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Progress in joining of advanced materials

Part 1: Solid state joining, fusion joining, and joining of intermetallics

G. Çam and M. Koçak

Advanced materials generally require novel joining techniques. Developments in new materials research should be conducted hand in hand with work on weldability and joining capacity aspects. Sound joint quality for any new material has always been considered a milestone in a research and development scheme for a new material, particularly in terms of widespread applications. Better understanding of the microstructuremechanical properties relationships of the bonded or welded joints will feed back to the materials development activities both in conventional and new materials areas. The two joining processes diffusion bonding and laser welding are considered in this literature review, since these processes are capable of joining a wide range of materials of interest in the aerospace industry, as well as in many other industrial applications, and offer remarkable advantages over conventional fusion welding processes. Of particular interest is the ability to join the more difficult aerospace alloys with minimal component distortion and high reproducibility of joint quality. The purpose of the review is to outline progress made in this area and to make suggestions for future work. Part 1 deals with solid state joining, fusion joining, and joining of intermetallics, while Part 2 will cover joining of metal matrix composites and joining of other advanced materials.

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INTRODUCTION

The joining of any material with another has always been a necessity in engineering applications. Welding or bonding of two materials almost always causes changes or deterioration of the microstructural and mechanical properties of the original materials in the joining region. Joining of two different materials (dissimilar joints) leads to a much more complicated situation where each material's own properties should be taken into account during the joining process and later during joint quality determination.

New or advanced materials generally require novel joining techniques. Therefore, developments in new structural materials research should be conducted in parallel with research into weldability and joining capacity aspects. Sound joint quality of any new material has always been considered a milestone in a research and development scheme, particularly in terms of widespread applications.

Various aspects of the similar and dissimilar joints of advanced materials made by laser welding, diffusion bonding, high vacuum-high temperature brazing, electron beam welding, or other conventional materials joining technologies still require a vast amount of research and development supported by the knowledge gained over many years of work on conventional materials. It is obvious that a better understanding of the microstructure-mechanical properties relationships of bonded or welded joints will feed back to the materials development and optimisation activities both in conventional and new materials areas.

The topic of weldability and extensive characterisation (microstructural and fracture mechanics) of the welded/bonded joints of some advanced materials is a promising applied research and development area which may attract considerable industrial interest if the industrial research projects are organised in a product oriented fashion and conducted with sufficient expertise.

Weldability aspects of some advanced materials still require further research and development. Such materials include:

- (i) titanium aluminide intermetallics
- (ii) Ni₃Al intermetallic alloys
- (iii) Fe₃Al intermetallic alloys
- (iv) oxide dispersion strengthened (ODS) alloys
- (v) metal matrix composites (MMCs)
- (vi) nickel based superalloys
- (vii) Al-Li alloys.

Most of these alloys are mainly used in aerospace industry. Although the use of welding in the aerospace industry is rather limited compared with other major industries, it has gradually increased over the last 20 years as a result of the development of welding methods (e.g. laser beam welding, friction stir welding, etc.) which have a less detrimental effect on local material properties and shape (minimum distortion) than more conventional arc welding.

The two joining processes diffusion bonding and laser beam welding are considered in this literature review since these processes are capable of joining a wide range of materials of interest in the aerospace industry, as well as in many other industrial applications, and offer remarkable advantages over conventional fusion welding processes. Of particular interest is the ability to join the more difficult aerospace alloys with minimal component distortion and high reproducibility of joint quality.

SOLID STATE JOINING PROCESSES

Among the modern joining techniques used in engineering, solid state processes probably have the longest history and a wide spectrum of processes are now classified under the generic term 'solid state'. Solid state joining processes operate without melting of the base metal, usually by the application of high pressure. Bonding is achieved by the introduction of mechanical, electrical, or thermal energy and/or diffusion. These processes differ in the times, pressures, and temperatures used and the methods of applying heat.

At one extreme, cold pressure welding requires extensive deformation but no significant heating and is, therefore, restricted to ductile materials. Other processes include inertia (or friction) welding and explosive welding, leading to the other extreme of diffusion bonding.

Friction welding is a rather specialised process for joining a cylindrical part to a stationary section. The cylindrical unit is spun at high speed. Light contact between the parts creates heat at the interface and cleans the surfaces to be joined. Axial pressure is applied, causing the parts to rotate against each other forming the joint. The cleanliness and solid state nature of the bond make the process attractive for joining of many materials.

Explosive bonding is achieved between two metallic surfaces by a directed shock wave produced by detonation of an explosive charge. While the process is often used for cladding of steel plate by conventional alloys, the process has more recently been applied to joining complex and dissimilar materials. Perhaps the latest application is the joining of tubes to tubesheets in heat exchangers.

Diffusion bonding takes place when two mating surfaces are subjected to pressure at elevated temperature for an extended period. Diffusion takes place across the interface and a bond is formed. An interlayer of some rapidly diffusing element is sometimes used to decrease bonding time. The diffusion bonding process is characterised by its ability to join materials with minimal deformation and, in like materials, the absence of any identifiable bond line, which is in contrast to the results of cold pressure welding.

Diffusion bonding

It is possible to join a wide range of materials in both like and dissimilar combinations by diffusion bonding. In addition, solid state diffusion bonding avoids in particular undesirable structural transformations, since the temperatures involved in the process are rather low. These prime advantages have led to extensive use of this method in a wide range of industries extending from the electronics and nuclear fields to manufacture of various engineering and aerospace components.

Another driving force extending the use of diffusion bonding is the increasing development of novel and advanced materials, such as MMCs, intermetallics, and ceramics, where fusion processes are not generally applicable or are of limited use. Another area where diffusion bonding is finding application is the bonding of ceramics to metals. Although reports of some diffusion bonding of dissimilar material combinations have appeared in the literature, more demanding applications are expected particularly in engine parts, ranging from automotive to industrial and aeroengine components. In these applications, joints which can withstand much more severe operating conditions than previously considered will be required.

The widest application area of diffusion bonding now is in the aerospace industry. It is often used in combination with superplastic forming (SPF) for the fabrication of aircraft and aerospace components.¹ The technique is based on the formation of a metallurgical bond between mating surfaces by diffusion controlled mechanisms, with minimal macroscopic deformation.

Diffusion bonding is a process in which premachined components are held under load at an elevated temperature while in a protective atmosphere. Loads which would not cause macrodeformation of the parent material(s) and temperatures of 0.5–0.8 T_m (where T_m is the melting point in kelvin) are employed. Holding times at elevated temperature can exceed 60 min, but this depends on the material types being bonded, the joint properties required, and the remaining bonding parameters.² Although the majority of bonding operations are performed under vacuum or in an inert gas atmosphere, certain bonds have also been produced in air.³

To form a bond it is necessary for the two metal surfaces to come into atomic contact and hence microasperities and



a initial point contact and oxide contaminant layer; *b* large voids with thinner oxide layer after some point yielding and creep; *c* some voids remaining with very thin oxide layer after final yielding and creep; *d* oxide layer eliminated after continued vacancy diffusion leaving few small voids; *e* completed bonding

1 Mechanism of diffusion bonding²

surface contaminants must be removed before bonding. Furthermore, the bond interface has to be protected from oxidation whether under vacuum or in inert gas. It is generally believed that solid state bonding is completed through two stages:⁴

- (i) plastic flow disrupts the oxide film to expose the clean metallic surface and produce intimate contact
- (ii) bonding is established by atomic interdiffusion and recrystallisation and/or grain growth across the bond interface.

The mechanism of diffusion bonding is shown schematically in Fig. 1. Diffusion bonding can be categorised into three main groups:

- (i) solid state diffusion bonding
- (ii) liquid state diffusion bonding or diffusion brazing

(iii) superplastic forming-diffusion bonding (SPF-DB). This depends on the type of pressurisation, use of interlayers, and formation or not of a liquid phase. Each of these types, discussed below, finds specific applications for a range of materials and geometries needing to be joined.

Solid state diffusion bonding

Solid state bonding is mainly carried out under vacuum or in other protective atmospheres, such as argon, with heat being applied by radiant, induction, direct, or indirect resistance heating. Pressure can be applied either uniaxially or isostatically. In the former, a low pressure (usually 3–10 MPa) is used to avoid macrodeformation of the parts, i.e. no more than a few per cent. This type of process therefore requires a good finish on the mating surfaces since the contribution to bonding by plastic yielding is restricted. In addition, the surfaces should be as clean as is practically possible to minimise surface contamination.

In hipping, much higher pressures (100–200 MPa) are used and thus surface finishes are not critical. A further advantage of this process is that the uniform gas pressurisation permits the bonding of complex geometries in contrast to the generally simple butt joints possible with uniaxial pressurisation.

Where difficult materials need to be joined in the solid state (and in particular for metal to ceramic joints), it is



a for integrally stiffened structure; b for sandwich structure

2 Principle of SPF–DB technique^{2–5}

possible to introduce single or multiple interlayers of other materials to assist in the bonding process and to modify post-bond stress distributions.

Liquid state diffusion bonding or diffusion brazing

Also known as transient liquid phase (TLP) bonding, liquid state diffusion bonding or diffusion brazing is applicable only to dissimilar material combinations or to like materials where a dissimilar metal insert is used. Solid state diffusion processes lead to a change of composition at the bond interface and the bonding temperature is selected such that the newly formed phase at the bond interface melts at this temperature. This thin layer of liquid spreads along the interface to form a joint at a temperature lower than the melting point of either of the parent metals. A reduction in bonding temperature leads to solidification of the melt and this phase can subsequently be diffused away into the parent metals by holding at the bonding temperature. The technique has been used particularly for the bonding of aluminium alloys² where eutectics can be formed with copper, silver, or zinc to aid the breakup of the stable aluminium surface oxide.

Superplastic forming-diffusion bonding

The SPF-DB technique was specifically developed within the aerospace industries and its industrial importance is such that it is now considered as a different diffusion bonding process. The process is used commercially for titanium and its alloys, these materials being ones that exhibit superplastic properties at elevated temperatures within defined strain rate conditions. These temperature and pressure conditions coincide with the conditions required for bonding and therefore the two processes have been combined into one manufacturing operation.

The aircraft industry benefits from the ease of diffusion bonding of titanium, a material that absorbs its own oxide film at elevated temperatures. One result of this, however, is the need to introduce a stopoff material (usually yttria based) to prevent bonding in those areas where it is not required, as shown schematically in Fig. 2.

Considerable attention is being directed towards the diffusion bonding of superplastic aluminium alloys, as SPF-DB has demonstrated substantial cost and weight savings in fabricating aircraft structures. The SPF-DB process has recently become an emerging technology in

aerospace industries for production of complex net shape parts made of high strength aluminium. Although aluminium SPF technology has already been developed for implementation in production, limited success in solid state bonding of aluminium, especially high strength aluminium alloy, has been reported to date.

The major difficulty in solid state bonding of aluminium is the stable and tenacious surface oxide film which can not be avoided under normal manufacturing conditions. Considerable effort has therefore been directed towards methods of achieving intimate metallic contact between mating surfaces in the presence of this film and hence the adaptation of the SPF–DB technique for aluminium.

FUSION JOINING PROCESSES

In addition to the conventional heat sources used in fusion welding processes, namely gas flame and arc heat sources, electromagnetically accelerated particle beams, such as electron, ion, and neutral beams, and special type beams (i.e. laser and plasma beams) with large outputs have been developed over the last 30 years and are now available as heat sources for fusion welding. Power beam welding processes are generally classified as those capable of delivering an energy density greater than $\sim 10 \text{ kW mm}^{-2}$ to the workpiece and which are thereby capable of deep 'keyhole' penetration. These processes comprise electron beam, plasma arc, and laser welding.

