Transient Liquid Phase Process in Ni-B Joining

Jae Pil Jung* and Choon Sik Kang**

*Department of Material Science and Engineering, The University of Seoul,
Junnong-dong, Dongdaemun-gu, Seoul 130-743, Korea

**Department of Metallurgical Engineering, Seoul National University,
Shilim-dong, Gwanak-gu, Seoul 151-742, Korea

With the use of the diffusion bonding system of Ni/B/Ni, the liquid layer at the Ni/B interface was studied. In the previous report we suggested that the intermediate layer of pure B which has a high diffusivity in Ni and a high melting temperature can reduce the bonding time of the TLP (Transient Liquid Phase) process. In the present study the Ni/B/Ni specimen was bonded at temperatures of 1433–1473 K in vacuum. As a result, a liquid metal in the bonding zone was formed by mixing the diffused atoms of the intermediate layer of solid state with the base metal. For this procedure incubation time of 25 s was required. The initial width and the maximum width of the liquid layer were 3.5 and 9 times, respectively, wider than the thickness of the intermediate layer. With a similar bonding procedure, pure carbon (C) can be used also as an intermediate layer.

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I. Introduction

TLP (Transient Liquid Phase) bonding has been suggested as a method for the bonding of heat resistant alloys⁽¹⁾, and a lot of papers on the bonding process and mechanism have been made^{(1)–(7)}. According to the previous reports, the process of TLP bonding is composed of the melting of an intermediate layer, the dissolution of a base metal, the isothermal solidification and the homogenization.

It takes a long time to complete the TLP bonding process mainly due to the amount of time taken for homogenization. In order to reduce the amount of time taken for bonding in the TLP process, a highly diffusive element of pure boron (B) was applied as an intermediate layer by the authors, and we found some possibilities for commercial alloys⁽⁸⁾⁽⁹⁾.

In case that B is used as an intermediate layer, the melting temperature of the intermediate layer is higher than the bonding temperature, and than that of the commonly used base metals like Ni- or Fe-alloys. Therefore in the diffusion bonding system of Ni/B/Ni, the intermediate layer is not melted at the bonding temperature. Tuah-poku *et al.*⁽⁴⁾ studied the Ag/Cu/Ag sandwich joint where the melting temperature of the intermediate layer is higher also than that of the base metal. In this case, however, the formation of liquid metal on the Ag/Cu/Ag-joint was not mentioned, and it took a long time for the TLP bonding.

In this study, we tried to investigate the formation of liquid metal, the width of liquid layer, the isothermal solidification, and the bonding procedure of the Ni/B/Ni-joint which took shorter time for the TLP bonding.

II. Experimental Details

1. Materials

Pure B-powder with purity 99.6% and size — 325 mesh was used as the intermediate layer. To simplify the bonding phenomenon, pure Ni, the basic element of Ni-base superalloys to which TLP bonding is applied commonly, was chosen as the base metal. In the bonding specimen of the Ni/B/Ni, the dimension of one of the two base metals is $10 \times 10 \times 20 \text{ mm}^3$, and the chemical composition of the base metal is given in Table 1.

The bonding surfaces of the base metals were polished by using Al_2O_3 -powder of $0.05 \mu\text{m}$ in diameter. On the polished surface, B-powder was coated as the slurry state mixed with methyl alcohol. The amount of B which is necessary to form the intermediate layer of a given thickness was weighed and evenly coated on the base metal. For example Fig. 1 shows the cross section of the glass on which B-powder is coated. In order to obtain a clear photographic image of intermediate layer, glass was used in place of Ni, the base metal, for transparency. The thickness of the intermediate layer ranged from 5 to $150 \mu\text{m}$.

2. Bonding condition

The Ni/B/Ni specimen was packed in a quartz tube in

Table 1 Chemical composition of the base metal (mass%).

Si	Zn	Fe	Bi	Pb	Ni
0.295	0.29	0.10	0.099	0.053	bal

Fig. 1 Cross-section of the glass on which B-powder is coated (B-thickness: 25 μm). In order to obtain a clear photographic image of the intermediate layer, glass was used in place of Ni, the base metal.

the vacuum condition of 1.6×10^{-1} Pa. The specimen was heated up to the bonding temperature of 1433–1473 K at the rate of 24 K/s in the induction furnace. After the specimen was held at the bonding temperature, it was quenched into the water of room temperature. The quenching produced eutectic layer in the bonding zone, and we assumed the width of the eutectic layer to be equal to that of the liquid layer at the bonding temperature just before quenching⁽⁴⁾.

