# Microstructural Development in Transient Liquid-Phase Bonding

W.F. GALE and E.R. WALLACH

The applicability of conventional models of the transient liquid-phase (TLP) bonding process to the joining of nickel using ternary Ni-Si-B insert metals is considered in this article. It is suggested that diffusion of boron out of the liquid and into the solid substrate before the equilibration of the liquid and solid phases can result in the development of significant boron concentrations in the substrate. This, in turn, leads to the precipitation of boride phases in the substrate during holding at bonding temperatures below the binary nickel-boron eutectic temperature. The formation of boride phases during holding at the bonding temperature is of importance, because first, it is not predicted by the standard models of the TLP process, and second, the borides are not removed by prolonged holding at the bonding temperature and therefore may influence the in-service properties of the joint. In contrast, when bonding above the binary nickel-boron eutectic temperature, localized liquation of the substrate takes place. This liquid region resolidifies following prolonged holding and does not result in the formation of persistent boride phases. Experimental support is presented for the formation of borides during bonding, and characterization of the boride phases formed in the substrate is described.

## I. INTRODUCTION

IN the transient liquid-phase (TLP) process, an insert is placed between two substrates which forms a liquid phase at the bonding temperature. The liquid is then gradually removed by interdiffusion with the substrates. One of the most attractive features of TLP bonding is that it seemingly provides a method of joining materials, such as nonweldable gamma-prime or oxide dispersion-strengthened alloys, without the extensive precipitation of second phases. Hence, the process should allow the retention of parent metal properties in fabricated components.

In order to understand the conditions required to allow the production of joints free from second phases, models of the TLP process have been proposed. Conventional models of the TLP bonding process[1,2,3] are based on binary alloy liquids. The binary alloy liquid can be produced either directly from a binary insert (for example, Ni-B) or from a single element insert that forms the binary liquid by reaction with the substrate. In these models, it is assumed that, after formation of the liquid, the solid and liquid phases initially equilibrate to their respective solidus and liquidus compositions. When equilibration is complete, solid-state diffusion of the melting point depressant (such as boron) in the substrate results in gradual isothermal solidification of the insert. According to the models, the process of isothermal solidification is completed without the precipitation of second phases during holding at the bonding temperature. The remaining melting point depressant can then be diluted in the substrate by a prolonged homogenization treatment. Hence, the precipitation of second phases on cooling (due to decreased solubility of the melting point depressant at lower temperatures) can be largely or entirely avoided.

In contrast to the binary alloy inserts considered in the conventional models, commercial TLP insert metals may consist of ternary alloys such as Ni-Si-B. In this article, it is proposed that with ternary Ni-Si-B inserts, deviations from the conventional models can occur. It is suggested that these deviations can result in the precipitation of boride phases at the bonding temperature during the initial stages of joint formation.

## II. EXPERIMENTAL TECHNIQUES

Transient liquid-phase bonds were fabricated using a Ni-4.5 pct Si-3.2 pct B (weight percentages) insert metal (American Welding Society designation BNi-3) in the form of 51 $\mu$m-thick melt-spun sheets and commercial-purity nickel substrates (99 wt pct Ni) in the form of discs of 35 mm in diameter and 2 mm in thickness. High-purity (99.98 wt pct minimum) nickel substrates were also employed, although this difference in impurity level was not found to be of importance for these substrates. Bonds were fabricated under a nominally zero load, using a series of holding times (0 to 12 hours) at two different temperatures (1065 °C and 1150 °C) under a vacuum of $5 \times 10^{-5}$ mbar.

The formation of second phases during holding at 1065 °C was monitored using X-ray diffraction (XRD) with a hot-stage Guinier camera. The results of this investigation were correlated with microstructural investigations conducted using light, scanning (SEM), and transmission electron microscopies (TEM). Samples for light and microscopies were prepared using electrolytic etching/polishing in a 10 pct solution of hydrochloric acid in methanol at −20 °C using a current density of 33 mA mm$^{-2}$. Scanning electron microscopy was performed using Camscan S2 and S4 microscopes. Transmission electron microscopy specimens were prepared by electropolishing (at 100 mA/30 V with a 50 pct methanol, 35 pct n-butanol, 15 pct perchloric acid electrolyte at a temperature of −10 °C) to perforation followed by ion milling (dual guns operating at 5kV/0.5

mA per gun, with gun-to-specimen angles of 12 deg) to extend the perforation back to the bond-line region. These foils were examined using PHILIPS* 400T instruments

---

*PHILIPS is a trademark of Philips Electronic Instruments Corporation, Mahwah, NJ.