Electron beams, which are easy to generate and offer relatively higher output, were the first high energy density beams to be commercially applied. Their most important disadvantage is the requirement of a vacuum working chamber, since the propagation range in air is extremely short. However, it is possible to weld much thicker plates using the electron beam welding process.

The plasma arc technique is the only arc welding process which is capable of achieving the energy density required for 'keyhole' penetration. In this technique, an arc is formed between a tungsten electrode and the workpiece, which is constricted and intensified by a copper nozzle surrounding the electrode, giving a plasma arc of a columnar form. The combination of high welding current and plasma gas flowrates results in deep penetration of the workpiece. The plasma arc technique is not only capable of high penetration keyhole welding, it can also be used as a low penetration weld surfacing technique.

Laser welding as an advanced industrial fabrication process is about 20 years old, but the technique already offers direct competition to electron beam and the more conventional welding processes. Laser beams possess a dual handicap of high investment and low thermal efficiency, but they have the great advantages of optical manipulation (i.e. ease of working), low distortion, greater accuracy and automation, and avoid the need for a vacuum working chamber in most cases. Some further details on the laser welding process are given below.

Laser beam welding process

Lasers are now attracting a great deal of interest as heat sources as a result of their potential to give extremely high energy density.⁶ Lasers may be classified according to their mode of operation as continuous wave (CW) or pulsed wave (PW). Early lasers capable of melting and cutting materials were of the solid state type with a pulsed output, whereas the continuous lasers did not have sufficient power output for processing the materials. However, the development of the high power CW CO₂ gas lasers and the PW Nd-YAG lasers in the last two decades led to the application of laser beams as a more general heat source in areas such as cutting, welding, heat treating, soldering, brazing, cladding, and hardfacing. Presently, lasers are applied to the welding of stators and rotors in generators, important gears,



weld direction

3 Principles of laser beam welding⁷

hot rolled silicon steel sheets, bimetallic saw blades, and tube-tubesheets of stainless steel. The welding of 50 mm diameter tube-tubesheets with a $3 \text{ kW } \text{CO}_2$ continuous laser can be completed in 8 s. Figure 3 is a schematic diagram of a laser beam welding operation.

In laser welding, when the laser beam impinges on the metal, it delivers its heat to the surface and further penetration beneath the surface relies on thermal conduction. The metal under the laser beam evaporates and a cavity or keyhole is formed through the thickness of the workpiece. By moving this keyhole along the joint between two pieces of metal, a weld is made as shown in Fig. 4.

Laser welding using a high power CO_2 or pulsed Nd-YAG laser can easily weld the specimen under atmospheric conditions. However, in the case of atmospheric laser welding, the generation of high density high temperature metallic vapour and its interaction with the laser beam (so called laser plasma) occurs and strongly affects the welded bead. This laser plasma can be suppressed by using inert gas (e.g. helium) as an assist gas. Another solution for the problem of laser plasma is the use of a low vacuum (a few thousand pascals).

Recognised characteristics of laser welding are deep penetration, narrow bead width, and narrow heat affected zone (HAZ) typical of high power density welding. This configuration is achieved in a keyhole welding mode in which the beam passes entirely through the joint to produce a full penetration weld (Fig. 4). Applications have generally used the downhand welding position. However, it is also possible to carry out all position welding for complex components.



4 Keyhole formation in laser beam welding

JOINING OF INTERMETALLICS Joining of titanium aluminides

During the past decade, an extensive effort has been devoted to developing titanium aluminide (Ti₃Al, designated as α_2 , and TiAl, designated as γ) based alloys. These alloys, which are still in the research and development stage, possess very good high temperature properties, such as oxidation, high temperature fatigue, and creep resistances, as a result of their high specific modulus, high recrystallisation temperatures, and low selfdiffusion. However, their room temperature ductility is intolerably low. Although the addition of β stabilisers seems to be the solution to their brittleness, large amounts of β stabilisers give rise to microstructures consisting mainly of β titanium. This means that these alloys therefore suffer from the disadvantages associated with a full β structure, e.g. reduced creep strength. Blackburn and Smith^{8,9} have found that the addition of

Blackburn and Smith^{8.9} have found that the addition of 13 at.-%Nb (or up to 4 at.-%V) to α_2 -Ti₃Al and the addition of 0.5–1.5 at.-%V to γ -TiAl improved their ductility. This discovery has stimulated an extensive study of Ti–Al based intermetallics, which has reached the point of evaluating their potential applications, mainly in the aerospace industry. Two types of α_2 -Ti₃Al based alloys with some room temperature ductility, namely Ti–26Al–11Nb (at.-%) (the first generation α_2 alloy, designated Ti–26–11) and Ti–25Al–10Nb–3V–1Mo (at.-%) (the second generation α_2 alloy, also known as super α_2 and designated Ti–25–10–3–1), are now available.

The joinability of Ti–Al based alloys is an important factor in determining their potential for wider use, since their fabrication is limited as a direct result of their low room temperature ductility. There is, therefore, increasing interest in fabrication of these alloys using joining, e.g. fusion welding and solid state bonding techniques.

Physical metallurgy of titanium aluminides

At present there are several ongoing projects on solid state (diffusion bonding) and fusion welding (LB) of γ -TiAl alloys, as well as the alloy development work at the GKSS Research Center. Therefore, the physical metallurgy of titanium aluminides is discussed in detail in this review. An excellent review of the physical and welding metallurgy of titanium aluminides has been conducted by Threadgill.^{10,11}

It is essential to comprehend the features of the Ti–Al equilibrium phase diagram in order to interpret the complex welding metallurgy of these alloys. It is perhaps surprising that the Ti–Al phase diagram is not fully known and, until very recently, even the most important parts of the titanium rich end were controversial. It now appears to be accepted that the α field extends to the γ field (Fig. 5).^{12–15} Three principal intermetallics are formed, namely α_2 -Ti₃Al, γ -TiAl, and TiAl₃, which has no Greek symbol. Other intermetallic



5 Modified Ti-Al phase diagram: after Pfullmann¹³

compounds may also exist, but their structures and stabilities are uncertain. Examination of the phase diagrams shows that solidification to α , β , or γ phases would be feasible, with only minor changes in the Ti/Al ratio. McCullough *et al.*^{12,16} have provided strong evidence that stoichiometric TiAl solidifies with α as the primary phase.

The greatest progress has been made in the Ti–Al alloys based on the α_2 -Ti₃Al intermetallic. This intermetallic exists as an ordered hcp (DO₁₉) structure at ambient temperatures over a range of compositions, although at elevated temperatures it exists as the bcc phase. On cooling from elevated temperatures, it is believed to transform to a disordered α phase, with long range order (α_2) being established at a slightly lower temperature.¹⁵

The structure of γ -TiAl is ordered fcc (L1₀) which, like α_2 -Ti₃Al, can exist over a reasonably wide range of compositions.¹⁵ Unlike α_2 -Ti₃Al, it does not undergo a phase change at elevated temperatures, although it does lose its long range order. However, the width of the γ -TiAl field diminishes significantly with increasing temperature.

It is believed that the TiAl₃ phase exists only as a line compound in the binary system. The structure of TiAl₃ is tetragonal (DO₂₂). Figure 5 illustrates the uncertainty in the region of the binary phase diagram between the TiAl₃ and γ -TiAl fields, although recent work by Schuster and Ipser¹⁷ suggests that a number of other compounds may exist in this region.

All titanium aluminides possess good high temperature strength and oxidation resistance. However, their limited ductility at low temperatures precludes their use in load bearing structures. Intense research activity has been undertaken to improve the room temperature ductility of these alloys, without compromising their high temperature performance, and some of the more significant developments are discussed below.

 α_2 -Ti₃Al aluminides. As the binary Ti–Al phase diagram in Fig. 5 shows, α_2 -Ti₃Al intermetallic forms over a range of aluminium contents from 22 to 36 at.-%.^{12,18,19} The intermetallic exhibits a hcp ordered crystal structure (DO₁₉ superlattice). Studies by Sastry and Lipsitt²⁰ on a near stoichiometric α_2 -Ti₃Al alloy indicated that on cooling the high temperature bcc β phase transforms allotropically to the hcp α phase and then orders extremely rapidly at temperatures just below the β transus temperature (1125–1150°C). They suggested that the low ductility of the ordered hcp structure (of the order of 1–2% elongation) results from a high degree of slip planarity and an absence of non-basal slip and twinning in the ordered structure.



a for 0–100 wt-%Nb, arrow indicates approximate position of Ti-24-11 α_2 alloy;²³⁻²⁶ *b* for 0–30 wt-%Nb section consisting of α_2 and β orthorhombic phases (O) and martensite transformation line M_8 , after Kim and Froes²¹

6 Pseudobinary Ti₃Al-Nb equilibrium phase diagram

The low temperature ductility of the α_2 -Ti₃Al alloy can be improved by adding β stabilisers, such as niobium, molybdenum, or vanadium. These alloying elements increase the number of slip systems available, refine the microstructure by lowering the β transus temperature, and also permit a small amount of retained β at ambient temperatures. Sastry and Lipsitt²⁰ showed that the presence of niobium improves α_2 -Ti₃Al ductility by reducing slip length and planarity and increasing the tendency for nonbasal slip. An improvement in the ductility of niobium containing alloys has also been attributed to the dispersal of slip by small islands of β phase. The results have led to much work on alloys such as Ti-24-11 (Ref. 21) and more recently Ti-25-10-3-1 (Ref. 22) directed towards finding microstructures giving optimum combinations of room temperature and high temperature properties. Unfortunately, the addition of these denser elements results in a material which is almost as dense as the conventional titanium alloys which it could replace. Figure 6a shows a Ti₃Al-Nb pseudobinary phase diagram developed from the work of several investigators.²³⁻²⁶ As illustrated, an increase in the niobium content promotes a decrease in the β transus temperature. It should be noted that this diagram indicates transformation on cooling directly from β phase to α_2 . However, it is more likely that transformation occurs from



a from light microscopy; *b* from TEM (bright field) 7 Images of α - β processed Ti-26-11 alloy³¹

 β to disordered α , which subsequently orders on cooling. The nominal composition of Ti-24-11 is indicated by the arrow in Fig. 6a.^{23,26} An equivalent 'effective' composition for Ti-25-10-3-1 would be located to the right of that for Ti-24-11 owing to its increased β stabiliser content. Kim and Froes²¹ also proposed a Ti₃Al-Nb pseudobinary phase diagram (Fig. 6b), which is somewhat more complicated than that illustrated in Fig. 6a. These authors reported an ordering of the β phase to a β_2 structure and the presence of an orthorhombic (O) phase based on Ti₂NbAl. Thermomechanical processing and heat treatment studies on both alloys have shown that the $\alpha_2 - \beta$ microstructures produced in these alloys closely resemble those of similarly processed conventional $\alpha-\beta$ titanium alloys.²⁷⁻³⁰ In many instances, structure-property relationships have also been shown to parallel those associated with conventional titanium alloys, although the room temperature ductility and toughness levels of the titanium aluminides are always appreciably lower. Light and transmission electron microscopy (TEM) bright field micrographs of $\alpha - \beta$ processed Ti-26-11 sheet in Fig. 7 (Ref. 31) show a close resemblance to $\alpha - \beta$ processed near α or $\alpha - \beta$ titanium alloys. The β processed or heat treated microstructures also parallel those of conventional alloys, as shown in Fig. 8 (Ref. 31) for β annealed Ti-26-10-3-1 alloy.