The bonded zone was analyzed by Scanning Electron Microscope (SEM) and Auger Electron Spectroscopy (AES).

III. Results and Discussion

1. Formation of liquid metal

Figure 2 shows the bonding surface of the Ni/B/Ni specimen at the early stage of bonding where the specimen was held for 25 s at 1453 K and the thickness of the intermediate layer was 25 μm . On the bonding surface only a melted mark appeared and some of B powders remained in a solid state. The melted mark was cross sectioned, and the microstructure of the sectioned area was found to be eutectic. In order to observe the eutectic zone easily, we used a thicker intermediate layer of 150 μm thickness, and the specimen was held for 180 s at 1453 K and quenched into water of room temperature. In Fig. 3(a) as well as in Fig. 2, some of B remained as in a solid state as powder on the bonding surface, and the eutectic zone was also observed.

In Fig. 3 the left hand side is the remaining intermediate layer of solid state B, and the right hand side is the base metal. The change of Ni- and B-concentration on the eutectic zone was measured by the AES (see Fig. 3(b)). The experimental result showed that B-concentration decreased gradually from the left to the right side.

Considering the results shown in Figs. 2 and 3, it seems that some of B has been diffused from the intermediate

Fig. 2 Bonding surface of the Ni/B/Ni specimen at the early stage of bonding (B-thickness: 25 μm , held for 25 s at 1453 K).

Fig. 3 The eutectic zone near the solid-state intermediate layer (a), and the profile of Ni- and B-concentrations by AES analysis (b). (Ni/B/Ni specimen, B-thickness: 150 μm , held for 180 s at 1453 K).

layer into the base metal due to the gradient of B-concentration. The diffused B will mix with the base metal, and if the melting point of the mixed base metal is lowered below the bonding temperature, then it will be melted.

In Fig. 4, the amount of liquid metal (i.e. eutectic

Fig. 4 Relation between the width of the eutectic layer and the square root of the holding time at 1433 K, 1453 K and 1473 K (Ni/B/Ni specimen, B-thickness: 25 μm).

layer) produced at the interface of the Ni/B/Ni is illustrated with the square root of holding time. Irrespective of the bonding temperatures of 1433, 1453 and 1473 K, the tendency to the width of the eutectic layer with holding time is similar.

When the holding time was less than 25 s, the eutectic layer could not be observed on the bonding zone. By increasing holding time more than 25 s, however, the eutectic layer was observed. That means it takes 25 s of incubation time to produce liquid metal by mixing solid state B with Ni.

2. Initial width of liquid layer

When all the solid state intermediate layer is dissolved, the bonding zone is filled with liquid metal. The width of the liquid layer at this moment can be defined as the initial width of the liquid layer, W_{IL} , like the other studies of TLP bonding⁽²⁾⁻⁽⁴⁾. In the Ni/B/Ni specimen the measured values of W_{IL} were 87 μm at 1433 K (holding time, $t_h=90$ s), 81 μm at 1453 K ($t_h=50$ s) and 80 μm at 1473 K ($t_h=45$ s). Figure 5 shows an example of the bonding zone filled with liquid metal.

W_{IL} can be calculated theoretically also as the function of W_0 by using mass balance of B, where W_0 means the thickness of the intermediate layer.

For the convenience of calculation, we set the following three conditions. First, the amount of B which had been diffused into the solid state base metal was neglected, because B-concentration on the Ni of solid state (i.e. solidus concentration) was much less than that of the liquid state (i.e. liquidus concentration) at a given temperature (see Fig. 6⁽¹⁰⁾). For example, at 1453 K the B-concentration on the Ni of liquid state is 3.15 mass% (13 at%), whereas on the solid state is 0.03 mass% (0.22 at%). Sec-

Fig. 5 Example of the bonding zone filled with the liquid metal (Ni/B/Ni specimen B-thickness: 15 μm , held for 250 s at 1453 K).