---

operating at accelerating voltages of 120 kV to produce bright-field and dark-field images as well as selected area (SADP) and microdiffraction patterns. In the figures shown in this article, the beam direction is denoted as $B$ and the operating reflection as $g$. Energy dispersive X-ray spectroscopy (EDS) was performed using Link Systems 860 analyzers attached to the 400T and S4 instruments.

## III. RESULTS AND DISCUSSION

### A. Mechanisms for Microstructural Development

In the standard models of the TLP process described in the Introduction, it is assumed that the liquid-solid equilibration and solid-state diffusion processes occur sequentially rather than simultaneously. It is more realistic, however, to assume that the two processes operate simultaneously.[4] Under these conditions, for the ternary Ni-Si-B insert between nickel substrate, there will be three processes occurring in parallel, namely:

(1) dissolution of nickel from the solid substrate into the liquid insert;
(2) diffusion of boron from the liquid insert into the solid substrate; and
(3) diffusion of silicon from the liquid insert into the solid substrate.

If the dissolution process is completed and the solid and liquid phases are equilibrated (to their respective solidus and liquidus compositions) before significant solid-state diffusion has taken place, then the behavior of the Ni-Si-B insert should be similar to that assumed in the conventional models. However, for cases in which significant solid-state diffusion occurs before equilibration is attained, then substantial deviations from the models would be expected. Thus, it is necessary to compare the relative rates of the dissolution and diffusion processes if the applicability of the conventional models to Ni-Si-B inserts is to be ascertained.

The kinetics of the dissolution process have been examined, for Ni-B inserts, by Nakao et al.[1,2] using an equation of the type

$$n = n_s \left[ 1 - \exp \left( -\frac{kАt}{V} \right) \right] \qquad [1]$$

in which $n$ = number of moles of solute in the liquid at time $t$;
$n_s$ = number of moles of solute in the liquid at equilibrium;
$k$ = constant (determined by Nakao et al. as 269 nm s$^{-1}$ at 1100 °C for Ni-B inserts in nickel superalloys);
$A$ = area of interface between the solid and the liquid;
$V$ = volume of the liquid phase;
$t$ = holding time.

Consider a 50 $\mu$m-thick insert held at 1100 °C for an arbitrary time of 1 minute. Under these conditions, it is predicted from Eq. [1] that the liquid-solid equilibration process is less than half completed (with $n = 0.48n_s$).

Having examined the dissolution process, consider the diffusion in the substrate of the elements boron and silicon. After equilibration, the liquid and adjacent solid have compositions fixed by the respective liquidus and solidus values. However, before equilibration, these constraints will not apply. In order to examine diffusion processes before equilibration, the insert and substrates are treated here as a continuum. In such circumstances, diffusion of a solute out of a finite interlayer into semi-infinite solid substrates may be represented by the following distribution:[5]

$$C(x,t) = \frac{1}{2} C_0 \left( \text{erf} \frac{h - x}{2 \sqrt{(Dt)}} + \text{erf} \frac{h + x}{2 \sqrt{(Dt)}} \right) \qquad [2]$$

where $C(x, t)$ = concentration of the solute as a function of distance from the center of the interlayer ($x$) and time ($t$);
$2h$ = width of the interlayer;
$D$ = diffusivity of the solute in the substrate; and
$C_0$ = initial solute concentration in the insert.

Using this equation, the boron concentration profile as a function of holding time at temperature may be obtained* for a 50 $\mu$m-thick BNi-3 interlayer with a boron

---

*This approach assumes that the diffusivity of boron is that observed in the solid substrate and ignores the greater diffusivity of boron in the liquid. This would tend to flatten the concentration profile in the liquid, which would, in turn, influence diffusion in the solid substrate. However, the boron concentration profile in the liquid predicted by Eq. [2] (when ignoring the higher diffusivity of boron in the liquid) becomes almost flat after 30 seconds at temperature. Thus, the difference in diffusivity of boron in the liquid and the substrate would not seem to be of overriding importance.

