CHAPTER 6

Diffusion Brazing

In brazing, wetting of the component surfaces is not always easy to achieve and when it does occur, the resulting alloying between the filler and components can cause excessive erosion of the parent materials, embrittlement of joints due to the formation of phases with inferior mechanical properties, and other undesirable effects. Thereafter, the upper working temperature of the assembly is also compromised by the presence of the lower-melting-point filler metal. These problems notwithstanding, brazes have the singular merit of being able to fill joints of irregular dimensions and produce well-rounded fillets at the edges of the joint.

Diffusion bonding sidesteps the need for wetting and spreading by a filler metal (see Chapter 1, section 1.1.7.3). Once formed, diffusion-bonded joints are stable to high temperatures so that the service temperature of the assembly can actually exceed the peak temperature of the joining process without risk of the joint remelting. While the formation of undesirable intermetallic phases can also occur in diffusion bonding, because there are usually fewer constituents involved, it is easier to select a safe combination of materials. However, diffusion bonding tends to be limited as a production process because it is not tolerant of joints of variable width, and moreover, its reliability is highly sensitive to surface cleanliness. High loads (typically 10 to 100 MPa (or 1.4 to 14 ksi) have to be applied during the bonding cycle to ensure good metal-to-metal contact across the joint interface. Also, the duration of the heating cycle is typically hours, compared with seconds for brazing, because solid-state diffusion is much slower than wetting of a solid by a liquid. These factors, and the absence of any significant fillets to minimize stress concentrations at the edges of joints (see Chapter 4, section 4.2.4), considerably limit the applications for diffusion bonding.

There exists a hybrid joining process that combines the good joint filling, fillet formation, and tolerance to surface preparation of conventional brazing, together with the greater flexibility with regard to service temperature and metallurgical simplicity that is obtainable from diffusion bonding. This process uses a molten filler metal to initially fill the joint gap, but during the heating stage, the filler diffuses into the material of the components to form solid phases and, in consequence, the remelt temperature of the joint is raised. This process is called diffusion brazing, sometimes also referred to as transient liquid-phase (TLP) joining, or transient liquid phase bonding (TLPB) [Nicholas 1998, 91–102]. It is an established joining and repair process that has been used for decades in the aerospace industry. Further information on its low temperature analogue, diffusion soldering, can be found in the companion volume Principles of Soldering. It is noteworthy that although diffusion soldering processes are, by definition, performed at process temperatures below 450 °C, the remelt temperature of joints can exceed the solidus temperature of common brazes.

6.1 Process Principles

The steps involved in making a diffusion-brazed joint are illustrated schematically in Fig. 6.1. The joint configuration generally comprises the two component parts and a filler preform inserted between them, and heating is commenced (stage 1). The latter is usually much thinner than 50 µm (2 mils), which is thinner than a typical braze preform. The components are clamped together with a compressive stress of a few megapascals and the assembly is then usually heated to above the liquidus temperature of the filler metal, which melts, wets the joint surfaces, fills the joint gap, and forms small edge fillets (stage
2. If the filler and base material are elemental metals and enter into a simple eutectic reaction, then melting can be brought about by heating the assembly to a temperature above the eutectic point. If this process temperature is below the melting point of the pure filler, then initially interdiffusion occurs in the solid state, which forms part of the first stage of the process. This results in depression of the melting point of the filler so that melting and wetting occur (stage 2).

Due to the generation of liquid in the joint, the necessary applied pressures are generally much less than those required for normal diffusion bonding, and typically in the range of 0.5 to 1 MPa (70 to 145 psi), but greater than those normally used during brazing (0–0.1 MPa, or 0–15 psi). This is important not only because it enables the joining operation to be less demanding in equipment terms but also because the pressure needed is only a small fraction of the yield stress of the parent material so that macroscopic deformation is avoided [Askelsen 1992].

If the assembly were then cooled, the joint would resemble a thin, but conventional, brazed joint in its properties and metallurgical characteristics. However, by maintaining the assembly at elevated temperature, the composition of the filler metal will change with time as alloying elements in the braze, added as melting-point depressants, diffuse away from the joint and into the parent metals. In consequence, the solidus temperature of the filler rises and solidification occurs isothermally (stage 3). Ultimately, the joint becomes essentially homogeneous with the parent metal (stage 4).

