THERMODYNAMIC MODELING AND EXPERIMENTAL INVESTIGATION OF BRAZED JOINTS USED IN AEROSPACE INDUSTRY

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Abstract

The kinetics of isothermal solidification during the TLP-brazing of nickel superalloys, Inconel 625 and 718, and stainless steel, SS 410, with BNi-2 filler alloy has been studied through a combination of modeling and experimental investigations. It was observed that the boron diffusion model and migrating solid/liquid interface model predicted the isothermal solidification times relatively accurately when nickel superalloys were used as base metals; however, silicon diffusion model was more accurate for stainless steel base metal due to the increased solubility of boron in the multi-component melt. A revision of boron diffusion model parameters was given for the SS 410/BNi-2 combination for better approximation of holding time and to calculate the composition of the residual liquid when the holding time was not long enough to complete the isothermal solidification.

Introduction

Inconel 625 and 718 superalloys are extremely versatile austenitic nickel based superalloys with excellent strength and good ductility at very high temperature. Typical applications include aero-engine hot section components, miscellaneous hardware, tooling and liquid rocket components involving cryogenic temperatures. However, like other austenitic nickel based superalloys that contain a substantial amount of Ti and Al, they are highly susceptible to the heat affected zone cracking during welding [1]. SS 410 is martensitic stainless steel that provides good corrosion resistance plus high strength and hardness. Typical applications include steam and gas turbine parts, pump and valve shafts, miscellaneous hardware, tooling and petroleum fractionating towers. However, due to hardenability, it is also highly susceptible to the heat affected zone cracking during welding [2]. Typical high temperature brazing with nickel based fillers that contain boron and silicon as melting point depressants are commonly used to join these alloys. However, these melting point depressants form eutectic structures that are extremely hard and contain very brittle intermetallic compounds with nickel and chromium which are detrimental to the mechanical properties of brazed joint [3-5]. One method to prevent the formation of these deleterious phases is transient liquid phase bonding (TLP), also known as diffusion brazing. The diffusion brazing process uses a low melting filler alloy to wet the contacting base material and that subsequently solidifies isothermally via a fast diffusing element, e.g. boron. Thus, at a relatively low melting temperature, diffusion brazing produces a joint that has a uniform composition profile and that is relatively more tolerant of surface oxides**,** geometrical defects and wide gaps [6]. These advantageous features have been exploited in a wide range of applications, from the production and repair of turbine engines in the aerospace industry to the connection of circuit lines in the microelectronic industry [7].

One of the most important parameters in the diffusion brazing process is the time required to complete the isothermal solidification to prevent the formation of the brittle eutectic phases in the resulting brazed joints. Tuah-Poku *et al.* [8] derived the expression for the holding time for silver/copper/silver sandwich joints based on stationary solid/liquid interface and their predicted values were found to be overestimated compared to the experimental findings. Lee *et al.* [9] suggested that diffusion of the solute into the base metal could actually take place during liquid homogenization, which could result in the formation of second phase precipitates and thus the holding time required for complete isothermal solidification would be considerably reduced. Other models based on migrating solid/liquid interface [4,10] and Fick's second law of diffusion have been used by other researchers [11-14] to predict the isothermal solidification completion times for pure nickel and nickel based superalloys with either binary Ni-P or ternary Ni-Cr-B filler alloys, and good agreement with the experimental values have been reported. However, such studies have not yet been carried out for transient liquid phase bonding of Inconel 625 and 718, and SS 410 base alloys with multicomponent filler alloy, such as BNi-2. One of the major limitations of the existing modeling approaches, when nickel based fillers are used for bonding, is that these models rely on the solubility of boron in pure nickel as a reference for isothermal solidification. However, the real systems are almost always multi-component and the validity of such assumption has to be verified experimentally. An increase in solubility will result into overestimation of time requirement to complete isothermal solidification and vice versa.

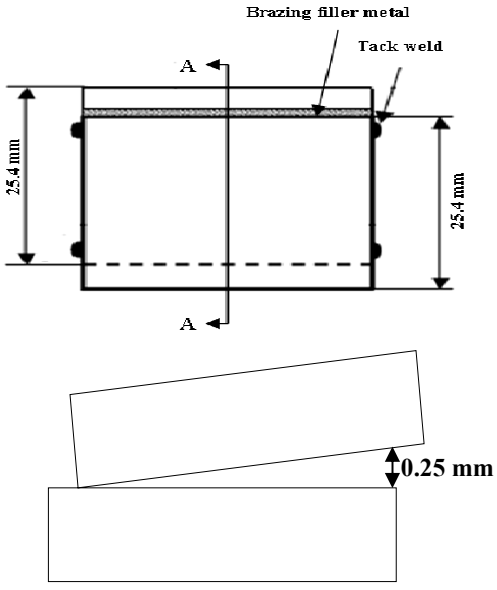
Although diffusion brazing is an excellent bonding technique, the time required to complete isothermal solidification is

usually long enough to discourage their potential applications in many industries. Therefore, a better understanding of the effect of other process variables, such as brazing temperature and joint gap, on the time required to complete isothermal solidification, is imperative to reduce the time requirement and thus to optimize the process.