---

diffusivity in the substrate of 6.22 × 10$^{-11}$ m$^2$ s$^{-1}$ (this diffusivity value was determined at a temperature of 1100 °C for the diffusion of boron out of a Ni-Cr-Si-B insert into nickel-based substrates by Kucera et al.[6]). Take, for example, a holding time of 1 minute; the concentration of boron in the nickel substrate at a distance of 10 $\mu$m from the edge of the insert is found to be 4990 moles m$^{-3}$ (which is equivalent to 3.2 at. pct). This value is considerably greater than the maximum solubility of boron in solid nickel (0.3 at. pct at the generally accepted eutectic temperature of 1093 °C to 1095 °C taken from the work of Schöbel and Stadelmier[7] by Massalski,[8] Moffatt,[9] and Portnoi and Romashov[10]). If a similar calculation is performed for silicon diffusion [using a silicon diffusivity in the substrate of 3.09 × 10$^{-14}$ m$^2$ s$^{-1}$ (Kucera et al.[6]) and again considering a distance of 10 $\mu$m from the insert], then it is found that no significant silicon diffusion will have occurred after 1 minute at temperature.

These calculations suggest that after 1 minute at the bonding temperature, a binary nickel-boron alloy will be produced in the substrate and that the maximum solubility of boron in this alloy will have been exceeded. As the normal bonding temperature of the ternary Ni-Si-B alloy (1065 °C) is below the binary nickel-boron eutectic

temperature, the precipitation of $Ni_3B$ borides in the substrate at the edge of the insert would be expected during holding at the bonding temperature once the solubility of boron in nickel has been exceeded. In contrast, at temperatures above that of the binary nickel boron eutectic, liquation of the substrate material would be expected once the solubility of boron in the solid nickel substrate is exceeded.

Any tendency to form boride phases during holding at the bonding temperature would be of importance for two reasons. First, such behavior is not predicted by the standard models of the TLP process, and the applicability of these models to ternary systems, such as Ni-Si-B, would need to be re-examined. Second, the formation of boride phases during holding at the bonding temperature has practical implications if these phases cannot be resolutioned by holding at the bonding temperature, since their presence would be expected to influence the mechanical properties of the bonded component. In comparison, the occurrence of liquation at the bonding temperature would present a lesser problem, as the liquid phase could be removed by prolonged holding. In the next section, an experimental investigation is made of the circumstances in which boride precipitation and substrate liquation occur.

## B. Experimental Verification of the Mechanisms

In the last section, it was suggested that isothermal solidification of ternary Ni-Si-B inserts could result in the precipitation of boride phases during holding at a bonding temperature below the binary Ni-B eutectic temperature. In contrast, when bonding above the binary eutectic temperature, boron diffusion into the substrate should merely result in liquation of the surrounding substrate. Thus, in order to support the proposed mechanism, evidence is required that borides are formed only during holding below the binary eutectic and are not formed above this temperature and that boride precipitation on cooling is not significant.

Experimentally, the formation of boride phases above and below the Ni-B binary eutectic temperature was compared. There has been considerable uncertainty regarding the exact value of the eutectic temperature. Eutectic temperatures in the range of 1080 °C to 1140 °C have been given in the literature.[11-14] A lower eutectic temperature of 1045 °C (suggested by Sobalev and Fedrov[15]) can be ignored, as this was determined from cooling curve data which are not applicable to the present problem, especially in view of the large hysteresis between heating and cooling observed in the Ni-B system.[7,16] Therefore, in the present work, temperatures clearly below (1065 °C) and above (1150 °C) the range of quoted Ni-B eutectic temperatures, have been chosen.

### 1. Below Ni-B binary eutectic temperature (1065 °C tests)

#### a. $Ni_3B$ precipitation

In hot-stage XRD studies using a Guinier camera, the precipitation of $Ni_3B$ was detected during holding at the bonding temperature of 1065 °C. This result is in agreement with the predictions made in the last section. Microstructural investigations were also undertaken to show that precipitation of $Ni_3B$ takes place in the substrate immediately adjacent to the insert, as predicted by the

mechanism proposed in the last section. After heating to the bonding temperature and then immediately cooling, a $Ni_3B/Ni$ eutectic was observed throughout the joint,[17] which indicates that complete melting had occurred. Melting takes place during heating to the bonding temperature, since the liquidus temperature of the foil is approximately 1054 °C. In addition, a small number of transgranular and substrate grain boundary $Ni_3B$ precipitates were observed (Figure 1). However, there was no marked precipitation at the substrate-insert interface, as was observed after longer hold times (see below). While this microstructure is consistent with the simple equilibrium models in which the borides form on cooling from the bonding temperature, subsequent developments show a marked divergence from this interpretation.

