WELDING RESEARCH

SUPPLEMENT TO THE *WELDING JOURNAL*, JUNE 1994
Sponsored by the American Welding Society and the Welding Research Council

A Novel Brazing Technique for Aluminum

A simplified and cost-effective method using an alloy powder mixture instead of a clad surface has been developed for brazing aluminum, copper and brass

BY R. S. TIMSIT AND B. J. JANEWAY

ABSTRACT. This paper describes a novel brazing technique for aluminum, in which at least one of the contacting aluminum surfaces is coated with a powder-mixture consisting of silicon and a potassium fluoroaluminate flux. Brazing is carried out by heating the joint to approximately 600°C in nitrogen gas at near-atmospheric pressure over a time interval of a few minutes. During heating, the flux melts at 562°C and dissolves the surface oxide layers on the aluminum, thus allowing the silicon particles to come into intimate contact with the bare metal. At temperatures exceeding 577°C, the silicon dissolves rapidly into the aluminum and generates *in-situ* a layer of Al-Si liquid alloy of eutectic composition. The filler metal forms a fillet around the joint by capillary action. A metallurgical bond is formed on cooling. The addition of Zn powder to the Si/flux powder mixture allows diffusion of Zn during brazing and modifies the resistance to corrosion of the brazed assembly.

The novel brazing technique may be exploited using elements other than silicon for generating filler metal. The only requirement on these elements, such as Cu, Ge, Zn, etc., is that they form a relatively low-temperature eutectic alloy with aluminum. The technique has been used successfully for brazing aluminum/Cu, Cu/Cu and Cu/brass in addition to aluminum/aluminum joints.

R. S. TIMSIT is with AMP of Canada Ltd., Markham, Ont., Canada,and B. J. JANEWAY are with Alcan International Ltd., Kingston R & D Center, Kingston, Ont., Canada.

Introduction

The joining of metal parts by brazing often involves the use of a filler metal characterized by a liquidus temperature above 450°C (842°F) but appreciably below the solidus temperatures of the core materials. On melting, the filler metal spreads between the closely fitted surfaces, forms a fillet around the joint and yields a metallurgical bond on cooling. Over the past several years, nitrogen furnace brazing (Refs. 1, 2) has been used in preference to other techniques for the large-scale joining of aluminum parts such as automobile heat exchangers and air-conditioning condensers (Refs. 2, 3). In these applications, at least one of the aluminum components is clad with filler metal consisting of an Al-Si alloy of near-eutectic composition such as AA4045, AA4047 or AA4343 (Ref. 4). These alloys contain 9 to 13 wt-% of Si and are characterized by a melting temperature (in a narrow range near 577°C) (Ref. 5) considerably lower than that of the core alloy (~660°C). Joining is carried out at approximately 600°C (1112°F) in the presence of a noncorrosive flux such as a fluoroaluminate salt (Refs. 1, 6) to remove native surface oxide films from the contacting aluminum surfaces. Oxide removal enhances wetting by the molten Al-Si eutectic alloy at the brazing temperature and eases liquid-metal penetration of the joint.

KEY WORDS

Brazing
Aluminum
Eutectic Reaction
Intermediary Powder
Si/Flux Powder Mix
Oxide Removal
Temperature Relation
Filler Metal Generation
Si, Cu, Ge vs. Mg
Low-Temp. Eutectic

The manufacture of clad aluminum brazing sheet is a multistep process that involves casting of the filler metal ingot, subsequent cladding to the aluminum core material by hot rolling and final cold rolling of the composite material to the desired thickness. The preparation of aluminum brazing sheet is thus relatively complicated and the manufacturing cost is correspondingly high. The present work was motivated by the need to simplify aluminum brazing sheet manufacture. The development of a brazing technique that obviates the use of clad material, without greatly affecting the industrial brazing practice evolved over the past several years for aluminum, would obviously be attractive. The present paper describes such a technique. The process is carried out in nitrogen gas and has been used successfully for brazing aluminum/Cu, Cu/Cu and Cu/brass in addition to aluminum/aluminum joints.

