Diffusion Brazing of Nickel Aluminides

Major anomalies in the form of borides appear on the Ni side of NiAl/Ni-Si-B/Ni joints, presenting a major deviation from conventional predictive models

BY S. V. OREL, L. C. PAROUS AND W. F. GALE

ABSTRACT. NiAl is a promising candidate material for high-temperature applications. However, NiAl suffers from poor low-temperature ductility and toughness. Thus, in many potential applications, NiAl would have to be used locally, in combination with Ni-based alloys, rather than to form entire components. Hence, suitable technologies are required for NiAl to Ni-based alloy joining. In view of the poor low-temperature ductility and strong alumina-forming tendency of NiAl, diffusion brazing seems to be the most suitable technology for joining NiAl to itself and to Ni-based alloys.

This paper examines the diffusion brazing of NiAl to Ni using Ni-Si-B interlayers and draws comparisons with previous work by authors on NiAl/Ni-Si-B/NiAl and Ni/Ni-Si-B/Ni diffusion brazing. The progression of micro-structural development in the NiAl/Ni-Si-B/Ni joints is compared with that expected from standard models of the diffusion brazing process in which dissolution of the substrate material, isothermal solidification and solid-state homogenization occur sequentially. Evidence is presented that, while events on the NiAl side of the NiAl/Ni-Si-B/Ni joints are not incompatible with standard diffusion brazing process, major anomalies occur on the Ni side of the joint. These anomalies involve the formation of borides, seemingly at the brazing temperature, when that temperature for the ternary Ni-Si-B liquid is below the Ni-B binary eutectic temperature and extensive liquation of the Ni substrate when the brazing temperature is above the Ni-B binary eutectic temperature. Isothermal solidification of the NiAl/Ni-Si-B/Ni joints is dominated by epitaxial growth of the Ni substrate into the joint and is far more rapid than in the case of NiAl/Ni-Si-B/NiAl joining. The origins of these differences are discussed.

S. V. OREL, L. C. PAROUS and W. F. GALE are with the Materials Engineering Program, Auburn University, Auburn, Ala.

KEY WORDS

Diffusion Brazing
Nickel Aluminides
Ni-Si-B Interlayers
Microstructural Dev.
Metallography
Sustrate Dissolution
Isothermal Solid.
Homogenization
Boride Formation
Boron Diffusion

Introduction

The intermetallic compound NiAl possesses an ordered B2 (body centered cubic based with a CsCl-type superlattice) crystal structure (Ref. 1). NiAl remains highly ordered up to its melting temperature (1638°C for Ni-50 at.-% Al, Ref. 2) and is characterized by a wide range of stoichiometry. Formation of continuous surface alumina layers allows NiAl to withstand highly oxidizing environments (Ref. 3). The density of NiAl containing 50 at.-% Ni is 5950 kg/m^3 (Ref. 4), which is approximately two-third that of Ni-based superalloys and the thermal conductivity of NiAl (70–80 W m^{-1} K^{-1}, Ref. 5) is almost eight times larger than for many Ni-based alloys (Ref. 4). These properties would be attractive for high-temperature applications in aggressive environments, such as gas turbine engines (Ref. 6). However, NiAl has poor low-temperature ductility and toughness (Ref. 7), and these characteristics impose limitations on potential applications. In many cases, NiAl would need to be employed locally within structures that are predominantly composed of conventional Ni-based superalloys.

Applications involving both NiAl and superalloys imply a requirement for suitable NiAl-superalloy joining technologies. Many common joining processes, such as fusion welding, diffusion welding or friction welding, are poorly suited to the joining of NiAl (due to the poor low-temperature ductility and strong alumina-forming tendency of this material). In contrast, diffusion brazing is conducted under isothermal conditions at relatively low temperatures and is tolerant of surface oxide layers. Hence, there has been some interest in diffusion brazing of NiAl based materials (Refs. 8–10).

Diffusion brazing of NiAl to NiAl can be accomplished by the use of Ni interlayers or by *in-situ* reaction of Ni and Al within the joint clearance. However, the high brazing temperatures required for these techniques are not tailored for joining of NiAl to superalloys. Furthermore, processes involving *in-situ* reactions are not readily compatible with capillary joint filling and therefore suffer from geometrical constraints. Hence, an investigation is underway of the adaptation of conventional Ni-based alloy joining

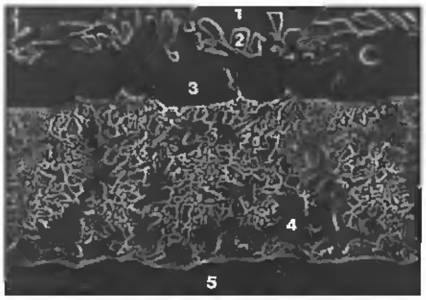

Fig. 1 — Cross-section of NiAl/Ni-Si-B/Ni joint after 5 min holding at a temperature of 1065°C. 1 — Ni substrate; 2 — borides; 3 — ingrown solid; 4 — eutectic; 5 — NiAl substrate.