After holding for 1 minute at the bonding temperature, in addition to the occasional precipitation of $Ni_3B$ as described above, the formation of a further prominent region of $Ni_3B$ precipitates in the vicinity of the original position of the substrate-insert interface was observed. The region of $Ni_3B$ was separated from the eutectic mixture by a region of primary proeutectic nickel. This became more prominent in samples held for longer times (3 minutes (Figure 2(a)) and 5 minutes) at the bonding temperature. After 5 to 10 minutes holding at the bonding temperature, this region stabilized, and similar results were achieved in samples given longer holding times (20 minutes (Figure 2(b)), 1, 3, 6, 7, and 12 hours).

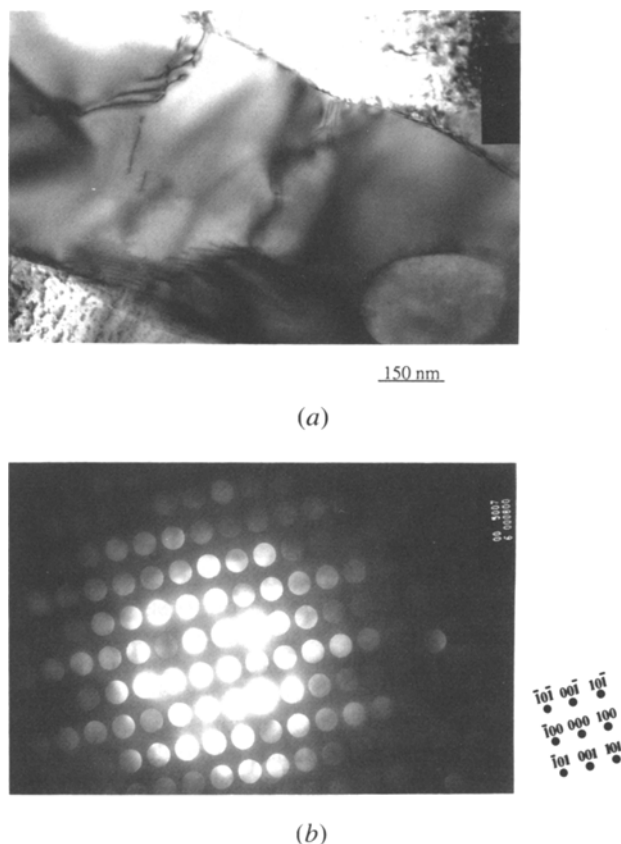The observations described above are consistent with the mechanism proposed for the formation of $Ni_3B$



150 nm

(a)



$\bar{1}0\bar{1}$ $00\bar{1}$ $10\bar{1}$
$\bar{1}00$ $000$ $100$
$\bar{1}01$ $001$ $10\bar{1}$

(b)

Fig. 1—$Ni_3B$ precipitation in a joint held for 1 min at 1065 °C. (a) bright-field micrograph and (b) microdiffraction pattern ($B$ = [010]).
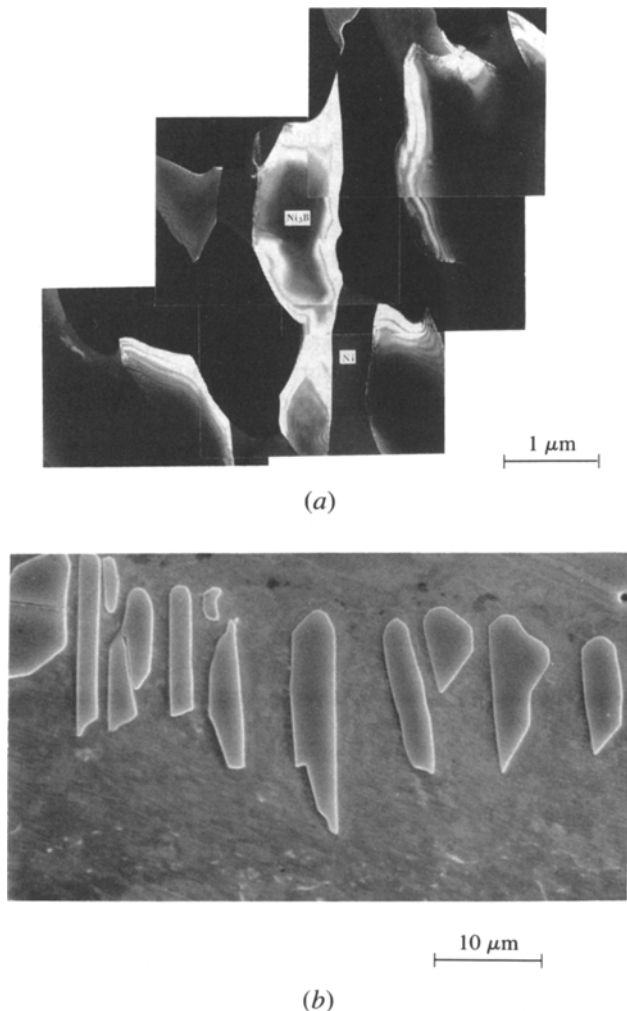
(a)