The objectives of this work are, thus, to calculate the time required to complete the isothermal solidification using different modeling approaches, and to study the effect of process variables during the transient liquid phase bonding of Inconel 625 and 718, and SS 410 with nickel based filler BNi-2, and to verify the predicted values with experimental investigations.

Experimental Procedures

In this work, wedge shape joint gap specimen model, shown in Fig. 1, was utilized. The specimen models consisted of two identical wrought Inconel 625 and 718, and SS 410 base alloys with a relative movement of 4 mm from each other to form an edge groove where the BNi-2 brazing filler paste was placed. The nominal compositions of the base and filler alloys are given in Table 1. The specimen was fixed by tack welds to form a variable brazing gap (0 – 250 μm).



A-A

Fig. 1 The wedge shape joint gap specimen

The samples were nicro-blasted and then acid cleaned. To prevent the oxide build-up, the base alloy was pre-plated with very thin layer of nickel (nickel flash) and subsequently vacuum brazed in an Argon atmosphere at a vacuum pressure of 106.6 Pa according to the matrix shown in Table 2. The brazed samples were prepared metallographically and studied under the optical and scanning electron microscopes (SEM) equipped with electron dispersive spectrometry (EDS) at Concordia University and the Université Polytechnique de Nantes, France.

Table 1 Nominal compositions of Inconel 625, 718, SS 410 and BNi-2

Alloy	Nominal Composition	Solidus (°C)	Liquidus (°C)
Inconel 625	Ni: 58% (min), Cr: 20 – 23%, Fe: 5%, Co: 1%, Mo: 8 – 10%, Nb(+Ta): 3.15 - 4.15%, Ti: 0.4%, Al: 0.4%, C: 0.1%, Mn: 0.5%, Si: 0.5%	1290	1350
Inconel 718	Ni (+Co): 50-55%, Cr: 17-21%, Fe: bal, Co: 1%, Mo: 2.8-3.3%, Nb(+Ta): 4.75-5.5%, Ti: 0.65-1.15%, Al: 2-8%, C: 0.8%, Mn: 0.35%, Si: 0.35%, B: 0.006%, Cu: 0.3%	1260	1336
AISI 410	Fe, <0.15%C, 11.5-13.5%Cr, >0.75%Ni, <1.0%Si, <0.04%P, <0.03%S	1480	1530

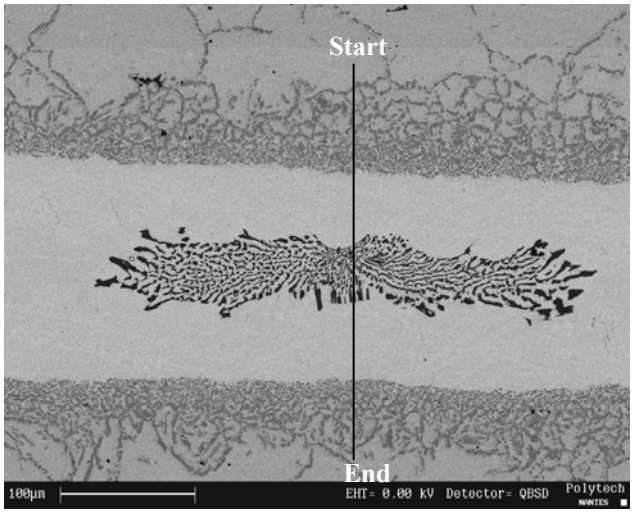
Table 2 Braze tests matrix

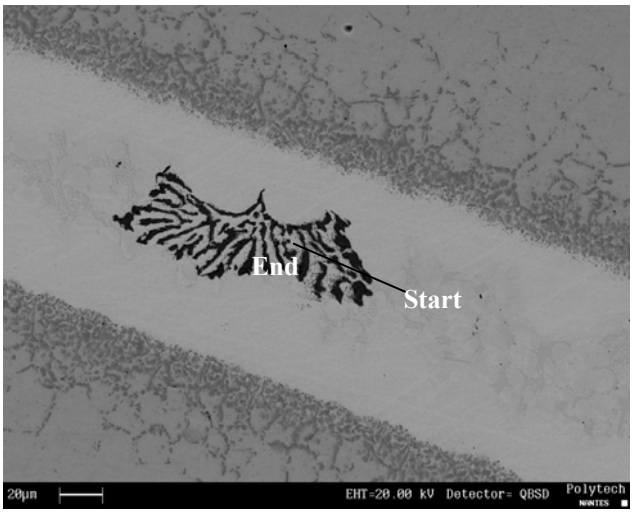
Temp. (K)	Holding Time (min)						
1325	10			50	60	70	90
1358			30	50		70	90
1394	10	20	30	50			90

