Development of the Copper-Tin Diffusion-Brazing Process

A fluxless silver-free process was developed that is suitable for fusion reactor components

BY S. P. S. SANGHA, D. M. JACOBSON AND A. T. PEACOCK

ABSTRACT. The copper-tin diffusion-brazing process has been studied with the objective of applying it to the joining of plasma-facing beryllium tiles to copper-based heat sinks in a nuclear-fusion reactor. The process is silver-free -- an essential requirement for this application -- and can be carried out at temperatures below 700°C (1292°F). This approach produces thin joints of essentially pure copper of high thermal conductance with the requisite strength. Satisfactory conditions for achieving robust joints under the constraints demanded by the nuclear-fusion application have been established. The roles of the process parameters -- thickness of the filler metal tin, the compressive loading applied to the components during the brazing cycle and the brazing temperature -- have been assessed.

Introduction

Diffusion brazing is a hybrid joining process that combines the features of liquid-phase joining and diffusion bonding and has the beneficial features of both techniques (Ref. 1). Diffusion brazing and its lower-temperature analog, diffusion soldering, use a molten filler metal to initially fill the joint clearance, but during the heating stage the filler diffuses into the material of the components to form solid phases, raising the remelt temperature of the joint. The steps involved in making a diffusion brazed (or diffusion soldered) joint are shown in Fig. 1. This process provides the ready means to fill joints that are not perfectly smooth or flat (a feature of liquid-phase joining), while offering greater flexibility with regard to service temperature. The process also provides the following consequential advantages:

- Facilitating the achievement of exceptionally good joint filling in large area joints.
- Allowing edge spillage from the joints to be tightly controlled and kept to a minimum.
- Attaining high thermal conductivity with copper, silver and gold systems, since the joint produced is composed of primary metal.

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

1) Preferably be a binary alloy, to keep the joint design and joining process as simple as possible.
2) Have a phase constitution that includes a relatively low melting point eutectic reaction to initiate the melting process.
3) Have as few brittle intermetallic compounds as possible, which should all melt at temperatures below or comparable to the joining temperature. This will reduce the establishment of diffusion barriers that can impede the process and lead to the formation of brittle interlayers.
4) The terminal primary metal phase should possess a wide range of solid solubility of the other constituents. This will minimize the risk of intermetallic phases precipitating during cooling of the assembly from the processing temperature and provide a greater process tolerance to the amount of filler metal introduced into the joint.

Examples of alloy systems that satisfy these conditions and lend themselves to viable diffusion soldering and brazing processes are silver-tin, gold-tin and nickel-boron (Ref. 1, Table 4.3).

The development of the copper-tin diffusion process was prompted by the need for a silver-free joining process capable of providing joints of high thermal conductance in the fabrication of plasma-facing components for nuclear-fusion reactors being developed for power generation (Ref. 2). Such components, notably the first wall and divertor, will be subject to severe nuclear and thermal radiation (Ref. 3). Their reliability and maintainability are crucial to power generation by nuclear fusion. These plasma-facing components must be clad with materials of low atomic number, Z, to minimize contamination of the plasma by the high Z elements (which can seriously poison the components) and to effectively spread the energy deposition over a large volume -- thereby minimizing local "hot spots" and consequent damage. Two candidate materials are being considered for this function: carbon fiber-reinforced carbon composites and beryllium. Since each material has distinct advantages and drawbacks, both are being actively evaluated.

In a reactor environment, silver has the propensity to transmute to cadmium, a volatile element with a high atomic weight that poisons the plasma and makes the use of silver-based brazes unacceptable for plasma-facing com-

KEY WORDS

Diffusion Brazing
Transient Liquid Phase Joining
Silver-Free Brazes Joining
Nuclear Fusion
Thermal Management

Fig. 1 — Schematic of steps to make a diffusion-soldered (or diffusion-brazed) joint.

Fig. 2 — Shear test sample geometry for the DIN 50162 test.

Fig. 3 — Plot of shear strength as a function of brazing temperature for diffusion-brazed assemblies, each comprising a foil of copper plated on both sides with a 2-μm-thick layer of tin sandwiched between copper-plated CuCrZr plates. The assembly was held for 5 min at the brazing temperature under a compressive load of 2.5 ± 0.5 MPa. The variation in shear strength is consistent with the progressive dissolution and dispersion of tin in copper and the concomitant reduction in the formation of the Cu₃Sn intermetallic phase.

Fig. 4 — Plot of shear strength as a function of tin layer thickness for diffusion-brazed assemblies with the same configuration as for Fig. 3.