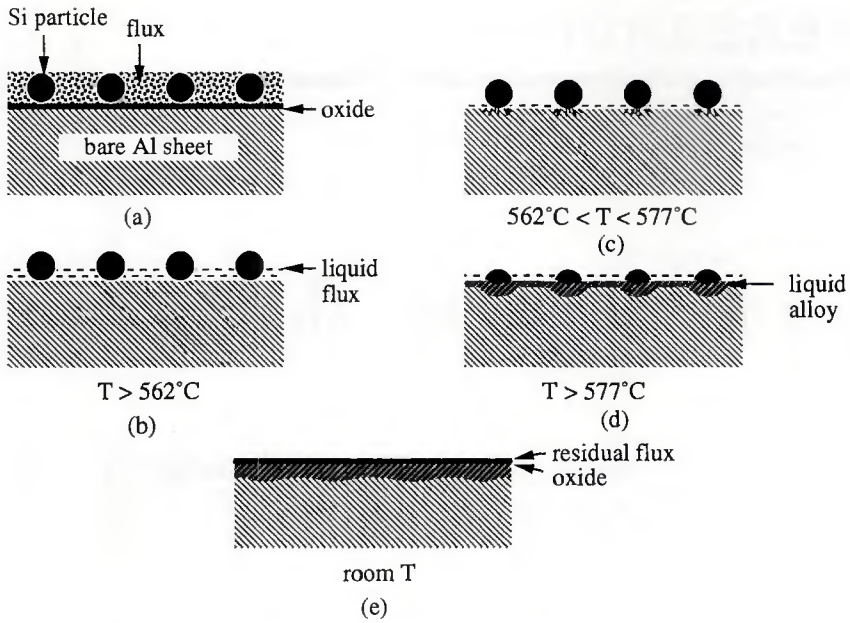


Fig. 1 — Successive steps in the novel brazing process. A — Deposition of a Si/flux powder mix on the aluminum surface. The Si particle dimensions range from ~1 to 100 μm; the flux particle dimensions do not exceed 1 μm; B — melting of the flux at 562°C and dissolution of surface oxide films; C — at 562°C < T < 577°C, solid-state interdiffusion of Si and aluminum; D — at T>577°C, rapid dissolution of Si to form localized pools of filler metal of near-eutectic composition, followed by coalescence of liquid metal pools; E — end of filler metal generation and solidification.

Brazing Process

The present brazing technique uses the "eutectic bonding" approach described in earlier publications (Refs. 7, 8), but avoids the need to coat the base metal surface with an intimately adhering layer of the eutectic-forming metal by electroplating or vacuum deposition. In the present technique, at least one of the aluminum surfaces is coated with a thin layer of a powder mix consisting of an element capable of forming a low-temperature eutectic with aluminum (*e.g.*, Si, Cu, Ge, Zn) and a flux capable of dissolving surface oxide films (Ref. 9), as illustrated in Fig. 1A. A commonly available noncorrosive flux (Ref. 6) was used in the present work. This flux consists of a mixture of $KAlF_4$ and $K_2AlF_5 \cdot H_2O$ powders in a molar ratio of the respective salts of approximately 13:1 (Ref. 10), and with a particle dimension of the order of 1 μm. For reasons to be addressed later, we will focus most of our attention on brazing using Si.

The surface coverage by the Si powder may range from a few to several tens of grams per square meter, depending on the joining application, and the weight ratio of Si-to-flux powder may vary typically from 1:1 to 1:3, also depending on the application. Considerably larger Si surface coverage may be used for specific applications. The Si powder particle dimensions may range from ~1 to 100 μm. Brazing is carried out by heating the joint at approximately 600°C in nitrogen gas at near-atmospheric pressure for a few minutes. During temperature ramp-up, the flux melts at ~562°C (1043°F) and dissolves the surface oxide layers on aluminum (Ref. 11), as illustrated in Fig. 1B. Sufficient flux must always be present to remove these oxides. Oxide dissolution must occur more rapidly than reoxidation of the aluminum surface, and it allows the Si particles to come into intimate contact with the bare metal. At this juncture, the large elemental concentration gradients at the aluminum/Si interface cause the aluminum and Si to interdiffuse — Fig. 1C. At temperatures exceeding 577°C (1070°F), it is found that the Si particles diffuse rapidly into the aluminum surface and generate *in situ* a layer of Al-Si liquid alloy of near eutectic composition — Fig. 1D. The filler metal penetrates the joint of interest by capillary action and forms a fillet, thus producing a metallurgical bond on cooling. Any unused filler metal remains on the aluminum surface to form a layer of Al-Si alloy of near-eutectic composition — Fig. 1E.

In this process, only one of the joined surfaces need be covered with the Si-flux mix because the molten flux spreads rapidly across the joint to remove surface oxide films from the mating surfaces. The quantity of filler material formed from one coated surface is generally sufficient to yield a good metallurgical bond. Because fillets are formed through capillary flow of the filler metal, brazing requires only minimal contact force at the joint interface.

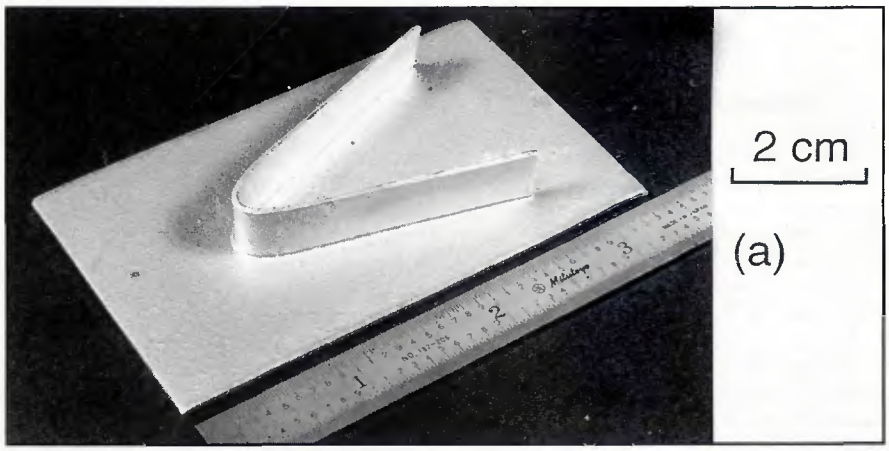
Procedures and Results

Preparation of Surfaces and Joints

The successful use of the novel brazing technique requires a uniform coating of Si-flux powder on the metal surfaces prior to brazing. In the present work, the uniform coating could be deposited from a water-based slurry after cleaning the surfaces chemically prior to dipping. Chemical cleaning was carried out as follows: the surfaces were first immersed for 5 s in a caustic bath consisting of 5% by weight NaOH in water at 65°C (149°F), rinsed in cold water, desmutted for ~2 s in an acid bath consisting of 50 wt-% HNO_3, rinsed in cold water and finally dried for a few minutes in a forced-air furnace. This procedure removes oil and grease residues and yields an aluminum surface that is uniformly wettable by water. The aluminum sheet was then dipped for a few seconds into a water-based slurry composed of 50 wt-% of the Si/flux powder and 50% distilled water at room temperature. Excess slurry was allowed to drip off following withdrawal, thus leaving the uniform powder coating on the sheet surface. The Si powder consisted of commercial-grade material of 99.1% purity, with Fe as the major contaminant.