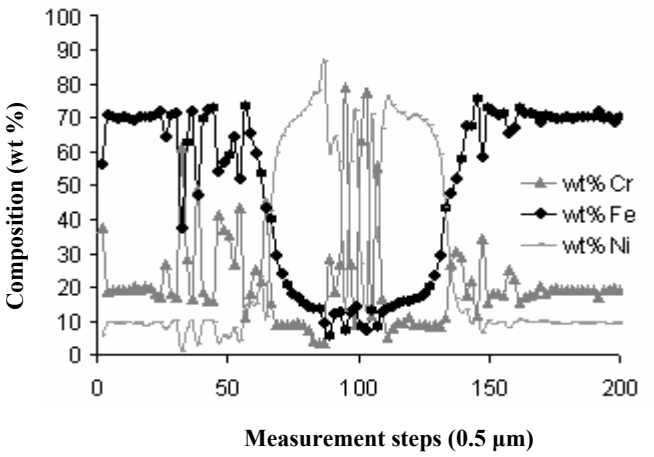
Microstructures of the Joint

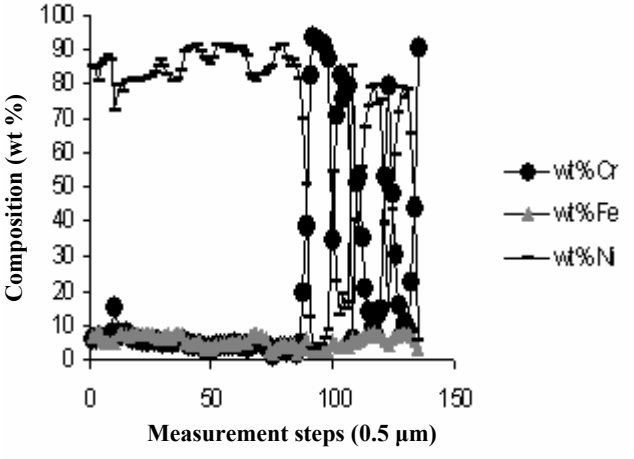
A typical micrograph of the SS 410/BNi-2 brazed joint and the corresponding EDS analyses is shown in Fig. 3. Intermetallic phases were formed along the centerline of the joint since the holding time was not long enough to complete isothermal solidification. The residual liquid that was present at the end of the temperature holding eventually transformed on cooling into eutectic constituents.

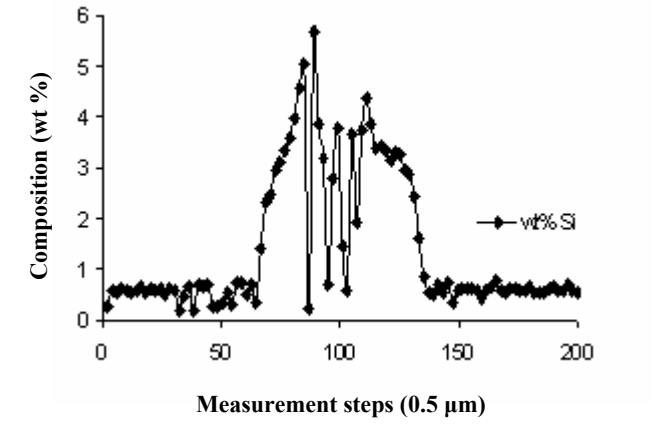
EDS analyses suggest that it consists of γ- nickel solid solution (both pro-eutectic and eutectic) and Cr and Ni rich borides, which are in agreement with the findings of other researchers [3,5,15]. A line scan through the centerline eutectics reconfirmed the findings, as shown in Fig. 4.











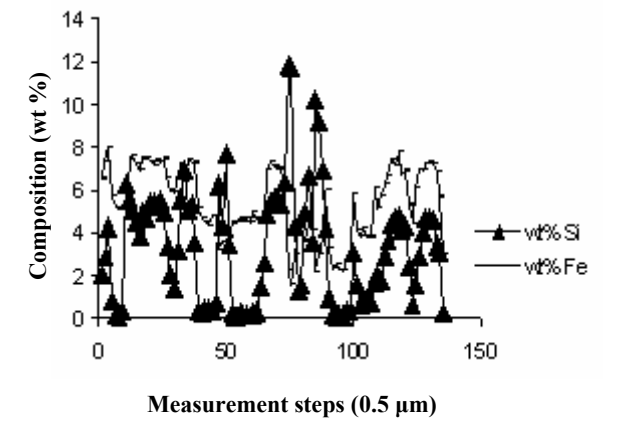


Fig. 3 SEM micrograph and the corresponding EDS analyses of a SS 410/BNi-2 joint brazed at 1394K for 50 minutes

