based mainly on iron, boron and silicon it seemed that they might be suitable for use as an insert materials for joining ferritic ODS alloys. Joints were also made with two commercial nickel-base brazing alloys as a comparison.

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TABLE I Composition (wt %) of materials used

Material	Ni	Fe	Cr	Ti	Mo	Y_2O_3	B	Si
BNi1a	Bal	–	14.0	–	–	–	3.2	4.5
BNi3	Bal	–	–	–	–		3.2	4.5
Fe foil	–	78.0	–	–	–	–	13.0	9.0
MA957	–	Bal	14.0	0.99	0.30	0.27	–	–

The aim of this study was to find or develop a foil based on the Fe–B–Si system which should be a suitable interlayer for TLP bonding the ferritic ODS alloy MA957. A series of bonding conditions and heat treatments were used to develop the optimum joint microstructure. The joints produced have been characterized by metallographic examination and tensile tests at room temperature and at 700 °C, the service temperature of this alloy.

2. Experimental procedure

The ODS ferritic alloy, MA957 was supplied by the INCO Alloys Ltd (Hereford, UK) in the form of a solid rod of diameter 25 mm and its composition in weight per cent is shown in Table I. The alloy was produced by the mechanical alloying technique, and was used for diffusion bonding in the as-received, fine grain state (typical grain size of 2 μm). The commercial Metglass nickel-base brazing foils BNi1a (25 μm thick) and BNi3 (50 μm), and the 20 μm thick iron-base foil (designated 2605S-2 and produced for magnetic applications) were supplied by Neomet Ltd. (Stockport, UK). The respective compositions in weight per cent for the foils are given in Table I.

The samples prepared for joining were in the form of discs of diameter 18.0 mm and a thickness of 4.0 mm. Surface preparation involved grinding to a 1200 grit finish (giving a root mean-square roughness of 2.0 μm) using water. Finally, samples were degreased in Inhibisol and stored in methanol until used for bonding. All the samples were joined in a vacuum of 4×10^{-4} mbar using radio frequency induction heating.

High-temperature differential scanning calorimetry (DSC) was used to establish the melting temperature of the iron-base foil. The DSC trace (Fig. 1) shows that the foil melts in the range 1150–1165 °C and, therefore, an optimum bonding temperature of 1190 °C was selected with a pressure of 4 MPa. The TLP bonds produced using the nickel-base foils were made at a temperature of 1100 °C and a pressure of 1.5 MPa. A fast heating rate of approximately $9\,^{\circ}\mathrm{C\,s^{-1}}$, to the bonding temperature was employed to prevent the premature diffusion of boron into the parent metal. All bonds were cooled to room temperature in vacuum after completion of the bonding cycle.

The quality of the joints formed was assessed initially by metallurgical examination. The bonds were inspected using both light and scanning electron microscopy for the formation of precipitates, phases, the extent of any porosity and compositional and microstructural homogeneity with the parent metal. Changes in the composition of the joint with hold time, and identification of precipitates and phases, was carried out using both energy dispersive spectroscopy (EDS) and laser microprobe mass spectrometry (LAMMS). One of the main advantages for using LAMMS as an analytical technique was its ability to detect qualitatively light elements, in particular boron, carbon and oxygen, which cannot be detected with EDS equipment available. The mechanical properties of the joints were measured at room temperature and at 700 °C using a strain rate of 1 mm min^{-1}.

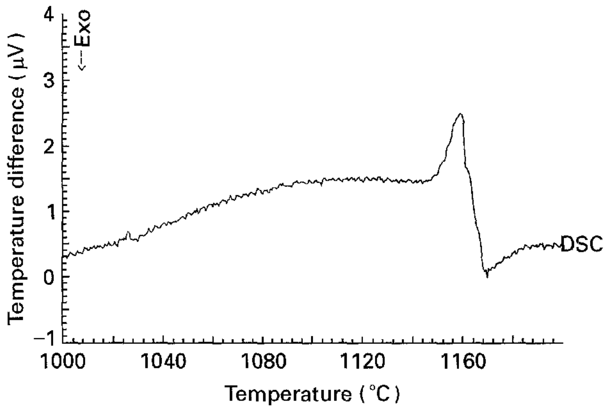


Figure 1 DSC trace showing the melting range for the iron-base foil (Fe–B–Si).

3. Results and discussion

3.1. TLP bonding using the nickel-base braze (BNi1a)

In metallurgical terms, a "good" joint can be classified as one free from precipitates, free from porosity and with a composition and microstructure as similar as possible to that of the parent alloy. The bond microstructures produced using the nickel-base brazing foil (BNi1a) are shown in Fig. 2.

The bond microstructures showed little change with hold time, but the thickness of the bond region was seen to increase noticeably. Initially, this increase in thickness was considered to be parent metal dissolution which is an equilibrating process in TLP bonding. However, EDS composition profiles (Fig. 3) taken across the joints, indicated that after a short hold of 4 min, the braze centre was rich in nickel (40–45 wt %) and only at a distance of about 25 μm from the braze/ODS interface (within the parent metal) did the concentration of nickel begin to drop significantly and the concentration of iron begin to increase. Increasing the hold time to 60 min further homogenized the composition of the joint, especially with respect to nickel, iron and silicon. The nickel profile spread out with increasing hold time and this corresponded to the