The aqueous slurries were found to be remarkably stable when used with cleaned aluminum surfaces. No effects of slurry aging on the brazing process were detected over a time interval of two years. Powder deposition was always performed after agitating the slurry to generate a reasonably uniform suspension of the heavy Si/flux powder in water. The Si/flux weight ratio in the slurry was varied between 1:2 and 1:3. Depending on the concentration of solids in suspension, surface coverage by the brazing mix ranging from 10^{-3} to 8×10^{-2} kg m^{-2} could easily be obtained on aluminum. After dipping, the coating was dried in a circulating air oven at 170°C (338°F) for 1 min. The deposit thus obtained was very uniform. The mating surface in the joint was similarly cleaned but was not necessarily coated with powder.

Other surface preparation and powder deposition techniques were used successfully for brazing. For example, vapor degreasing was used to remove residual oil and other organic contaminants from the aluminum surfaces. Because this decontamination procedure does not yield a surface readily wettable



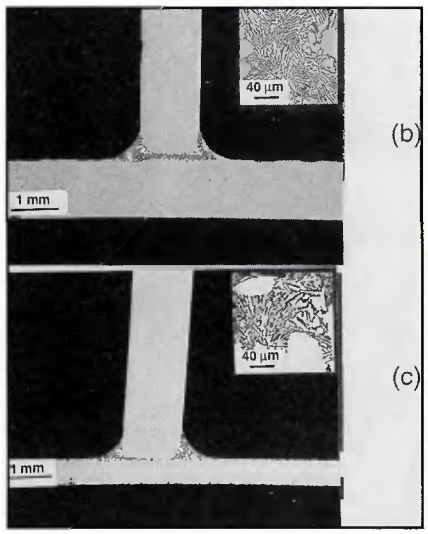


Fig. 2 — A — External appearances of a typical joint between two AA3003 aluminum sheet specimens. Only the horizontal sheet was coated with Si/flux mix; B — metallurgical cross-section from a typical AA3003 joint. The gray precipitates in the AA3003 components are Al-Fe-Mn-Si constituents. Inset: enlarged view of fillet. The dark needle-like particles consist of Si precipitated from solution during cooling; C — metallurgical cross-section from a joint formed by conventional brazing wherein the vertical component was joined to a coupon of AA3003 clad on both sides with AA4045 (Ref. 4). Inset: enlarged view of fillet; the Si precipitates are appreciably coarser than those generated by the novel brazing technique as explained in the text.

by water, deposition of a uniform Si/flux coating required the addition of a wetting agent to the aqueous slurry (Ref. 2). As an alternative to this procedure, a uniform coating could also be deposited from an alcohol-based slurry without prior chemical cleaning of the aluminum, since alcohol dissolves residual organic contaminants from surfaces. However, nonaqueous slurries are generally not environmentally benign. As an additional alternative for deposition, Si/flux coatings of acceptable uniformity were generated on a chemically clean surface by electrostatic spraying.

In the present work, the efficacy of the brazing technique was evaluated by mechanically assembling the clean and coated test components in the desired joint configuration, heating the assembly in a nitrogen furnace at the selected temperature for time intervals of approximately 2 min, and examining the brazed joint(s) after cooling.

Aluminum/Aluminum Joints

Figure 2A shows the external appearance of a typical joint formed between two AA3003 aluminum sheet specimens (the compositions of the aluminum alloys used in the present work are listed in Table 1). In this example, only the sheet shown horizontally in the figure was coated with the Si-flux mix. Brazing was carried out at 600°C, thus, significantly above the eutectic reaction temperature, to induce rapid Si diffusion into the aluminum as will be described later. Note the uniformity of the filler. Figure 2B shows a metallurgical cross-section from a typical joint. The dark needle-like particles in the fillet are Si particles precipitated from solution during cooling after dissolution of the Si powder into the aluminum. The fine precipitates in the base metal consist largely of $Al_{15}(FeMn)_3Si_2$ constituents usually present in AA3003. For comparison, Fig. 2C shows a metallurgical cross-section obtained from a joint similar to that illustrated in Fig. 2A but formed by conventional brazing wherein the vertical AA3003 specimen was joined to a coupon of AA3003 clad with AA4045 (Ref. 4). No Si powder was used in forming the latter joint, although flux was introduced, since the filler metal is generated on melting of the clad alloy at approximately 577°C (Ref. 4). The fillets in the two figures are essentially identical. Generally, the Si precipitates in fillets formed from clad alloys, as in Fig. 2C, are appreciably coarser than those generated by the novel brazing technique. The difference in the coarseness of Si precipitates in the two brazing processes may relate to differences in filler metal compositions. We recall that the filler metal in the novel technique is produced from the AA3003 base alloy rather than from AA4045.