Diffusion brazing provides a means to fill joints that are not perfectly smooth or flat (a feature of liquid-phase joining), while offering greater flexibility with regard to joint configurations and mechanical properties than can be obtained from diffusion bonding. Owing to the features of the process, including the high degree of control applied to the process parameters, the following additional advantages may be obtained:

- Good reproducibility of the process
- High dimensional control of the joint width, i.e., narrow tolerances
- Facilitation of exceptionally good joint filling in large area joints, which ensures leak tightness. This is especially important where the joint forms part of a hermetic enclosure.
- Attainment of very narrow joints, typically less than 50 μm (2 mils), which benefits properties such as mechanical properties and thermal conductivity
- Ability to tightly control edge spillage of the molten filler and even prevent it altogether

An alloy system suitable for diffusion brazing should have the following characteristics:

- It should be based on a simple alloy binary or ternary system to keep the joint design and joining process as simple as possible.
- It should have a phase constitution that includes a relatively low-melting-point eutectic reaction to initiate the melting process.
- It should have as few intermetallic compounds as possible. Those that do exist should be stable over a wide range of composition and ideally melt at temperatures below or comparable with the joining temperature. This reduces the propensity for diffusion barriers to become established that would impede the isothermal solidification process and the proliferation of brittle phases in the joint.
- The terminal primary metal phase should possess a wide range of solid solubility of the other constituents to minimize the risk of

![Fig. 6.1 Schematic illustration of the steps involved in making a diffusion-brazed joint](image)
intermetallic phases precipitating during cooling of the assembly from the processing temperature and to provide a greater tolerance of the process to the amount of filler metal introduced into the joint.

A selection of representative examples of alloy systems that satisfy these conditions and lend themselves to viable diffusion brazing processes is shown in Table 6.1.

### 6.2 Examples of Diffusion Brazing Systems

One of the first diffusion brazing processes to be exploited was developed for joining nickel-base superalloys using the Ni-4B eutectic braze (melting point = 1090 °C, or 2084 °F) [Duvall, Owczarski, and Paulonis 1974]. Nickel-12P eutectic braze (melting point = 880 °C, or 1616 °F) has also been used in the same application [Ikawa, Nakao, and Isai 1979].

Both boron and phosphorus play a dual role, being very effective melting-point depressants and fast-diffusing elements. This second characteristic is especially advantageous for diffusion brazing because boron and phosphorus diffuse rapidly out of the molten filler at the joining temperature and become widely dispersed in the parent metals. In consequence, isothermal solidification takes place rapidly at the joining temperature as the composition of the nickel filler tends toward pure nickel. Because boron brittles many filler metals, this makes the production of ductile preforms difficult. One solution to this problem has been the development of surface enriched brazing foils. These are produced free of boron and are therefore ductile, and the boron is added to the surface region by a vapor phase process. Ductile nickel-base preforms for diffusion brazing are now normally made by rapid solidification technology. The formation of eutectic nickel and iron alloys with boron and phosphorus having deep eutectic wells makes them amenable to foil manufacture

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### Table 6.1 Selected material combinations used for diffusion brazing

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Filler metal</th>
<th>Process temperature</th>
<th>Remelt temperature</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Cu/Ni/Ni interlayers</td>
<td>1150 1920</td>
<td>1400 2550</td>
<td>Shalz et al. [1994]</td>
</tr>
<tr>
<td>Alumina/kovar</td>
<td>Ni/Ti/Ni interlayers</td>
<td>980 1800</td>
<td>984–1310 1805–2390</td>
<td>Zhang, Qiao, and Jin [2002]</td>
</tr>
<tr>
<td>Cobalt alloys</td>
<td>Ni-4B</td>
<td>1175 2145</td>
<td>1475 2685</td>
<td>Duvall, Owczarski, and Paulonis [1974]</td>
</tr>
<tr>
<td>Nickel alloys</td>
<td>Ni-4B</td>
<td>1175 2145</td>
<td>1450 2640</td>
<td>Duvall, Owczarski, and Paulonis [1974]</td>
</tr>
<tr>
<td>Nickel alloys</td>
<td>Ni-4.5Si-3.2B</td>
<td>1065 1950</td>
<td>1450 2640</td>
<td>Gale and Orel [1996]</td>
</tr>
<tr>
<td>Cobalt alloys</td>
<td>Ni-12P</td>
<td>1100 2010</td>
<td>1450 2640</td>
<td>Ikawa, Nakao, and Isai [1979]</td>
</tr>
<tr>
<td>Inconels (Ni-Cr-Fe alloys)</td>
<td>Ni-7Cr-3Fe-2B-4.5Si (AMS 4777)</td>
<td>1150 2100</td>
<td>1400 2550</td>
<td>Wu, Chandel, and Li [2001]</td>
</tr>
<tr>
<td>Ferritic superalloys</td>
<td>Ni-4.5Si-3.2B</td>
<td>1100 2010</td>
<td>1400 2550</td>
<td>Khan and Wallach [1995]</td>
</tr>
<tr>
<td>Steel (including stainless)</td>
<td>Ni-20CrNi-B powder compact</td>
<td>1000 1830</td>
<td>Not determined</td>
<td>Zhuang and Eagar [1997]</td>
</tr>
<tr>
<td>Copper</td>
<td>Sn</td>
<td>690 1275</td>
<td>1080 1975</td>
<td>Singh, Jacobson, and Peacock [1998]</td>
</tr>
<tr>
<td>Silver alloys</td>
<td>Ag-30Cu</td>
<td>825 1515</td>
<td>950 1740</td>
<td>Tsuchi-Oku, Dollar, and Massalski [1988]</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Ti-30V</td>
<td>1675–1760 3050–3200</td>
<td>&gt;2095 &gt;3800</td>
<td>Schwartz [1987]</td>
</tr>
<tr>
<td>Titanium aluminate</td>
<td>Cu powder mixture</td>
<td>1150 2100</td>
<td>&gt;1350 &gt;2460</td>
<td>Gale et al. [2002]</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>Cu-50Ni</td>
<td>975 1785</td>
<td>1700 3090</td>
<td>Norris [1986]</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>Cu-15Cu-15Zn</td>
<td>700 1290</td>
<td>700(a) 1290(a)</td>
<td>Elahi and Fenn [1981]</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>550 1020</td>
<td>550(a) 1020(a)</td>
<td>Niemann and Wille [1978]</td>
</tr>
<tr>
<td></td>
<td>Zn-1Cu</td>
<td>525 975</td>
<td>525(a) 975(a)</td>
<td>Ricks et al. [1989]</td>
</tr>
<tr>
<td></td>
<td>Ag-29Cu</td>
<td>510 950</td>
<td>660 1220</td>
<td>Bushby and Scott [1995]</td>
</tr>
</tbody>
</table>