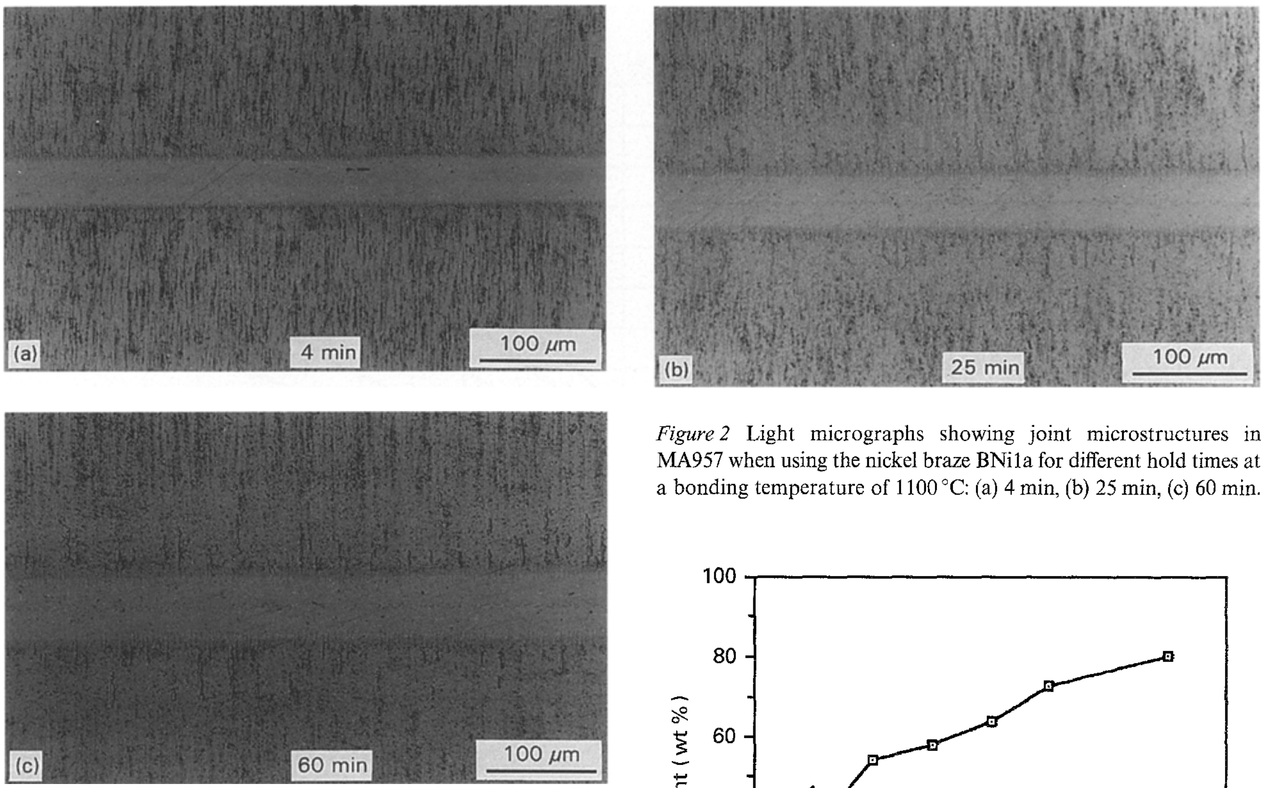


Figure 2 Light micrographs showing joint microstructures in MA957 when using the nickel braze BNi1a for different hold times at a bonding temperature of 1100 °C: (a) 4 min, (b) 25 min, (c) 60 min.

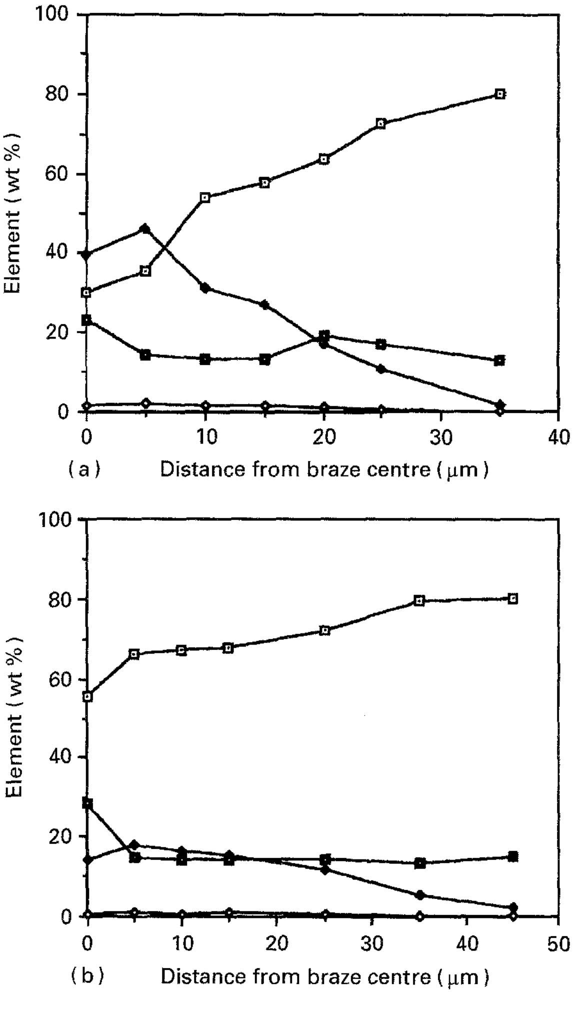


Figure 3 EDS composition profiles taken across bonds in MA957 made using the nickel braze BNi1a: (a) 4 min hold, (b) 60 min hold, (□) Fe, (◆) Ni, (■) Cr, (◇) Si.

increase in thickness of the joint. The EDS analysis indicated 15–19 wt % nickel remained in the joint region and reference to the Schaeffler diagram in Fig. 4, suggests that enough nickel was present at the joint to stabilize the γ-Fe phase.

The photomicrographs indicate clearly the formation of precipitates both at the braze/parent metal interface and in the parent metal near the bond region where the precipitates appear to have segregated along grain boundaries. Precipitates also formed at the braze centre and were seen more clearly using SEM as shown in Fig. 5. LAMMS spectra taken from precipitates at the centre (Fig. 6a), indicate the formation of silicides of iron, nickel and chromium whilst spectra obtained from the braze/parent metal interface show the precipitates to be both borides and silicides of iron and chromium, see Fig. 6b. The spectra in Fig. 6b also have peaks for carbon and oxygen and these could either be from the agglomeration of TiC/TiO_2 particles at the interface or due to the formation of chromium carbides (e.g. $Cr_{23}C_6$) or from surface oxides. The formation of precipitates based on silicon and boron would be expected at the centre of the braze on cooling after a short hold time at the bonding temperature. However, for longer hold times (e.g. 60 min), the melting point depressants should have diffused away and a precipitate-free region should have been produced on cooling [3]. Instead, increasing the hold time at the bonding temperature not only failed to remove the braze centre-line precipitates, but the chromium concentration associated with these precipitates was found to increase, see Fig. 7. This suggests that the precipitates observed may be forming at the bonding temperature and not during the cooling stage. The lowest eutectic temperatures for iron and chromium silicides (1190 and 1335 °C) obtained from the respective phase diagrams in Fig. 8, are higher than the bonding temperature (1100 °C); accordingly, silicide precipitates would be expected to form at the bonding temperature. If this consideration is true, then an increase in precipitation (shown by the increase in chromium concentration associated with these precipitates) with hold time would be seen, as appears to be the case. This would, therefore, also explain the persistence of these silicides at the braze centre with hold time.

