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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.

KEY WORDS

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

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-

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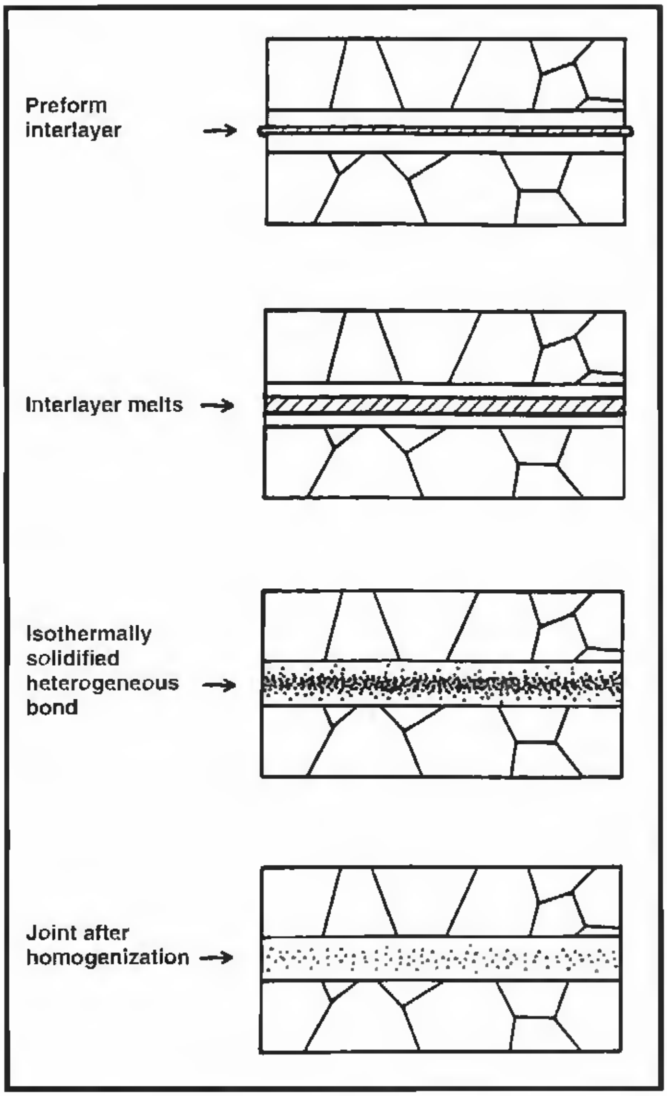

Fig. 1 — Schematic of steps to make a diffusion-soldered (or diffusion-brazed) joint.

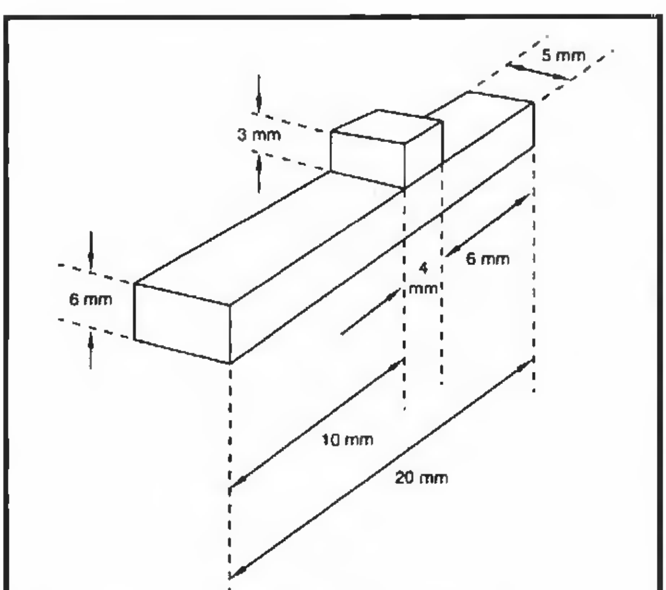

Fig. 2 — Shear test sample geometry for the DIN 50162 test.