(a) Estimated, but not measured
by melt spinning (see Chapter 1, section 1.3.2.2). This process excels at producing thin (20–50 μm, or 0.8–2.0 mils) and highly uniform foil preforms that are ideal for diffusion brazing processes.

Another melting-point depressant that is widely used in melt-spun foils is silicon. However, silicon diffuses much more slowly in nickel than do boron and phosphorus. As a result, relatively persistent silicides tend to form in joints during diffusion brazing operations, which can cause embrittlement [Khan and Wallace 1995]. Nevertheless, it has been shown that nickel silicide can be completely dispersed and solid solution achieved in a diffusion-brazed joint between nickel alloy (Inconel) components made with a nickel-iron-silicon-boron alloy held at 1150 °C (2100 °F) for 120 minutes [Wu, Chandel, and Li 2001].

Diffusion brazing of aluminum alloys that contain silicon can be accomplished using a copper or brass preform [Timisit and Janeway 1994]. The brazing temperature needs to be above 530 °C (990 °F) for the copper preform and 510 °C (950 °F) for the brass preform. The role of zinc is as a melting-point depressant. Joint strengths above 100 MPa (15 ksi) can be obtained. Aluminum-lithium alloys, which have high specific stiffness, are difficult to join by brazing because the lithium stabilizes the native oxide in the form of lithium-rich spinels. However, they may be joined by diffusion brazing using copper interlayers and applied pressures in the region of 5 MPa (0.7 ksi) at a process temperature of 530 °C (990 °F). The partial oxygen pressure in the process chamber needs to be below 2 MPa (3 × 10⁻⁷ psi) and the faying surfaces scrupulously cleaned for joining to be successful [Urena et al. 1996]. Diffusion brazing of aluminum/boron fiber composites 6061 Al-50%B has been achieved using Al-12Si brazing foils for use on the space shuttle [Schwartz 2003]. The process temperature must be kept low to prevent reaction between the aluminum and boron and reduction of mechanical properties. The boron fibers or tapes will often be coated with silicon carbide to aid protection in this regard.

Titanium alloys can be diffusion brazed with copper. Copper plays the role of a temporary melting-point depressant, diffuses readily in titanium, and can be applied as a thin layer to faying surfaces by electroplating. Some care may be needed in the applicability of this approach because copper stabilizes the beta phase in titanium and decreases the beta-to-alpha transition temperature. Tantalum alloys are often joined by diffusion brazing as a means of achieving high-temperature service without using an exceptionally high-melting-point braze. Ti-30V braze, when used with an extended heating cycle at 1675 to 1760 °C (3050–3200 °F), to form a diffusion-brazed joint to tantalum alloys, results in a joint remelt temperature that exceeds 2095 °C (3800 °F) [Schwartz 2003, 98]. The high reactivity to tantalum, when hot, with most gases means that vacuum is required for brazing and a thin surface coating of copper or nickel is often required as an additional measure to slow reaction with residual species in the vacuum.