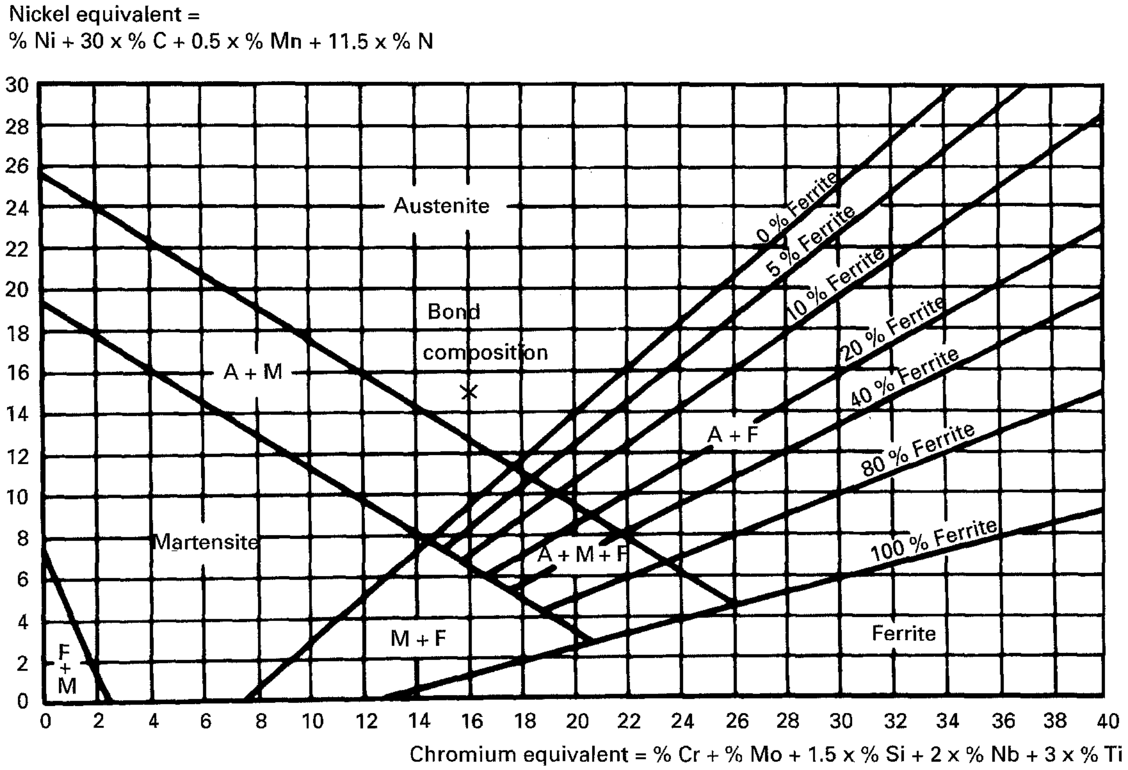


Figure 4 The γ-iron phase is stabilized at the braze centre as shown by the Schaeffler diagram [5].

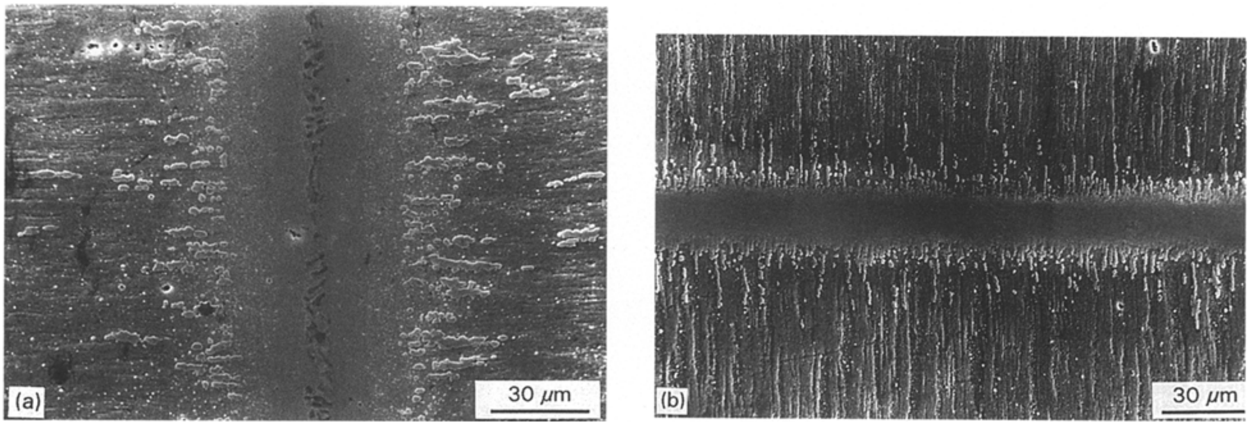


Figure 5 Scanning electron micrographs showing the formation of precipitates at bonds in MA957 when using (a) braze BNi1a, (b) braze BNi3 (chromium absent)

As a comparison with the BNi1a foil, a TLP bond was also made using BNi3 (contains no chromium but has the same boron and silicon content as the BNi1a foil). The microstructure was found to be similar to that in bonds made using BNi1a, with the formation of γ-Fe phase stabilized in the bond region (Fig. 5b). However, although similar boride and silicide precipitates were again observed at the braze/parent metal interface, no precipitates were observed at the centre of the joint. It seems, therefore, that the retention of silicon (to form silicides) within the bond made using BNi1a is strongly influenced by the initial high concentration of chromium (14 wt %) present in the BNi1a foil.