The mechanical properties of these alloys are strongly dependent on microstructure, which in turn can be controlled by thermomechanical processing. Luetjering *et al.*³² have recently described studies on super α_2 (Ti₃Al–Nb–Mo–V) which demonstrate the potential of microstructural control.



a from light microscopy; *b* from TEM (bright field), arrows indicate β strips between α_2 platelets

8 Images of β annealed Ti-26-10-3-1 castings³¹

Alloy systems based on Ti₃Al-Nb (α_2) and super α_2 are now available in preproduction quantities for evaluation and although alloy development is still underway, it is unlikely that the compositions will change markedly in the near future. At this stage, it is not clear whether the two phase $\alpha_2 + \beta$ microstructures required for room temperature ductility have adequate high temperature stability and creep properties.

The achievement of some room temperature ductility in α_2 -Ti₃Al based alloys by alloying with niobium has also initiated increasing interest in developing α_2 -Ti₃Al based MMCs, which are expected to surpass the monolithic α_2 -Ti₃Al alloys in some properties such as fatigue and creep resistance.³³ Another alternative approach is considered to be the exploitation of eutectic reactions in titanium alloys in order to produce in situ composites with good flow and creep resistances via relatively simple casting technologies. These alloys offer, in addition to the possibility of controlling the interlamellar spacing, the advantages of microstructural and thermal stability (including interfacial stability) inherent in eutectic microstructures. These alloys are also expected to offer improved high temperature properties compared with their monolithic counterparts. Recently, several investigations were conducted on these alloys. Wu *et al.*^{34,35} have reported that ternary Ti–Al–Si alloy with hypoeutectic and eutectic microstructures containing the intermetallic phases Ti₃(Al,Si) and Ti₅(Si,Al)₃ have promising high temperature mechanical properties. However, their room temperature ductility and fracture toughness were found to be relatively low. Wagner et al.^{36,37} have also investigated the effects of niobium additions on silicon containing α_2 -Ti₃Al based eutectic alloys and found

that niobium addition improved oxidation resistance dramatically. However, no beneficial effect on room temperature ductility and fracture toughness was obtained.

Rapid solidification processes offer a judicious way of controlling microstructure, extending the solubility range of alloying elements, and producing metastable or amorphous phases. In the case of eutectic alloys, microstructural control (interlamellar spacing, eutectic grain size, and eutectic structure) is of prime concern. Metastable or amorphous phases are generally not formed in eutectic alloys. Es-Souni *et al.*³⁸ have investigated the effect of rapid solidification on the microstructure of α_2 -Ti₃Al based eutectic alloy containing silicon and niobium and reported a substantial microstructural refinement in the melt spun ribbons in comparison to the arc melted alloys. The melt spinning technique, and also more sophisticated rapid solidification techniques such as gas atomisation, seem to be promising ways of producing fine scale microstructures.

Dutta and Banerjee³⁹ reported superplasticity in $Ti_3Al + 11$ at.-%Nb alloy, which was consumable arc remelted under vacuum, β forged, and hot rolled well below the $\alpha_2 - \beta$ transus (1100°C) to obtain a fine grained equiaxed $\alpha_2 - \beta$ microstructure with an average grain size of about 4 μ m. They attained a maximum tensile elongation of 520% at 980°C and at a strain rate of $3.3 \times 10^{-4} \, \text{s}^{-1}$. More recently, superplasticity in Ti-25Al-10Nb-3V-1Mo (at.-%) quinary alloy, known as super α_2 , has been reported by Yang et al.,40 with ductilities of up to 570% when deformed at 980°C and a strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$. In another work, Ghosh and Cheng⁴¹ reported 800% tensile elonga-tions in super α_2 alloy at even lower temperature (950°C) and at a strain rate of the order of 10^{-4} s⁻¹. Ridley *et al.*^{42,43} have also studied the superplasticity of super α_2 with an $\alpha_2 + \beta$ duplex microstructure (with mean grain size 3 μ m). They showed that enhancement of superplastic strain to failure can be achieved for constant velocity testing (decreasing strain rate) and not for constant strain rate deformation. Consequently, specimens were pulled to failure at a constant velocity of 10% min⁻¹, with an initial strain rate of $1.66 \times 10^{-3} \text{ s}^{-1}$. These authors reported that the material showed maximum strain rate sensitivity factor m values >0.4 at temperatures of 960-980°C, with a maximum tensile elongation of 1350% at 960°C. They concluded that there is potential use for the SPF-DB process with super α_2 . More recently, Guo *et al.*⁴⁴ studied the superplasticity and diffusion bonding of Ti-14Al-21Nb-3Mo-1V (wt-%) super α_2 alloy. They reported elongations of ~573% at 950°C and a strain rate of 4.52×10^{-5} s⁻¹, which increased to 1096% as temperature was raised up to 980°C at the same strain rate, whereas elongation of Ti-14Al-21Nb (wt-%) ternary α_2 alloy was reported to be 477% at 950°C and a strain rate of 1.49×10^{-5} s⁻¹. These authors also reported that increasing the strain rate decreased superplasticity; super α_2 alloy exhibited 385% tensile elongation at 950°C and a strain rate of $4.9 \times 10^{-4} \text{ s}^{-1}$ (Ref. 5). They also noted that the SPF-DB technique is suitable for α_2 -Ti₃Al based alloys. Nanophase α_2 -Ti₃Al alloys produced by mechanical attrition have also been reported,45 although it is not clear whether the expected increase in strength and ductility has been realised.

It can be estimated from the phase diagrams that the β to α_2 phase transformation will be a critical event in the joining of these materials. Work by Baeslack *et al.*^{46,47} and Weykamp *et al.*⁴⁸ on the kinetics of the phase transformation has shown it to be rather sluggish and that the reaction is even slower in the more complex super α_2 alloys.

 γ -*TiAl aluminides.* The γ -TiAl aluminides possess properties superior to those of the α_2 -Ti₃Al alloys, such as lower density (3·7–3·9 g cm⁻¹), higher elastic modulus, and better high temperature mechanical properties and oxidation

resistance, but their room temperature ductility is lower.⁴⁹ Extensive research in the late 1980s led to identification of several engineering alloys based on Ti-(47–49)Al with room temperature plastic elongation values up to 3.5% and improved strength. Remarkable improvements in fracture toughness and creep properties have also been achieved recently, making γ -TiAl aluminides potentially viable engineering alloys.^{50–53} There is a ductile to brittle transition temperature for γ -TiAl aluminides, which lies between 550 and 700°C depending on the alloy composition.⁴⁹ At elevated temperatures, these alloys can exhibit very high ductilities. Although there has been an extensive effort devoted to the development of more ductile γ -TiAl alloys and the ambient temperature ductilities of known γ -TiAl alloys are less than those of the α_2 -Ti₃Al alloys.

Chen⁵⁴ has conducted quenching studies of binary Ti–Al alloys and of some ternary systems. Although his results show no clear evidence for the formation of the β phase at high temperatures, this may have been a result of insufficient soaking time before quenching to achieve equilibrium. Furthermore, the position of the $\alpha/\alpha + \gamma$ boundary at high temperatures is significantly affected by the vanadium con-tent of the alloy. Huang and Siemers⁵⁵ have reported dilatometry and solidification data which also indicate that the α phase is stable up to the melting point and that binary alloys containing 50-54 at.-%Al will solidify as a. These authors further point out that comparison with other data may be difficult, as oxygen (an α stabiliser) contents are not always known. Degawa et al.56 have reported that oxygen had an adverse effect on the ductility of y-TiAl castings, whereas its effect on strength appeared to be marginal. These authors proposed that the oxygen content of γ -TiAl alloys should be below 2000 ppm for optimum ductility. It is likely that the effects of other alloying elements on solidification and solid state transformation will be pronounced, since the alloying elements most often used to promote ductility are β stabilisers. In other work, Kobayashi et al.57 studied the microstructures of rapidly solidified alloys and again reported that the α field extends to the γ field.

A number of approaches to alloying of γ -TiAl to improve ductility have been suggested and useful reviews have been conducted by Kim⁴⁹ and Khan et al.⁵⁸ Sastry and Lederich⁵⁹ have proposed the use of ductile phase reinforcement, in which small (200 µm) particles of ductile titanium or niobium alloys are incorporated into the material at the level of 10-20 vol.-%. This is reported to have led to increased toughness, provided that excessive reaction between the ductile phase and the matrix could be avoided. More conventional approaches have proposed the addition of 1-10 at.-% of elements such as vanadium, chromium, manganese, tungsten, molybdenum, niobium, and tantalum, either singly or in combination. The amount of aluminium and the type and amount of ternary or quarternary additions determines whether the crystal structure is single phase, equiaxed γ , or duplex lamellar $\gamma + \alpha_2$. The relative amounts of equiaxed and duplex γ present in the final microstructure also depend strongly on the heat treatment and cooling rate from process temperatures.

The γ -TiAl alloys that are of engineering importance are the two phase alloys Ti-(45-49)Al-(1-3)X-(1-5)Y-(0·1-1)Z, where X = V, Mn, and/or Cr, Y = Nb, Ta, W, and/or Mo, and Z = Si, C, B, N, Ni, Fe, P, Se, or Te.⁵¹ In the two phase $\alpha_2 + \gamma$ alloys, vanadium, chromium, and manganese improve ductility, whereas niobium, silicon, tungsten, and tantalum improve oxidation resistance. In single phase alloys, niobium and tantalum are used as strengthening additions as well as to improve corrosion resistance. Unfortunately, it seems that alloying elements that improve ductility will decrease the oxidation resistance^{49,60} and the reverse is also true. However, small additions of Group Vb and Group VIb elements, such as telurium, selenium, and phosphorus, improve oxidation resistance without compromising ductility.⁶⁰ Furthermore, small additions of carbon and nitrogen are known to improve creep resistance and silicon yields some improvements in oxidation resistance and room temperature ductility.⁵¹ Small additions of boron and silicon refine the microstructure. Since small variations in the alloy content will result in significant shifts in the $\alpha_2 + \gamma$ phase boundary, it is obvious that alloy compositions will have to be precisely defined.

The mechanisms by which these alloying additions improve the ductility is complex. Yamaguchi⁶¹ has shown that deformation in γ -TiAl is predominantly by mechanical twinning and that this can be enhanced by manganese additions, an observation also reported by Hug and Veyssiere.⁶² Hanamura *et al.*⁶³ and Tsujimoto and Hashimoto⁶⁴ have also reported that small additions of manganese to γ -TiAl improve room temperature ductility. However, it is not clear to what extent the mechanical properties are influenced by compositional factors or by effects of microstructure. Dogan *et al.*⁶⁵ have investigated the effect of manganese (1 at.-%) on the fracture behaviour of Ti-48.5 at.-%Al, which has a microstructure of lamellar two phase $\alpha_2 + \gamma$ and found that the manganese addition did not improve the ductility.