Fig. 6 The Ni-B phase diagram⁽¹⁰⁾.

ondly, the volume change of the Ni-B alloy by melting was neglected. Finally, the average concentration of B on W_{IL} was assumed as $(X_3 + X_4)/2$, where X_3 and X_4 was the liquidus concentration of B on the interface of 'Ni/liquid layer' and 'B/liquid layer' respectively as shown in Fig. 7. Accurate Ni-B phase diagram (Fig. 6) is more complicated than Fig. 7. As the bonding temperature of 1433–1473 K is higher than the melting temperatures of the Ni-B intermetallic compounds, Fig. 6 can be simplified to Fig. 7.

The derivation of mass balance equation is as follows.

$$W_0 \cdot \rho_B \cdot 100 = W_{\text{IL}} \cdot \rho_{\text{IL}} \cdot (X_3 + X_4)/2 \quad (1)$$

where

$$\rho_{\text{IL}} = f_B \cdot \rho_B + f_{\text{Ni}} \cdot \rho_{\text{Ni}} \quad (2)$$

$$\begin{aligned} f_B &= V_B / (V_B + V_{\text{Ni}}) \\ &= \{(X_3 + X_4)/2 / \rho_B\} / [(X_3 + X_4)/2 / \rho_B \\ &\quad + \{100 - (X_3 + X_4)/2\} / \rho_{\text{Ni}}] \end{aligned} \quad (3)$$

Fig. 7 Schematic illustration of Ni- and B-concentrations on the Ni/B boundary when liquid metal is producing at the bonding temperature of 1433–1473 K.

$$f_{Ni} = V_{Ni} / (V_B + V_{Ni})$$

$$= \{ [100 - (X_3 + X_4)/2] / \rho_{Ni} \} / \{ (X_3 + X_4)/2 / \rho_B + [100 - (X_3 + X_4)/2] / \rho_{Ni} \} \quad (4)$$

W_0 : W_{IL} (μm)
 ρ_{IL} : density of W_{IL} (g/cm^3)
 ρ_B : density of B (g/cm^3)
 ρ_{Ni} : density of Ni (g/cm^3)
 f_B : partial molar volume of B in W_{IL}
 f_{Ni} : partial molar volume of Ni in W_{IL}
 V_B : volume of B in W_{IL}
 V_{Ni} : volume of Ni in W_{IL}

From eqs. (1)–(4), eq. (5) and W_{IL} can be obtained.

$$W_0 \cdot \rho_B \cdot 100 = (W_{IL} - W_0) \cdot \rho_{Ni} \cdot (X_3 + X_4)/2 + W_0 \cdot \rho_B \cdot (X_3 + X_4)/2 \quad (5)$$

$$W_{IL} = W_0 [1 + \{200 \cdot \rho_B / (X_3 + X_4) \cdot \rho_{Ni}\} - \rho_B / \rho_{Ni}] \quad (6)$$

W_{IL} is varied with W_0 , X_3 and X_4 , if ρ_B and ρ_{Ni} are constant. When the bonding temperature is determined, X_3 and X_4 will become constant also, and in this case W_{IL} is linearly proportional to W_0 .

The calculated W_{IL} by eq. (6) and the measured one are listed in Table 2. The constant values for calculating eq. (6) are $\rho_B = 2.34 \times 10^3 \text{ kg}/\text{m}^3$ and $\rho_{Ni} = 8.9 \times 10^3 \text{ kg}/\text{m}^3$. The values of X_3 are 3.26 mass% at 1433 K, 3.15 mass% at 1453 K and 3.05 mass% at 1473 K. X_4 are 15.37 mass% at 1433 K, 15.61 mass% at 1453 K and 15.85 mass% at 1473 K. The values of X_3 and X_4 are calculated from the phase diagram of Ni–B (Fig. 6)⁽¹⁰⁾ by assuming that the solidus and the liquidus line between 1473 K and the eutectic points of 1366 K and 1308 K are linear.

As shown in Table 2, we can see that the calculated

Table 2 Comparison of the calculated and the experimentally measured values of W_{IL} , when W_0 was 25 μm .

Bonding temperature (K)	Calculated W_{IL} (μm)	Measured W_{IL} (μm)
1433	89	87
1453	88	81
1473	88	80

W_{IL} 's correspond well to the measured ones, and W_{IL} is about 3.5 times wider than W_0 .

In some results of the TLP bonding^{(2)–(4)}, however, W_{IL} is equal to the thickness of the intermediate layer of W_0 . Tuah-poku *et al.*⁽⁴⁾ analyzed the dissolution process of Ag/Cu/Ag joint where, similarly Ni/B/Ni, the melting point of intermediate layer is higher than the bonding temperature. In this case W_{IL} is also regarded as equal to W_0 .