Heat treatments were carried out to further homogenize the bond with respect to the high concentration of nickel in the joint region and also to remove the precipitates. A temperature of 1300 °C was used for a 2 h hold and the effect of this treatment is shown in Fig. 9a. From the EDS profile (Fig. 9b) it is clear that the bond region is more homogeneous and the level of nickel has been considerably reduced. The large precipitates (probably borides) at the braze/parent metal interface seem to have gone into solution but smaller and more irregular precipitates (likely to be the stable chromium silicides and borides) are still visible on either side of the joint region. An additional effect of the heat treatment has been to increase the agglomeration of the strengthening precipitate dispersion and to increase the degree of porosity at the bond region. The solution of the boride precipitates at the high heat-treatment temperature would in the short term, increase the concentration of boron in regions adjacent to the bond interface. As a result, localized melting would increase parent metal dissolution leading to further agglomeration of the precipitate

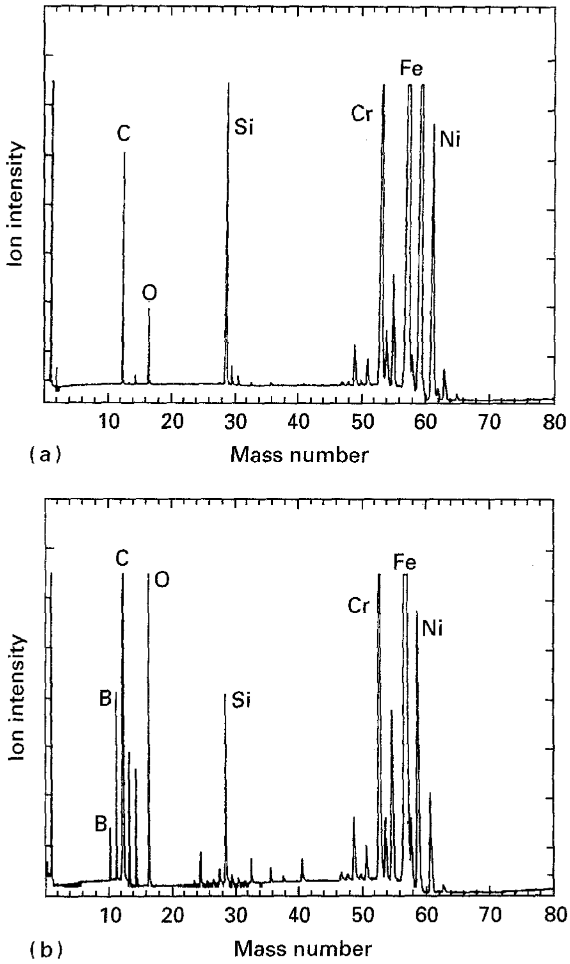


Figure 6 LAMMS spectra taken from a joint in MA957 made using the nickel braze (BNi1a) from: (a) precipitates at the braze centre; (b) precipitates at the braze/parent metal interface.

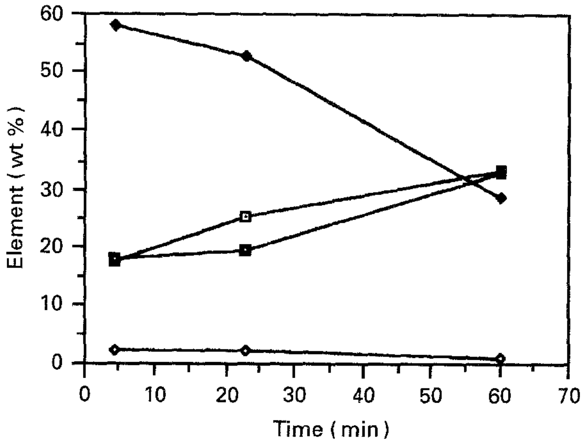


Figure 7 EDS analysis of the braze centre in MA957 showing the changes in composition with hold time when using the nickel braze, BNi1a. (□) Fe, (◆) Ni, (■) Cr, (◇) Si.

dispersion (see Fig. 9a). The pores that are seen are large and round suggesting gaseous porosity due to argon released from the melted ODS alloy (argon is usually used during the mechanical alloying process and becomes occluded in the metal).

3.2. TLP bonding using the iron-base foil (2605S-2)

The microstructures of joints produced using the iron-based foil for different hold times are shown in Fig. 10. With a hold time of 2 min, similar precipitate formation was seen on either side of the joint region as had been observed in bonds made using the nickel brazing foil, BNi1a. As the hold time at the bonding temperature was increased from 2 min to 30 min the formation of boride precipitates in the vicinity of the joint decreased and none were observed for the 30 min hold. Although the iron-base foil contained more silicon and boron than the nickel-base foil, a sufficient hold time allowed the melting-point depressants to diffuse out of the filler so that precipitate-free joint was produced. EDS composition profiles taken across the bonds (see Fig. 11) show a ferritic joint, which after 30 min at the bonding temperature resulted in a composition virtually the same as that of the parent metal. LAMMS spectra taken from the precipitates in the parent metal near the joint region show peaks for iron, chromium, and boron, see Fig. 12a. These precipitates are borides of iron and chromium probably of the form $(Fe,Cr)_2B$ [4]. Observation of the braze/parent metal interface also shows an agglomeration of the precipitate strengthening phase (TiC/TiO_2) present in the parent metal. This is more noticeable in the initial stages of bonding as clearly demonstrated by Fig. 10a, for a 2 min hold. The EDS profile in Fig. 11a shows high titanium concentration at approximately 10 μm from the centre of the braze which is at the original foil/parent alloy interface (initial foil thickness was 20 μm). LAMMS analyses further confirmed that these agglomerations corresponded to the precipitate strengthening phase, as peaks for titanium, carbon and oxygen were recorded (Fig. 12b). In the later stages of bonding, agglomeration was seen to occur quite noticeably along grain boundaries, to which boron segregates on diffusion into the parent alloy. Melt-back is essentially an equilibrating process which occurs in the liquid filler at the bonding temperature. As the liquid filler is not in equilibrium and supersaturated with respect to boron and silicon, extensive inter-diffusion at the liquid filler/parent metal interface results in parent metal dissolution. This process continues until the joint region is fully equilibrated with the parent metal. However, the erosion of the parent metal immediately in contact with the liquid filler is a concommitant side effect.

3.3. Mechanical testing

Initial metallurgical examination showed that the TLP bonds made using the iron-base foil produced acceptable joint microstructures compared with bonds produced using the nickel braze, BNi1a. However, it was necessary to assess the quality of these bonds by tensile testing both at room temperature (RT) and at elevated temperature (700 °C). Preliminary tensile tests were carried out to compare typical bond strengths and to investigate the effect on joint properties of microstructural features developed during the bonding process.