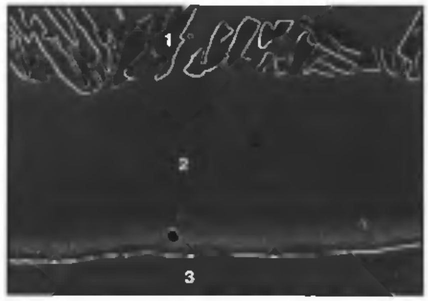

Fig. 2 — Cross-section of NiAl/Ni-Si-B/Ni joint after 2 h holding at a temperature of 1065°C. 1 — borides; 2 — eutectic free joint; 3 — NiAl substrate.

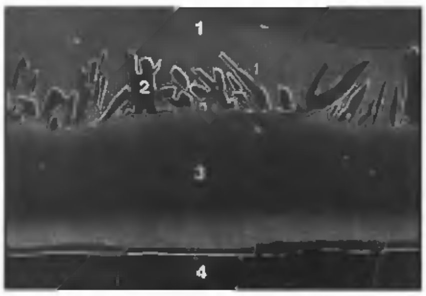

Fig. 3 — Cross-section of NiAl/Ni-Si-B/Ni joint after 6 h holding at a temperature of 1065°C. 1 — Ni substrate; 2 — borides; 3 — eutectic-free joint; 4 — NiAl substrate.

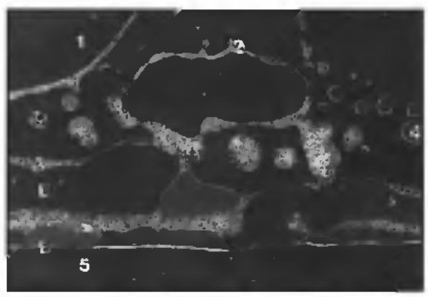

Fig. 4 — Cross-section of NiAl/Ni-Si-B/Ni joint after 20 min brazing at 1150°C. 1 — Ni substrate; 2, 3 — eutectic; 4 — globular eutectic deposits; 5 — NiAl substrate. Line D-D corresponds to the original joint clearance.

technology to the fabrication of joints between NiAl-based materials and Ni-based alloys. In view of the current rapid changes in the design of NiAl-based materials, the present paper concentrates on the fundamental mechanisms of joining in a NiAl/Ni-Si-B/Ni model system. The progression of diffusion brazing is considered with respect to microstructural development in the joint region. The paper discusses differences between NiAl/Ni-Si-B/Ni joints (examined experimentally in the present work) and NiAl/NiSi-B/NiAl and Ni/Ni-Si-B/Ni joints (studied in previous investigations by the authors (Refs. 11–13).

Experimental Technique

Investigation of diffusion brazing of NiAl to Ni was carried out using cast, near stoichiometric NiAl (Ni-48 at.-% Al) with a grain size of around 150 µm, and commercial purity Ni (99.5 wt-% Ni). The brazing filler metal was a 51-µm-thick melt-spun amorphous metallic foil conforming to the AWS BNi-3 specification (Ni-4.5 wt-% Si-3.2 wt-% B) and having a solidus temperature of 984°C (1803°F) and a liquidus temperature of 1054°C (1929°F). NiAl/Ni-Si-B/Ni joints were produced using 2.5-mm (0.1-in.) thick NiAl and Ni substrates with a 1000-grit SiC finish. Each substrate had a faying surface area of 245 mm^2 (0.38 in.^{2}).

To diminish the effect of heating rates on the development of the joining process at the early stages of brazing, a Gleeble 1500 system was used for fabrication of short brazing time joints (0–S min duration). In this system, the sample is resistance heated by the application of an electric current directly to the sample. Brazing was conducted under a 10^{-2} Pa (10^{-4} mbar) vacuum atmosphere at temperatures of 1065°C (1949°F) and 1150°C (2102°F) for times ranging from zero (heating only) to 5 min. Fifty-µm-thick tungsten spacers were inserted between the faying surfaces (bracketing the brazing foil) to maintain a constant joint clearance. The use of a constant joint clearance provided a reference for the accurate location of joint microstructural features. With the joint geometry employed, a heating rate of 14°C/s (25°F/s) and a cooling rate of 5°C/s (9°F/s) were obtained in the Gleeble system. Load control was employed to maintain an applied pressure of 0.4 MPa.

For longer brazing times (20 min to 21 h at 1065° and 1150°C), brazing was conducted in a 10^{-2} Pa vacuum furnace with radiant heating. A heating rate of 2°C/s (3.6°F/s) and a cooling rate of 1.5°C/s (2.7°F/s) were used (these values represent the maximum heating and cooling rates that could be achieved with the furnace and specimen geometry employed). These runs employed a deadload of 500 g (1.35 lb). To diminish heat transfer between the specimen and the dead load, alumina spacers were placed between the load and the joint assembly. In the case of both the radiant heated and Gleeble brazes, the temperature during brazing was monitored by a thermocouple spot welded to the sample.

The progression of diffusion brazing was studied by characterization of the microstructure of joints after cooling to room temperature. Cross-sections of joints were prepared for metallographic examination. These cross-sections were subjected to electrolytic etching at 3 V in a solution consisting of 30 vol-% of acetic acid, 30 vol-% of lactic acid, 20 vol-% of hydrochloric acid, 10 vol-% of nitric acid, and 10 vol-% of distilled water. The microstructure of the joint region was studied using light microscopy (LM) and scanning electron microscopy (SEM). Joint compositional profiles were determined using SEM based energy-dispersive x-ray spectroscopy (EDS).