A number of interesting variants of diffusion brazing have been reported. One of these makes use of a filler of near-eutectic composition Ag-29Cu for joining aluminum. The unusual feature here is that the filler metal has a higher melting point (779 °C, or 1434 °F) than the parent metal, aluminum [Bushby and Scott 1995]. In this case, the process relies on the formation of a low-melting-point ternary eutectic alloy between silver, copper, and aluminum at 505 °C (941 °F). When the assembly is heated above this temperature, solid state interdiffusion across the interface between the three metal constituents results in a ternary alloy, which melts. The copper diffuses out of the joint faster than the silver. The latter forms the intermetallic compound Ag₂Al at the center of the joint, which remains solid at the joining temperature. Raising the holding temperature to the melting point of the Ag₂Al intermetallic compound (567 °C, or 1053 °F), but still below the melting temperature of the parent metal, removes it from the joint. Aluminum casting alloys and aluminum-boron composites can be diffusion brazed by plating commercial Al-7.5Si filler metal with copper. Provided the copper is sufficiently thin and well diffused after brazing, the mechanical and corrosion resistance of the aluminum parts are not compromised. The joining process temperature can be as low as 540 °C (1000 °F). Using the same idea, the filler metal foil or coating can be dispensed with altogether if certain combinations of different metals or alloys are being joined. This approach has been used in the development of a diffusion brazing process for joining Zircaloy 2 (Zr-1.5Sn-0.25(Fe,Ni,Cr)) to stainless steel at approximately 950 °C (1740 °F). The process relies on a eutectic reaction between iron and zirconium at 934 °C (1713 °F) [Owczarski 1962].
Diffusion brazing is not limited to metal components but can also be applied to ceramic parent materials. A nickel foil, 100 μm (4 mils) thick and coated both sides with a 3 μm (120 μm) layer of copper has been used as an interlayer in diffusion brazing components of alumina [Shalz et al. 1994]. The joining operation was carried out in vacuum at 1150 °C (2100 °F), which is above the melting point of copper (1085 °C, or 1985 °F). At this temperature, the copper melts and alloys with the nickel, leading to isothermal solidification. At the same time, the nickel diffuses toward the alumina interface where it forms NiO-Al2O spinel, which provides a strong bond. An applied pressure of 5 MPa (700 psi) ensures good initial interfacial contact, so although the volume of liquid is small, it is still sufficient to fill the joint gap. A lower-temperature process for joining alumina to Kovar (Fe-29Ni-17Co) makes use of a titanium foil 0.3 mm (12 mils) thick sandwiched between 15 μm (0.6 mil) thick nickel foils [Zhang, Qiao and Jin 2002]; alternatively, the three foils could be replaced by a so-rolled trifoil or a titanium foil plated both sides with nickel. The trifoil is held between the aluminum and Kovar components under a comparatively low uniaxial pressure of 30 to 40 kPa (4.3–5.7 psi). When the assembly is heated in vacuum, titanium diffuses across the interface with the nickel foils to form a eutectic that melts at 942 °C (1728 °F). The nickel layers are progressively replaced by layers of Ti6Ni intermetallic, which melts at 984 °C (1803 °F), and the thickness of the titanium core is correspondingly reduced. Heating the assembly above 980 °C (1796 °F) for at least 20 min is sufficient to form a joint with a shear strength of about 80 MPa (11 ksi), provided the joint is stress relieved by a subsequent heat-treatment at 400 °C (750 °F) [Qiao, Zhang and Jin 2003]. Bonding to the alumina is accomplished by the formation of an NiTiO interfacial phase. This process is a hybrid of active brazing, involving titanium, and diffusion brazing.

In place of foils, powder mixtures can be used to affect diffusion-brazed joints. This opens the possibility of applying the filler metal by other means such as screen printing and syringe dispensing (when in a suitable binder). This has been demonstrated for an active diffusion-brazed joint made between Fecralloy (Fe-30Cr-5Al-0.06Y2O3) and calcia-stabilized zirconia (CSZ) [Li and Xiao, 2001]. Starting with a powder mixture of equivalent composition Fe-20Cr-5Al and heating to 1000 °C (1830 °F), the aluminum melts, dissolves some chromium, and is then able to wet the ceramic. Chromium is consumed by the formation of chromates at that interface, while both aluminum and chromium dissolve in iron, forming a solid solution. Consequently, the braze solidifies at the joining temperature. Further information on active brazes is given in Chapter 7.

Another embodiment of diffusion brazing involves conducting the joining operation with a temperature gradient imposed. Aluminum alloys have been joined using copper foils in this manner. The temperature gradient forces the liquid interface to move slowly through the joint and into the parent materials until it runs out of copper and solidifies. For reasons not fully understood, as the interface moves, it tends to adopt a rippled, sine wave profile, which greatly reduces any tendency of the joint to fail when stressed in shear [Shelley 1998]. Unfortunately, the complexity of the equipment required to develop the necessary controlled temperature gradient limits the applicability of this novel approach.