One major attractive feature of the new brazing process is a capability for introducing additional materials into the surfaces to enhance selected properties. For example, the addition of Zn powder to the Si/flux mix leads to diffusion of Zn into the coated surfaces without adversely affecting the generation of filler metal. Figure 3 shows a typical distribution with depth of Zn introduced by this method. The concentration profile was obtained by wavelength-dispersive Electron Micro-Probe Analysis (EMPA) of a cross-section of AA3003 sheet coated with a Si-flux-Zn powder mix deposited from a water-based slurry. The Zn surface coverage was 4.3×10^{-3} kg m^2 and the weight ratio of Si to Zn was approximately 1:1. The joint was brazed at 600°C using a procedure identical to that described earlier. The presence of an appreciable quantity of Zn over a depth of ~100 µm, with a maximum of ~1% by weight near the surface, was found to enhance the resistance to corrosion of the surface (Ref. 12).

Although the brazed joints illustrated above were formed with AA3003 core components, it was verified that the brazing technique may be used with a wide

Table 1 — Aluminum Alloy Composition Limits in Wt-%

AA Alloy	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	Others
1050	0.25	0.4	0.05	0.05	0.05	0.05	—	0.03	
1100	0.95 Si+Fe		0.05–0.2	0.05	—	0.1	—	—	0.15
3003	0.6	0.7	0.05–0.2	1.0–1.5	—	0.1	—	—	0.15
3102	0.4	0.7	0.1	0.05–0.4	—	0.3	—	0.1	0.15
4045	9–11	0.8	0.3	0.05	0.05	0.1	—	0.2	0.15
6061	0.4–0.8	0.7	0.15–0.4	0.15	0.8–1.2	0.25	0.04–0.35	0.15	0.15
X-800	0.05	0.19	0.31	1.11	0.27	—	—	0.008	0.15

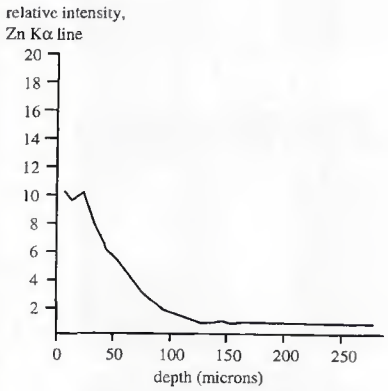


Fig. 3 — Typical distribution of Zn dissolved into aluminum during brazing, by introducing Zn powder into the Si/flux mix. The curve shows the relative intensity of the Zn Kα line as a function of distance from the surface. The analysis was carried out by wavelength dispersive EPMA on a cross-sectional brazed specimen prepared from AA1100 alloy.

range of aluminum alloys such as the extrusion alloys AA1050, AA3102 and others. Figure 4 illustrates the generation of filler metal on surfaces of a commonly used sheet alloy such as AA1100, AA6061 and X-800. In all cases, the efficacy of filler metal generation was determined by coating the surfaces with a layer of the brazing mix and heating as described above. The metallurgical structure of the solidified filler metal shown in Fig. 4A is essentially identical to that observed with other alloys such as AA1050, AA3102 and others. The quantity of eutectic liquid formed corresponds approximately to the thickness of the surface layer carrying the dark Si precipitates. Although this thickness is only approximately 20 μm in these illustrative examples, the quantity of filler metal may be considerably larger because it is controlled largely by the initial Si powder coverage on the surface, as will be shown later. As in Fig. 2, the dark needlelike particles near the surface consist of Si precipitated from solution on cooling.

The cross-sections shown in Fig. 4B and 4C were obtained respectively from AA6061 and X-800 specimens after attempting to generate filler metal. Note that the surface in Fig. 4B is severely disrupted and that an appreciable quantity of unreacted Si remains imbedded in the surface. The lower Mg concentration in X-800 appears to lead to appreciably less surface disruption, as indicated in Fig. 4C, but considerable unreacted Si was also left over on that surface. In all cases, no significant amount of filler metal was produced. These observations are typical of all those made on aluminum alloys containing more than approximately 0.1 wt-% of Mg. The absence of a generation of filler metal in Mg-bearing aluminum alloys is attributed in part to impairment of the liquid flux to dissolve Al_2O_3 in the presence of Mg, due to the formation of MgF_2 at elevated temperatures (Ref. 11). It is also attributed to the lack of formation of a free-flowing liquid of eutectic composition in the Al-Mg-Si system at ~600°C (Ref. 5). However, the increased state of disruption of the surface (following attempted brazing) observed with increased Mg concentration in the alloy points to some metallurgical reactions between the Si coating and the base alloy before formation of MgF_2. The nature of these reactions was not investigated.

Magnesium-containing aluminum alloys can be brazed by cladding the surface with any aluminum alloy free of Mg, and generating the filler metal from the clad (Ref. 13). The metallographic structure of the fillet is generally found to be nearly identical to those illustrated in Fig. 2. Filler metal could be generated with a clad layer thickness as small as ~45 μm. These observations indicate that Mg diffusion from the core alloy and across the clad layer is generally too slow to have an appreciable effect either on the activity of the molten flux or on filler metal formation, over the time intervals used in the brazing process.