Encouraging levels of room temperature ductility and fracture toughness can be achieved in γ -TiAl based alloys containing minor additions of alloying elements such as vanadium, chromium, manganese, or niobium by appropriate choice of composition and process variables.⁴⁹ For a given two phase alloy composition, microstructural variations directly influence the room temperature ductility, which ranges from 0.5 to 4% plastic elongation.^{50,64,66-68} Recent research has also revealed ductile Ti + ~47.3 at.-%Al alloy, which has ductility that can exceed 40%, even at room temperature with compressive testing.⁶⁹

These findings have triggered extensive research activity to improve the room temperature ductility of γ -TiAl. Attempts have involved alloying with various additional elements and selecting alloy compositions which lead to two phase microstructures consisting of α_2 -Ti₃Al and γ -TiAl.⁷⁰ The mechanical properties of the two phase alloys (which possess a microstructure consisting of equiaxed γ grains and colonies of thin parallel α_2 and γ lamellae) are superior to those of single phase material,66,71-73 with strength and ductility being particularly dependent on the volume fraction of the lamellar colonies. However, the two phase alloys' fracture toughness of 16 MPa $m^{1/2}$ (Refs. 49, 66-68, 74, 75) is lower than that of the fully lamellar microstructure with large grain sizes, which is typically lower than 16 MPa $m^{1/2}$ (Refs. 66–68, 74–76). Two phase $\alpha_2 + \gamma$ alloys are heat treated in the $\alpha + \gamma$ phase field to yield a microstructure consisting of two distinct morphologies, namely equiaxed γ grains and colonies of thin parallel α_2 and γ lamellae. That these improvements in properties are associated with the complex series of solid state phase transformations which such alloys undergo was first appreciated at a stage where a number of groups^{12,13,16,77,76} produced modifications to the high temperature region of the appropriate portion of the Ti–Al phase diagram. There has been a lack of systematic work to locate precisely the high temperature boundaries in this system and in particular to investigate whether the alloying elements considered desirable exert their influence via effects which are primarily 'microstructural' or 'compositional' in nature.

Another successful approach which has been reported is the use of the Martin Marietta XD process to produce an alloy containing a dispersion of TiB₂ particles (XD composite). Patterson *et al.*⁷⁹ claimed that the particulate reinforcement is directly responsible for grain size refinement, which

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in turn results in improved casting and thermomechanical process characteristics.

Recently, superplastic behaviour in γ -TiAl has been attained. A structure composed of γ -TiAl with 3 vol.- $\%\alpha_2$ -Ti₃Al was obtained in a titanium aluminide containing 36 wt-%Al after undergoing a compressive strain of 80% at 1000°C with a strain rate of 10^{-3} s⁻¹ and subsequently held at 925°C for 24 h. The grain size was found to be about 8 µm. This alloy exhibits superplastic behaviour within the strain rate interval $0.83 - 1.6 \times 10^{-3} \text{ s}^{-1}$ with an m value of 0.4. The largest extension to rupture of 250%was obtained at 925°C and $8.0 \times 10^{-4} \text{ s}^{-1}$ (Ref. 80). A maximum elongation of >100% in γ -TiAl at 1100°C at a strain rate range of 10^{-3} s⁻¹ was also reported by Mitao et al.⁸¹ For y-TiAl based alloys, superplastic behaviour was also achieved in the following manner. A mixture of elemental powders of titanium and aluminium (50 at.-%), after undergoing a mechanical alloying process, was hot pressed at 900°C for 1 h under a pressure of 100 MPa. This resulted in a compact having a relative density of 99.8% and an ultrafine grain structure ($0.1 \,\mu m$) consisting mainly of the y-TiAl intermetallic compound. Grain growth up to 2 µm occurred after an anneal at 1200°C for 10 h. The material lost its brittleness after the final heat treatment and the compressive deformation of the compact at 900°C was presumed to proceed by superplastic flow.⁸¹ In more recent work, Maeda et al.82 attained a tensile elongation of 230% in y-TiAl at 1000°C and a strain rate range of 10^{-5} s⁻¹. The strain rate sensitivity of rolled γ -TiAl based Ti-48Al-2Cr alloy was measured in the temperature range 1000–1200°C for two different grain sizes by Ĉlemens et al.⁸³ It was shown that superplastic behaviour can be found even for relatively coarse grained material (27 µm) at temperatures above 1100°C.

On heating, γ -TiAl alloys will undergo changes in the equilibrium α_2/γ ratio (with α being more stable at higher temperatures) and eventually (at least under equilibrium conditions) a complete transformation of γ to α will take place. According to the phase diagram proposed by McCullough *et al.*^{12,16} there is a phase change at about 1130°C from $\alpha_2 + \gamma$ to $\alpha + \gamma$ and eventually complete transformation to α .

 $TiAl_3$ aluminides. Although alloys based on the TiAl_3 stoichiometric composition have been developed, these alloys are not yet as well optimised as other titanium aluminides and are still a long way from commercial production. However, the low density, high specific strength, good elevated temperature properties, and excellent oxidation resistance have provided an incentive for alloy development. The DO₂₂ structure is derived from the fcc (L1₂) structure, which generally exhibits some ductility. Several authors have reported that Ti-Al-X alloys with the L1₂ structure can be produced by alloying with copper,^{84–87} nickel and zinc,^{84,85,87} iron,^{87–89} boron,⁸⁶ mangan-ese,^{84,85,87,90} chromium,^{84,87,90,91} cobalt,⁸⁷ or paladium.⁹² Studies on the Ti–Al–Mn and Ti–Al–Cr systems have indicated lower hardness values than in TiAl₃, together with good compressive ductility, and some tensile ductility. Mechanical data about TiAl₃ alloys are very scarce, but properties comparable to or better than those of γ -TiAl alloys have been reported at ambient and elevated temperatures. Zhang et al.⁸⁴ have suggested that quarternary Ti-Al-Mn-V alloys are the most promising.

No indications of phase changes with temperature have been reported following preliminary differential thermal analysis (DTA) studies,⁸⁴ but other intermetallic compounds, which could result in loss of ductility, were observed in these alloys before homogenisation. Tarnacki and Kim⁸⁶ found that rapid solidification in alloys containing boron or manganese still resulted in the L1₂ structure and that



a for decomposition of high temperature β phase in α_2 alloy (schematic), after Weykamp *et al.*,⁴⁸ *b* for α_2 and super α_2 alloys as determined by dilatometry⁴⁷

9 Continuous cooling transformation curves

boron and manganese formed second phases which markedly strengthened the matrix, increased the hardness, and refined the microstructure. In copper containing alloys, however, rapid solidification had little effect, but these authors reported that all rapidly solidified alloys appeared to be brittle. Hoellrig and Ogilvy,⁹³ who supported this observation, investigated spray deposition of various TiAl₃-X alloys. They reported that a slow cooling rate from deposition temperature to ambient temperature was required to prevent cracking of the sprayed preforms.

Welding metallurgy of titanium aluminides

 α_2 -Ti₃Al aluminides. Although published data are limited, there is no evidence to suggest that the α_2 based alloys suffer from any major weldability difficulties in terms of susceptibility to hot cracking, etc. David *et al.*⁹⁴ have carried out sigmajig tests on a Ti-24Al-11Nb alloy and reported that the resistance to solidification cracking was quite acceptable. The major problem with this alloy is its very low ductility at ambient temperature and the consequent risk of solid state cracking.

The most significant factor in the joining of α_2 alloys is the β to α phase transformation, which is comparatively sluggish and much slower than the similar γ and α transformation which is critical in the welding of ferrous alloys. It is rather difficult to quantify the comparison, but it is worth noting that a cooling rate as slow as 50 K s⁻¹ in super α_2 alloys still suppresses any β decomposition, whereas such a cooling rate in common C-Mn steels would ensure complete transformation. Several authors^{46-48,95} have concluded that rapid cooling of α_2 and super α_2 alloys from the β phase results in little or no β decomposition and that the microstructure consequently consists primarily of retained ordered β_2 . Although this phase is comparatively ductile, it has marginal notch toughness and is therefore not always a desirable constituent. Furthermore, it is thermodynamically unstable and exposure at elevated tem-



10 Knoop hardness (500 g load) v. cooling rate for α_2 and super α_2 alloys continuously cooled from 1200°C (Ref. 47)

peratures in service may lead to transformation to the equilibrium α_2 phase.

Less rapid cooling from the β phase field will yield a very hard α_2 martensitic structure, with virtually no retained β phase,^{48,95} together with the formation of O and ω phases.^{94,96} Although this martensitic structure exhibited very high strength, it was very brittle and therefore clearly undesirable. In order to obtain the most desirable microstructure in α_2 alloys, which consists of a fine $\alpha_2 - \beta$ mixture, it is necessary to cool quite slowly from the β phase field and this requires either the application of very high preheats before welding to slow down the cooling rate or the development of specific post-weld heat treatment (PWHT) schedules to produce desirable microstructures. Weykamp et al.48 have proposed a schematic continuous cooling transformation (CCT) diagram (Fig. 9a), which shows the various transformations in α_2 . It can be seen that, as might be expected, the diffusion controlled transformations are favoured at slow cooling rates and shear at higher cooling rates. Baeslack and Broderick⁴⁷ have also proposed a preliminary CCT diagram for α_2 and super α_2 alloys, which is given in Fig. 9b. This diagram clearly demonstrates the effect of various alloy compositions on the rate of transformation in these alloys. Figure 10, from the same work, shows the effect of cooling rate on the hardness of the alloy. As can be seen from Fig. 10, the peak hardness value corresponds to fairly modest cooling rates, particularly in the more highly alloyed super α_2 alloys.

Thus, joining processes in which the cooling rates can be closely controlled are likely to be particularly useful in producing the desirable weld microstructure. In this respect, processes such as electron beam welding followed by beam rastering to slow the cooling rate are promising.

The degree of the ordering of the β phase appears to depend on the previous thermal history,⁹⁷ since it will determine the Ti/Al ratio in this phase. Furthermore, variations in the degree of β ordering may be present across a weldment. Kestner-Weykamp *et al.*⁹⁷ have pointed out that the degree of β ordering may be of more than academic interest, since the higher diffusivity expected for the disordered β phase will adversely influence creep resistance. Peters and Bassi⁹⁸ have reported two additional phases in super α_2 alloys existing as precipitates, namely a hcp ω phase and an O phase. These precipitates only appear after long periods at elevated temperatures and are thus unlikely to form as a result of welding unless the cooling rate is extremely slow.

There is considerable evidence to suggest that the ductility of α_2 (Ref. 99) and super α_2 (Ref. 100) aluminides can be influenced by hydrogen. It has been suggested that hydrogen embrittlement is associated with the formation of a hydride phase, possibly TiNbH (Ref. 99), TiH₂ (Ref. 101), or Ti₃AlH (Ref. 102). Recent publications by Eliezer *et al.*¹⁰³ and Schwartz *et al.*¹⁰⁴ have concluded that the mechanisms of hydrogen embrittlement are very complex and that hydrogen behaves in a different manner in the α_2 and β phases, with hydride formation being much more likely in the former. Furthermore, diffusion rates for hydrogen are appreciably higher in the β phase.

Hydrogen embrittlement could be quite important in several joining processes, especially in slag shielded arc welding, where hydrogen is unavoidably introduced into the weld pool. Fortunately, such processes are not normally used for titanium based alloys. It is possible that any effects of hydrogen will be most significant in joining processes in which high hardness α_2 martensite is formed, which will have very low ductility even in the absence of hydrogen.

 γ -TiAl aluminides. No solidification cracking problems have been reported for γ -TiAl aluminides, but the major challenge is again the ability to cope with the lack of ambient temperature ductility. Non-equilibrium solid state phase transformations have not been fully investigated, but it is well established that significant changes in the equilibrium α_2/γ ratio will take place on heating and a phase transformation to α will occur at high temperatures. In the alloys containing β stabilisers, it is likely, but not demonstrated, that some β phase may form at very high temperatures. However, this is not likely to be a major problem.