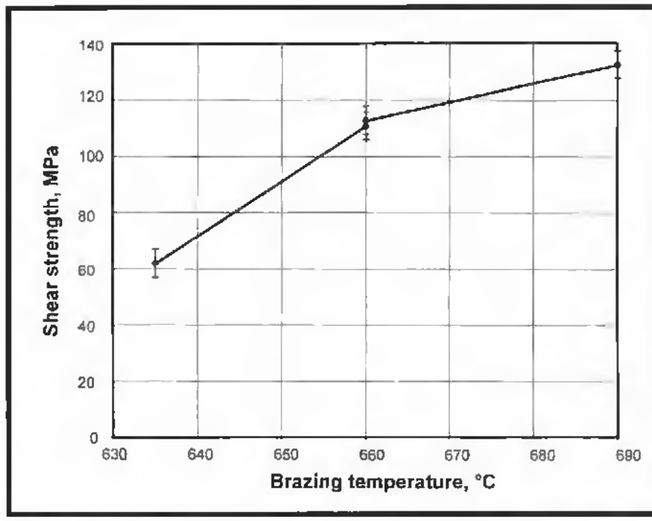

Fig. 3 — Plot of shear strength as a function of brazing temperature for diffusion-brazed assemblies, each comprising a foil of copper plated on both sides with a 2-µm-thick layer of tin sandwiched between copper-plated CuCrZr plates. The assembly was held for 5 min at the brazing temperature under a 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 Cu_3Sn intermetallic phase.

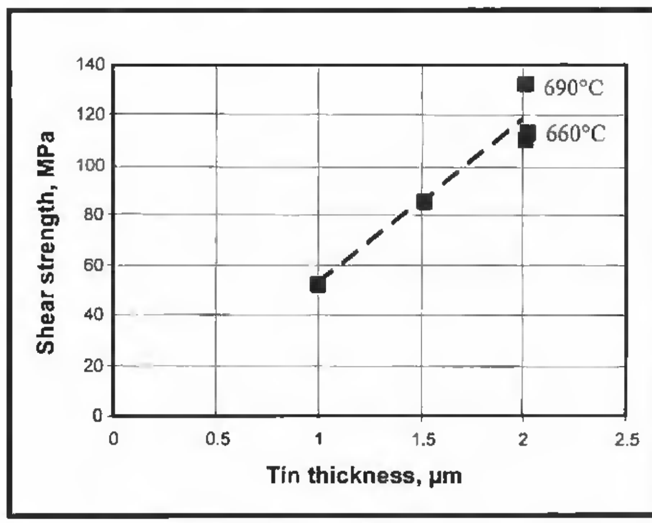

Fig. 4 — Plot of shear strength as a function of tin layer thickness for diffusion-brazed assemblies with the same configuration as for Fig. 3.

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.

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

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

Components, (50 × 25 × 6 mm)/ Sample Number		Tin Thickness (μm)	Compressive Loading (MPa)	Heating Method	Brazing Temperature (°C)	Brazing Temperature (°F)	Time at the Brazing Temperature (min)	Shear Strength (MPa)
CuCrZr	1	2	3	resistance	585	1085	5	<20
	2	2	3	resistance	690	1274	10	58 ± 57
DS Copper	3	2	3.5	resistance	635	1175	5	62 ± 12
	4	2	3.5	resistance	660	1220	5	111 ± 20
	5	2	4	resistance	660	1220	5	113 ± 20
	6	2	4	resistance	690	1274	5	133 ± 45
CuCrZr	7	1	4	resistance	600	1112	5	<20
	8	1.5	4	resistance	600	1112	5	42 ± 11
	9	1	4	resistance	650	1202	5	53 ± 29
	10	1.5	4	resistance	650	1202	5	86 ± 34
CuCrZr	11	2.5	0.03	induction	760	1400	3	<20
	12	2.5	0.03	induction	760	1400	6	<20
	13	2.5	0.03	induction	760	1400	10	<20
	14	5	0.03	induction	760	1400	3	<20
	15	5	0.03	induction	760	1400	6	<20
	16	5	0.03	induction	760	1400	10	<20
	18	8	0.03	induction	760	1400	3	<20
	19	8	0.03	induction	760	1400	6	<20
	20	8	0.03	induction	760	1400	10	<20

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) 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 × 25 × 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 Cr_2Zr 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 ~2×10^{-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 ~1.5×10^{-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 pm) 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 pm, 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