Development of the Copper-Tin Diffusion-Brazing Process

The crucial parameters for a copper-tin diffusion-brazing process were temperature, thickness of the tin layer, the upper limit on the tin-to-copper thickness ratio and pressure to the joint. To achieve mechanically sound joints by copper-tin diffusion brazing, it is vital that all the tin is sufficiently dispersed and incorporated heat sinks. The steps followed to achieve a successful copper-tin diffusion-brazing process are described below.

ponents (Ref. 4). The transmutation also affects the mechanical integrity of the braze when a significant fraction is transmuted into cadmium. Copper-tin diffusion brazing was selected as a possible silver-free joining solution for attaching the beryllium components to copper-based heat sinks. The steps followed to achieve a successful copper-tin diffusion-brazing process are described below.
within the copper primary phase — not left as unreacted tin or combined with copper in brittle intermetallic phases. In nuclear-fusion applications where one of the components is a thick block of copper, this metal dwarfs the quantity of tin in the vicinity of the joint, thus the tin-to-copper ratio is not a critical issue.

With regard to temperature, a perceived application requirement for joining the fusion reactor components was to keep the brazing temperature and time as low as possible to prevent the formation of unacceptably thick (>12 μm) Cu-Be intermetallic layers that may have undermined the mechanical integrity of the joint (Refs. 5, 6).

The first stage of the process development was carried out using CuCrZr and dispersion-strengthened (DS) copper components and omitting beryllium (Ref. 7). In this way, the basic aspects of the process could be assessed in isolation of issues relating to the formation and growth of copper-beryllium intermetallics.

Assemblies were produced to determine the effect on the mechanical integrity of the joints by the following:

1. Increasing the brazing temperature from 585°C (1081°F) to 690°C (1274°F) for a constant tin thickness of 2 μm and under a compressive loading of 3.5 ± 0.5 MPa.
2. Varying the thickness of the plated tin layer at constant temperature and compressive loading.
3. Reducing the compressive loading by a factor of 100 from -3 MPa down to 0.03 MPa (30 kPa).

Tiles 50 x 25 x 6 mm of the copper alloys were used as the test pieces. These specimens were coated with pure copper to prevent deleterious reactions between the molten tin and the Cr2Zr precipitates in the CuCrZr. Initially, the plated layer of copper was 2 μm thick; when later found to be insufficient to buffer the tin in the joint from the intermetallic precipitates, the copper coating was increased to 8 μm. The components were clamped together under a compressive loading of 3.5 ± 0.5 MPa and separated by a foil preform of soft copper electroplated on both sides with tin, in a range of thicknesses from 1.5 to 2.5 μm. The assemblies were diffusion brazed over a range of temperatures from 585 to 690°C (1081 to 1274°F) in a vacuum of -2 x 10^-5 mbar, held at peak temperature for 5 min and slow-cooled in a vacuum.

Two heating arrangements were used: 1) a vacuum hot-press was provided with resistance heating emanating from the platen of the press, and 2) heating was supplied from an rf coil maintained in a vacuum of -1.5 x 10^-5 mbar and using a 40-kW, 20-kHz supply. The advantages of the latter were faster heating and cooling and the magnetic stirring of the molten metal provided by the rf excitation. However, this facility did not allow the application of compressive loading above 30 kPa.

These test assemblies and the conditions used in their preparation are listed in Table 1.

After the joining operation, the brazed assemblies were cut and sliced into modified DIN 50162 shear test pieces — Fig. 2. At least three samples from each assembly, representative of identical processing conditions, were subjected to proof-shear testing using a Denison 6161 Universal Tensile Tester. Other specimens cut from each of the assemblies were polished and examined metallographically.

### Results and Discussion

These trials have succeeded in demonstrating the effect of the different process parameters on the mechanical integrity of copper-tin diffusion-brazed joints. Figure 3 shows the increase in shear strength as the joining temperature was raised from 635 to 690°C (1175 to 1274°F), while Fig. 4 shows the influence of tin layer thickness (from 1 to 2 μm) on this parameter. These results all correspond to a constant time at the peak brazing temperature of 5 min.