Fig. 4 Line scans through centerline eutectics of a SS 410/BNi-2 joint brazed at 1325K for 50 minutes

EDS compositional analyses in Fig. 3 and 4 revealed a significant amount of silicon in the center of the joint that might form nickel silicides, which is in accordance with the findings of Jang *et al.* [5]. This can be understood from the following solidification phenomenon [3]: During brazing, γ-nickel first solidified isothermally from the faying surfaces into the melt. Upon cooling the primary γ- nickel solidified as nodular dendrites which enriched the remaining melt with boron, silicon and chromium. As cooling proceeded, binary eutectic of γ- nickel and nickel boride solidified, further enriching the melt of chromium. Subsequently, binary eutectic of γ- nickel and chromium boride solidified. The remaining portion of the melt, which is further enriched in silicon will eventually transform into the ternary eutectic of γ-nickel, nickel boride and nickel silicides. Since the multi-component melt is rich of nickel, similar solidification phenomena are expected for Inconel 625, 718 and SS 410/BNi-2 combinations when the holding time is not sufficient to complete isothermal solidification.

Conventional TLP models assume that solute diffusion in the base metal takes place under equilibrium conditions and thus the formation of boridic precipitates is avoided. However, because of rapid boron diffusion and its low solubility, parent metal close to the brazing gap is quickly oversaturated with boron which produces strong precipitation of borides having a very dense arrangement [16]. This was evident in all brazed joints microstructures, irrespective of brazing temperature, holding time and joint gap. It suggests that diffusion of solute atoms into the base alloy could actually take place during base metal dissolution and liquid homogenization. These borides produce brittleness and decrease the formability of the joint [17]. In order to obtain superior mechanical properties, it is necessary to dissolve these borides or to dilute them to a degree where they have no or minimum negative effects. Solid solution in the joint gap with no or minimum precipitates in the base metals would form an ideal brazed joint. Some researchers [7,17] suggested the necessity of homogenization heat treatment after complete isothermal solidification to achieve comparable properties between the base and filler alloys.

Mathematical Modeling of Isothermal Solidification Time

Boron Diffusion Model:

For unsteady state diffusion of a specie from a source with initial thickness 2w, which is of the order of diffusion distance $(Dt)^{0.5}$, into a semi-infinite substrate, solute distribution in the substrate is represented by [18]:

$$C_{(y,t)} = C_m + \frac{1}{2}(C_0 - C_m)\left\{ erf\ \frac{y+w}{\sqrt{4Dt}} - erf\ \frac{y-w}{\sqrt{4Dt}} \right\} \quad \text{.....(1)}$$

where, C_m = initial solute concentration in the base metal; C_o = initial solute concentration in the interlayer; $C_{(y,t)}$ = solute concentration as a function of distance from the centre of the interlayer (y) and time (t); D = diffusion coefficient of the solute in the substrate.

Holding time can be estimated considering the fact that isothermal solidification is completed when the solute concentration at the centre of the interlayer is reduced to the solidus value C_s. Substituting $C_{(y,t)} = C_s$ at y = 0 yields the following equation:

$$C_s - C_m = (C_0 - C_m)\left\{ erf\ \frac{w}{\sqrt{4Dt_f}} \right\} \quad \text{.....(2)}$$

Migrating Solid/liquid Interface Model:

Modeling based on migrating solid/liquid interface gives the following expression [7]:

$$t_f^{1/2} = \frac{2h}{\gamma * 4 * D^{1/2}} \quad \text{.....(3)}$$

where t_f is the time required to complete isothermal solidification, D is the diffusion coefficient, 2h is the maximum width of the brazed insert following homogenization of liquid and γ is a dimensionless parameter that accounts for the moving boundary which can be determined from the following expression:

$$\frac{C_\alpha - C_m}{C_\beta - C_m} = \gamma\sqrt{\pi}\exp\gamma^{1/2}(1 + erf(\gamma)) \quad \text{.....(4)}$$

C_α and C_β are the solute concentration in the solid phase and the liquid phase at the interface, respectively. The value of γ was first calculated by taking C_α and C_β as the average values of boron concentration in solidus (0.3 at%) and liquidus (16.3 at%) of Ni-B binary system over the brazing temperature range (1325 -1394K).