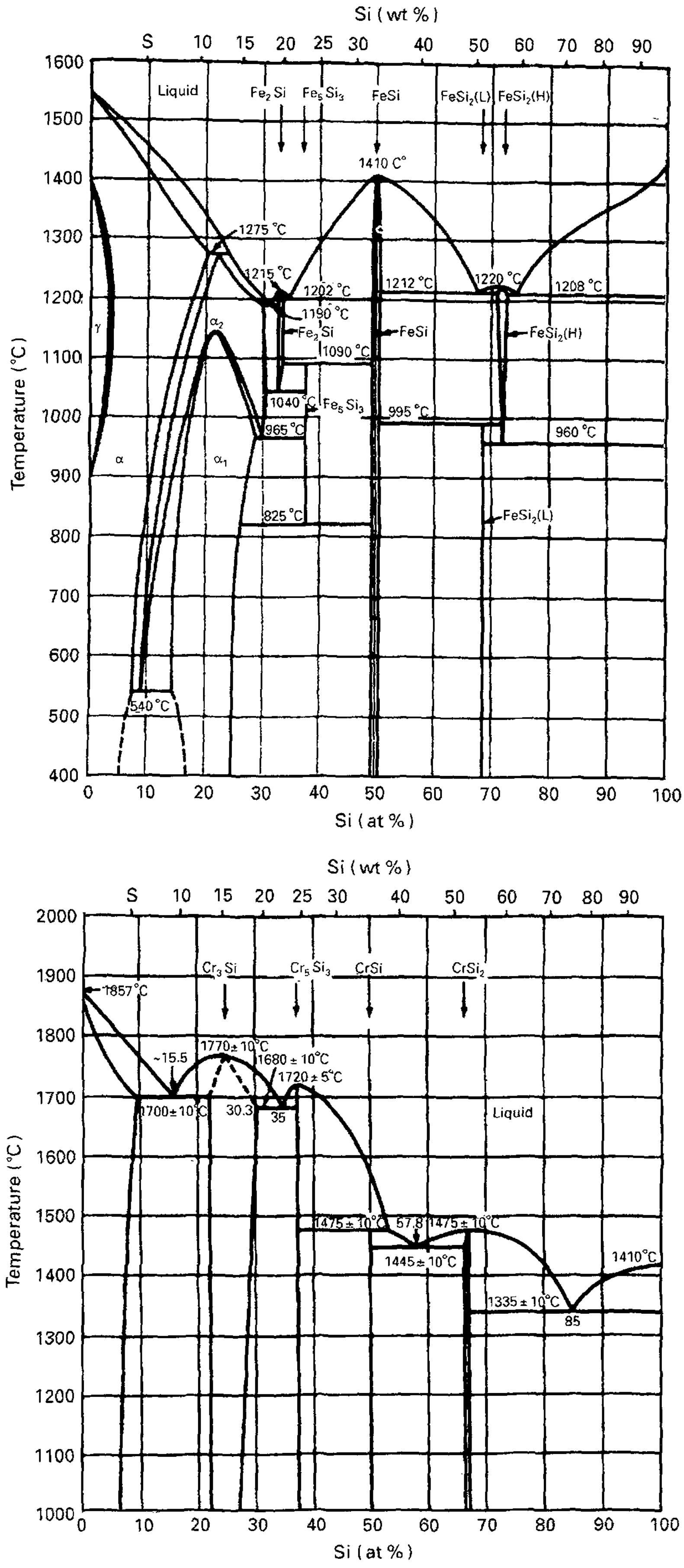


Figure 8 Binary phase diagrams for: (a) iron silicides, and (b) chromium silicides [6].

3.3.1. Room-temperature tensile tests

Joints made using the nickel-base foil, BNi1a, at RT gave a tensile strength (TS) of 662 MPa, which is 54% of the parent metal strength (see Fig. 13). The bond failed at the braze/parent metal interface and, as the fractograph in Fig. 14a shows, the failure mode was by cleavage resulting in flat fracture surfaces. The location of brittle failure at the bond interface appeared to

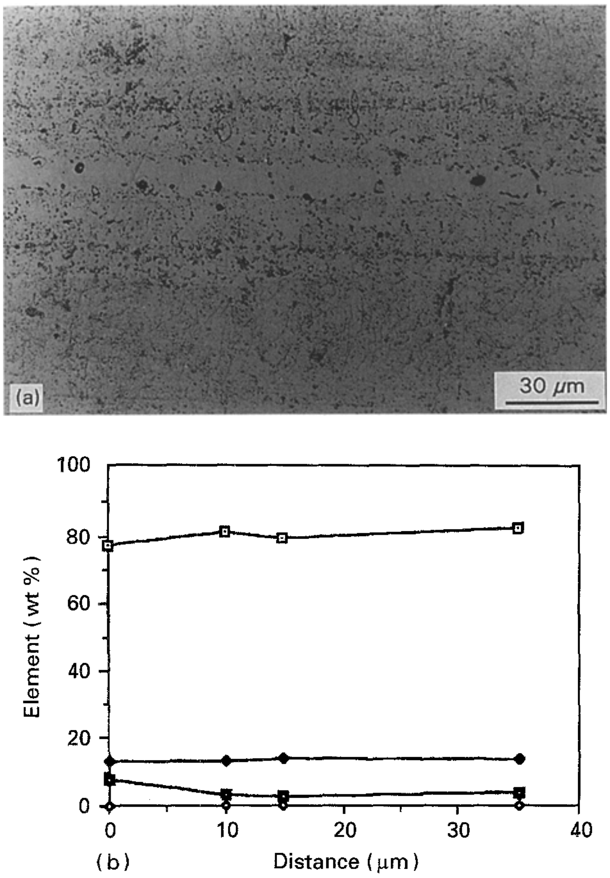


Figure 9 Joint microstructure produced in MA957 using the nickel braze, BNi1a: (a) after heat treatment at 1300 °C for 2 h; (b) EDS composition profile after the heat treatment. (□) Fe, (◆) Cr, (■) Ni, (◇) Si.