Results and Discussion

In this section, microstructural development in NiAl/Ni-Si-B/Ni joints is discussed and compared to the NiAl/Ni-Si-B/NiAl and Ni/Ni-Si-B/Ni systems and to standard models of the diffusion brazing process. Microstructural development in the NiAl/Ni-Si-B/Ni joints (Figs. 1–4) is discussed as a function of brazing temperature and holding time.

Comparison of the NiAl/Ni-Si-B/Ni and NiAl/Ni-Si-B/NiAl systems.

In previous work by the authors, it was reported that the progression of diffusion brazing in NiAl to NiAl joints made with Ni-Si-B interlayers (Ref. 12) was not incompatible with standard models of the diffusion brazing process (Refs. 14, 15). These models consider diffusion brazing to progress through three sequential stages. These three stages are as follows:

1) *Dissolution of the Substrate.* Dissolution of the substrate material into the joint occurs after melting of the interlayer and brings the compositions of the liquid and adjacent solid phases to those of the liquidus and solidus, respectively. These compositions result in the establishment of local equilibrium between the liquid and adjacent solid phases and hence remain fixed during the subsequent isothermal solidification stage. The extent of substrate dissolution required to

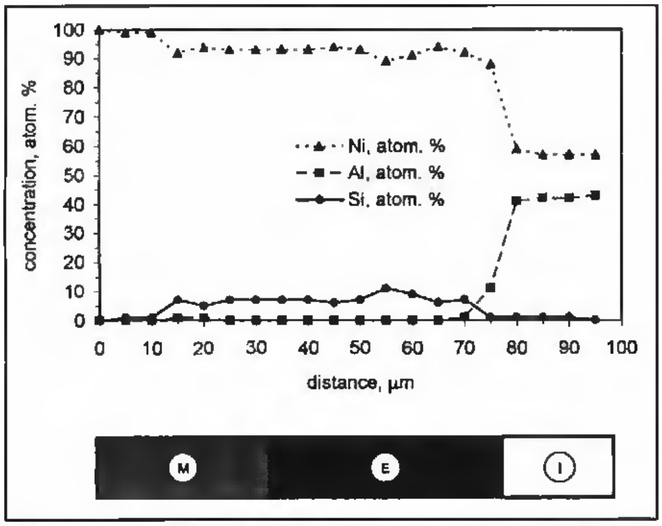

Fig. 5 — Compositional profile for NiAl/Ni-Si-Bl/Ni joint after 0 min holding at 1065°C. M — substrate Ni; E — eutectic; I — substrate NiAl.

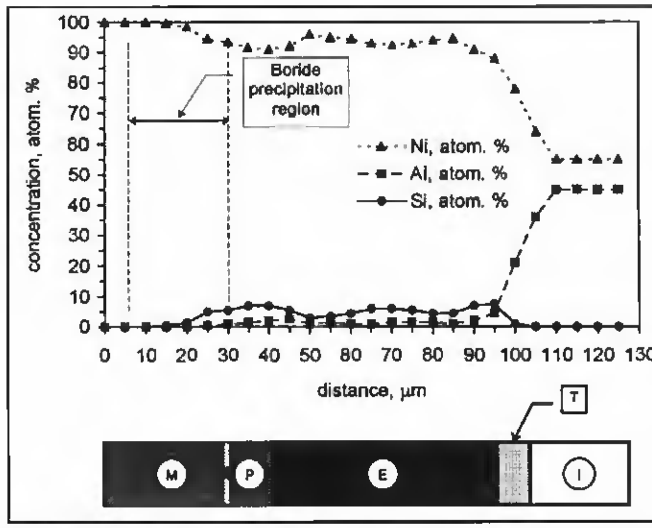

Fig. 6 — Compositional profile for NiAl/Ni-Si-B/Ni joint after 5 min holding at 1065°C. M — substrate Ni; P — ingrown proeutectic Ni; E — eutectic; I — substrate NiAl.

establish local equilibrium depends on the brazing temperature and the shape of the filler-substrate phase diagram.

2) *Isothermal Solidification.* Following the dissolution stage, diffusion of (melting point depressant) solute from the liquid into the substrate results in advance of the solid phase into the joint. This process continues until the liquid is eventually entirely removed.

3) *Homogenization.* When solidification is complete, the residual gradient in solute concentration between the joint line and substrates is removed by solid-state diffusion of the solute into the bulk substrate material.

The extent to which these three processes are applicable to NiAl/Ni-Si-B/Ni joints will now be discussed.

In fixed (50-µm) joint clearance NiAl/Ni-Si-B/NiAl diffusion brazements, a rapid increase with brazing time in the aluminum content of the eutectic was observed (for example, the as-placed filler metal was aluminum-free, whereas, after 1 min at 1065°C, the eutectic was observed to have average aluminum content of 6 at.-%). These observations suggest that dissolution of the NiAl substrates into the liquid was both rapid and occurred to a significant extent.