As shown by the data, when a temperature approaching 690°C (1274°F) was used together with a compressive loading of 4 MPa and a tin layer thickness of 2 μm, joint strengths exceeding 130 MPa were consistently obtained in a 5-min dwell at the brazing temperature. When loading was reduced below 3.5 MPa, fusion of the original interfaces became inadequate, which resulted in

---

**Table 1** — Summary of Process Conditions Used for the Preparation of the Brazed Assemblies

<table>
<thead>
<tr>
<th>Components, (50 x 25 x 6 mm)</th>
<th>Sample Number</th>
<th>Tin Thickness (μm)</th>
<th>Compressive Loading (MPa)</th>
<th>Heating Method</th>
<th>Brazing Temperature (°C)</th>
<th>Time at the Brazing Temperature (min)</th>
<th>Shear Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCrZr</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>resistance</td>
<td>585</td>
<td>5</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>resistance</td>
<td>690</td>
<td>10</td>
<td>58 ± 57</td>
</tr>
<tr>
<td>DS Copper</td>
<td>3</td>
<td>4</td>
<td>3.5</td>
<td>resistance</td>
<td>635</td>
<td>5</td>
<td>62 ± 12</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>3.5</td>
<td>resistance</td>
<td>660</td>
<td>5</td>
<td>111 ± 20</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4</td>
<td>3.5</td>
<td>resistance</td>
<td>660</td>
<td>5</td>
<td>113 ± 20</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4</td>
<td>3.5</td>
<td>resistance</td>
<td>690</td>
<td>5</td>
<td>133 ± 45</td>
</tr>
<tr>
<td>CuCrZr</td>
<td>7</td>
<td>1</td>
<td>4</td>
<td>resistance</td>
<td>600</td>
<td>5</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.5</td>
<td>4</td>
<td>resistance</td>
<td>600</td>
<td>5</td>
<td>42 ± 11</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1</td>
<td>4</td>
<td>resistance</td>
<td>650</td>
<td>5</td>
<td>53 ± 29</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.5</td>
<td>4</td>
<td>resistance</td>
<td>650</td>
<td>5</td>
<td>86 ± 34</td>
</tr>
<tr>
<td>CuCrZr</td>
<td>11</td>
<td>2.5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>3</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>2.5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>6</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>2.5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>10</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>3</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>6</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>10</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>5</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>3</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>8</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>6</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>8</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>10</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>8</td>
<td>0.03</td>
<td>induction</td>
<td>760</td>
<td>10</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>
CuCrZr

Cu foil with Sn coating (partly reacted)

Theoretical Considerations

Attempts have been made to model diffusion-brazing processes, sometimes referred to as transient liquid phase (TLP) brazing, in order to understand the significance of the various process parameters and their interrelationship. These modeling studies are reviewed by Zhou, Gale and North (Ref. 9). The analysis is most straightforward for binary alloy systems comprising solid solutions or simple eutectics that do not include intermetallic compounds. Intermetallic phases that might form between the composition of the low-melting-point constituent and the final primary metal solid solution will hinder the dissolution process because the low-melting constituent then has to diffuse through the intermetallic; plus, diffusion in the intermetallics is generally much slower than in the primary metal. To quickly complete the brazing reaction, the processing temperature must be set above that of the melting point of the highest melting temperature intermetallic.

In the copper-tin system, the temperature chosen for the joining operation was close to or above the melting point of the stable Cu₃Sn phase, i.e., at 660°C (1220°F) or above. However, even at this temperature, for the fully reacted end product to be primary copper, tin has to diffuse through the intermetallic phases. This not only limits the reaction rate, but also makes the theoretical analysis of the process more complex. Furthermore, the rapidly declining solubility of tin in copper (as the temperature is reduced to room temperature) promotes re-precipitation of Cu₃Sn and adds a further level of complication to the analysis.

The analytical model of Tuah-Poku, Dollar and Massalski (Ref. 10) was applied to the tin-copper transient liquid phase reaction in the temperature range 676°C (1249°F), the decomposition tem-
perature of the Cu₃Sn (i.e., ε) phase, and 756°C (1393°F), the decomposition temperature of the γ-phase — Fig. 8. This model provides a method for estimating the time, t, to complete isothermal solidification. It is based on simplifying assumptions that each surface of the base metal (in this case, copper) is semi-infinite and is covered by a layer of solute or melting point depressant (MPD) (in this case, tin) whose composition at the solidifying interface is maintained at the composition Cₐ, the solubility limit of the solute in the base metal at the process temperature. The further assumption was made that the metallurgical system behaves like a solid solution, or simple binary eutectic. Solving Fick's diffusion equations under this set of conditions yields the following relationship:

\[ t = \frac{\pi W_o^2 (C_8 - C_{al})}{16D_α} \]  

where \( W_o \) is the thickness of the melting-point depressant interlayer, \( C_8 \) is the initial concentration of the MPD, which is unity for pure tin, and \( D_α \) is the diffusivity of the solute in the base metal.