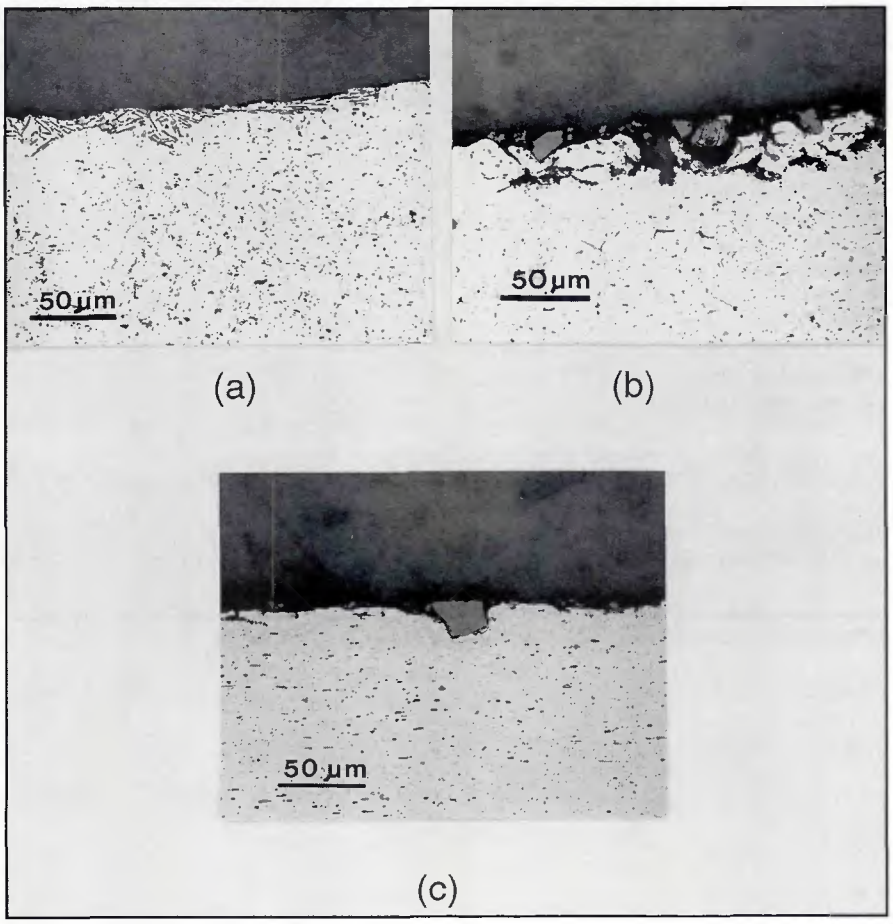


Fig. 4 — Cross-sections obtained from specimens of commonly used aluminum alloys. A — AA1100; B— AA6061; C — X-800.

Aluminum/Cu Joints

Aluminum/Cu joints were brazed by the novel process using the Si/flux brazing mix. It was surmised that the technique could be used since a ternary eutectic exists at 524°C (975°F) in the Al-Cu-Si system (Ref. 14). Formation of a ternary liquid alloy of near-eutectic composition would yield the required filler metal. Prior to brazing, the aluminum component (AA1100) was cleaned chemically as described previously. The Cu section was prepared from commercial-purity material. It was cleaned by etching for 1 min in a 50 vol-% solution of nitric acid, rinsing in distilled water and drying with an air blower. The aluminum surface was coated with Si/flux powder using a water-based slurry. Typical surface coverage by Si and flux were respectively ~8 x 10^{-3} kg m^{-2} and 25 x

10^{-3} kg m^{-2}. Brazing was carried out by heating to 584°C (1083°F) in nitrogen gas to cause rapid melting of the flux and then reducing the temperature to below 548°C (1018°F) as quickly as possible by cutting off power to the furnace and increasing the nitrogen gas flow. The reason for cooling rapidly (~1 min) is explained below.

Figure 5 shows a typical metallographic cross-section obtained from an aluminum/Cu lap joint. Note the presence of a relatively wide interdiffusion layer consisting of a eutectic material. Careful examinations by EPMA identified one phase as $CuAl_2$. The composition of the second phase was found to range from $\sim Cu_{0.4}Al_{0.5}Si_{0.1}$ to $\sim Cu_{0.2}Al_{0.5}Si_{0.3}$. The eutectic material was separated from the Cu component of the joint by a coherent intermetallic layer of approximate composition $Cu_{0.7}Al_{0.3}$ with a thickness of ~4 μm. Exposure of the joint to temperatures higher than ~548°C (1018°F) for time intervals exceeding ~1 min led to excessive dissolution of Cu into the aluminum sheet. This dissolution stems from the large solubility of Cu in Al in that temperature range (Ref. 5). Despite the presence of a relatively large quantity of intermetallic phase in the interdiffusion layer, the brazed joint was not found to be brittle. Any effect of the Si surface coverage on the strength of the Al/Cu joint remains to be investigated.

Brazing of an aluminum/Cu joint in the presence of Si probably occurs as follows: liquid metal is first formed by initial dissolution of Si into aluminum to form a layer of Al-Si eutectic liquid at a temperature exceeding 577°C (1071°F). As explained earlier, wetting of the Cu surface by the molten eutectic metal immediately leads to Cu dissolution to generate a molten ternary alloy. This alloy then constitutes the filler metal whose composition ranges from $\sim Cu_{0.3}Al_{0.62}Si_{0.08}$ to $Cu_{0.02}Al_{0.97}Si_{0.01}$ (Ref. 14) depending on temperature. This conjecture about the filler metal generation mechanism stems from observations that aluminum/Cu joints could not be brazed at temperatures lower than 577°C, *i.e.*, below the eutectic temperature of the Al-Si system.