Compositional profiles obtained as a function of holding time at a brazing temperature of 1065°C in the present investigation of NiAl/Ni-Si-B/Ni brazements are shown in Figs. 5–10. In the NiAl/Ni-Si-B/Ni joints with a 50-µm fixed joint clearance, a rapid increase in the aluminum content of the eutectic was observed. For example, after 5 min holding at a brazing temperature of 1065°C (Fig. 6), the average aluminum content of the eutectic was around 2 at.-% (the BNi-3 filler metal was initially aluminum-free). The aluminum content of the eutectic was lower for the NiAl/Ni-Si-B/Ni joints than for the NiAl/Ni-Si-B/NiAl joints. For example, after 20 min holding time at 1065°C the aluminum concentration in eutectic was around 12 at.-% for the NiAl to NiAl joints compared to 6 at.-% for the NiAl to Ni joints held for 20 min at 1065°C (see Ref. 12, Fig. 7). However, it should be born in mind that in the NiAl/Ni-Si-B/Ni joints there was only a single aluminum source, as compared to two sources in the NiAl/Ni-Si-B/NiAl joints. Hence, it can be seen that dissolution of the NiAl substrate was significant in both cases.

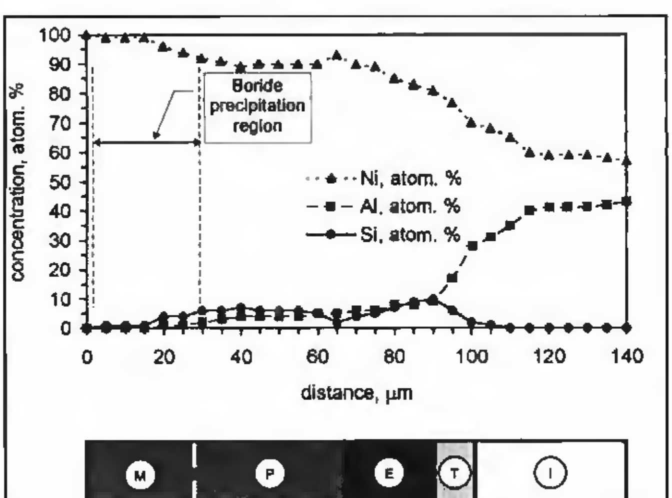

Fig. 7 — Compositional profile for NiAl/Ni-Si-Bl/Ni joint after 20 min holding at 1065°C. M — substrate Ni; P — ingrown proeutectic Ni; E — eutectic; I — substrate NiAl.

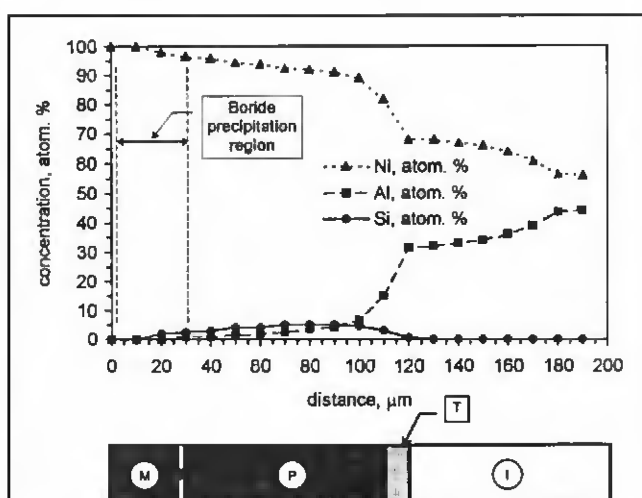

Fig. 8 — Compositional profile for NiAl/Ni-Si-B/Ni joint after 2 h holding at 1065°C. M — substrate Ni; P — ingrown proeutectic Ni; I - substrate NiAl.

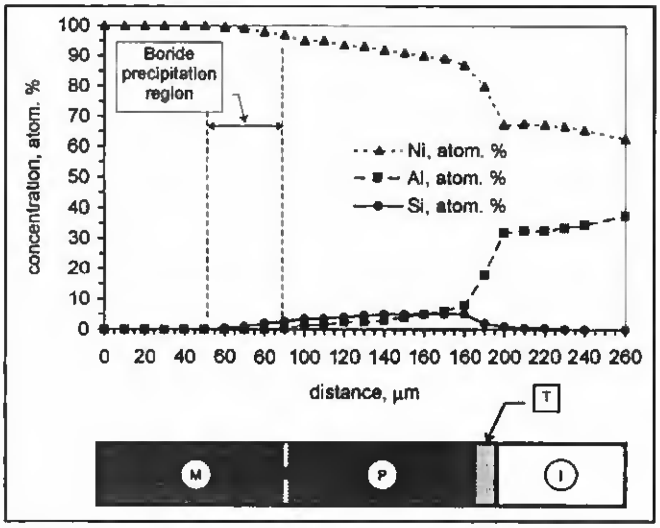

Fig. 9 — Compositional profile for NiAl/Ni-Si-B/Ni joint after 6 h holding at 1065°C. M — substrate Ni; P — ingrown proeutectic Ni; I — substrate NiAl.