In the Ni/B/Ni specimen, the liquid layer will be produced by mixing between the diffused atoms of the intermediate layer and of the base metal. The B-concentration in W_{IL} of the Ni/B/Ni specimen, for example, on the range of 3.15–15.7 mass% at 1453 K⁽¹⁰⁾, is much less than that in W_0 of nearly 100%. That means B in the intermediate layer should be diffused into the base metal continuously until its concentration is reduced from 100% to the range of 3.15–15.7 mass%. During this process, the base metal which contains B on the range of 3.15–15.7 mass% will be melted continuously, and the width of the liquid layer increase. This will make W_{IL} wider than W_0 in the case of Ni/B/Ni.

3. Max. width of liquid layer

As the holding time at a bonding temperature increases, the width of the liquid layer at the bonding zone of Ni/B/Ni will also increase gradually. Finally it reaches to maximum value of W_M , and from this moment isothermal solidification begins. As shown in Fig. 4, the measured values of W_M were 138 μm at 1433 K ($t_h = 830 \text{ s}$), 146 μm at 1453 K ($t_h = 575 \text{ s}$) and 158 μm at 1473 K ($t_h = 300 \text{ s}$).

The derivation of mass balance equation for calculating W_M is as follows.

$$W_0 \cdot \rho_B \cdot 100 = W_M \cdot \rho_M \cdot X_3 \quad (7)$$

where

$$\rho_M = f'_B \cdot \rho_B + f'_{Ni} \cdot \rho_{Ni} \quad (8)$$

$$f'_B = V'_B / (V'_B + V'_{Ni}) = (X_3 / \rho_B) / \{X_3 / \rho_B + (100 - X_3) / \rho_{Ni}\} \quad (9)$$

$$f'_{Ni} = V'_{Ni} / (V'_B + V'_{Ni}) = \{(100 - X_3) / \rho_{Ni}\} / \{X_3 / \rho_B + (100 - X_3) / \rho_{Ni}\} \quad (10)$$

ρ_M : density of liquid metal at W_M (g/cm^3)

f'_B : partial molar volume of B in W_M

f'_{Ni} : partial molar volume of Ni in W_M

V'_B : volume of B in W_M

V'_{Ni} : volume of Ni in W_M

Table 3 Comparison of the calculated and the experimentally measured W_M , when W_0 was 25 μm .

Bonding temperature (K)	Calculated, W_M (μm)	Measured, W_M (μm)
1433	220	138
1453	227	146
1473	234	158

From eqs. (7)–(10), eq. (11) and W_M can be obtained.

$$W_0 \cdot \rho_B \cdot 100 = [(W_M - W_0) \cdot \rho_{Ni} + W_0 \cdot \rho_B] \cdot X_3 \quad (11)$$

$$W_M = W_0 \cdot \{1 + (\rho_B / \rho_{Ni}) \cdot (100 - X_3) / X_3\} \quad (12)$$

W_M is varied with W_0 and X_3 , if ρ_B and ρ_{Ni} are constant. When the bonding temperature is determined, X_3 will be also constant, and in this case W_M is linearly proportional to W_0 .

The calculated W_M by eq. (12) and the measured one are listed in Table 3. The same constant values (X_3 , ρ_{Ni} , ρ_B) in eq. (6) are also used in the calculation of W_M . As shown in Table 3, calculated W_M 's are 220 μm at 1433 K, 227 μm at 1453 K and 234 μm at 1473 K, and they are larger than the measured ones. The reason seems that by the wetting phenomenon some liquid metal on the bonding zone flows out and spreads on the surface of the base metal. Therefore the amount of the liquid metal within the bonding zone will decrease, and it can cause the measured W_M to become smaller than the calculated one.

The calculated values of W_M 's are nearly $9W_0$ (see Table 3). These values are larger than the result of Tuah-poku *et al.*, $W_M \approx 4.9W_0$ at Ag/Cu/Ag joint⁽⁴⁾. The results of our and Tuah-poku's studies should be different because of the difference in the base metals, the intermediate layers, and the liquidus concentrations X_3 , which are used in both studies.

4. Isothermal solidification

As illustrated in Fig. 4, the Ni/B/Ni specimen was isothermally solidified by holding it for 17930 s at 1433 K, 14975 s at 1453 K and 12600 s at 1473 K. Figure 8 shows the example of isothermally solidified joint.