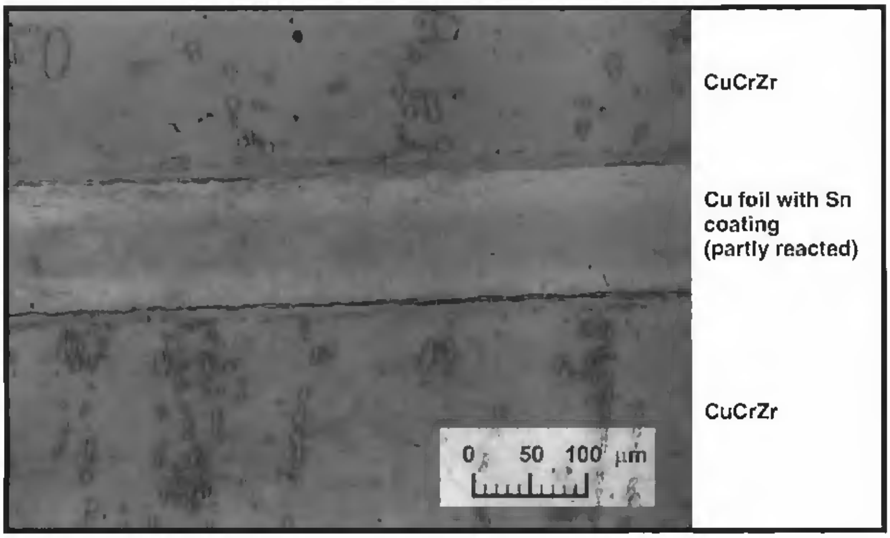

Fig. 5 — Micrograph of a joint made between a copper-plated CuCrZr tile and a copper foil coated with a 2.5-µm-thick layer of tin at 760°C (1400°F) under a compressive loading of 30 kPa, showing incomplete fusion across the joint interface and absence of Cu_3Sn intermetallic phase.

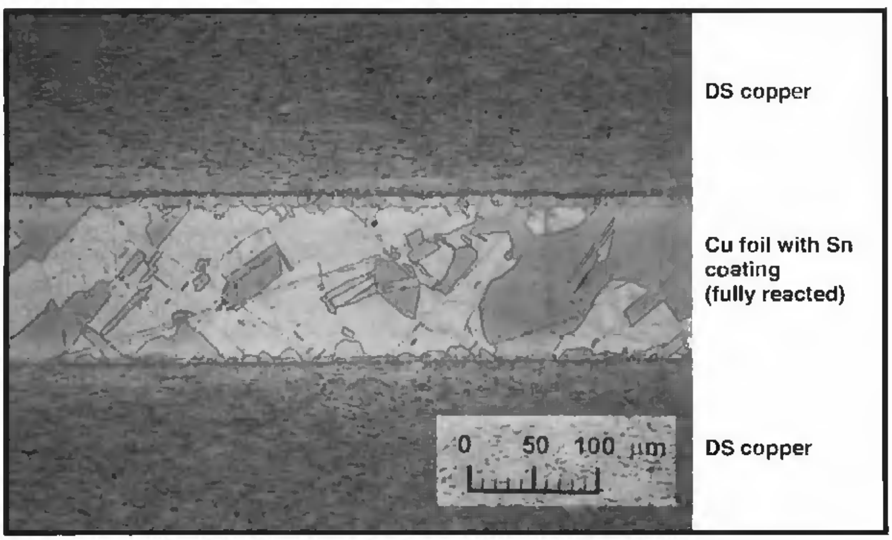

Fig. 6 — Micrograph of a well-reacted joint in a dispersion-strengthened copper assembly formed at 690°C (1274°F) shown after etching. There is no visible evidence of residual intermetallic Cu_3Sn phase at the interface between the reaction zone and the copper components in this sample.

weak joints, even when the thickness of the tin layer was maintained at 2.5 µm and the temperature was raised to 760°C (1400°F). The reduction of the loading led to incomplete joint filling and variable fusion of the mating surfaces, as shown in Fig. 5. Even at an applied loading of 3 MPa and a peak temperature of 690°C maintained for 10 min, fusion of the interfaces was irregular, giving rise to measured joint strengths that varied widely from about 20 to 168 MPa and averaged at 58 MPa. By comparison, the measured shear strengths at an applied load of 4 MPa were found to vary in a proportionately narrower range, from 78 to 197 MPa, with an average value of 133 MPa. Therefore, the minimum pressure that needs to be applied to achieve joints with a reasonable consistency in shear strength is judged to be 4 MPa. This condition is achievable in a fairly standard hydraulic press or in a jig designed with bolts that contract differentially onto the assembly. A microsection through such a joint is shown in Fig. 6.