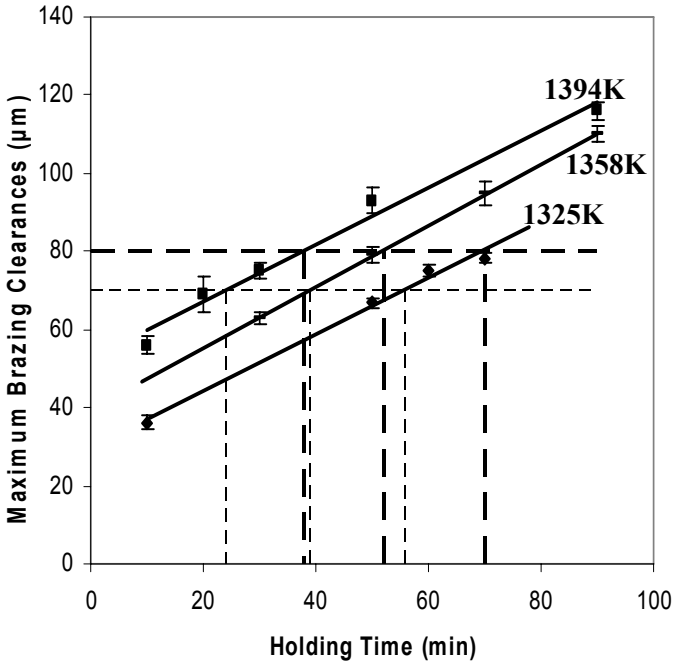
For γ < 0.1, a linear relationship exists among t_f, D and 2h [19]. Nakao *et al.* [20] developed the following linear expression:

$$t_f^{1/2} = J\left(\frac{2h}{D^{1/2}}\right) \quad \text{.....(5)}$$

where J is a constant and is related to γ by equation (3). Plotting the values of $t_f^{1/2}$ against $(2h/D^{1/2})$, the value of J, the slope of the straight line, can be determined.

Silicon Diffusion Model:

Like boron, silicon also acts as a melting point depressant which diffuses out from the joint towards the base metal. Using the average silicon composition in the isothermally solidified joint from EDS analyses, solute distribution law, equation 1, can be used to calculate the activation energy and frequency factor. Hence, this approach does not neglect the effect of any element in the multi-component melt on the solubility of the melting point depressant which will result into better approximation of holding time requirement for complete isothermal solidification than the other two models.



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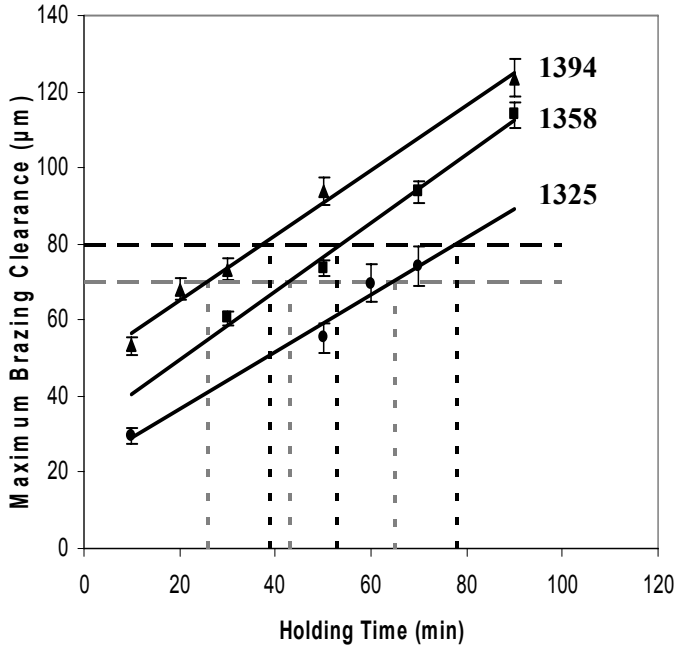
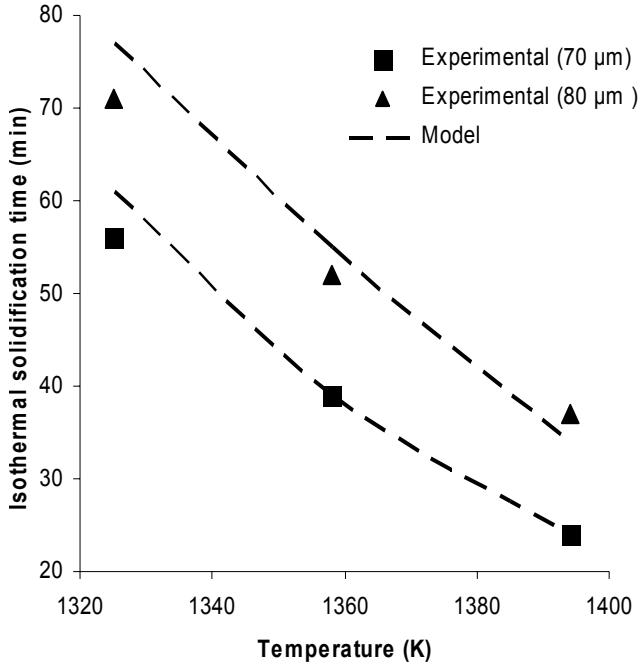


(b)

Fig. 5 Effect of holding time on the maximum brazing clearance of (a) Inconel 625/BNi-2 and (b) Inconel 718/BNi-2 combinations