10 μm

(b)

Fig. 2—Development of a distinct region of Ni₃B precipitation at the original insert-substrate interface: (a) dark-field TEM micrograph ($g$ = (021) Ni₃B) of sample held for 3 min at 1065 °C and (b) SEM micrograph of sample held for 20 min at 1065 °C.

in the substrate during holding at the bonding temperature. The possibility that these borides were produced by diffusion of boron from the insert into the substrate before the onset of melting of the insert can be eliminated for the following reasons. First, the region of marked boride precipitation was not produced after holding below the solidus temperature of insert (984 °C). Second, between the solidus and liquidus temperature of the insert, the substrate borides only occurred adjacent to the portion of the insert that had melted.

In summary, the possibility of boride precipitation in the substrate (during heating or on first reaching the bonding temperature) before the onset of melting of the insert can be eliminated. However, evidence is required to show that other precipitation, occurring on cooling from the bonding temperature, is not involved. Whereas boride precipitation in the substrate could be observed after 12 hours at the bonding temperature, the insert metal liquid phase is largely removed after 2 hours holding at the bonding temperature and completely absent after 7 hours holding.[17] When the liquid phase is no longer present, it follows that the maximum boron concentra-

tion in the joint region must have decreased to a value less than that of the solidus. Thus, in these circumstances, the only source of boron for Ni₃B precipitation during cooling is from decreases in the solubility of boron in solid nickel on cooling from the bonding temperature. Hence, if precipitation on cooling is to account for the prominent formation of borides at the original substrate-insert interface, then a mechanism for the preferred precipitation of Ni₃B on the interface is required: two possibilities need to be considered, namely, that

(1) the interface constitutes a favored site for processes such as boron segregation or the preferential nucleation of borides and
(2) the presence of silicon in the region of the interface in some way increases the activity of boron so as to promote the formation of borides.

In practice, however, both of these mechanisms can be dismissed. Generally, growth of proeutectic nickel into the liquid takes place epitaxially, and therefore, the original solid-liquid interface does not constitute a preferential site for segregation, nucleation, etc. Furthermore, EDS analyses[17] show that following 20 minutes at the bonding temperature, there is no obvious step in the silicon concentration profiles (that could in any way account for a change in boron activity) associated with the original solid-liquid interface, whereas precipitation could still be observed following 12 hours holding at temperature.

In summary, evidence has been presented which suggests that Ni₃B precipitation in the substrate occurs during the first few minutes of holding at the bonding temperature at the edge of the liquid (and not before the onset of melting of the insert). Further holding results in interdiffusion, and this serves to remove the liquid, whereas the borides remain stable. In contrast, a suitable explanation for this type of precipitation on cooling could not be formulated, and it seems likely that the formation of this region of borides does not occur as a result of precipitation on cooling from the bonding temperature. Thus, after the completion of isothermal solidification, an isolated band of borides remains in the substrate adjacent to the original liquid-solid interface.

b. $M_{23}X_6$ precipitation

In addition to the precipitation of Ni₃B in the substrate, the precipitation of an $M_{23}X_6$-type phase [in the present case, M and X are nickel and (presumably) boron, respectively] was observed in the substrate. The Ni₂₃B₆ phase was found to form with a cube-cube orientation relationship (Figure 3) with the nickel matrix so that