It has been reported^{105,106} that hydrogen can form previously unknown hexagonal hydrides in some γ -TiAl alloys under high pressures and temperatures. The same authors have also detected cubic δ titanium hydrides and other undetermined precipitates in γ -TiAl alloys after hydrogen charging. Eliezer *et al.*¹⁰³ and Schwartz *et al.*¹⁰⁴ have pointed out that γ -TiAl alloys would be expected to have good resistance to hydrogen embrittlement, except under the most extreme conditions. Although there is no direct evidence to support this point of view, it is not likely that hydrogen would be of major concern in the welding of γ -TiAl alloys.

 $TiAl_3$ aluminides. No studies on the weldability or welding metallurgy of TiAl_3 based alloys have been reported, but it is known from studies on the processing of these alloys that any operation involving rapid cooling of the joint is likely to lead to cracking. No information is available on the non-equilibrium cooling and possible transformations which may take place. Because of the high aluminium content of TiAl_3 alloys, joining processes such as diffusion bonding may require an interlayer and it is likely that these alloys may not be able to withstand the severe plastic deformation required in processes such as friction welding.

The complexity of the binary Ti–Al phase diagram in the range between the TiAl and TiAl₃ compounds,^{17,18} where several other intermetallic compounds may exist, will also have a significant effect on the microstructure and hence performance of joints cooled under non-equilibrium conditions. This aspect will obviously require further investigation when progress has been made on the more critical shortcoming of the undesirably low ductility of these alloys.

Welding of titanium aluminides

Solid state joining of α_2 -Ti₃Al aluminides. Work at TWI^{107,108} has demonstrated that diffusion bonding of α_2 -Ti₃Al alloys presents few problems in terms of producing a sound weld and that 25 at.-%Al has no apparent effect on the excellent quality of the bonds which can normally be made in titanium alloys. It is reasonable to assume that the same will be true of the super α_2 compositions. However, no data yet exist on the properties of such welds, particularly at elevated temperatures. Figure 11 (Ref. 108) shows microstructures at the bond line in specimens diffusion bonded above and below the β transus and the partial transform-



a bonded at 1070°C (above β transus temperature) under 3.44 MPa pressure for 2 h; *b* bonded at 1035°C (below β transus temperature) under 3.44 MPa pressure for 2 h

11 Diffusion bonds in Ti-26-11: arrows indicate bond line ×400

ation which occurs at the higher temperature is evident. A good quality bond can however be obtained at lower temperatures. Ridley et al.^{42,43} have reported some initial studies on diffusion bonding of super α_2 with a 3 mm thickness. Trials of isostatic diffusion bonding were carried out at various temperatures below the β transus temperature (reported to be 1080-1085°C) and satisfactory bonds were obtained at temperatures of 1030 and 1050°C. At the latter temperature, the alloy contains about 80% β phase. The authors believed that considerable potential for SPF-DB exists. More recently, Guo et al.44 reported a shear strength of 797.6 MPa in super α_2 diffusion bonded without interlayer at 990°C under pressure of 9 MPa for 70 min, which approached the shear strength of the base metal. They also reported that there are good prospects for α_2 -Ti₃Al based alloys to be formed using the SPF-DB technique.

Cox et al.¹⁰⁹ successfully demonstrated the potential for diffusion bonding of α_2 -Ti₃Al alloys using capacitor discharge heating. Depending on the conditions used, either a solid state or a fusion weld was produced, but the authors reported higher shear strengths in solid state bonds made with higher electrode force and that these properties exceeded those found in fusion welds by a significant margin. Shear stress values of up to 355 MPa were reported for bonds in 1.7 mm thick sheet. Under these conditions, peak hardness values of around 380 HK were observed at the bond line.

Friction welding offers an attractive method of joining these materials and some success has been obtained using inertia welding in the USA⁴⁶ and linear friction welding at TWI.^{108,110} However, these studies were again confined to α_2 compositions and it was found that in both process variants the region close to the bond line developed unfavourable microstructures consisting of retained β and α_2 martensite. This is reflected in the hardness data shown in Figs. 12 (inertia welding) and 13 (continuous drive). Although the microstructures are difficult to identify by optical microscopy, recent studies by Baeslack *et al.*^{108,110}



12 Knoop microhardness traverse for inertia friction weld in 19 mm diameter α_2 rod⁴⁶

using TEM have confirmed the presence of α_2 martensite and retained β at the bond line, with more β being present in welds made at a higher frequency where the cooling rate would have been faster.

Stotler et al.111 conducted successful flash welding of α_2 -Ti₃Al alloys in 0.5 × 0.2 in (12.5 × 5 mm) sections and reported encouraging mechanical property data. Their limited microstructural data show that the bond line structure consisted of fine α_2 and retained β phases, but no hardness measurements were reported. Further studies by the same authors¹¹² demonstrated that the changes in the microstructures are related to variations in process parameters. They suggested that some control of cooling rate, and in turn microstructure, can be achieved by varying the die opening and upset distance. Increasing the former caused a decrease in the cooling rate, whereas increasing the latter increased the cooling rate. Increasing the upset distance also resulted in the displacement of the more heated material into the flash, reducing the width of the HAZ and generally increasing the strength of the weld. Martensitic microstructure was the predominantly produced structure over the range of conditions studied, but the scale of the microstructure varied significantly. In contrast to expectation, the weld with the highest hardness exhibited the best ambient temperature mechanical properties (ultimate tensile strength 490 MPa). The authors attributed this to the greater degree of forging in this weld. Additionally, considerable scatter in hardness data was reported, with low strength welds failing at the weld line at a stress of 158-167 MPa. These very low values could be attributed to the small cracks possibly introduced during the joining process.

Baeslack *et al.*¹¹³ reported some limited data on the joining of an α_2 -Ti₃Al alloy to a Ti-6Al-2Sn-4Zr-2Mo-0·1Si alloy by diffusion bonding, linear friction welding, and capacitor discharge spot welding. The microstructures of the welds were characterised in detail by optical microscopy, TEM, and electron probe microanalysis. Evidence of elemental diffusion across the interface was found in the diffusion bonds, promoting a corresponding microstructural gradient. In contrast, the linear friction welds demonstrated intense and highly localised mechanical mixing with minimal interdiffusion. The microstructure, subjected to intense mechanical work, had undergone complete dynamic recrystallisation of the β grains. Spot welds showed no evidence of mechanical mixing or interdiffusion.

Fusion welding of α_2 -Ti₃Al aluminides. Limited data in literature from the USA suggest that a number of fusion weld processes can be successfully adapted to the joining of α_2 type alloys,^{46,94,114-117} but published information on fusion welds in the super α_2 types is very scarce. Studies on α_2 and super α_2 have mostly concentrated on process optimisation and very limited mechanical data other than hardness and bend data are available.

Baeslack *et al.*⁴⁶ studied the welding of Ti-26-11 and found that the weld microstructure and mechanical properties had a strong dependence on the cooling rate experi-



○ 14–21/14–21, 25 Hz, edge; □ 14–21/14–21, 25 Hz, centre; ◇ 14–21/14–21, 12·5 Hz, centre; × 14–21/14–21, 50 Hz, centre; • 6242/14–21, 25 Hz, centre

13 Hardness traverses across linear friction welds in α_2 alloy illustrating effect of welding frequency¹¹⁰

enced during the weld thermal cycle. It was found out that moderate cooling rates associated with conventional gas tungsten arc (GTA) welding $(25-75 \text{ K s}^{-1})$ promote the formation of an extremely fine, acicular α_2 microstructure (hcp (DO₁₉) superlattice) which exhibits low ductility and high susceptibility to solid state cracking during weld cooling. It was also found that improvements in GTA weld ductility and cracking resistance could be achieved by using slower weld cooling rates (<10 K s⁻¹) to produce a coarser α_2 platelet + retained β microstructure.⁴⁶ However, it is practically rather difficult to achieve such cooling rates as they require heating of the workpiece to relatively high temperatures during the welding operation.⁹⁵

Increases in the peak hardness of the fusion zone and the HAZ were reported by Baeslack *et al.*⁴⁶ and David *et al.*⁹⁴ The data of David *et al.* also demonstrate the dependence of the peak hardness and HAZ width on the process parameters. As expected, the width of the HAZ increased with increasing energy input, but the peak hardness also increased with increased heat input. The authors attributed this to the increased retention of β phase in the lower heat input welds and consequent reduction in the quantity of fine α_2 martensite. They also suggested that an ω phase, as observed by Strychor *et al.*,⁹⁶ may be present. However, no firm evidence to support this view was given. The microstructure and hardness data of David *et al.*,⁴⁶ who also reported low peak hardnesses and attributed this to the retention of β phase.

Baeslack et al.¹¹⁵ also conducted laser welding of an α_2 -Ti₃Al alloy in 1.7 mm thick sheet using a Nd-YAG laser. They reported that the application of pulsed Nd-YAG laser welding produced crack free weldments in Ti-26-11. The extremely rapid cooling rates provided by this high energy density welding process suppressed the β to α transformation and promoted the formation of a relatively ductile, ordered β microstructure (bcc (B2) microstructure, CsCl type) within the fusion zone. Although this β (B2) phase is highly metastable, it is possible to stabilise the microstructure and develop acceptable mechanical properties. Transmission electron microscopy examination of the fusion zone of welded specimens demonstrated almost complete retention of the β phase, which existed as a fine equiaxed ordered β_2 structure, suggesting dynamic recrystallisation had occurred on cooling. Only isolated formation of α_2 was observed at prior β grain boundaries and at dislocations. The extensive β retention was reflected in the hardness traverse which showed an appreciable drop in the fusion zone hardness compared with that in the HAZ, shown in Fig. 14a.



14 Knoop hardness traverses across Nd-YAG laser welds in α₂-Ti₃Al alloy

In subsequent studies, Baeslack et al.^{116,117} investigated the influence of PWHT at temperatures between 565 and 850°C followed by slow cooling on β decomposition in the fusion zone of a Nd-YAG laser welded Ti-26-11 alloy. However, they found that low temperature PWHT increases fusion zone hardness and significantly lowers bend ductility (Fig. 14b). The authors attributed this reduction in ductility to partial decomposition of the metastable β fusion zone microstructure to an extremely fine α_2 microstructure. Hardness values in the HAZ were unaffected by the heat treatment. In particular, Baeslack et al. sought evidence for the β decomposition to an ω phase reported by Strychor et al.96 after heat treatment at 400°C, but found none. They also demonstrated that the ductility of pulsed Nd-YAG laser welds in the Ti-26-11 alloy increases with increasing PWHT temperature, with a bend ductility following PWHT at 850°C being almost equivalent to that of the $\alpha-\beta$ processed base metal. This is probably a result of the microstructural coarsening at higher PWHT temperatures with a corresponding improvement in weld ductility. However, more detailed evaluation of PWHT, especially at higher temperatures, will be required to develop acceptable laser weld mechanical properties.

Baeslack et al.46 and David¹¹⁸ have investigated autogenous tungsten inert gas (TIG) welding of α_2 -Ti₃Al alloys. Baeslack *et al.* reported epitaxial growth of coarse β grains from the HAZ, which had transformed to a fine α_2 microstructure in both the fusion zone and HAZ. The near HAZ structure was both finer and harder than the fusion zone microstructure and no retained β phase was reported. Baeslack¹¹⁴ has proposed that cooling rates of the order of 25 K s^{-1} or slower would be required to generate the optimum $\alpha_2 + \beta$ microstructure and this could necessitate the maintenance of interpass temperatures of about 600°C. Cieslack et al.⁹⁵ have calculated that a higher temperature of about 795°C is required to achieve a cooling rate of 0.1 K s⁻¹, which would produce an equilibrium $\alpha_2 + \beta$ microstructure for similar material. David¹¹⁸ did not conduct a detailed study of the microstructure of TIG welds, but did comment that the alloy was resistant to solidification cracking.