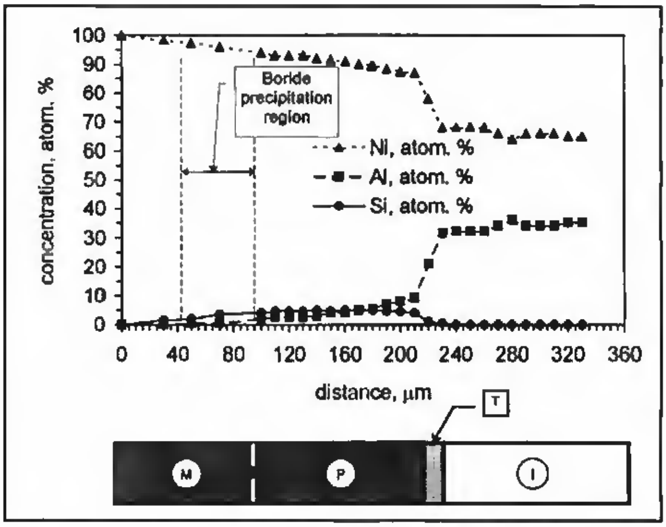

Fig. 10 — Compositional profile for NiAl/Ni-Si-B/Ni joint after 21 h holding at 1065°C. M — substrate Ni; P — ingrown proeutectic Ni; I — substrate NiAl.

During NiAl to NiAl joining, isothermal solidification occurred through the epitaxial ingrowth of Ni-enriched B2-type phase (Ref. 12). Evidence was also found for the formation of an $L1_2$ (Ni_3(Al, Si)) layer at the ingrowing B2 to liquid interface in brazements subjected to holding times in the range 20 min to 2 h at 1065°C. Protracted holding at the brazing temperature was required to bring about complete isothermal solidification in NiAl/Ni-Si-B/NiAl joints. Throughout most of the joint, isothermal solidification was only completed after a holding time of 21 h at 1065°C. Furthermore, the ingrowing B2 fronts were highly irregular (due to a cellular mode of epitaxial growth (Ref. 12)), and this resulted in isolated regions of the (21 h at 1065°C) joint where residual eutectic was observed. With the NiAl/Ni-Si-B/Ni joints examined in the present work, no evidence was found for the advance of the B2 phase (or other NiAl-based phases) from the NiAl substrate into the joint either during or after isothermal solidification (as can be seen from the compositional profiles shown in Figs. 5–10). Instead, as will be discussed in the next section, isothermal solidification of these joints was dominated by the rapid growth of Ni into the joint.

As a result of the irregular rate of isothermal solidification in the NiAl/Ni-Si-B/NiAl joints (due to cellular growth of the B2 phase into the joint), a distinct overlap was observed between the isothermal solidification and homogenization stages. With the NiAl/Ni-Si-B/Ni joints, a similar process was not observed. Given the dominant role in the isothermal solidification process of rapid growth of Ni into the joint, an opportunity for (cellular) growth of the B2 phase into the joint was not available.

Comparison of the NiAl/Ni-Si-B/Ni and Ni/Ni-Si-B/Ni Systems

The nature of microstructural development during joining of Ni-based alloys using Ni-Si-B interlayers was found to deviate from that predicted by conventional models of diffusion brazing (Refs. 14, 15) in which dissolution and isothermal solidification operate sequentially. One of the authors (Ref. 11) had previously suggested that diffusion of boron from the liquid into the solid substrate can take place before the melted interlayer and adjacent substrate reach local equilibrium. In such a case, dissolution and isothermal solidification would operate simultaneously rather than sequentially. Hence, fixed liquid and adjacent solid compositions (*i.e.*, local equilibrium at the liquid-solid interface) would not be established during the early stages of isothermal solidification. In these circumstances, substantial boron concentrations could develop in the solid adjacent to the liquid. These concentrations would be limited only by the (high) diffusivity of boron in solid Ni (a diffusivity of 6×10^{-11} m^2s^{-1} at 1100°C was estimated by Kucera, *et al.* (Ref. 16), for diffusion of boron into Ni-based substrates out of a Ni-Cr-Si-B liquid).

When the brazing temperature (*e.g.*, 1065°C) of a ternary Ni-Si-B filler metal is less than the substrate (*e.g.*, Ni) boron eutectic temperature (1093°–1095°C for Ni-B (Ref. 17)), boride formation in the substrate becomes possible at the brazing temperature. In contrast, when brazing is conducted above the substrate-boron eutectic temperature, extensive liquation of the substrate could occur (Ref. 11). Experimental support has been offered for the formation of Ni_3B and $M_{23}B_6$ borides in Ni substrates adjacent to a Ni-Si-B liquid when brazing is conducted at a temperature (1065°C) below that of the Ni-B binary eutectic. This evidence was based on correlation of hot-stage x-ray diffraction data with room-temperature cross-sectional transmission electron microscopy investigations. Furthermore, evidence has been offered that brazements produced in the same Ni/Ni-Si-B/Ni system at a temperature of 1150°C underwent liquation of the substrate in regions that were not contiguous with the main liquid layer.