In the TLP bonding, the isothermal solidification is known as the diffusion controlled process of the melting point depressant just as B⁽²⁾⁻⁽⁵⁾⁽¹¹⁾. Considering this and our experimental results, isothermal solidification of the Ni/B/Ni joint will also be the diffusion controlled process of B.

During isothermal solidification, the width of liquid layer decreased linearly as the square root of holding time increased as shown in Fig. 4. Based on these results, during isothermal solidification, the width of the liquid layer at time t (W_t) can be given as in eq. (13).

$$W_t = W_M - k \sqrt{D(t - t_M)} \quad (13)$$

k : const.

D : diffusivity of B in solid Ni at bonding temperature

t_M : the time taken for W_M

Fig. 8 Isothermally solidified joint of Ni/B/Ni (B-thickness: 15 μm , held for 7920 s at 1453 K).

The time taken for isothermal solidification, t_f , can be also derived from eq. (13). When the specimen solidified isothermally, W_t becomes zero. In this case, the t of eq. (13) becomes t_f , and we can get t_f as follows:

$$t_f = A \frac{W_M^2}{D} + t_M \quad (14)$$

A : const.

Equation (14) is a form similar to the results of Liu *et al.*⁽⁵⁾ and others⁽⁴⁾⁽¹¹⁾.

5. Bonding procedure

Figure 9 shows the schematic illustration for the change of B-concentration at the Ni/B interface during the bonding process. During the bonding, B-concentration at the intermediate layer will vary in the order of $0' \rightarrow 1' \rightarrow 2' \rightarrow 3' \rightarrow 4 \rightarrow 5 \rightarrow 6$, and at the base metal

Fig. 9 Schematic illustration for the change of B-concentration at the Ni/B/Ni interface during bonding (BM: base metal side, IM: intermediate layer side).

adjacent to the intermediate layer, it will vary in the order of $0 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow 3' \rightarrow 4 \rightarrow 5 \rightarrow 6$. The numbers 0 and 0' mean the compositions of the base metal and the intermediate layer respectively before bonding. The interface will isothermally solidify from 4 to 5, and homogenized at 6.

This procedure is a little different from the illustration reported by Duvall *et al.*⁽¹⁾. The difference in the two cases is caused by the different procedure for the formation of liquid metal on the joint. That means, in case of the Ni/B/Ni specimen, liquid metal is formed by mixing the diffused atoms of the intermediate layer with the base metal, whereas in case of Duvall *et al.*, liquid metal is formed by the simple melting of the intermediate layer.

Fig. 10 Examples of isothermally solidified joint (a) 'Rene80(upper)/B/AISI 304(lower)' (B-thickness: 15 μm , held for 14400 s at 1453 K), (b) 'Ni/C/Ni' (C-thickness: 5 μm , held for 900 s at 1618 K).

Using B as an intermediate layer, we can also bond other metals such as Cu, Fe- and Ni-alloys⁽⁸⁾⁽⁹⁾⁽¹²⁾. Pure carbon (C), interstitial element like B, can be also used as an intermediate layer to bond isothermally in a short time. For example, Figure 10 shows the Rene80/B/AISI304- and Ni/C/Ni-joint of liquid phase diffusion bonding.

IV. Conclusion

With the use of the diffusion bonding specimen of Ni/B/Ni, the formation of liquid metal, the width of liquid layer at the Ni/B interface, and the bonding procedure were studied. The obtained results are summarized as follows.

(1) At the early stage of bonding, the incubation time of about 25 s was required for producing liquid metal in the bonding zone.

(2) The initial width of liquid layer was calculated as $W_{IL} = W_0 [1 + \{200 \cdot \rho_B / (X_3 + X_4) \cdot \rho_{Ni}\} - \rho_B / \rho_{Ni}]$. The calculated W_{IL} was nearly equal to $3.5 \cdot W_0$, and it corresponded well to the measured one.

(3) The maximum width of liquid layer was calculated as $W_M = W_0 \cdot \{1 + (\rho_B / \rho_{Ni}) \cdot (100 - X_3) / X_3\}$, and the calculated W_M was nearly equal to $9 \cdot W_0$.

(4) With similar bonding procedure of the Ni/B/Ni, Rene80/B/AISI304 and Ni/C/Ni specimens were also bonded.

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