A detailed assessment of the HAZ in TIG welds of a similar alloy has recently also been undertaken by Baeslack *et al.*¹¹⁹ These authors have discriminated between the microstructures observed in the near HAZ and far HAZ. In the near HAZ, where significant β grain growth had occurred, β decomposition on cooling was primarily caused by fine, acicular α_2 phase, with more martensite closer to the fusion boundary. In the far HAZ, only partial transformation to β took place, this being along α_2 grain boundaries and by the nucleation and growth of β transversely across the α_2 grains, with the expected increase in the degree of transformation with an increase in peak temperature.

Cox et al.¹⁰⁹ conducted capacitor discharge resistance welding of an α_2 -Ti₃Al alloy. They reported that the cooling rate was so fast that again the microstructure consisted predominantly of retained β . No cracking was encountered in these welds.

The alloy Ti-25-10-3-1, also known as super α_2 , is a second generation α_2 -Ti₃Al alloy which contains a higher β stabiliser content than Ti-26-11. This higher β stabiliser content, and in particular the presence of slowly diffusing molybdenum, would be expected to promote more sluggish β decomposition kinetics such that a potentially more crack resistant β (B2) microstructure may be produced at the moderate cooling rates experienced during GTA welding. Baeslack and Broderick⁴⁷ investigated the effect of cooling rate on the structure and hardness of a Ti-26-10-3-1 titanium aluminide. They found that the on cooling bcc to hcp phase transformations in Ti-26-10-3-1 closely parallel those in Ti-26-11, but initiate at appreciably longer times. They concluded that the retention of a relatively soft β (B2) microstructure at cooling rates down to 25 K s⁻¹ indicates the potential for producing conventional GTA welds without solid state cracking. Conversely, these slow transformation kinetics will make the practical generation of thermally stable Widmanstatten $\alpha_2 + \beta$ microstructures in fusion weldments very difficult owing to the extremely slow cooling rates required.

Baeslack and Threadgill¹⁰⁷ have performed CO₂ laser welding for a Ti-26-10-3-1 alloy. In earlier work,⁴⁶ the lack of response to etching together with the fairly low maximum hardness (about 375 HK0.5) indicated a substantial amount of retained β in the microstructure, although the increase in the hardness compared to the parent material was an indication of the presence of some α_2 martensite. These lower hardness values confirm the expectation that β to α transformation is more sluggish in the more highly alloyed super α_2 . Baeslack¹¹⁴ has also referred to other preliminary work on CO₂ laser welding of super α_2 , where a predominantly β_2 microstructure was observed, again with extensive solid state cracking, indicating a greater susceptibility to cracking in the ordered β_2 microstucture. The same author has also reported similar experiences in capacitor discharge resistance welding of super α_2 , where again the microstructure consisted of ordered β_2 , and where cracking occurred during cooling. In contrast, Baeslack et al.^{115,116} also reported that no cracking was observed in Ti-26-11 α_2 alloy (1.7 mm thick) welded by pulsed Nd-YAG laser welding, despite the suppression of the β to α transformation. Unfortunately, there are very limited data on the weldability of super α_2 alloys.

Solid state joining of γ -TiAl aluminides. Diffusion bonding is considered to be one of the most suitable joining techniques for γ -TiAl aluminides. For instance, Nakao et al.¹²⁰ successfully demonstrated the potential for diffusion bonding of a binary γ (38 wt-%Al) alloy at temperatures of 1000–1200°C. They reported that reasonable mechanical properties can be obtained with tensile test failure away from the interface at room temperature, although bond line failures occur at elevated temperatures. Post-weld heat treatments led to recrystallisation of the bond, which in





turn improved the high temperature mechanical properties, giving tensile failures away from the bond line. It was also proposed that only limited migration takes place across the interface. However, some migration was induced following PWHT, giving rise to tensile test failures in the base metal at elevated temperatures.

Yan et $al.^{121}$ also reported some success in diffusion bonding of a Ti-45Al alloy, with and without the use of interlayers. They demonstrated that good bond strengths were achieved without interlayers at high bonding temperatures (1200°C) and pressures (<40 MPa). The use of interlayers (titanium and vanadium) produced sound welds, but a PWHT was necessary to optimise the mechanical properties. The improvement of mechanical properties by PWHT is shown in Fig. 15. Attempts to identify an interlayer which would permit TLP bonding failed owing to tendencies to form high temperature eutectics or other stable intermetallics. However, copper based interlayers may prove to be useful.

Later, Yan et al.¹²² investigated solid state bonding of Ti–48Al (at.-%) alloy consisting of γ -TiAl as the matrix and α_2 -Ti₃Al as the second phase with sputter coated interlayers of interest (containing titanium, vanadium, niobium, chromium, and manganese) in a thickness range of $0.5-1.5 \,\mu\text{m}$. It was found that the bondability of titanium aluminide is improved by interlayers of vanadium, chromium, and manganese and that bonding can be carried out at relatively low temperatures or pressures, i.e. 1000°C and 20 MPa. Although the resulting bond line microstructures were different from that of the parent material and the bond properties were relatively poor, a post-bond heat treatment (PBHT) at 1340°C produced a lamellar structure of $TiAl + Ti_3Al$ in the bond region and thus improved the bond properties, including deformability at high temperatures. However, since vanadium, chromium, and manganese all decrease the oxidation resistance of TiAl,49 the oxidation resistance of bonds made with these interlayers may be a potential cause for concern. Yan et al.^{122,123} suggested the use of a niobium interlayer in addition to vanadium, chromium, or manganese to improve oxidation resistance while maintaining the ductility of bonds, since niobium additions to y-TiAl alloys significantly improve its oxidation resistance.49

Yan and Wallach¹²³ have also reported success in diffusion bonding of γ -TiAl. They have pointed out that surface finish, bonding temperature, and pressure are important parameters, as expected. They suggested that solid state bonding of γ -TiAl should be carried out at temperatures of at least 1100°C to obtain joints with acceptable mechanical properties. A rougher surface finish (i.e. with 1200 grit emery paper) rather than a polished

surface should be chosen to increase plastic deformation at the interface and thus to promote recrystallisation at the bond line and in turn greater bond strength. However, an even rougher surface (rougher than 1200 grit finish) is not beneficial since the resulting larger interface voids take longer to remove by the various diffusion processes during bonding, although more local plastic deformation can occur with rougher surfaces. Furthermore, to avoid the use of high temperature and high pressure simultaneously, a two stage bonding process is used which comprises first high pressure at a low temperature for a short time and second low pressure, but at a high temperature for a longer time.

Solid state diffusion bonds produced using 1200 grit surface finish, joined in two stages (1000°C and 40 MPa for 5 min, followed by 1200°C and 5 MPa for 30 min), exhibited the best results. However, the shear strength of the joint was below that of the parent material. The same authors also investigated TLP diffusion bonding of y-TiAl using low melting and high melting alloys. They reported that the low melting filler alloys based on Ti-Cu or Ti-Ni react with the base material and form intermetallic particles at the interface during bonding, leading to void formation during PWHT. In order to avoid this, homogenisation of bonds (or optimisation of properties) has to be carried out in two steps; first, use of a low temperature for a long time until the intermetallic particles dissolve into the base material (i.e. 1020°C for 40 h), and second, use of a high temperature to optimise the microstructure and properties of bond regions (i.e. 1340°C for 40 min). Therefore, these alloys should be used only when bonding at a low temperature is of particular interest.

For TLP bonds made with high melting filler alloys (i.e. V–49Ni (at.-%) or Ti–38Mn (at.-%)), homogenisation at high temperature can be used directly to achieve optimised properties, since no intermetallic particles form during bonding. Hence, the properties of bonds made with these two high melting alloys were better than those of bonds made using low melting alloys. Furthermore, filler alloy elements, such as vanadium and manganese, can significantly improve the ductility of γ -TiAl. The room temperature bend properties (four point bending), namely strength and ductility, of bonds made with a filler alloy of V–49Ni (at.-%) (thickness 1 µm) at 1250°C and 2 MPa for 10 min and homogenised at 1340°C for 1 h were comparable with those of the parent material.

Another success in diffusion bonding of γ -TiAl (~47·3 at.-%Al) has been reported.¹²⁴ Sound bonded joints for mechanical testing without microvoids and oxide films, such as TiO₂ or Al₂TiO₅, on the bonded interfaces were produced at a temperature of 1200°C for 3·84 ks at 15 MPa pressure. However, a PBHT at 1300°C was necessary to optimise the tensile properties of the joint, resulting in fracture in the base material at a temperature of 1000°C.

Cam et al.^{125–128} have recently also demonstrated that both cast and rolled γ -TiAl alloys can be successfully bonded by solid state diffusion bonding. The bonds produced using 1200 grit surface finish exhibited the best results. Defect free bonds were produced without difficulty and recrystallised γ grains with varying sizes were formed at the bond interfaces. For cast γ -TiAl alloy, higher bonding temperatures and pressures provided better results, the best bond quality being achieved by bonding at 1200°C and a pressure of 20 MPa, without PBHT (Fig. 16a). The effect of PBHT was also studied and it was found that the bond strength of bonds produced at lower temperatures (i.e. 975°C) can be improved by heat treatment (Fig. 16b).¹²⁶ For rolled y-TiAl alloy, the highest shear strength of 540 MPa was achieved by bonding at 1000°C using 20 MPa pressure for 5 h, which produced indiscernible bond lines (Fig. 17).¹²⁸ Defect free bonds with reasonable shear strengths (300-440 MPa) could be produced even with pressure as low as 5 MPa for a bonding time of 8 h.



a as bonded at 1100°C under 30 MPa pressure for 1 h; *b* after PBHT at 1340°C for 1 h

16 Micrographs showing bond regions in cast *y*-TiAl alloy: arrows indicate bond line¹²⁶

Electron beam diffusion bonding of a Ti-48Al-2Cr-2Nb alloy was also investigated at TWI.¹²⁹ Defect free bonds were achieved and no obvious change in hardness with distance from the bond line was observed. However, no mechanical data were reported.

Inertia friction welding is being considered as another alternative solid state joining technique for γ -TiAl aluminides. However, work¹³⁰ on inertia friction welding of Ti-48Al-2Cr-2Nb (at.-%) alloy showed that cracking occurred in the outer periphery and central heat and deformation zone (HDZ). No PWHT was carried out in this work.

Initial attempts at linear friction welding of γ -TiAl alloys have been made at TWI,¹⁰⁷ but the welds showed extensive cracking. However, the joint quality was generally reasonable, with extensive grain refinement in the bond owing to dynamic recrystallisation. In an attempt to eliminate cracking, further welds were made with lower friction and forge forces and sound welds could be produced.¹²⁹ Horn¹³¹ has also claimed that crack free welds in 6 and 8 mm diameter bars of an alloy believed to be Ti–48Al were produced by rotary friction welding, but he gave no detailed welding



17 Micrograph showing bond region in rolled y-TiAl alloy bonded at 1000°C under 20 MPa pressure for 5 h: arrows indicate bond line¹²⁸

conditions. A slight hardness increase across the weld was observed, as shown in Fig. 18. Furthermore, success was also reported in joining the same material to an X55CrMnNiN-22-9-5 austenitic stainless steel by the same process, although attempts to weld the aluminide to an X22CrNi17 ferritic steel led to extensive interface cracking as a result of very high hardness levels in the steel.