In the Ni/Ni-Si-B/Ni system, it should be noted that, once borides formed in the substrate at the brazing temperature, these remained stable with further holding. Thus a situation was observed in which the eutectic was completely removed from the braze joint after 2 h holding at 1065°C, whereas borides formed in the substrate during holding for between 1 and 20 min at the same brazing temperature remained stable after 12 h holding. It should be noted that epitaxial growth of the Ni substrate into the joint did not produce a detectable microstructural discontinuity corresponding to the original solid-liquid interface. Furthermore, diffusion of Si from the liquid into the substrate smoothed out the chemical discontinuity at the original solid-liquid interface. Hence, the original location of the solid-liquid interface would not represent a preferential site for nucleation of borides on cooling to room temperature (in samples subjected to protracted holding periods). Thus, the preferential formation of borides on the substrate side of the original solid-liquid interface does not seem to be consistent with precipitation on cooling from the brazing temperature.

The progression of isothermal solidification in the NiAl/Ni-Si-B/Ni system paralleled that in Ni/Ni-Si-B/Ni joints. Borides closely resembling those formed (at the 1065°C brazing temperature) in Ni/Ni-Si-B/Ni joints were observed in the Ni substrate immediately adjacent to the original solid-liquid interface of NiAl/Ni-Si-B/Ni joints (held for times of 5 min and longer at a temperature of 1065°C, as shown in Fig. 1). After 2 h holding at 1065°C, the joint was completely isothermally solidified, as evidenced by the absence of eutectic on cooling back to room temperature (Fig. 2). In contrast, the borides formed in the Ni substrate immediately adjacent to the original location of the solid-liquid interface remained stable (Fig. 3) for all holding times examined (up to 21 h at 1065°C).

When an 1150°C brazing temperature (*i.e.*, above the 1093°–1095°C Ni-B binary eutectic temperature) was employed, substantial liquation of the Ni substrate (Fig. 4) was observed. As with Ni/Ni-Si-B/Ni joints produced at 1150°C (Ref. 11), substrate liquation involved both penetration down Ni-Ni grain boundaries and the formation of globular eutectic deposits, which were not contiguous with the main liquid seam — Fig. 4.

Isothermal solidification of the NiAl/Ni-Si-B/Ni joints was dominated by motion of a solid Ni front into the liquid. This front grew epitaxially from the Ni substrate. As isothermal solidification continued, a distinct layer of Al depletion formed in the NiAl substrate due to loss of aluminum to the liquid (which acted as an aluminum sink). The Al-depleted layer was found to increase in thickness from around 5 to 10 µm (depending on lateral position in the joint) for a brazement held for 5 min at 1065°C (Fig.6) to around 7 to 15 µm for a brazement held for 6 h at 1065°C — Fig. 9. However, as indicated in the last section, no evidence was found for a significant advance of solid from the NiAl substrate into the joint. After the brazements were held for 2 h at the 1065°C brazing temperature, a layer whose composition was close to that of Ni_3Al had formed at the interface between the Al depleted zone and the (now fully resolidified) main joint.

1. The maximum solubility of B in Ni is 0.3 at.-% (Ref. 17). Similar data are not available for NiAl; however, prominent boride formation was observed in a NiAl + 1.2 at.-% B alloy (Ref. 18).

Mechanisms Governing Microstructural Development in NiAl/Ni-Si-B/Ni Joints

Comparison of the present investigation of NiAl/Ni-Si-B/Ni joining with previous studies by the authors of NiAl/Ni-Si-B / NiAl and Ni/Ni-Si-B/Ni joining (Fig. 11) has revealed the following:

1) The time taken to complete isothermal solidification in the NiAl/Ni-Si-B/Ni system was comparable with that in the Ni/Ni-Si-B/Ni system, but was far smaller than that for NiAl/Ni-Si-B/NiAl.

2) Isothermal solidification in the NiAl/Ni-Si-B/Ni system was dominated by epitaxial growth of the Ni substrate into the joint.

3) Microstructural development on the Ni side of the NiAl/Ni-Si-B/Ni joints was incompatible with standard models of diffusion brazing; whereas, behavior on the NiAl side of the joint exhibited no obvious deviations from these models.

A potentially important factor in the occurrence of isothermal solidification by growth of Ni, rather than NiAl, into the joint is aluminum redistribution. Epitaxial growth of solid NiAl into the (initially aluminum-free) braze joint would require a supply of aluminum to the liquid, whereas this is not the case for Ni. Unfortunately, in the absence of a detailed quaternary Ni-Al-Si-B phase diagram, a convincing analysis of aluminum redistribution is not possible.

In seeking an explanation for the observed character of the isothermal solidification process, perhaps the most obvious would be a markedly reduced boron diffusivity in NiAl compared to Ni. In such a case, isothermal solidification would be dominated by diffusion of boron from the liquid into the Ni substrate. Furthermore, in such a circumstance, the rapid development of a high substrate boron concentration (thus leading to either boride formation or liquation depending on the brazing temperature) would only be expected for the Ni substrate and not the NiAl substrate.

Experimentally, it was noted that the distance from the braze interface at which boride formation could be observed (after the brazements were cooled to room temperature) was far greater for the Ni substrate than for the NiAl substrate. For example, marked boride precipitation extended through a distance of 1 mm (0.04 in.) from the braze interface of Ni/Ni-Si-B/Ni joints held for 2 h at 1065°C. In contrast with NiAl substrates, brazements prepared under similar conditions only showed detectable boride precipitation within 100 µm of the main braze joint.