The minimum suitable temperature for a diffusion brazing process is not simply determined by the melting point of the filler or that of the alloys generated by reaction. If it is desired that the end product of reaction is a solid solution across the joint and that there are no residual interfacial intermetallic phases present, then the solubility limit of the minor constituents in the primary metal phase is also crucially important. This issue was highlighted in the development of a fluxless copper-tin diffusion brazing process, which makes use of tin-coated copper foils (100 μm, or 4 mils, thick), sandwiched between copper-coated components [Sangha, Jacobson, and Peacock 1998]. With the aim of avoiding the formation of the brittle Cu6Sn (α) intermetallic phase by reaction of tin with copper, a process temperature exceeding the melting point of this phase of 676 °C (1249 °F) was chosen. The effect of brazing temperature on joint strength is shown in Fig. 6.2. However, in addition, it was found that only when the maximum thickness of the tin layer was restricted to 2.5 μm (100 μm) was it possible to consistently suppress the formation of the Cu6Sn intermetallic phase. This is due to the substantial decline in the solubility of tin in copper as the temperature falls toward ambient room temperature. Whereas copper can accommodate up to 16% tin at 520 °C (970 °F), the solubility reduces to a mere 1% at 200 °C (390 °F). Figure 6.3 shows a section through an
optimized joint made at 690 °C (1275 °F), using the copper-tin diffusion brazing process, with 2.0 μm (80 μin.) of tin, showing an absence of visible particles of the intermetallic Cu₃Sn intermetallic phase.

The diffusion brazing process based on copper-tin has been successfully employed in producing heat exchangers for Sterling engines by a layer manufacturing technique, as described in section 6.5.

6.3 Modeling of Diffusion Brazing

Attempts have been made to model diffusion brazing processes in order to understand the significance of the various process parameters and their interrelationship [Tuah-Poku, Dollar and Massalski 1988; Nakagawa, Lee, and North 1991; MacDonald and Eagar 1992; 1998; Zhou, Gale and North 1995]. The analysis is simplest for binary alloy systems comprising solid solutions or simple eutectics, which do not include intermetallic compounds. Some of the limits of these models are highlighted in Nicholas [1998, 94–101]. Even so, further refinements to the models continue to be made, including the treatment of ternary systems [Sinclair, Purdy, and Morral 2000].

In their review of the subject, Zhou, Gale, and North [1995] split the process of diffusion brazing (involving the relatively simple configuration of a homogeneous filler between two components of the same base material) into four stages, which are identical to those enumerated in section 6.1:

1. Heating of the assembly from room temperature to the filler melting temperature, during which significant interdiffusion occurs between the parent material and the filler metal. This part of the process is particularly important when the filler metal layer is very thin.
2. Dissolution of the base material into the molten filler, resulting in the width of the liquid zone increasing. At the same time, the temperature increases from the melting point to the joining temperature.
3. Isothermal solidification at the joining temperature, as a result of diffusion of one or more constituents of the filler into the base metal (and vice versa).
4. Homogenization of the joint and base metal.

In the simplest case considered, the parent material and filler are both elemental metals and enter into a single eutectic reaction, and no intermediate intermetallic compounds form. The diffusion brazing process can then be represented on the generic eutectic phase diagram shown in Fig. 6.4.

Analytical models of diffusion brazing make use of the following assumptions:

- There are no initial barriers to direct contact between the parent material and filler metal...
so that metal-to-metal interface formation can occur instantaneously when the components are brought into contact. This means that the effect of surface oxides in inhibiting or retarding diffusion across interfaces is neglected.

- It is implicitly assumed that the components and filler are pressed together under sufficient applied stress, that any asperities yield so that contact is rapidly established across the entire surface areas of abutment.
- The parent and filler metals are initially homogeneous.
- The classical Fick’s diffusion equations apply.
- The parent metal has a semi-infinite surface at the joint interface, in the simplest case.
- Mass conservation applies; in particular, there is no loss of the low-melting-point constituent from the edges of the joint.
- The influence of grain boundaries is not taken into account.

If intermetallic phases form between the filler and that of the final primary metal solid solution, the situation becomes more complicated. In particular, the intermetallic phases hinder the dissolution process because the low-melting constituent then has to diffuse through the intermetallic phase. Diffusion in intermetallic compounds is generally much slower than in pure metals.