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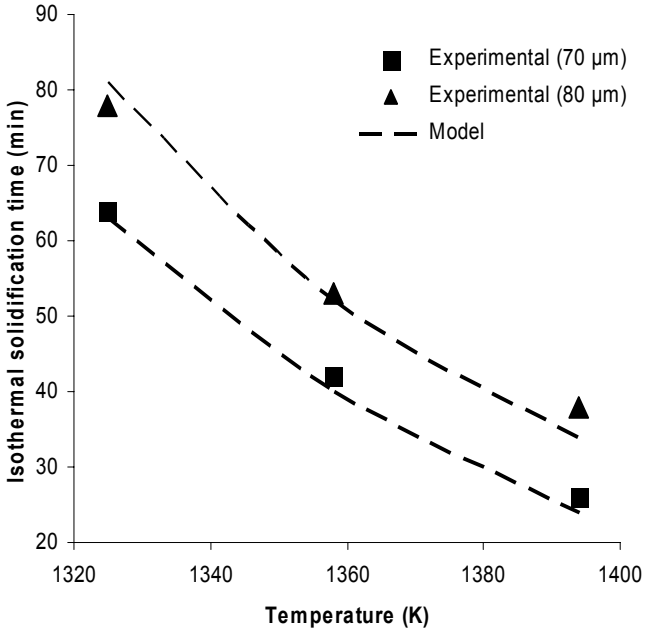
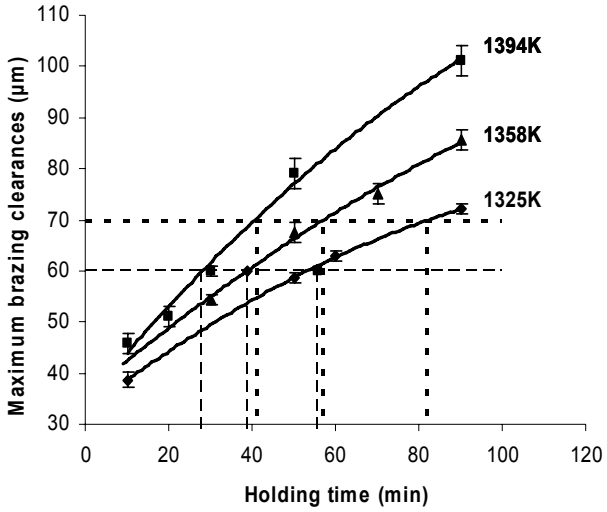


(b)

Fig. 6 Comparison of predicted isothermal solidification times from boron diffusion model with experimental investigations for (a) Inconel 625/BNi-2 and (b) Inconel 718/BNi-2 combinations

Experimental Verifications

In the wedge gap brazed joint, a distinction is made between areas of free of brittle phase and brittle phase containing seam sections. The beginning of brittle phase stabilization marks the maximum brazing clearance (MBC) for the combination of base metals and filler alloy brazed at a particular temperature and holding time. Figure 5 shows the maximum brazing clearances for the Inconel 625/BNi-2 and Inconel 718/BNi-2 combinations brazed at 1325K, 1358K and 1394K with different holding times ranged from 10 to 90 minutes.



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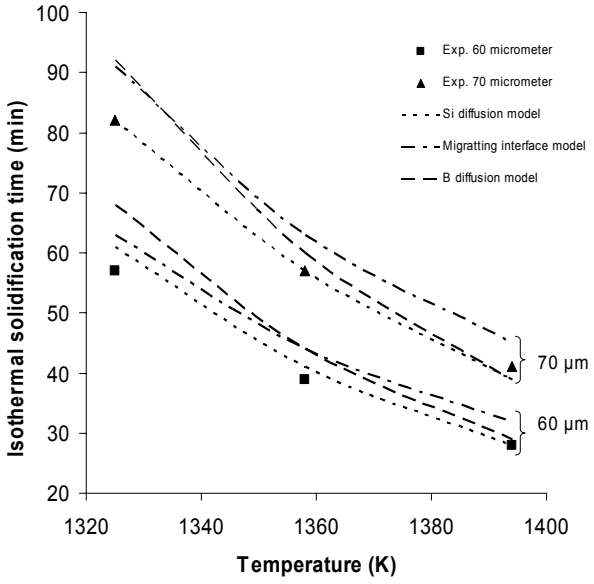

(b)

Fig. 7 (a) Effect of holding time on the maximum brazing clearance for SS 410/BNi-2 combination; (b) Comparison of predicted isothermal solidification times with experiments

Conversely, if a specified MBC is taken, the corresponding brazing time will represent the isothermal solidification time for that brazing clearance. Significant reduction of holding time was observed with increasing brazing temperatures and with decreasing joint gap.