In the aluminum/Cu joint just discussed, no intimate contact existed initially between the metal components because the metal surfaces were separated by the Si-flux particulate. It is worth noting that aluminum/Cu joints may also be brazed by introducing only flux into the joint and heating to ~565°C (1049°F) to melt the flux and generate an intimate aluminum/Cu contact interface. Subsequent interdiffusion of Al and Cu leads to filler metal formation since the Al-Cu system is characterized by a eutectic reaction at ~548°C (Ref. 5). In practice, this procedure often leads to nonuniform fillets because brazing is not initiated uniformly along a joint but begins instead where surface asperities of the core components are in mechanical contact.

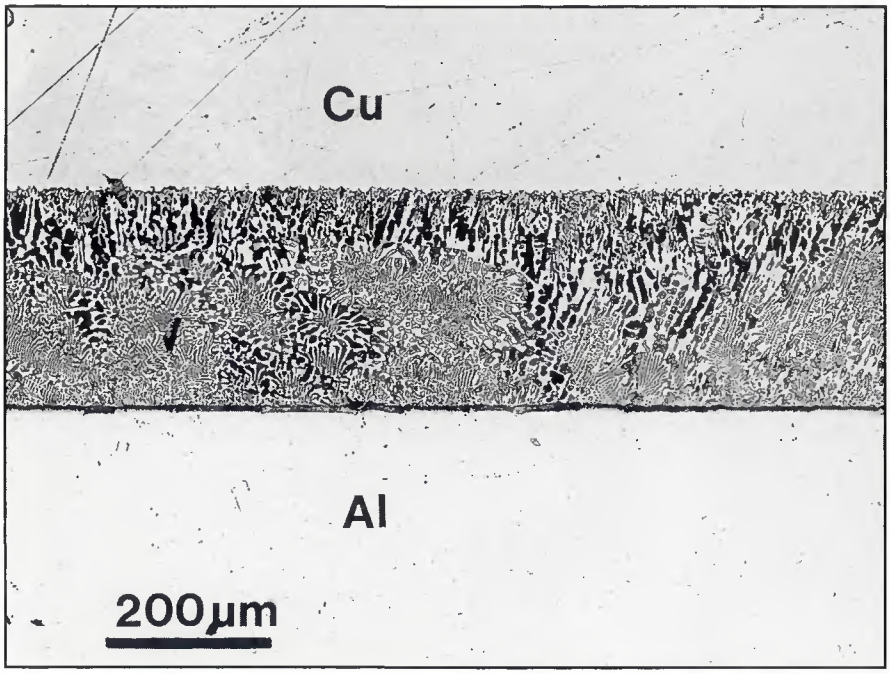


Fig. 5 — Typical metallographic cross-section from an aluminum/Cu lap joint. The relatively wide interdiffusion layer consists of a eutectic material made up of $CuAl_2$ and αCu-Al phase.

Cu/Cu and Cu/Brass Joints

Joining of Cu/Cu and Cu/brass joints was also successfully performed using the novel brazing technique. The brass consisted of 70/30 Cu-Zn material of commercial purity. Prior to Si/flux deposition, the components were cleaned by dipping for 1 min in a 50 vol-% nitric acid solution, rinsing in deionized water and drying. The brazing mix was deposited from a water- or isopropyl alcohol-based slurry to generate typical surface coverage of Si and flux of ~10 x 10^{-3} and 30 x 10^{-3} kg m^{-2}, respectively. Brazing was carried out at an elevated temperature as the eutectic reaction between Cu and Si occurs at 803°C (1477°F) (Ref. 5). It was found that excellent fillets were formed in Cu/Cu and Cu/brass joints by heating for a few minutes respectively at 900°C (1652°F) and at 876°C (1609°F) in nitrogen gas. Here again, the brazing temperature was significantly above the eutectic temperature to induce rapid Si dissolution and rapid formation of filler metal. Metallographic cross-sections from typical brazed joints are illustrated in Fig. 6. Note the excellent fillet geometry. Examinations by EMPA indicated that the fillets formed in Cu/Cu joints were rich in copper, consisting of 90 to 95 at-% Cu. Fillets formed between Cu and brass were characterized by an average composition of $\sim Cu_{0.84}Si_{0.05}Zn_{0.11}$. The sequence of metallurgical reactions leading to these fillet compositions was not investigated

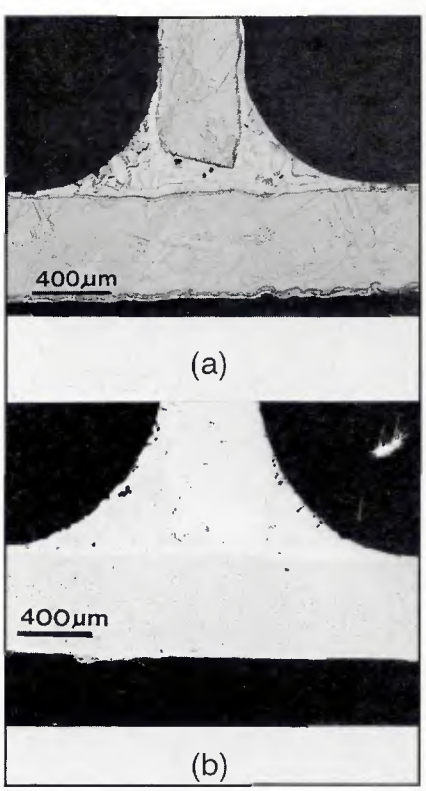


Fig. 6 — Metallographic cross-sections from typical brazed joints. A — Cu/Cu; B — Cu/brass. The compositions of the fillets formed in A and B correspond respectively to $\sim Cu_{0.9}Si_{0.1}$ and $Cu_{0.84}Si_{0.05}Zn_{0.11}$.