Assuming a negligible boron solubility in both NiAl and Ni[1], the boron diffusivities in Ni and NiAl can be roughly estimated. In such a circumstance, the boron diffusion distance in the substrate for a given brazing time/temperature can be taken as the maximum distance from the braze interface at which borides were precipitated in the relevant substrate. Using an $x \approx \sqrt{(Dt)}$ approach (where x is the boron diffusion distance, D is the diffusion coefficient of boron in the relevant substrate at the brazing temperature and t is the brazing time) boron diffusivities of the order of $10^{-10} m^2s^{-1}$ in Ni (1065°C) and $10^{-12} m^2s^{-1}$ in NiAl were obtained for a 1065°C bonding temperature. These data support the suggestion that the experimental observations of isothermal solidification time and microstructural development in NiAl/Ni-Si-B/NiAl can be correlated with a higher boron diffusivity in Ni than in NiAl.

The microstructures observed in the NiAl/Ni-Si-B/ Ni joints discussed in this paper differ dramatically from those expected from standard models of the diffusion brazing process. These differences will now be summarized. Standard models treat the diffusion brazing process as consisting of three discrete sequential stages, namely: dissolution, isothermal solidification and homogenization. The dissolution stage establishes local equilibrium across the solid-liquid interface by modifying the compositions of the liquid and adjacent solid to those of the liquidus and solidus respectively. Thus, on entering the isothermal solidification

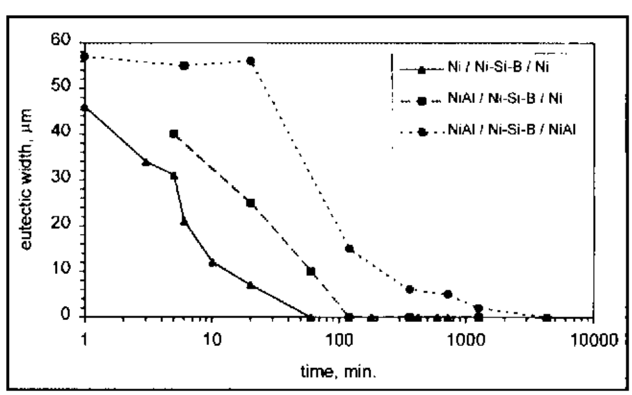

Fig. 11 — Eutectic width vs. brazing time for Ni/Ni-Si-B/Ni (Refs. 11, 19, 20), NiAl/Ni-Si-B/Ni (present work), and NiAl/Ni-Si-B/NiAl (Ref. 12) joints held at 1065°C. Eutectic width values for 0 min holding time were 55 µm for Ni/Ni-Si-B/Ni joints, 53 µm for NiAl/Ni-Si-B/Ni joints, and 50 µm for NiAl/Ni-Si-B/NiAl joints.

stage, the compositions of the liquid and adjacent solid are already fixed and there is no possibility of the formation of second phases (such as borides) during isothermal solidification. In contrast, the boride precipitation observed within the nickel substrate of the Ni/Ni-Si-B/NiAl bonds examined in the present work closely resembles that occurring at the brazing temperature in Ni/Ni-Si-B/Ni joints. Thus, a direct contradiction exists between the microstructures observed in the present work and standard models of the TLP process.

In response to the contradiction observed between standard diffusion brazing models and the microstructures of NiAl/Ni-Si-B/Ni joints, the authors propose an alternative mechanism in which the dissolution and isothermal solidification steps occur in parallel, rather than sequentially. In such a parallel mechanism, isothermal solidification would commence before the establishment of local equilibrium at the solid-liquid interface results in the maintenance of fixed solid and liquid compositions. If the transfer of boron from the liquid phase to the solid is not limited by maintenance of the composition of the solid to the solidus value, then the high diffusivity of boron in nickel would rapidly result in the development of a significant boron concentration in the nickel substrate. In contrast, silicon is far less mobile in nickel than boron and so rapid transfer of silicon to the nickel substrate would not occur. Thus, the nickel substrate would be transformed into a binary Ni-B alloy.

The effect of the formation of a binary Ni-B alloy on the microstructure nickel substrate depends on the difference between the brazing temperature employed for the ternary Ni-Si-B interlayer and the binary Ni-B eutectic temperature. When a brazing temperature below the Ni-B binary eutectic temperature is employed, transfer of boron to the Ni substrate would result in the formation of borides once the (small) solid-solubility of boron in nickel was exceeded. In contrast, when a brazing temperature above the binary Ni-B eutectic temperature is employed, liquation of the nickel substrate will occur once the solubility of boron in nickel is exceeded. The boron diffusivity in NiAl is far lower than in Ni, and hence in the case of the NiAl substrate, isothermal solidification proceeds only relatively slowly. Thus, there is sufficient time for the establishment of local equilibrium across the solid-liquid interface (and hence the development of fixed solid and liquid compositions) before the occurrence of significant isothermal solidification. Hence, the formation of borides at the brazing temperature would not be expected in the case of the NiAl substrate and was not observed experimentally.

Conclusions

An examination of the diffusion brazing of NiAl to Ni using Ni-Si-B interlayers has been undertaken. The results of this investigation can be summarized as follows:

1) The progression of the diffusion brazing at the NiAl substrate side of the joints was not incompatible with that predicted by standard diffusion brazing models. No qualitative changes were found with respect to the two brazing temperatures studied (1065° and 1150°C).