Thickening the tin layer from 2 to 5 µm and 8 µm to improve joint filling at the lower loading of 0.03 MPa introduced a new problem, formation of an interfacial layer of brittle Cu_3Sn that considerably compromised mechanical strength. Raising the joining temperature to 760°C did not provide the desired compensation to sufficiently disperse the tin away from the joint and into the copper alloy to eliminate the Cu_3Sn intermetallic phase — Fig. 7. The copper-tin phase diagram shown in Fig. 8 (Ref. 8) indicates that the solubility of tin into the copper primary phase declines noticeably as the temperature is lowered. Therefore, the re-precipitation of the Cu_3Sn phase on cooling from the joining temperature may be the cause of the Cu_3Sn intermetallic phase being present in the joints made at 760°C using tin thickness in excess of 2.5 µm, rather than insufficient dissolution of tin into the copper.

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 that 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 Cu_3Sn 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 intervening γ- and β-CuSn 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 Cu_3Sn 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 temperature of the Cu_3Sn (*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 $C_{\alpha L}$, 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:

$$t = \frac{\pi W_0^2}{16 D_\alpha}\left(\frac{C_B}{C_{\alpha L}}\right)^2 \qquad (1)$$

where W_o is the thickness of the melting-point depressant interlayer, C_B 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-CuSn phases to the primary copper. Accordingly, the diffusivity $D_{\overline{\alpha}}$ is now the aggregate value for the tin diffusion through to the copper and the $C_{\alpha L}$ must be replaced by the value $C_{\alpha\beta}$, 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

$$t = \frac{\pi W_0^2}{16 D_{\overline{\alpha}}}\left(\frac{C_B}{C_{\alpha B}}\right)^2. \qquad (2)$$

As shown by MacDonald and Eager (Ref. 11), this equation can be represented in nomograph form — Fig. 9. The value of $D_{\overline{\alpha}}$ is not readily available from the literature, but can be calculated from the variables in Equation 2, which have been experimentally determined. The value of $D_{\overline{\alpha}}$ estimated for a tin layer thickness of 2 µm, which takes ~10 min to react with and completely disperse in copper at 680–690°C (1256–1274°F), is 2×10^{-13} m²/s.

Using this value of $D_{\overline{\alpha}}$, the brazing time required to fully react tin layers 5 and 10 µm thick is estimated to be 90 and 360 min, respectively — clearly far in excess of the 5 min at 690°C or ~10 min above 680°C used in the current work. These values help explain why it was not possible to completely react and disperse the tin when the thicker coatings of tin were used.

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 $D_{\overline{\alpha}}$ calculated from Equation 2 lies almost midway between the measured value of ~5×10^{-11} m²/s for the diffusion of tin in Cu_3Sn at 707°C (1305°F) and the corre-