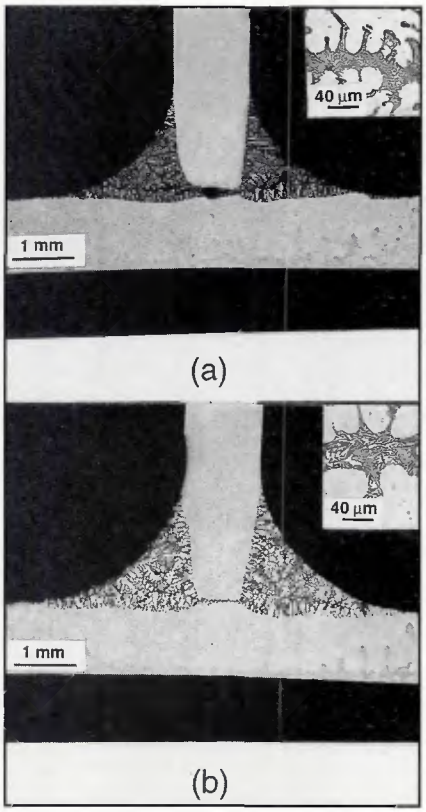


Fig. 7 — Metallographic sections of AA3003 aluminum joints brazed with: A — Cu/flux; B — Ge/flux. The insets show magnified views of the fillets. The fillet in A consists of the Al-$CuAl_2$ eutectic. The dark particles in the fillet in B consist of Ge and Al-Ge-Fe-Mn consituents.

because the present focus is a description of the novel brazing technique. It is expected that the metallurgical structure of the fillets would be affected not only by the base alloy composition and solidification time, but also by the brazing temperature. In the present work, the use of a brazing temperature appreciably higher than the Cu-Si eutectic reaction temperature may have led to Si depletion from the Cu-Si liquid filler metal by diffusion into the base metal. This would have affected the compositions of the solidified phases as is evident from the Cu-Si phase diagram (Ref. 5). Similar effects may have occurred during solidification of the Cu/brass joints.

Because copper oxides are unstable at elevated temperatures, it was surmised that Cu-rich materials might braze at elevated temperatures in the presence of Si powder alone, without the use of flux. It was verified experimentally that this conjecture is incorrect. This observation pointed to a surprising efficacy of the fluoroaluminate flux, which is used primarily for brazing aluminum (Refs. 1, 2) to remove oxide films from copper and brass at the elevated temperatures used in this work.

Brazing with Elements Other Than Si

Although the work reported above has focused on Si as the intermediary material for brazing, the brazing technique may use other elements to generate filler liquid. The only fundamental requirement is that these elements form a relatively low-temperature eutectic with at least one of the metals in the joint. Several elements such as Cu, Ge, Zn, La, Ca and Ba form a low-temperature eutectic with Al (Ref. 5); however, use of these metals for brazing aluminum may not always be desirable. Similarly for Cu/Cu joining, the selection of an intermediary metal from Ge, La, Nd, Sb, Se, and Sr, all of which form low-temperature eutectics with Cu (Ref.5), should require careful considerations for reasons outlined below.

For aluminum brazing, one of the major advantages of Si is its relative inertness in water at room temperature and its ensuant compatibility with aqueous slurries. Powder deposition from water-based slurries is straightforward and widely used in industry in various applications because it is simple, environmentally benign and requires no special handling. The chemical inertness of Si in water accounts for the absence of any effect of slurry aging on brazing. This is not necessarily the case with other potential intermediary metals for aluminum brazing. For example, Zn powder oxidizes rapidly in water to yield aqueous slurries that become unusable after only a few hours. For commercial applications, the use of Zn in an organic carrier such as an alcohol mitigates oxidation but generally does not represent an environmentally acceptable solution. In addition, the large Zn concentration in the Al-Zn eutectic (~90 at.-%) (Ref. 5) leads to a large coating weight requirement for the brazing of aluminum, which is not advantageous for many practical applications. Similarly, the chemical reactivity of other elements such as Ba and Ca in air or water and in many organic liquids precludes use of these metals as brazing materials. The reactivity of copper with water (Ref. 15) may also preclude powder deposition from aqueous Cu slurries for brazing aluminum. In the following, the use of brazing elements other than Si is illustrated only to show the broad applicability of the principles on which the novel brazing process is based.