2) Marked deviations from conventional models of the diffusion brazing process were observed at the Ni side of the joints. A prominent layer of borides was formed in the substrate adjacent to the original solid-liquid interface when the brazing temperature was below the Ni-B binary eutectic temperature. When the brazing temperature was taken above the Ni-B binary eutectic temperature, substantial liquation of the Ni substrate took place. This type of boride precipitation was consistent with previous observations of substrate boride formation at the brazing temperature after complete melting of the interlayer in Ni/Ni-Si-B/Ni joints.

3) Isothermal solidification of the NiAl/Ni-Si-B/Ni joints occurred by epitaxial growth of the Ni substrate into the joint. This has been correlated with differences in boron diffusion behavior between the Ni and NiAl substrates.

Acknowlegments

The authors wish to express their thanks to Easo George, Oak Ridge National Laboratory, for the supply of the NiAl substrate material; and to Thomas Edwards, Allied Signal, for the provision of the BNi-3 filler metal.

References

1. Baker, I., and Munroe, P. R. 1989. Properties of B2 compounds. *Proceedings High Temperature Aluminides & Intermetallics*, eds. S. H. Whang, *et al.*, pp. 425–451. The Minerals, Metals & Materials Society.

2. Nash, P., Singleton, M. F., and Murray, J. L. 1991. *Phase Diagrams of Binary Alloys*, ed. P. Nash, 1:181–183. ASM International, Materials Park, Ohio.

3. Doychak, J. K., and Mitchell, T. E. 1985. High temperature oxidation of ß-NiAl. *Materials Research Society Symposium Proceedings*, 39:476–484.

4. Darolia, R., Lahram, D. F., Field, R. D., Dobbs, J. R., Chang, K. M., Goldman, E. H., and Konitzer, D. G. 1992. Overview of NiAl alloys for high temperature structural applications. *Proceedings Ordered Intermetallics — Physical Metallurgy and Mechanical Behavior*, eds. C. T. Liu, *et al.*, pp. 679–698. Kluwer Academic Publishers.

5. Miracle, D. B. 1992. The Physical and mechanical properties of NiAl. *Acta Metallurgica et Materialia* 41(4): 649–684.

6. Dimiduk, D. M., Miracle, D. B., and Ward, C. H. 1992. Development of intermetallic materials for aerospace systems. *Materials Science and Technology*, 8:367–375.

7. Stoloff, N. S. 1985. High temperature ordered intermetallic alloys. *Materials Research Society Symposium Proceedings*, 39:4–24.

8. Moore, T. J., and Kalinowski, J. M. 1993. Diffusion brazing NiAl with self generated filler metal. *Materials Research Society Symposium Proceedings*, 288: 1173–1178.

9. Darolia, R. 1993. NiAl for turbine airfoil applications. *Structural Intermetallics, Proceedings First International Symposium on Structural Intermetallics*, eds. R. Darolia, *et al.*, pp. 495–505. The Minerals, Metals & Materials Society.

10. Strum, M. J., and Henshall, G. A. 1994. Liquid assisted diffusion bonding of NiAl. *Proceedings Advanced Joining Technologies for New Materials II*, pp. 5–19, AWS.

11. Gale, W. F., and Wallach, E. R. 1991. Microstructural development in transient liquid phase bonding. *Metallurgical Transactions* A, 22A: 2451 to 2457.

12. Orel, S. V., Parous, L. C., and Gale, W. F. 1994. Transient liquid phase bonding of NiAl using Ni-Si-B interlayers. *Proceedings Advanced Joining Technologies for New Materials II*, pp. 76–88, AWS.

13. Gale, W. F., and Wallach, E. R. 1991. Influence of isothermal solidification on microstructural development in Ni-Si-B filler metals. *Materials Science and Technology*, 7:1143–1148

14. Tuah-Poku, I., Dollar, M., Massalski, T. B. 1988. A study of the transient liquid phase bonding process applied to a Ag/Cu/Ag sandwich joint. *Metallurgical Transactions* A, 22A: 2451–2457.

15. Nakao, Y., Nishimoto, K., Shinozaki, K., and Kang, C. Y. 1989. Theoretical research on transient liquid insert metal diffusion bonding. *Proceedings Superalloys 1988*: 775–783. Metallurgical Society of AIMF.

16. Kucera, J., Buchal, A., Rek, A., and Stransky, K. 1984. Redistribution of boron in the vicinity of Ni-B brazed joints. *Kokove Materialy* 22: 250–262.

17. Schöbel, Von J. D., Stadelmaier, H. H. 1965. The binary system nickel-boron. *Z. Metallkunde* 56:856–859.

18. Lee, J. H., Choe, B. H., and Kim, H. M. 1992. Effect of boron in two-phase (NiAl $+Ni_3Al$) alloy. *Materials Science and Engineering* A152: 253–258.

19. Gale, W. F. Unpublished material.

20. Gale, W. F. 1991. Joining of Ni-based substrates using Ni-Si-B and Ni-P Alloys. Ph.D. thesis, University of Cambridge.