It has been observed that the predicted isothermal solidification completion times for nickel superalloys were in very good agreement with the experimentally determined values, as shown in Fig. 6, with an error of ±8%. Besides the uncertainties of experimental measurements, the small deviations could be attributed to the following model assumptions: (i) The value of C_s was taken as 0.3 at% to simplify the variation of boron solubility in the multi-component melt. This is the maximum solubility of boron in pure nickel and remains almost constant in the holding temperature range (1325-1394K); (ii) The assumptions associated with Fick's second law of diffusion might have contributed some errors to the calculations.

However, for stainless steel base metal, both the boron diffusion model and the migrating solid/liquid interface model overestimated the time required to complete isothermal solidification, especially at low temperature bonding operation, as shown in Fig. 7. Significant amount of iron and chromium was dissolved in the joint due to the dissolution of base metal, and the assumption of 0.3 at % solubility of boron as a reference for forming solid solution would no longer be appropriate. An increase of solubility will result into overestimation of time requirement for complete isothermal solidification, as evident from the model predictions at lower temperature. This suggests that at lower temperature range of investigation (1325-1358K), the solubility limit of boron in the multi-component melt must have increased. The eutectic temperature in Ni-B binary system is 1366K, and it is expected that for a nickel based multi-component system, the eutectic point will be at lower temperature than the binary eutectic, e.g. the eutectic temperature for BNi-2 filler alloy is 1244K. The dissolution of the base metal in the liquid filler metal could eventually shift the eutectic point, however, it is obvious that the eutectic temperature will still be lower than 1325K, since, otherwise, no isothermal solidification would have taken place at that temperature. The increased boron solubility at lower temperature range (1325 – 1358K) is, thus, reasonable since the solubility limit is the maximum at the eutectic temperature. Silicon diffusion model does not neglect the effect of any element in the multi-component melt and the predicted times were almost accurate.

Computational Thermodynamics

Considerable reduction of time required to complete isothermal solidification has been observed with the increase of brazing temperature and/or with the decrease of initial joint gap for all the three combinations. However, when the material limits the temperature and the complex geometry does not allow the joint gap to be narrow enough to have a reduced isothermal solidification time, it is necessary to predict the extent of formation of brittle eutectic phases which are mainly borides with little amount of silicides as discussed before. It is, therefore, necessary to determine the boron

composition in the residual liquid at the end of holding time, and an accurate boron diffusion model has no alternative in this regard. The revision of boron diffusion model for the SS 410/BNi-2 combination is, thus, necessary.

Revision of Boron Diffusion Model for SS 410/BNi-2:
Since the times predicted for isothermal solidification at 1358 and 1394K were within the uncertainty limits of the experimental measurements, 0.3 at% boron solubility, for a joint to be solidified isothermally, was considered reasonable for this temperature range. Diffusion coefficients were obtained for the two brazing temperatures: 1358 and 1394K. The revised values of activation energy and frequency factor were found to be 198.2 kJ/mol and 0.00676 m^2s^{-1}, respectively. Using the revised diffusion coefficient at 1325K, and the time required for isothermal solidification for an initial joint gap of 70 μm from Fig. 7, the reference solubility (C_s) for a joint to be solidified isothermally was determined as 0.33 at%. The revised model parameters are summarized below:

Activation energy, Q = 198.2 kJ/mol;
Frequency factor, $D_0 = 0.00676\ m^2/s$;
$C_s = 0.30$ at%; $1358\ K \leq T \leq 1394K$
$= 0.33$ at%; $1325\ K \leq T \leq 1358K$

The residual liquid width and its composition can now be determined using the revised boron diffusion model and EDS analysis, taking the dissolution of the base metal into consideration. Computational thermodynamics coupled with kinetic model of diffusion can be applied to predict the amount of these deleterious phases evolved from the residual liquid at the end of isothermal solidification. Since solidification of residual liquid takes place under non-equilibrium conditions, Scheil simulation, using multicomponent thermodynamic database, can be used in this regard using the composition of the residual liquid.

Summary and Conclusions

In contrary to the conventional TLP models, extensive volume and grain boundary precipitation of borides were observed in all brazed samples. Therefore, it is obvious that diffusion of solute atoms into the base alloy actually takes place during base metal dissolution and liquid homogenization.

Diffusion modeling using Fick's second law and migrating solid/liquid interface was successful in predicting the isothermal solidification times for the Inconel 625/BNi-2 and Inconel 718/BNi-2 combinations; however, silicon diffusion model was more accurate for SS 410/BNi-2.

The overestimation of predicted times, for the SS 410/BNi-2 combination, by boron diffusion model, and migrating solid/liquid interface model at lower temperature, was due to the increased solubility of boron in the multi-component melt. A revision of boron diffusion model parameters was given for low temperature bonding operation (1325 – 1358K) which can be used to determine the time required for isothermal solidification as well as the boron composition in the residual liquid at the end of holding time when isothermal solidification is not completed. The revision of boron solubility at lower temperature can also be incorporated in the migrating solid/liquid interface for better approximation of holding time required for isothermal solidification.