Applying this approach, but not taking into account solute dissolution during the heating stage (stage 1 above) nor density changes on solidification, Tuah-Poku, Dollar, and Massalski derived a relatively simple relationship between the reaction time \( t \) on the one hand and the thickness of the low-melting-point interlayer \( W_0 \); the diffusivity of the filler metal B in the base metal A \( D_B \); the initial concentration of the filler metal \( C_B \), normally unity; and the concentration of the filler metal at the solidifying interface \( C_{cal} \), which is identical to the solubility limit of the filler in the base metal at the process temperature. This situation can be described by:

\[
t = \frac{\pi W_0^2 \left( \frac{C_B}{C_{cal}} \right)^2}{16D_B} \quad \text{(Eq 6.1)}
\]

A refinement to Eq 6.1 has been made by MacDonald and Eagar [1998], which takes into account movement of the solid/liquid interface and density changes on solidification. This adds the following terms to the above equation: \( \rho_L \), \( \rho_S \) (density of the liquid and solid, respectively, on either side of the solidifying interface) and \( \beta = M/2D_\alpha t \), where \( M \) denotes the position of the interface. The modified equation is:

\[
t = \frac{W_0^2 \beta \rho_SC_B}{16D_B \left( \beta \rho_SC_{cal} \right)^2}
\]

According to both equations, the layer of liquid in a stable diffusion brazing process should reduce in thickness with time, in proportion to \( t^{1/2} \). This square root dependence has been observed when diffusion brazing nickel and nickel alloy components with an Ni-B interlayer [Nicholas 1998, 96–98].

The simpler equation (Eq 6.1) has been applied in the analysis of the copper-tin diffusion brazing at 700 °C (1290 °F), i.e., in the temperature range between 676 °C (1249 °F), the decomposition temperature of the Cu3Sn phase, and 756 °C (1393 °F), the decomposition temperature of the \( \gamma \) phase, for which the diffusion data are available. In this case, there is a complication because, in order for the fully reacted end product to be primary copper, tin has to diffuse through the intervening \( \gamma \) and \( \beta \) copper-tin phases (see Fig. 6.5). This not only limits the
reaction rate but adds complexity to the theoretical analysis. Furthermore, the rapidly declining solubility of tin in copper as the temperature is reduced toward room temperature promotes re-precipitation of Cu₃Sn and introduces a further issue for consideration.

In order to use the previously described analytical models, an average diffusivity, $D_\bar{a}$, is defined, which takes account of the diffusion of the low-melting-point filler through any intervening intermetallic compounds to primary phase. Furthermore, the term $C_{\text{sol}}$ is replaced in Eq 6.1 by $C_{\text{sol}}^b$, the limit of solubility of the filler in the base metal at the joining temperature. As shown by MacDonald and Eager [1992], this equation can be represented in nomograph form, reproduced in Fig. 6.6. The value of $D_\bar{a}$ is not readily available from the literature but can be calculated from the variables in Eq 6.1 after some limited experimental work to determine the time required for complete solidification to occur for the given thickness of the low-melting-point phase.

The estimated value of $D_\bar{a}$ for tin in copper, corresponding to a tin layer thickness of 2 µm (80 µin.) and a bonding time of $\sim$10 min at 680 to 690 °C (1256–1274 °F), is $2 \times 10^{-13}$ cm²/s. Using this value of $D_\bar{a}$, the bonding time required to fully react tin layers 5 µm (200 µin.) and 10 µm (400 µin.) thick are 90 and 360 min, respectively, which are far in excess of the bonding time used in the copper-tin diffusion brazing process development. These long diffusion times help to explain why it was not possible to completely react and disperse the tin into copper solid-solution when tin coatings of these thicknesses were tried. There is another contributory factor responsible for a residual copper-tin phase, Cu₃Sn, to be present at the end of the bonding cycle. The diminishing solubility of tin in copper as the diffusion-brazed assembly is cooled down to room temperature will cause this phase to re-precipitate out of copper solid solution.

It is worth pointing out that the aggregate diffusivity value, $D_\bar{a}$, calculated from Eq 6.1 lies...
almost exactly between the measured value of \(5 \times 10^{-11}\) cm\(^2\)/s for the diffusion of tin in Cu\(_3\)Sn at 707 °C (1305 °F) and the corresponding value of \(9 \times 10^{-10}\) cm\(^2\)/s for tin diffusion in pure copper [Brandes and Brook 1992]. These values of diffusivity are therefore consistent with one another, especially taking into account the respective melting points of pure copper (1085 °C, or 1985 °F) and of the \(\gamma\) phase (676–756 °C, or 1249–1393 °F). As a general rule for metals, diffusivity generally decreases as the melting point increases.