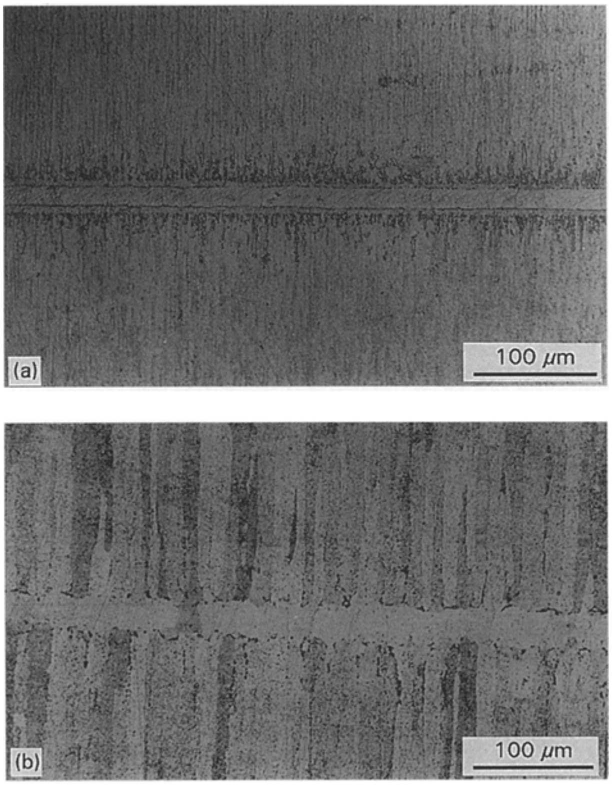


Figure 10 Light micrograph showing changes in joint microstructure with hold time when using the iron-base foil: (a) 2 min, (b) 30 min.

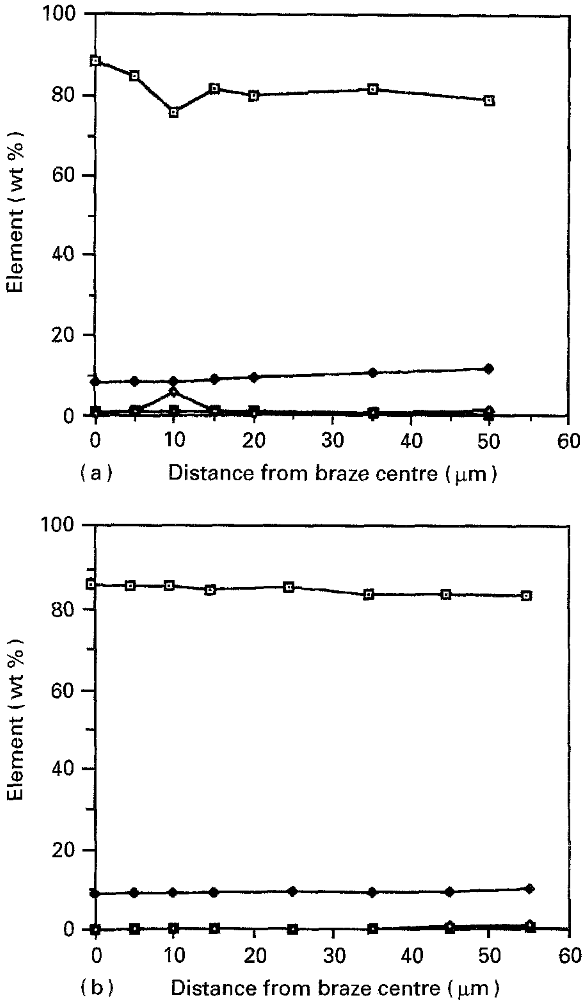


Figure 11 EDS composition profiles taken across bonds made using the iron-base foil. (a) 2 min hold, (b) 30 min hold. (□) Fe, (◆) Cr, (■) Si, (◇) Ti.

correspond to the location of silicide–boride precipitates that were seen to form in this region during the bonding process. The heat-treated bonds gave a lower TS value of 430 MPa and the fractograph in Fig. 14b indicates failure mainly by microvoid coalescence. This fracture behaviour was confirmed by the earlier light micrographs (Fig. 9a), which show that heat treatment, while removing some precipitates at the bond interface, also resulted in considerable porosity.

Room-temperature testing bonds produced after 30 min with the iron-base foil gave a TS value of 1095 MPa, which is 90% that of the parent metal (Fig. 13). A lower TS of 723 MPa was obtained for bonds held for a short time (10 min) at the bonding temperature. This was not surprising because a longer hold at the bonding temperature results in a joint visibly free from boride precipitates. The failure of both of these bonds was not in the braze but in the parent metal, adjacent to the joint region. The fractographs in Fig. 14c show that the failure in bonds produced both at 10 and 30 min was by transgranular cleavage attributable to precipitate formation. The fractograph in Fig. 14d also shows two modes of failure as the direction of the growing crack deviates on leaving the parent alloy and follows the braze/parent metal interface.

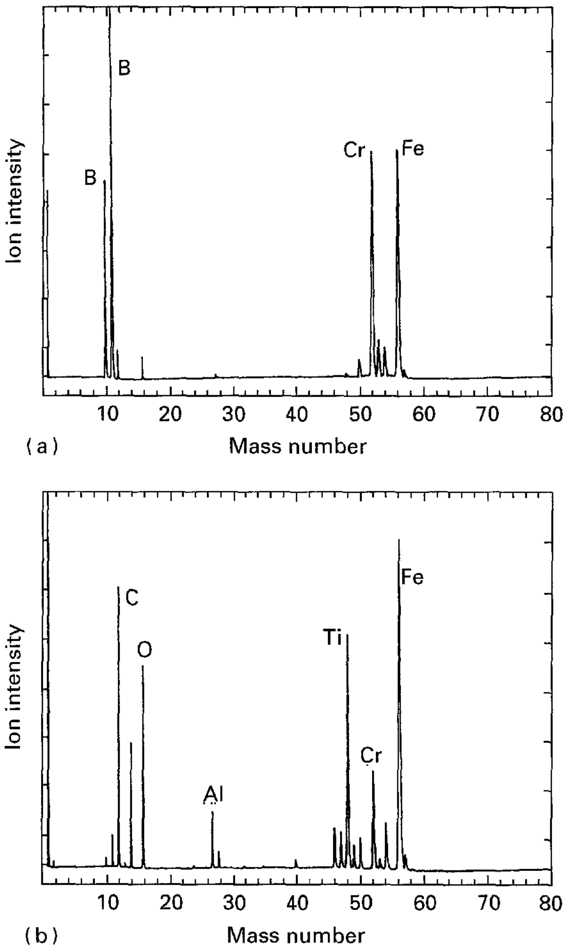


Figure 12 LAMMS spectra from bonds in MA957 made using iron-base foil: (a) precipitates formed at the parent/metal interface; (b) agglomerations along the bond interface.