$$(001)_{Ni} \parallel (001)_{Ni_{23}B_6}$$

$$[100]_{Ni} \parallel [100]_{Ni_{23}B_6}$$

The Ni₂₃B₆ precipitation occurs as follows. After short hold times (3 minutes at temperature), the precipitation of Ni₂₃B₆ occurs on substrate grain boundaries generally with a platelike morphology, although more angular morphologies were also observed. Following longer hold times (5 to 10 minutes), this process occurs to a greater extent, and after 20 minutes at temperature, the Ni₂₃B₆ can be observed to pin the grain boundaries (Figure 4).
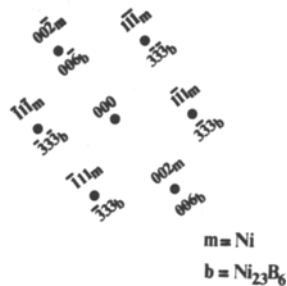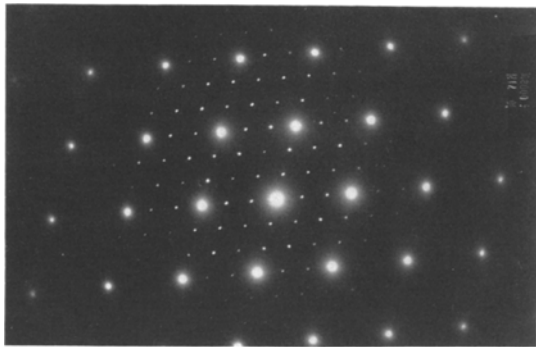
Fig. 3—SADP ($B$ = [110]) showing cube-cube orientation relationship of Ni and $M_{23}X_6$ phases.

Second phases were also observed on twin boundaries after 20 minutes. Plates of $Ni_{23}B_6$ are precipitated "back-to-back" on the twin boundary, and simultaneous growth of the $Ni_{23}B_6$ with a faceted morphology takes place into the substrate matrix on either side of the twin boundary.

After the initial precipitation of $Ni_{23}B_6$ on interfaces, transgranular precipitation occurs (after 5 minutes at temperature). Precipitates were usually found to form in colonies rather than with an even distribution, although some isolated precipitates could be observed. The colonies were observed in association with dislocation clusters, generally with a central precipitate or precipitates surrounded by smaller precipitates (Figure 5). This be-
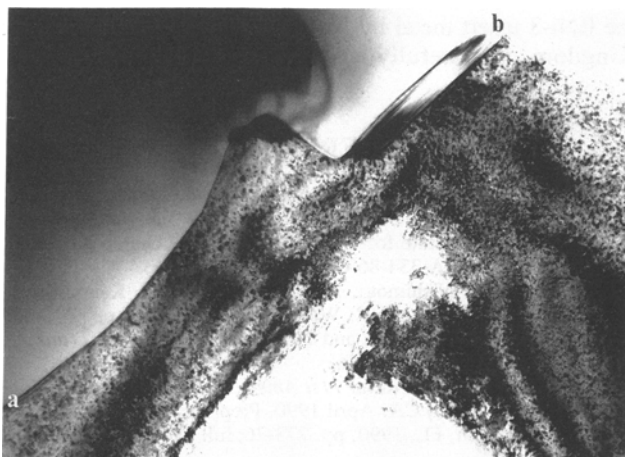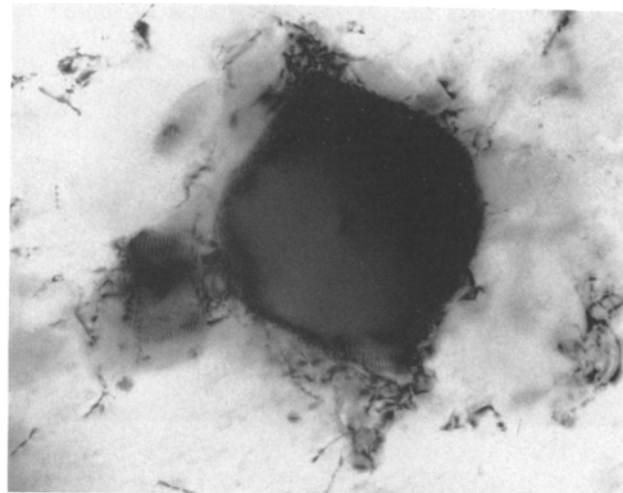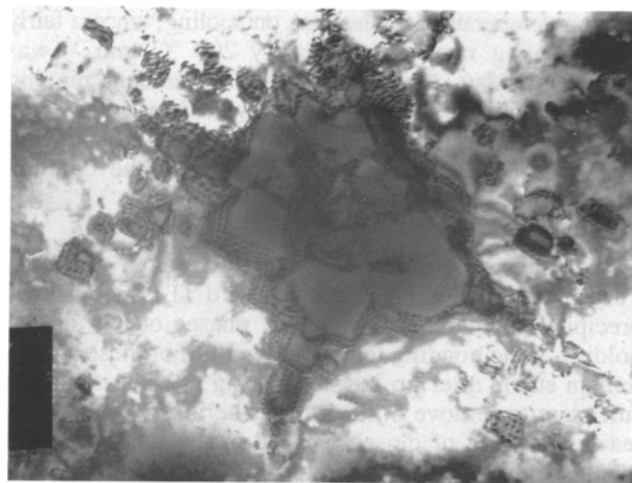