Fusion processes for γ -TiAl aluminides. Patterson et al.^{79,132} have studied autogenous electron beam welding of a near γ -TiAl composite, Ti–48Al (at.-%) containing 6.5 vol.-%TiB₂ (XD composite), and reported a significant susceptibility to solid state cracking. The authors suggested that this could be overcome by reducing the cooling rate to less than 300 K s⁻¹ or by applying a preheat at 250°C. They observed a significant increase in the weld zone hardness, with higher hardness levels produced at higher welding speeds owing to the higher cooling rates.

Similar studies on a binary Ti–48Al alloy¹³² demonstrated that a slower cooling rate of about 100 K s⁻¹ was required to avoid solid state cracking. Patterson *et al.*^{79,132} also reported some microstructural evaluations of electron beam welds both in the composite material and in the binary alloy. The microstructure of the fused composite material was not studied conclusively, although it was reported that an acicular phase rich in titanium and boron was observed. In the binary alloy,¹³² coarsening of the lamellar $\alpha_2 + \gamma$ microstructure occurred in the HAZ. The authors could not define the exact weld metal microstructure in the composite alloy, although it was suggested that the predominant phase was metastable α_2 with some γ colonies. They also suggested that solidification processes are dominated by epitaxial growth.







19 Ni-Al phase diagram

Electron beam weldability of γ -TiAl alloys was also investigated at TWI.¹²⁹ It was found that welds both with and without preheat showed extensive cracking, although the welds produced with preheating at 500 or 625°C exhibited less extensive transverse cracking. The rapidly cooled microstructure obtained from the run without preheat was predominantly equiaxed, whereas the slower cooled runs exhibited a predominantly lamellar duplex $\alpha_2 + \gamma$ microstructure.

In unpublished work at TWI,¹⁰⁷ the CO₂ laser welding of a Ti–48Al–2Cr–2Nb alloy was investigated. Initial trials resulted in extensive cracking away from the weld and some porosity was also noted at the lower welding speeds. No detailed study of the weld microstructure was conducted, although it was suggested that it was possibly a mixture of two phases, which were almost certainly α_2 and γ . However, further microstructural study is required to characterise these deposits fully. It was also noted that there was a significant increase in hardness in the fusion zone and this appeared to be more pronounced at higher welding speeds. Although no detailed microstructural evaluation was carried out, this was suggested to be a result of the formation of α_2 martensite.

General comments on titanium base intermetallics

The successful integration of titanium aluminides into gas turbine systems requires their joining both to themselves and to conventional titanium alloys. Appropriate welding procedures to join titanium aluminides have yet to be established in order to fully use them commercially. Diffusion bonding has been shown to be a successfully applicable joining technique for both α_2 and γ based alloys. The SPF–DB technique is also believed to be promising for production of hollow turbine blades from γ -TiAl alloys. Further work is, however, needed to provide more mechanical data and detailed evaluation of microstructures remain to be completed, particularly for fusion welding processes of γ -TiAl based alloys. The SPF–DB and laser (CO₂ and Nd-YAG) welding of γ -TiAl will be investigated at the GKSS Research Center. Two industrial projects have already been established to work on the topic.

Joining of other intermetallics

Physical metallurgy of nickel aluminides

A number of excellent reviews on the physical metallurgy and mechanical properties of nickel and iron aluminides can be found in the literature, the most recent being by Liu and Kumar,¹³³ Miracle,¹³⁴ Noebe *et al.*,¹³⁵ and Threadgill and Dance.¹²⁹

Several intermetallics are formed between nickel and aluminium, namely Ni₃Al, Ni₅Al₃, Ni₂Al₃, and NiAl (Fig. 19). Of these intermetallic compounds Ni₃Al and NiAl are of commercial interest. The most familiar intermetallic in the Ni–Al system is Ni₃Al, which is also referred to as γ' and has a fcc (L1₂) structure, which is the strengthening phase in commercial nickel based superalloys. The compound exists over a narrow composition range and has a melting point of 1395°C. It can be used in the temperature range of the superalloys, i.e. up to 1100°C, which is 80% of the melting point of Ni₃Al, so it can not be expected to extend this temperature range.

The γ' -Ni₃Al intermetallic is highly ductile in the form of single crystals but extremely brittle in polycrystalline form and its strength exhibits an anomalous temperature dependence. The reason for the brittle behaviour was until recently believed to be intrinsically weak grain boundaries in polycrystalline γ' -Ni₃Al.¹³³ Early studies on its mechanical behaviour established that polycrystalline γ' -Ni₃Al generally fails by intergranular fracture with little or no ductility owing to its intrinsically weak grain boundaries. However, more recent studies^{136,137} have shown that addition of a few parts per million of boron can dramatically improve ductility by becoming segregated to grain boundaries and improving their cohesion. Other elements, in particular iron, chromium, and zirconium, can also improve the tensile ductility of γ' -Ni₃Al at room temperature.



20 Temperature dependence of 0.2% flow stress of crystalline y'-Ni₃Al (Ref. 147)

However, recent studies by George et al.¹³⁸⁻¹⁴² have demonstrated that the grain boundaries may be intrinsically ductile in polycrystalline γ' -Ni₃Al and that the cause of room temperature brittleness in polycrystalline form may be related to environmental effects, in particular moisture, and to microcracks introduced during processing. These authors first reported that the grain boundaries in boron free γ' -Ni₃Al containing 0.26%Zr are not intrinsically brittle, which means that the principal role of boron in ductilising γ' -Ni₃Al may be related to the suppression of environmental effects.¹³⁸ Room temperature ductilities of 6-9% in water, 11-13% in air, and 48-51% in oxygen were observed, indicating that moisture plays an important role in embrittlement of grain boundaries. However, the role of zirconium in ductility has not been investigated. Another study by Liu¹⁴³ on grain boundary fracture of binary γ' -Ni₃Al alloy showed that the elimination of moisture by testing in dry oxygen does not suppress brittle fracture and lead to extensive ductility. These authors also pointed out that boron eliminates environmental embrittlement and that both boron and zirconium improve the ductility of γ' -Ni₃Al (Ref. 139) by strengthening grain boundaries.

George et al. achieved elongation of 23.4% in an equiaxed polycrystalline boron free γ' -Ni₃Al in ultrahigh vacuum,¹⁴⁰ which is a clear indication of intrinsic ductility of polycrystalline γ' -Ni₃Al. Moreover, the ductility increased systematically with increasing vacuum. However, the fracture mode was still intergranular in the absence of moisture and strengthening would be needed. Other recent work by George et al.¹⁴¹ showed that boron (when added in sufficient quantities, i.e. 100 wt-ppm) effectively suppresses environmental embrittlement in γ' -Ni₃Al both in air and in water. At low boron levels (50 wt-ppm), boron eliminates environmental embrittlement only in air. The ductility is strongly strain rate sensitive in water, increasing strain rate alleviating environmental embrittlement. Furthermore, a sufficient amount of boron changes the fracture mode from intergranular to transgranular. Cohron et al.¹⁴² also studied the effect of low pressure hydrogen on the grain boundary brittleness of γ' -Ni₃Al. It was reported that low pressure hydrogen does not embrittle polycrystalline γ' -Ni₃Al, suggesting that molecular hydrogen does not dissociate very efficiently into atomic hydrogen on γ' -Ni₃Al surfaces. Furthermore, moisture free hydrogen is not as harmful to the ductility of γ' -Ni₃Al as the water vapour in air. It was also observed that the fracture mode was predominantly transgranular and elongation of more than 40% was achieved in the absence of any hydrogen induced embrittlement. Lee et al.144 also studied the effect of hydrogen and water pressures in the range of 10^{-3} -10³ Pa on tensile ductilities of undoped and boron doped γ' -Ni₃Al. It was reported that boron doped γ' -Ni₃Al is insensitive to water



21 Effect of boron content on HAZ cracking tendency in γ' -Ni₃Al autogeneous electron beam welds¹⁵⁰

vapour, while undoped γ' -Ni₃Al is severely embrittled by water vapour at pressures greater than about 10^{-3} Pa.

The NiAl intermetallic exists over a much wider composition range compared with γ' -Ni₃Al and has a bcc (B2) structure with a melting temperature of 1638°C. The melting point of NiAl is about 300°C above those of the superalloys. It also has a lower density, a higher elastic modulus, and a higher thermal conductivity than γ' -Ni₃Al. Furthermore, it possesses excellent oxidation resistance. Thus, NiAl has been regarded as a potential substitute for superalloys for high temperature applications for more than 40 years. However, it exhibits low room temperature ductility and poorer creep performance than the best superalloys. Although some ductility has been achieved by boron doping, NiAl based polycrystalline alloys with sufficient room temperature ductility and creep performance are considered to be unlikely.

Joining of nickel aluminides

There has been great interest in the development of γ' -Ni₃Al for high temperature engineering applications (including steam and gas turbine components, diesel engine components, and a variety of structural components in energy conversion systems) since the discovery that its yield strength unusually increases with temperature up to 700°C (0.58 of the melting temperature), as shown in Fig. 20.^{145–147} The discovery of ductilisation of γ' -Ni₃Al alloy development, including study of hot workability, mechanical properties, oxidation and corrosion behaviour, and weldability. The weldability aspect in particular is considered to be of some commercial value. An excellent review of the existing data on joining of nickel aluminides was conducted by Ash *et al.*¹⁴⁸

The first work concerning the weldability of $Ni_3Al + B$ alloys containing iron¹⁴⁹ showed that iron additions increased susceptibility to fusion zone and HAZ cracking during autogenous GTA welding. This susceptibility to cracking in these alloys was attributed to intrinsically weak grain boundaries. However, later work¹⁵⁰ demonstrated that the cracking behaviour was affected by the boron content of the alloys (*see* Fig. 21) and the best cracking resistance was obtained for a boron content of 0.02 wt-%. Increasing boron content above 0.02 wt% increased the hot cracking tendency.

It was also found out that the addition of 10.7 wt-%Fe (Ref. 151) and 1.7 wt-%Hf (Ref. 152) improved the resistance to HAZ cracking. However, levels above 10.7 wt-% tended to promote formation of the β -NiAl. There was no clear indication that intergranular β formation increased cracking tendency, although β is usually considered as an undesirable microconstituent owing to its intrinsic

brittleness. Autogenous GTA welds made on as cast γ' -Ni₃Al with hafnium additions showed severe HAZ cracking as a result of hafnium, aluminium, and nickel microsegregations in the original solidification structure. In contrast, defect free autogenous electron beam and GTA welds were made on wrought sheet and powder metallurgy compacts with the same nominal composition as a result of the absence of microsegregation.

More recently, Santella and Sikka^{153,154} investigated the weldability of cast γ' -Ni₃Al based alloys (IC221 types) containing 7.7%Cr, 1.5%Mo, and 0–3%Zr using TIG welding with or without a 3.0 wt-%Zr filler. It was reported that although increasing zirconium levels reduce the susceptibility to cracking, most γ' -Ni₃Al based alloys exhibit marginal resistance to solidification cracking. Autogenous welds showed a greater susceptibility to cracking at lower zirconium levels (i.e. 1.5%Zr) could only be welded crack free by using a high zirconium filler. In work at TWI,¹²⁹ electron beam weldability of cast γ' -Ni₃Al alloy was studied. However, the welds contained significant numbers of solidification cracks. The number of cracks was reduced by reducing the welding speed, but it did not eliminate cracking.