In copper-tin diffusion brazing in the temperature range of 676-756°C (1249-1393°F), the process involves more than the dissolution of the base metal and its isothermal resolidification that accompanies diffusion of the solute. Here, the reaction is only complete once the tin diffuses through the intervening γ- and β-Cu₃Sn phases to the primary copper. Accordingly, the diffusivity \( D_α \) is now the aggregate value for the tin diffusion through to the copper and the \( C_{al} \) must be replaced by the value \( C_{ap} \), the limit of solid solubility of tin in copper at the joining temperature (shown as 8 at.% in Fig. 8). Equation 1 can then be rewritten as

\[ t = \frac{\pi W_o^2 (C_8 - C_{ap})}{16D_α} \]  

Equation 2 represents an approximation of the real situation. Some of the simplifying assumptions of the analytical model of Tuah-Poku, Dollar and Massalski (Ref. 10) are dealt with in the review article of Zhou, Gale and North (Ref. 9). One assumption is that there is mass conservation during the process, i.e., no liquid loss from the joint edges under the action of the compressive loading. In fact, for tin thickness in the range 1-5 μm, no expulsion of liquid tin was observed; the joint edges remained sharply defined and fillet-free. It was reassuring to observe that the aggregate value of \( D_α \) calculated from Equation 2 lies almost midway between the measured value of \( 5 \times 10^{-11} \text{ m}^2/\text{s} \) for the diffusion of tin in Cu₃Sn at 707°C (1305°F) and the corres-


DE = 2 x 10^{-13} m²/sec

Tin Thickness Process Time

<table>
<thead>
<tr>
<th>Tin Thickness (µm)</th>
<th>Process Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.2†</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

† measured

Time to achieve complete solid solution (hours)

10,000 m

<table>
<thead>
<tr>
<th>Concentration of MPD at solubility limit (in the base metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W₀ Diffusivity (log m²/sec)</td>
</tr>
<tr>
<td>Foil thickness (µm)</td>
</tr>
</tbody>
</table>

Application of Copper-Tin Diffusion Brazing to Plasma-Facing Components

For this application, it was necessary to qualify the copper-tin diffusion-brazing process for beryllium-to-copper assemblies. The beryllium components used were typically 50 x 25 x 3 mm, coated on the surface to be joined with a copper layer 10-12 µm thick. Sputter-ion plating was used to apply an adherent copper coating to the beryllium. In this process, the component was made to be the cathode of a glow discharge into which the coating material was sputtered. The electric field around the substrate provided kinetic energy to the ions of the depositing metal, which assisted adhesion of the depositing species. The beryllium tiles were chemically cleaned to remove all surface contamination. The copper ion-plated beryllium tiles were diffusion brazed to both CuCrZr and DS copper (strengthened high-copper alloys used in nuclear-fusion technology) at various temperatures and times between 585 to 660°C (1085 to 1220°F), using the procedure described above.

The copper-plated beryllium/strengthened copper diffusion brazed assemblies were assessed in the same manner as copper/copper assemblies, with shear test and metallographic samples prepared and evaluated. A joint between a CuCrZr plate and a beryllium tile ion plated with copper that was prepared at 660°C (1220°F) is shown in Fig. 10. There was no evidence of residual intermetallic Cu₃Sn phase at the interface between the reaction zone and the copper components in this sample.

Conclusions

A study of copper-tin diffusion brazing was made to identify the crucial process parameters needed to optimize this joining process. Key parameters that were identified in practical trials were the thickness of the tin layer and the loading applied to the joint during the brazing cycle. It was established that the tin layer thickness must be controlled to 2 µm, within a tolerance of ±0.5 µm, to obtain strong joints. A compressive load of 4 MPa is adequate, while one of 3 MPa is too low. The precise joining temperature is less critical, provided that it is 680°C (1256°F) or higher, sufficient to destabilize the brittle Cu₃Sn intermetallic compound. There is a risk of re-precipitating this intermetallic phase on cooling, if the heating operation does not adequately disperse the tin into the copper layers.
due to the diminishing solubility of tin in copper as the joined assembly is cooled down to room temperature. This fact helps to explain why the thickness of the tin layer is highly critical, in contrast with the silver-tin diffusion-soldering process, where the solubility of tin in silver is essentially maintained constant as the temperature is reduced.

With regard to the application of this diffusion-brazing process to plasma-facing components for nuclear reactors, the initial concern about the relatively long reaction time at elevated temperatures (required for diffusion brazing and the resulting promotion of interfacial copper-beryllium intermetallic phases) was not borne out in practice as indicated by the high strengths of the joints obtained in beryllium/strengthened copper assemblies (up to ~230 MPa), both when produced under a pressure of 150 MPa in a hot isostatic press and 4 MPa in a uniaxial press.

Acknowledgment

The authors wish to thank the NET Team at Garching, Germany, for their financial support.

References