Fig. 4—Bright-field. TEM micrograph showing substrate grain boundary (denoted by a-b) pinning by $M_{23}X_6$ precipitates (sample held for 20 min at 1065 °C).



500 nm

(a)

500 nm

(b)

Fig. 5—Bright-field TEM micrographs showing the formation of transgranular $M_{23}X_6$ clusters in the substrate (samples held for 1 h at 1065 °C) (a) single central precipitate and adjoining smaller precipitates and (b) central precipitate colony containing low-angle boundaries and surrounded by smaller precipitates.

havior could arise either from nucleation of the smaller precipitates on pre-existing dislocations in the substrate or from nucleation of the smaller precipitates on the interfacial dislocations formed in the matrix around the large central precipitate. The latter of these explanations seems most likely, as similar clusters were not evident before the onset of $Ni_{23}B_6$ precipitation.

Direct evidence for the precipitation of $Ni_{23}B_6$ at temperature was not obtained from the hot-stage XRD studies. However, the occurrence of pinning of substrate grain boundaries suggests that the boride phases were present during a period of significant grain growth. Significant grain growth could occur only during holding at the
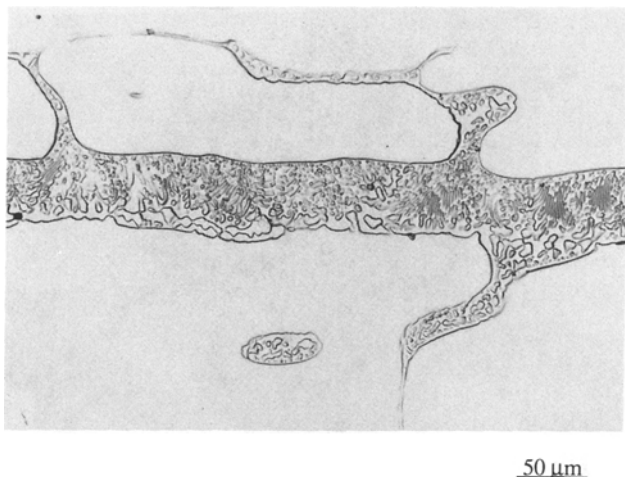
Fig. 6—Light micrograph showing the formation of transgranular and grain boundary deposits of Ni plus $Ni_3B$ eutectic mixture in the substrate of a sample held for 5 min at 1150 °C.

bonding temperature, rather than on cooling, since a fairly rapid cooling rate (approximately 200 °C min$^{-1}$) was employed. Also, the extent of grain boundary pinning increased with holding time, which would not be the case for precipitation on cooling. This suggests that as with $Ni_3B$, the $Ni_{23}B_6$ borides were formed at the bonding temperature.

### c. Summary

In summary, evidence has been presented that contrary to the predictions of the standard TLP models, the precipitation of $Ni_3B$ and $Ni_{23}B_6$ phases occurs during holding at the bonding temperature. Both of these phases remain stable after prolonged holding (12 hours) that is sufficient to remove borides from the insert metal. This leaves a region of closely spaced brittle borides which would be expected to have a profoundly detrimental influence on joint properties.

### 2. Above binary eutectic temperature (1150 °C tests)

After holding above the binary Ni-B eutectic temperature, the region of separate $Ni_3B$ precipitates in the substrate, distinct from the insert metal, was not seen. Instead, extensive formation of the Ni plus $Ni_3B$ eutectic mixture was found to have taken place along substrate grain-boundaries (Figure 6). In addition, isolated globules of eutectic mixture were also observed transgranularly in the substrate. These results are in accord with the proposed mechanism in which substrate liquation, rather than boride precipitation at this higher bonding temperature, is expected. On cooling, the liquid forms the regions of eutectic mixture observed in the substrate. Some $Ni_{23}B_6$ precipitation was also encountered, however, to a much lower extent than at 1065 °C. This precipitation did not result in pinning of substrate grain boundaries. Again, these results would seem to be consistent with the precipitation on cooling, rather than at the bonding temperature.