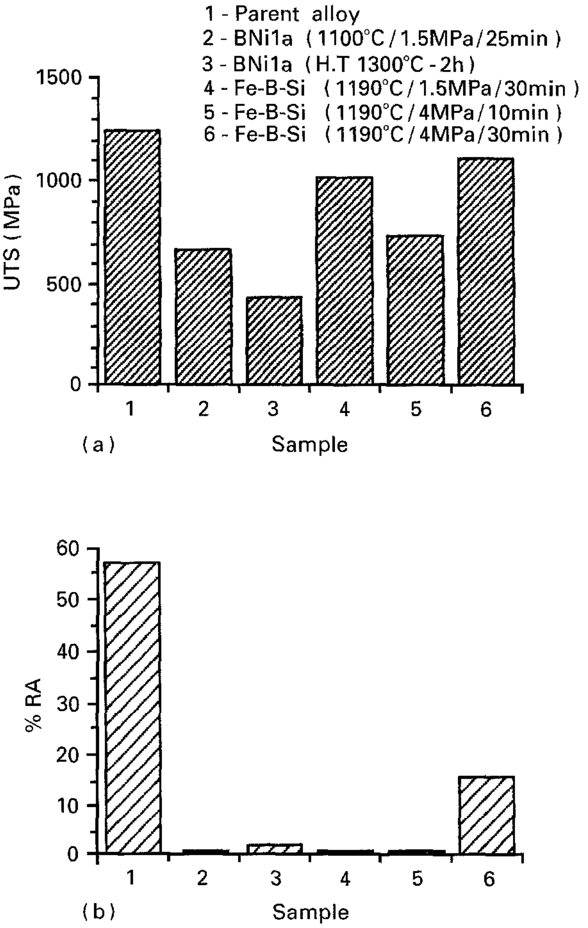


Figure 13 A Comparison at room temperature of the tensile properties of bonds made using the nickel braze (BNi1a) and the iron-base foil.

The RT tensile tests have shown that although near-parent-metal strengths are possible using the iron-base foil, the brittle failure in the parent metal adjacent to the bonds suggests that the presence of boron and silicon in the vicinity of the joint can have a severe embrittling effect. This is also evident in the very low percentage reduction in area (% RA) values measured. Some improvement, however, is seen when the bonds are either heat treated or given a long hold time at the bonding temperature, and this is attributed to the dispersion of boron and silicon further away from the joint region.

3.3.2. High-temperature tensile tests

Tensile tests carried out at a temperature of 700 °C gave bond properties which again corresponded well with the metallographic observations. The bonds produced with the nickel-base foil gave tensile strengths comparable with those of the parent metal (see Fig. 15). The bonds failed at the braze/parent metal interface, and the fractograph in Fig. 16a shows a dimpled surface fracture morphology characteristic of ductile failure. Although high bond strengths were recorded, the presence of embrittling precipitates gives the bond very low %RA values, see Fig. 15. Joints tensile tested after heat treatment at 1300 °C at 2 h gave poor bond strengths compared with as-bonded

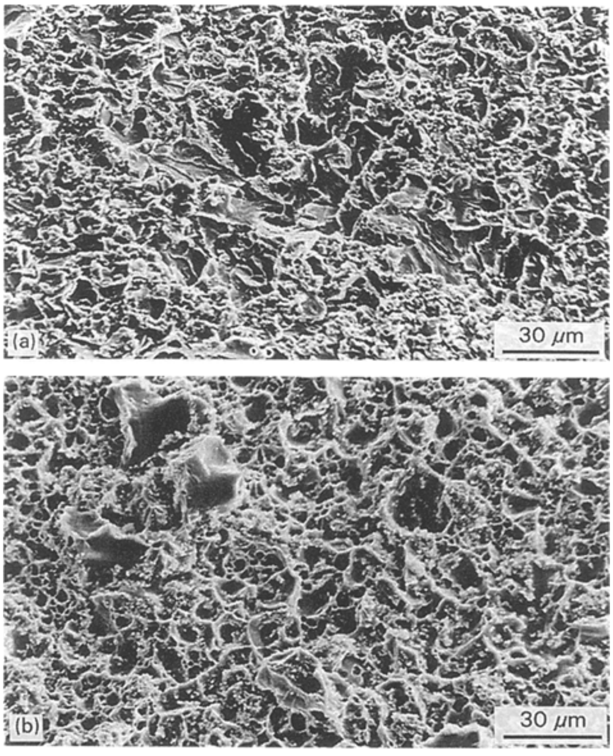
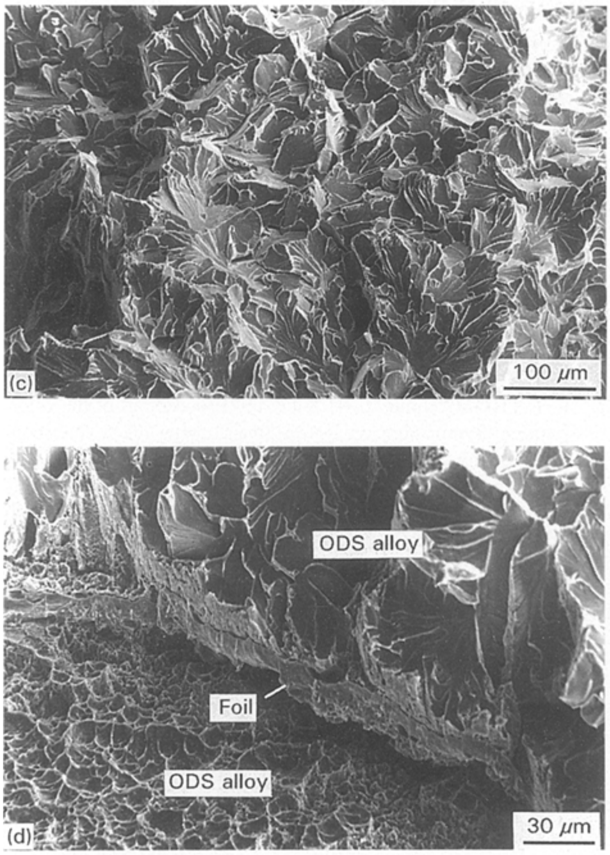


Figure 14 (*a*,*b*) Fractographs of tensile tests carried out at room temperature of bonds made using the nickel braze (BNi1a). (a) Tested in the as-bonded condition. (b) Tested after heat treatment at 1300 °C for 2 h. (c, d) Fractographs of tensile tests carried out at room temperature of bonds made using MA957. (c) Fracture surface using iron-base foil (1190 °C, 4 MPa, 30 min). (d) Fracture surface using iron-base foil showing the "two-mode failure".