Schulson¹⁵⁵ has pointed out that the larger the grains, the higher is the stress concentration factor in the vicinity of the boundary and the lower is the applied stress necessary to nucleate a crack. This implies that the HAZ cracks caused by welding residual stress would be fewer in number for fine grained intermetallic compounds than for coarse grained ones. Chen and Chen¹⁵⁶ demonstrated that the grain size of γ' -Ni₃Al has an influence on the resistance to HAZ cracking. They reported that it is possible to achieve crack free laser welds in γ' -Ni₃Al containing 200 and 500 ppm boron. They also reported that a grain size of about 20 μ m or less for the γ' -Ni₃Al containing 200 ppm boron and of less than 18 μ m for the γ' -Ni₃Al containing 500 ppm boron should be required to obtain weldments free from HAZ cracking. Although significant weld cracking problems were reported for boron doped γ' -Ni₃Al alloys for welding speeds above 13 mm s⁻¹ (Ref. 149), butt welds made with welding speeds up to 356 cm min^{-1} have been performed by Chen and Chen¹⁵⁶ on fine grained (12–15 µm) γ' -Ni₃Al specimens containing 500 ppm boron. However, no mechanical data have been reported.

Molian *et al.*¹⁵⁷ studied the \dot{CO}_2 laser welding of cast γ' -Ni₃Al containing boron and observed that cracking occurred in the fusion zone and HAZ. They reported that the hardness of the weld zone was substantially higher than that of the base material, which was attributed to the highly concentrated heat input of the laser beam resulting in refinement in the grain structure in the fusion zone and the HAZ. However, they also reported that room temperature tensile properties of the laser beam weldments were comparable with properties of the base material.

Although some γ' -Ni₃Al alloys are readily weldable, a complex interaction between hot ductility and strength determines the weldability of individual alloys based on material properties and specific welding parameters. Heat affected zone cracking was observed in γ' -Ni₃Al with 10 wt-%Fe and 0.05 wt-%B (IC25), which had zero ductility above 800°C. Another γ' -Ni₃Al based alloy, containing 10 wt-%Fe and 0.02 wt-%B (IC103), which recovered some ductility at higher temperatures, was not subject to HAZ cracking. Based on these observations, the third γ' -Ni₃Al based alloy, containing 1.5 wt-%Hf and 0.02 wt-%B (IC50), which demonstrated hot ductility behaviour similar to that of IC25, was expected likewise to be susceptible to HAZ cracking. However, this was not the case and was believed to be a result of the higher thermal conductivity of IC50 leading to shallower thermal gradients, so that the imposed thermal stress was less severe and never exceeded the fracture stress.



22 Effect of APD structure on hot ductility of Ni₃Al + 8 at.-%Cr alloy^{148,158}

A γ' -Ni₃Al alloy, when suitably processed either to decrease the severity of thermally induced welding stresses, limit the zero ductility range, or increase fracture stress over the range of temperatures encountered in the HAZ, is more resistant to HAZ cracking. The first of these is most readily accomplished by using a preheat or post-heat and by increasing the heat input. Alloying and heat treatment are the only means of improving ductility and fracture stress.

Chromium additions to γ' -Ni₃Al alloys have proven beneficial for both of these latter goals. Work conducted by Edwards *et al.*¹⁵⁸ has demonstrated that the presence of an antiphase domain (APD) structure in Ni₃Al + Cr alloys improves hot ductility and weldability. This APD structure in the alloy containing 8 at.-%Cr can be produced by heating to 1270°C and subsequent oil quenching. The presence of an APD structure is effective in dispersing slip and reducing the tendency for intergranular fracture in these alloys, since this is the fracture mode at higher temperatures. In this alloy, the ductility can be improved over a useful temperature range below 800°C, as shown in Fig. 22.^{148,158}

Recently, linear friction welding of cast γ' -Ni₃Al alloy was also studied at TWI.¹²⁹ However, difficulties were experienced with cracking of the parent material, although the weld region was defect free. Cracking was attributed to the propagation of small casting defects under the very aggressive mechanical vibrations experienced by the material during the process. Results indicated that the linear friction welding method has potential for defect free welding of γ' -Ni₃Al. Further work is, however, needed to demonstrate this.

Transient liquid phase diffusion bonding (TLPDB) has also recently been demonstrated to be a viable method of joining NiAl based alloys.^{159,160} Gale and Orel¹⁵⁹ satisfactorily bonded NiAl based alloy using a Ni-4·5Si-3·2B (wt-%) melt spun ribbon (AWS Bni-3) interlayer. Strum and Henshall¹⁶⁰ bonded NiAl by depositing pure nickel and aluminium on two opposing surfaces of a joint by electron beam evaporation, heating to 800°C in vacuum, and then holding for 4 h at 1200°C under a partial pressure of argon to reduce evaporation losses. Single phase NiAl was formed across the joint. However, variation in composition was not detected and, moreover, no mechanical data were reported.

Physical metallurgy of iron aluminides

The binary Fe–Ni phase diagram is still not well defined and there are several versions in the literature. Although a number of intermetallics exist in the Fe–Al system (Fig. 23), Fe₃Al and FeAl are the compounds of industrial interest. However, the phase boundaries of Fe₃Al and FeAl are not accurately known, since these compounds have similar crystal structures; Fe₃Al is also an ordered solid solution alloy with a bcc (DO₃) structure, whereas FeAl exhibits a bcc (B2) structure.



23 Fe-Al phase diagram

Iron based intermetallics have attractive electrical, magnetic, and corrosion resistance properties. Other features, such as the low cost of iron and aluminium and the low density and adequate strength at temperatures below $600^{\circ}C$ (Fig. 24), make Fe₃Al alloys potential candidates for structural applications. Furthermore, they do not contain large quantities of more strategic elements. However, their low ductility at room temperature, a sharp reduction in their strength above $600^{\circ}C$, and poor creep performance impeded their use. Binary Fe₃Al alloys have been found to be susceptible to embrittlement by water vapour at room temperature.¹⁶¹

Iron based intermetallics can be alloyed to improve room temperature ductility and it is possible to produce alloys with reasonable properties. This subject has been discussed in detail in a review by Liu and Kumar.¹³³ Studies have shown that increasing the purity of Fe_3Al changes the



24 Hot deformation behaviour of iron aluminide alloy FA-129 with composition Fe-0.2C-5Cr-28Al-0.5Nb: initial condition B2 structure (Ref. 148)

failure mode from intergranular to transgranular.^{162,163} In addition, ternary alloying additions, such as boron, zirconium, and molybdenum, improve the ductility of these alloys.^{164–168} The room temperature ductility of FeAl can also be improved by grain refinement (which is also beneficial to γ' -Ni₃Al when the grain structure is stabilised with TiB₂ particles). High temperature properties can also be improved by alloying with molybdenum, niobium, zirconium, titanium, and TiB₂.

Joining of iron aluminides

The weldability of Fe₃Al alloys is very sensitive to composition and welding parameters.¹⁶⁹ Furthermore, excessive fusion zone and HAZ grain growth, which can increase cracking sensitivity, has been observed for Fe₃Al GTA weldments.¹⁶⁹ Three possible methods have been suggested for improving cracking resistance in Fe₃Al weldments:

- (i) removal of water vapour from the environment (which is only a problem in GTA welding)
- (ii) alloying to decrease yield stress, increase fracture stress, and enhance cross-slip
- (iii) refining of slip path length using grain size refinement or an APD structure.

The weldability of a variety of binary and more complex Fe_3Al based alloys containing chromium, niobium, manganese, and boron in various combinations, using electron beam and TIG welding, has been studied by David *et al.*^{169,170} Of all the alloys investigated, alloy FA-129 (Fe-15·9Al-5·5Cr-1·0Nb-0·05C (wt-%)) had the best welding characteristics.¹⁷⁰ It was also demonstrated that defect free welds could be produced in this alloy. High cooling rates created fine disordered B2 domain structures in both the HAZ and fusion zone which can result in material which is more resistant to cracking. Therefore, current research is focused on correlating the effects of cooling rate on domain size and cracking resistance.

David and Zacharia¹⁷¹ conducted further welding studies of Fe₃Al based alloys and reported that a wide range of compositions could be crack free welded by using elec-



tron beam and TIG welding. The alloys contain about 5.5 wt-%Cr, about 1 wt-%Zr, 0.01 wt-%B, and 0.05 wt-%C in four different combinations. All the alloys studied were demonstrated to be crack free welded using electron beams. However, the use of TIG welding always produced cracks at high travel speeds for all the alloys, even at lower travel speeds for boron containing alloys. Studies on the electron beam and TIG welding of Fe₃Al based alloys (Fe-8Al + Cr (wt-%)) at TWI¹²⁹ also showed similar results. Crack free welds were produced by electron beam welding even without use of a preheat. It was observed that the weld metal grains grew epitaxially on HAZ grains and that the fusion zone grains were equiaxed and much finer than the parent material grains. Marginally lower hardness values were observed in the fusion zone (Fig. 25a). Ultimate tensile strength values of 600 MPa and elongations of 2-4% were obtained at room temperature. Fracture occurred predominantly at the weld centreline and the fracture mode was intergranular. Crack free welds were also produced by TIG welding (with a travel speed of 105 mm min^{-1}) without the use of a preheat. However, higher travel speeds $(120 \text{ mm min}^{-1})^{-1}$ resulted in transverse cracks. Microstructures similar to those obtained in electron beam welding were observed. The major differences were the increased width of the weld when using TIG welding and the 5-10 times larger grain size in the fusion zone. The increased weld width (wider softened region) is also seen in the hardness profile of the TIG weld (Fig. 25b). Ultimate tensile strength values of ~ 550 MPa and elongations of $\sim 7\%$ were obtained at room temperature. Failure invariably took place in the fusion zone, at the centre, and the fracture mode was predominantly intergranular.

Wilson et al.¹⁷² also demonstrated that capacitor discharge spot welding can successfully be used to weld Fe-24Al (at.-%) alloy. However, no detailed microscopy or mechanical property determinations were conducted.

Maziasz et al.¹⁷³ studied the effect of compositional variations on the TIG weldability of FeAl based alloys containing 0.24 at.-%B for room temperature ductility. They have reported that weldable FeAl alloys can contain small amounts of molybdenum and zirconium. However, boron is very detrimental to weldability of FeAl based alloys, since it causes hot cracking. It is also not known whether additions of boron in smaller quantities could be tolerated. Further work is needed to clarify this aspect.

General comments on nickel and iron base intermetallics

Ordered intermetallic alloys, such as γ' -Ni₃Al, NiAl, Fe₃Al, and FeAl have great potential for applications at elevated temperatures. Some of these alloys can be successfully welded, while others are prone to cracking either during or after welding. Many factors, such as composition and welding parameters and processes, can play an important role in the weldability of nickel and iron aluminides. In a broad sense, the weldability of nickel and iron aluminides is limited by either subsolidus or a combination of subsolidus HAZ and fusion zone cracking. These phenomena are attributed to inherent low ductility, excessive grain growth, or environmental embrittling mechanisms. Both micro- and macroalloying may improve weldability. The role of APD substructures, which have been shown to improve hot ductility and weldability in chromium modified γ' -Ni₃Al alloys, remains to be investigated for iron aluminides. Weldability of ductile intermetallics shows great promise, although a full understanding of their welding metallurgy is lacking. There is also a very limited number of mechanical data reported in the literature. Further work is needed to fully understand the welding of these materials.

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