Since prolonged holding will gradually remove the eutectic-forming liquid phase, the formation of these eutectic deposits in the substrate would seem to be a lesser problem than the formation of persistent borides, which occurs during holding at lower temperatures.

## IV. CONCLUSIONS

A study has been made of microstructural development during bonding of nickel substrates using Ni-Si-B insert metal. The results of this investigation are now summarized.

1. A mechanism for microstructural development has been proposed in which the formation of a binary Ni-B alloy in the substrate before equilibration of the liquid and solid phases to their respective liquidus and solidus compositions results in the formation of boride phases during holding at the bonding temperature when this is below the binary Ni-B eutectic temperature. This differs substantially from previous models of the TLP process in which it is assumed that borides are not formed at the bonding temperature.
2. Experimental evidence has been presented for the formation of $Ni_3B$ in the substrate at the original substrate-insert interface after 1 minute at a bonding temperature of 1065 °C (i.e., below the binary Ni-B eutectic temperature). This observation is consistent with the proposed mechanism.
3. The formation of $Ni_{23}B_6$ in the substrate also takes place during holding at the 1065 °C bonding temperature, and this results in substrate grain boundary pinning.
4. Above the binary Ni-B eutectic temperature (at 1150 °C), extensive liquation of the substrate is produced, especially at substrate grain boundaries. This result is consistent with the proposed mechanism.

## REFERENCES

1. Y. Nakao, K. Nishimoto, K. Shinozaki, and C. Kang: *Transient Insert Metal Diffusion Bonding of Ni-Base Cast Superalloy MM007*, International Institute for Welding, Abingdon, United Kingdom, Document No. IA-334-86-OE, 1986.
2. Y. Nakao, K. Nishimoto, K. Shinozaki, and C. Kang: *Superalloys, 1988*, TMS-AIME, Warrendale, PA, 1989, pp. 775-83.
3. I. Tuah-Poku, M. Dollar, and T.B. Massalski: *Metall. Trans. A*, 1988, vol. 19A, pp. 675-86.
4. C.H. Lee and T.H. North: *71st American Welding Society Convention*, Anaheim, CA, April 1990, Preprint, American Welding Society, Miami, FL, 1990, pp. 273-76; full paper to be published in *Weld. J.*
5. J. Crank: *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, Oxford, United Kingdom, 1975, pp. 15.
6. J. Kucera, A. Buchal, A. Rek, and K. Stransky: *Kovove Mater.*, 1984, vol. 22, pp. 250-62.
7. Von J.D Schöbel and H.H. Stadelmaier: *Z. Metallkd.*, 1965, vol. 56, pp. 856-59.

8. *Binary Alloy Phase Diagrams*, 1st ed., T.B. Massalski, ed., ASM, Metals Park, Ohio, 1986, pp. 366-71.
9. W.G. Moffatt: *Handbook of Binary Phase Diagrams*, Genium Publishing Corporation, Schenectady, NY, 1986.
10. K.I. Portnoi and V.M. Romashov: *Poroshk. Metall.*, 1972, vol. 5, pp. 48-56.
11. R.P. Elliott: *Constitution of Binary Alloys*, 1st Suppl., McGraw-Hill, New York, NY, 1965, pp. 127-28.
12. P.T. Kolomystev: *Doklady Akad. Nauk Tadzh. SSR*, 1962, vol. 144, pp. 112-17.
13. K.I. Portnoi, V.M. Romashov, V.M. Chubarov, M.Kh. Levinskaya, and S.E. Salibekov: *Poroshk. Metall.*, 1967, vol. 2, pp. 15-21.
14. M. Hansen and K. Anderko: *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, NY, 1958, p. 256.
15. A.S. Sobalev and T.F. Fedrov: *Neorgan. Materialy*, 1967, vol. 3, pp. 723-26.
16. E. Lugscheider, O. Knotek, and H. Reimann: *Monatsh. Chem.*, vol. 105, 1974, pp. 80-90.
17. W.F. Gale and E.R. Wallach: University of Cambridge, Cambridge, United Kingdom, unpublished research, 1991.