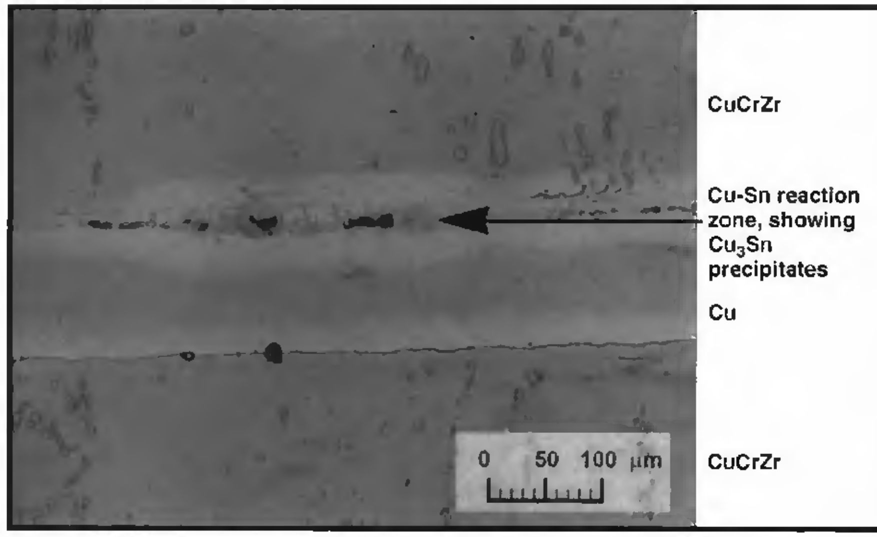

Fig. 7 — Micrograph of a joint made between a copper-plated CuCrZr tile and a copper foil coated with a 5-µm-thick layer of tin at 760°C (1400°F) under a compressive loading of 30 kPa, showing the presence of Cu_3Sn intermetallic phase at the joint interface.

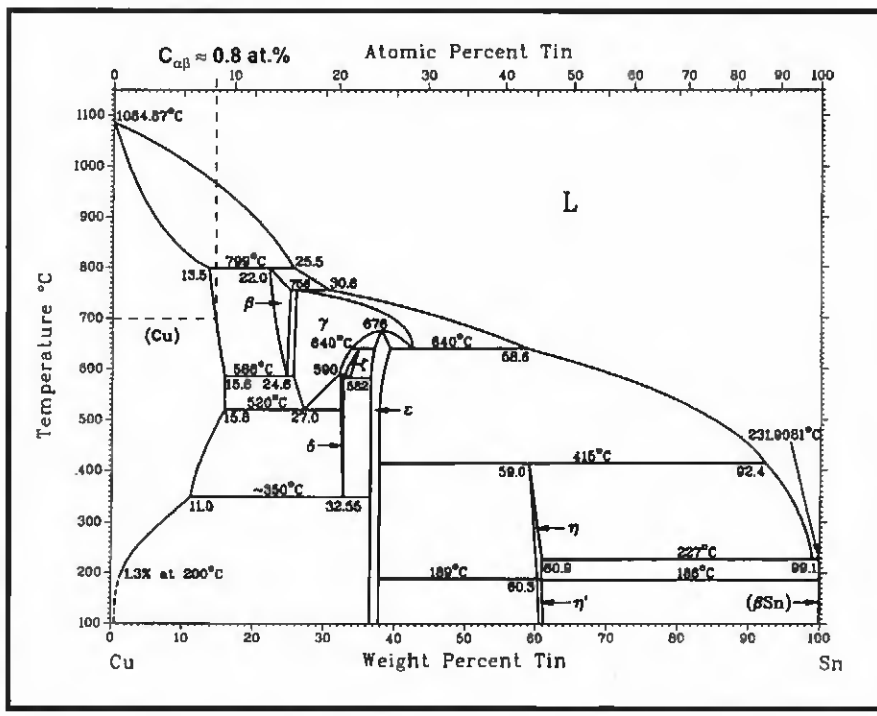

Fig. 8 — The copper-tin phase diagram (see Ref. 8 figure on p. 965).