This example shows the value of the simple analytical model for providing general guidelines. However, as Zhou, Gale, and North [1995] have pointed out, some caution needs to be observed in the use of the analytical models of transient liquid-phase bonding that have been proposed, and they cannot be relied on for quantitative purposes. In the first place, the resolution of such a joining process into a number of discrete processes is at variance with what actually occurs in practice. Classical diffusion theory yields a parabolic relationship for base metal dissolution as a function of time at constant temperature. Such behavior is not generally observed.

Grain boundaries are well known to play a major influence on the rate of diffusion and, therefore, on the kinetics of the diffusion brazing process. Grain boundaries are high-diffusivity paths, with diffusivity values typically four orders of magnitude higher than those for volume diffusion for the same element close to the melting point, although the aggregate rate of material transport along grain boundaries is limited by virtue of their narrow width, which is typically \(~1\) nm (0.04 \(\mu\)m). Grain boundaries will also enhance diffusion rates by increasing the area of a solid surface because they form grooves where they emerge at the free surface. The density of grain boundaries is directly related to the grain size of a material, so the grain boundary effect on diffusion brazing can be seen in the enhancement of the diffusion brazing process as grain size is reduced, all other parameters remaining unchanged. This effect has been confirmed in the diffusion brazing of silver and nickel components [Nicholas 1998, 97–98]. It is widely held that future work on the modeling of TLP bonding should focus on a numerical model that encompasses all the mass transport mechanisms that occur during the process, namely, volume diffusion in each of the phases present, grain boundary diffusion, and interfacial diffusion between the constituent phases. This will be a formidable undertaking, all the more so where there are more than two elemental constituents and where transitory phases form and dissociate during the bonding process. Such an approach has been investigated by Ohsasa, Shinmura, and Narita [1999] for analyzing the TLP bonding of nickel using the Ni-15.2Cr-4.0B ternary alloy braze.

### 6.4 Application of Diffusion Brazing to Wide-Gap Joining

Diffusion brazing has been effectively adapted to bridging wide gaps. As detailed in Chapter 4, section 4.3.4.2, powder mixtures comprising the braze and a “gap filler” are used mostly for wide gap brazing and require the application of pressure to minimize the formation of gross voiding or porosity. If these constituents and the process conditions are judiciously chosen, it is possible...
to achieve a reaction between the braze and “gap filler,” which leads to isothermal solidification and complete dispersion of the braze into the gap filler and parent materials.

One approach that has been followed for joining titanium aluminide is to apply a composite mixture of the aluminide and copper powder (with particle sizes less than 44 \( \mu \)m, or 1.7 mils, and 53 \( \mu \)m, or 2.1 mils, respectively), in the form of a slurry to the joint [Gale et al. 2002]. The components of titanium aluminide with the slurry interlayer were then pressed together under a compressive load of 4 MPa (580 psi) and heated to 1150 °C (2100 °F) for 10 min. This process temperature is above the melting point of copper (1085 °C, or 1985 °F), but over 200 °C (360 °F) below that of the titanium aluminide. In consequence, the copper melts and diffuses into the aluminide, solidifying at the process temperature. As applied, the layer of slurry was 500 \( \mu \)m (20 mils) thick but contracted to a final joint width of about 200 \( \mu \)m (8 mils). As bonded, the joints registered a four-point bend strength of 580 MPa (85 ksi). Gale [1999] has also reviewed the application of diffusion brazing (TLPB) to the joining of other structural inter-metallic compounds.

A different scheme, but still involving powders, has been applied to large root-opening 304 stainless steel joints [Zhuang and Eagar 1997]. In this case, individual particles of nichrome (Ni-20Cr) powder, less than 44 \( \mu \)m (1.7 mils) in size, were coated with a layer of Ni-10P by electroless deposition, with the deposit typically making up 16 wt% of the processed powders. The powder was compacted into 10 mm discs in a die under 350 MPa (51 ksi) compression. Subsequent heating of the 314 stainless steel assemblies at 1000 °C (1830 °F) with compacts held in place under a compressive load of 0.29 MPa (42 psi) and protected in a vacuum of better than \( 4 \times 10^{-1} \) mPa (\( 3 \times 10^{-5} \) torr) led to isothermal solidification and achieved full densification. The coating ensured that liquid existed between individual particles of nichrome, and this considerably aided the formation of fully dense joints, with tensile strengths that approached that of the stainless steel base metal (~580 MPa, or 85 ksi), for joints 1 to 4 mm (40–160 mils) wide. While the phosphorus evidently provided fluxing of the stainless steel surfaces, the resulting phosphides that formed represented the weakest link in the joints. Trials using coated 304L stainless steel powder in place of the nichrome gave poorer results, namely, significant porosity and weaker joints. It is believed that, being soluble in iron, both the nickel and phosphorus in the coating dissolved into the steel particles and isothermal solidification occurred before most of the shrinkage could occur.