Significant reduction of isothermal solidification time has been observed with decreasing joint gap and with increasing brazing temperature. No significant grain growth has been observed in the base metal in the temperature zone being investigated, however, before adopting higher brazing temperature, the susceptibility of base alloy to grain growth should be carefully studied.

Acknowledgments

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References

[1] Chen, W., Chaturvedi, M. C., Richards, N. L, "Effect of boron segregation at grain boundaries on heat-affected zone (HAZ) cracking in wrought Inconel 718," *Metallurgical and Materials Transactions A,* Vol. 32, No. 4 (2001), pp. 931-939.

[2] Penso, J. A. *et al, ASME, Pressure Vessel and Piping,* Vol. 395 (1999), pp. 243-253.

[3] Tung, S. K., Lim, L. C., Lai, M. O., "Solidification phenomena in nickel base brazes containing boron and silicon," *Scripta Materialia,* Vol. 34, No. 5 (1996), pp. 763-769.

[4] Sakamoto, A., Fujiwara, C., Hattori, T., Sakai, S., "Optimizing processing variables in high-temperature brazing with nickel-based filler metals," *Welding Journal,* Vol. 68, No. 3 (1989), pp. 63-71.

[5] Jang, J. S. C., Shih, H. P., "Evolution of microstructure of AISI 304 stainless steel joint brazed by mechanically alloyed nickel base filler with different silicon content," *Journal of Materials Science Letters*, Vol. 22, No. 1 (2003), pp. 79-82.

[6] Campbell, C. E., Boettinger, W. J., "Transient liquid phase bonding in the Ni-Al-B system," *Metallurgical and Materials Transactions A*, Vol. 31, No. 11 (2000), pp. 2835-2847.

[7] Ojo, O. A., Richards, N. L., Charturvedi, M. C., "Effect of gap size and process parameters on diffusion brazing of Inconel 738," Science and Technology of Welding and Joining, Vol. 9, No. 3 (2004), pp. 209-220.

[8] Tuah-Poku, I., Dollar, M., Massalski, T. B., "A study of the transient liquid phase bonding process applied to a silver/copper/silver sandwich joint," *Metallurgical and Materials Transactions A*, Vol. 19, No. 3 (1988), pp. 675-686.

[9] Lee C. H., North, T. H., Nakagawa, H., "Isothermal solidification during TLP-brazing (modeling and

experimental justification)," *Proc 71st American Welding Society Convention*, Anaheim, CA, 1990, pp. 243-246.

[10] Ramirez, J. E., Liu, S., "Diffusion brazing in the nickel-boron system," *Welding Research*, Oct. (1992), pp. 365-75.

[11] Ojo, O. A., Richards, N. L., Chaturvedi, M. C., "Isothermal solidification during transient liquid phase bonding of Inconel 738 superalloy," *Science and Technology of Welding and Joining*, Vol. 9, No. 6 (2004), pp. 532-540.

[12] Gale, W. F., Wallach, E. R., "Microstructural development in transient liquid-phase bonding," *Metallurgical and Materials Transactions A*, Vol. 22, No. 10 (1991), pp. 2451-7.

[13] Ohsasa, K., Shinmura, T., Narita, T., "Numerical modeling of the transient liquid phase bonding process of Ni using Ni-B-Cr ternary filler metal," *Journal of Phase Equilibria*, Vol. 20, No. 3 (1999), pp. 199-206.

[14] Shinmura, T., Ohsasa, K., Narita, T., "Isothermal solidification behavior during the transient liquid phase bonding process of nickel using binary filler metals," *Materials Transactions*, Vol. 42, No. 2, pp. 292-297.

[15] Shiue, R. K., Wu, S. K., Hung, C. M., "Infrared repair brazing of 403 stainless steel with a nickel-based braze alloy," *Metallurgical and Materials Transactions A*, Vol. 33, No. 6 (2002), pp. 1765-1773.

[16] Zorc, B., Kosec, L., "Comparison of brazed joints made with BNi-1 and BNi-7 nickel-base brazing alloys," *Revista de Metalurgia*, Vol. 36, No. 2 (2000), pp. 100-107.

[17] Lugscheider, E., Partz, K. D. "High temperature brazing of stainless steel with nickel-base filler metals BNi-2, BNi-5 and BNi-7," *Welding Research*, June (1983), pp. 160-164.

[18] Crank, J., The mathematics of diffusion, 2nd edition, Oxford University Press, (Oxford, UK, 1975), p. 41.

[19] Shewman, P., Diffusion in solids, 2nd edition, (New York, 1989), p. 41.

[20] Nakao, Y.,Nshimoto, K., Shinozaki, K., Kang, C. Y., *J. Q. Japan Welding Society*, Vo. 7 (1989), pp. 47-53.