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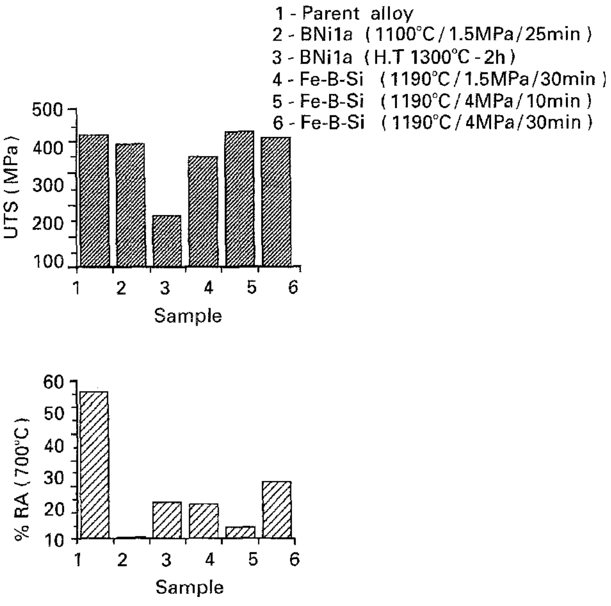

Figure 15 A comparison of the tensile properties at elevated temperature (700 °C) of bonds made using the nickel braze (BNi1a) and the iron-base foil.

samples. The weakness of the joints after heat treatment was attributed to the increase in porosity seen in the bond region and was thought to be due to argon gas released by melting of the parent metal.

Joints made with the iron-base foil gave higher bond strengths than those achieved with the nickel-base foil, and similar to that of the parent alloy.

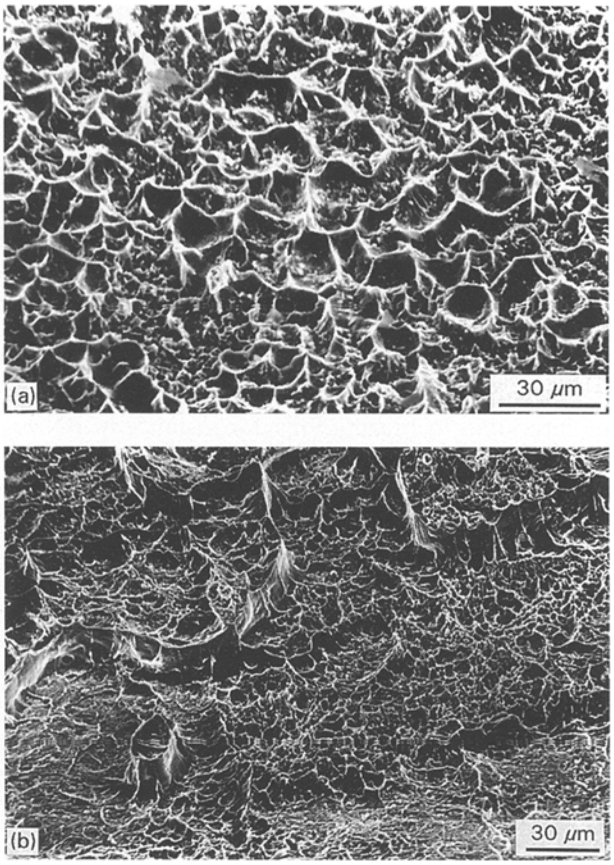

Figure 16 Fractographs of tensile tests carried out at 700 °C of bonds made (a) using the nickel braze (BNi1a), (b) using the iron-base foil.

Bonding time (10 and 30 min) had little effect on the bond strengths, and failure occurred at the braze/parent metal interface and not in the parent metal, as observed in RT tensile tests. The fractograph in Fig. 16b shows equiaxed dimples characteristic of ductile failure. A longer hold at the bonding temperature resulted in an improvement in the ductility of the joint, seen by the increase in %RA in Fig. 15.

Intermetallic precipitates at the bond seem to have less effect on joint strength in elevated temperature tests than in tests at RT. However, the failure tended to occur at the braze/parent metal interface. Metallurgical examination has shown that melting of the filler results in erosion of the parent metal interface leading to extensive agglomeration of the strengthening precipitates. Therefore, it would be reasonable to attribute the failure of the bonds to the plane of weakness associated with this melt-back region which results in the depletion of strengthening precipitates and oxides.

4. Conclusion

A novel interlayer based on the ternary Fe–B–Si system is found to be a suitable interlayer for TLP bonding giving superior metallurgical and mechanical properties compared with the commercially available nickel braze, BNi1a. Transient liquid-phase bonding using the iron-base interlayer produces near-parent metal properties, however, two fundamental problems with using foils have been identified, namely;

(i) excessive parent metal dissolution leading to the agglomeration of the strengthening precipitates and oxides in the parent metal matrix, and hence the subsequent failure of the bonds at the braze/parent metal interface during high-temperature tensile tests;

(ii) the high concentrations of boron and silicon present in the vicinity of the joint appear to have an embrittling effect which is more severe at room temperature than at higher temperature (700 °C), and which results in failure in the parent metal near the bond region.

Furthermore, this work has shown that the addition of chromium to brazing foils, for instance in BNi1a, to enhance oxidation resistance appears to have a detrimental affect on TLP bonds. The formation of embrittling, intermetallic precipitates based mainly on silicon within the braze was found to reduce joint strengths particularly at room temperature, and their formation was shown to be directly attributed to the higher chromium level in the nickel brazing alloy.

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