Zorc and Kosec [2000] have used a system of parallel wires to reinforce a joint gap with a braze used to wet and fill the interstices. By operating a diffusion brazing cycle, under compressive loads, continuous joints between the parent material and the reinforcement wires were achieved. Because the joints between the parent materials and the wires were not interrupted by layers of relatively weak braze, the resulting joints between common engineering materials (copper, steels) proved to be exceptionally tough and reasonably strong. The wire reinforcements, in all cases, 2 mm (80 mils) in diameter, were either copper or copper-plated steels used in conjunction with copper parent material or of various steels to match steel components. A selection of silver- and nickel-base brazing alloys and copper-phosphorous eutectic (Cu-7.3P, or BCuP-2) were used and the joining operations, which were carried out above their respective melting (solidus) temperatures. Extremely high pressures were applied for the duration of the diffusion brazing operation ranging between 2.4 GPa (350 ksi) for the copper combination, to 4.1 GPa (590 ksi) for the steel parent materials and reinforcements. The high pressures noticeably flattened the wires and punched them into the surfaces of the parent materials. These are somewhat extreme conditions, which are likely to greatly limit the practical application of this approach.

### 6.5 Application of Diffusion Brazing to Layer Manufacturing

Diffusion brazing offers an effective means for manufacturing parts with geometries that are difficult, if not impossible, to achieve using conventional manufacturing technology. This has been convincingly demonstrated for heat exchangers designed for use with Sterling engines.

A Sterling engine makes use of an external source of heat, which is supplied to a gas. The hot gas drives a piston, which converts the heat into useful work. Residual heat must then be rapidly removed from the gas in readiness for the next cycle. The heat removal is achieved by
passing the gas through specially designed cooler elements. The design required 1800 oval tubes 0.7 mm × 0.9 mm (28 × 35 mils) in an annular zone of a finned copper cylinder 68 mm (2.7 in.) long for carrying the gas to be cooled. The central hollow space of the copper cylinder was to contain the water coolant. This heat exchanger module is shown in plan and cross section in Fig. 6.7. The manufacture of these items presented severe problems in respect of the oval holes. Even circular holes of this fine size would be difficult to drill conventionally because of their length. A possibility that was considered was machining a series of notched annular rings, each 1 mm (40 mils) thick and of increasing diameter that would have to be shrink fitted together. However, this approach was ruled out as difficult, expensive, and unlikely to be technically successful. The solution was to fabricate the coolers using a layer manufacturing process involving bonding copper sheets or laminations together by diffusion brazing [Bocking, Jacobson, and Bennett 2000].

The laminations, of oxygen-free high conductivity (OHFC) copper, were 0.455 mm thick, and 185 such sheets were required for each assembly (which included blanking plates at either end for spigots). It was decided to produce the holes by photochemical machining, which is eminently suitable for cutting fine detail in thin sheets. In all, six coolers were required for each engine. Accordingly, they were all built together in a single operation, and each sheet was etched with the layer patterns for all six coolers, as shown in Fig. 6.8. Following photochemical machining, the sheets were plated on each side, with 2.0 ± 0.5 μm (8 ± 2 μin.) of pure tin. The sheets were then stacked in a jig, provided with three alignment pins to ensure that they registered correctly, as shown in Fig. 6.9. The stack was then pressed between a pair of steel plates at a pressure of approximately 3 MPa (440 psi). The pressure was applied by means of steel bolts positioned along the central cavity in each of the six heat exchanger modules. An appropriate torque was applied to give a compressive loading of ~90 kN (10 tons) on each bolt. This gave an overall pressure of close to 2 MPa (290 psi). A further 1 MPa (145 psi) of compression was provided by the thermal expansion mismatch between the tool steel press and the copper as the assembly was heated to a bonding temperature of 820 °C (1510 °F). The bonding operation was
carried out in a vacuum oven with a residual pressure of 10 Pa (1.5 × 10⁻⁴ psi). The heating rate used was 5 °C/min (9 °F/min), and the assembly was held at the peak joining temperature for 10 hours to ensure sustained thermal equilibrium throughout. Four of the six fully machined heat exchanger modules demonstrated good hermeticity and absence of blockages of any of the fine holes through the seepage of filler (Fig. 6.10). The two units that were not leak-tight had two small leaks, which were ascribed to inadvertent contamination of the tin plating from residual photoresist. These leaks were subsequently sealed with a solder applied to the inner walls of the two heat exchangers and were perfectly usable thereafter.

This successful trial clearly demonstrated the capabilities of layer manufacturing combined with diffusion brazing for manufacturing metal products with complex internal features. It envisaged that this approach could be developed into an important rapid manufacturing method [Bocking et al. 1997].

REFERENCES