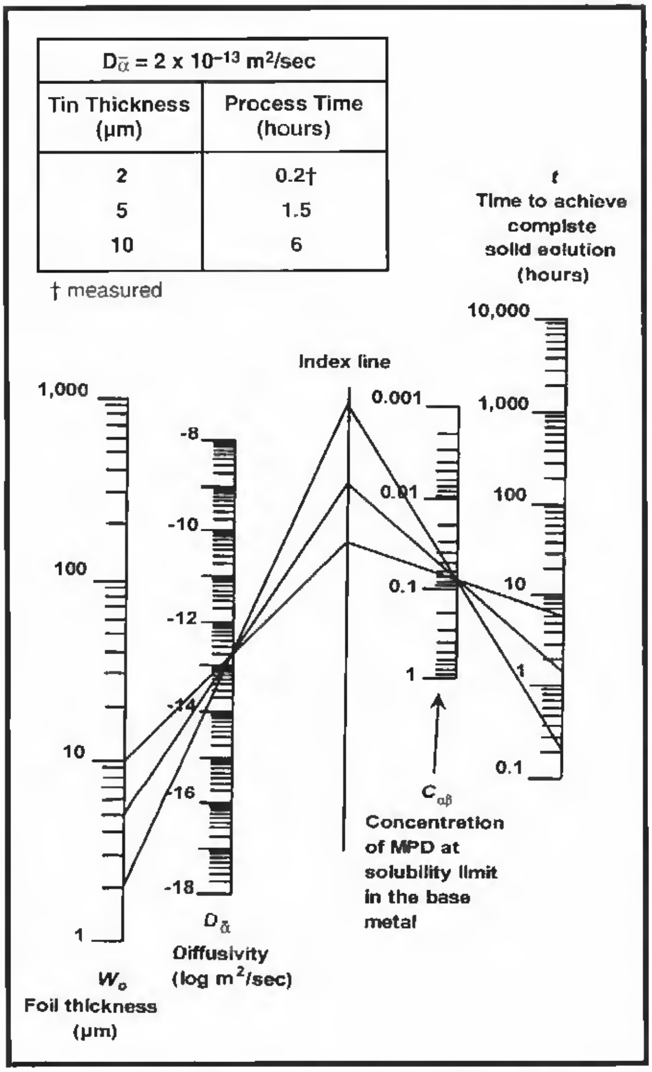

Fig. 9 — Nomograph based on Equation 1 illustrating the relationship between brazing time, tin thickness, concentration of MPD and the diffusivity of the filler metal.

sponding value of ~9 × 10^{-16} m²/s for tin diffusion in pure copper (Ref. 12). These values of diffusivity are all consistent with one another, especially taking into account the respective melting points of pure copper, >1085°C (>1985°F) and of the γ-phase, 676–756°C.

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 × 25 × 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 Cu_3Sn phase at the interface between the reaction zone and the copper components in this sample. Such joints produced in a hot isostatic press (HIP) at 150 MPa isostatic pressure maintained at 720°C (1328°F) for 90 min achieved shear strengths in excess of 230 MPa. Parallel diffusion-brazing trials carried out in a hot press involving uniaxial loading of 4 MPa at 660°C (1220°F) maintained for 5 min produced assemblies with an average shear strength of 199 ± 40 MPa and a maximum measured shear strength of 238 MPa. The standard deviation in the measured shear strengths became progressively narrower as the brazing temperature was raised from 660 to 720°C (1220 to 1328°F).

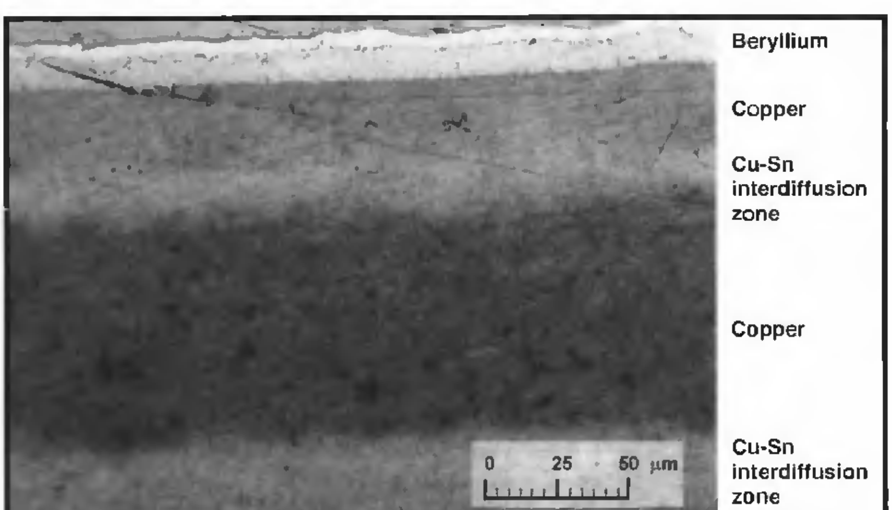

Fig. 10 — Micrograph of a well-reacted joint in a copper alloy (coated with copper) / beryllium (ion plated with copper) assembly formed at 660°C (1220°F). There is no visible evidence of residual intermetallic Cu_3Sn phase at the interface between the reaction zone and the copper components in this assembly.

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 Cu_3Sn 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

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