Figure 7A and B show metallographic cross-sections of AA3003 aluminum joints brazed respectively with Cu/flux and Ge/flux powder mixes. The Cu- and Ge-containing powders were deposited from an isopropyl alcohol and an aqueous slurry, respectively, to yield surface coverages of 45.8×10^{-3} kg m^2 for Cu and 15×10^{-3}kg m^{-2} for Ge. The Cu/flux and Ge/flux weight ratios were respectively 1:1 and 1:2. Brazing was carried out at 600°C in nitrogen gas as described earlier. Note that metallurgical bonds are formed in the two cases. As mentioned earlier, the filler metal formed with the Cu and Ge powders stems from the eu-

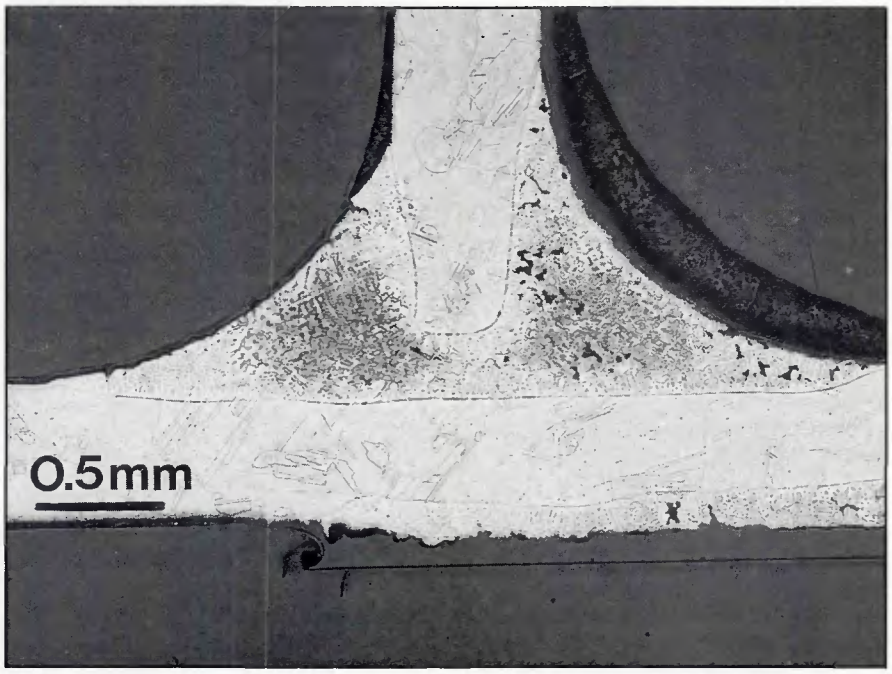


Fig. 8 — Metallographic cross-section from a typical Cu/Cu joint brazed with Ge/flux powder. The fillet consists of fine dendrites made up of two Cu-Ge solid solutions of approximate compositions $Cu_{0.92}Ge_{0.08}$ and $Cu_{0.08}Ge_{0.2}$ (ζ phase).

tectic reaction with Al at 548°C and 420°C (Ref. 5) in each case, respectively. In both cases, the joints were heated to 600°C to melt and generate rapid spreading of the flux. As expected, the fillet in Fig. 7A consists of the Al-$CuAl_2$ eutectic. The dark particles in the fillet shown in Fig. 7B consist of Ge and Al-Ge-Fe-Mn constituents. The Mn and Fe present in the latter constituents originate from the base alloy.

Figure 8 shows a metallographic section from a typical Cu/Cu joint brazed with Ge/flux powder. The brazing mix was deposited from the aqueous slurry mentioned above. Brazing was carried out in nitrogen gas at 700°C (1292°F) to take advantage of the Ge-Cu eutectic reaction at 644°C (1191°F) (Ref. 5) to generate filler metal. Note again the excellent metallurgical bond. Examinations by EMPA revealed that the fillet consisting of fine dendrites was composed largely of two Cu-Ge solid solutions of approximate compositions $Cu_{0.92}Ge_{0.08}$ and $Cu_{0.8}Ge_{0.25}$.

Formation Rates of Filler Metal

For the range of Si surface coverage discussed in this paper, empirical observations suggested that all the available Si dissolves into aluminum in a matter of seconds at the brazing temperature. Measurements of the formation rate of filler metal thus required the use of a rapid heating technique. These measurements were carried out using a rapid thermal anneal (RTA) furnace identical to the type used in the semiconductor industry (Ref. 16).

In the RTA furnace, the specimen is placed on a quartz tray that slides into a narrow quartz tube of rectangular cross-section. Banks of halogen lamps, controlled automatically by a temperature controller, provide the source of energy. The temperature monitoring system consists of a chromel/alumel thermocouple in contact with the specimen and fed back to control electronics. The furnace is capable of generating an elevated steady-state surface temperature in a small fraction of a minute. The steady-state temperature is controlled to 2°C (4°F). The furnace atmosphere is controlled by a flow of purge gas. All experiments described in this paper were carried out in nitrogen gas at a steady-state temperature of 600°C.

The Si dissolution times were determined by heating AA1100 aluminum coupons, each coated with a selected surface coverage of Si/flux mix, and measuring the depth to which Si had dissolved during a selected time interval at the brazing temperature. The coupons were 25 x 75 mm (1 x 3 in.) and ~1mm (0.04 in.) thick and were heated separately. Diffusion depths were measured from metallurgical cross-sections after cooling. The surface coverages by Si powder were sufficiently large to generate reasonably wide dissolution zones. These coverages ranged from 30 x 10^{-3} to 80 x 10^{-3} kg m^{-2}. The Si/flux weight ratio was ~1:3. The substrate surface temperature was monitored by pressing the control thermocouple junction lightly through the brazing mix into contact with the substrate.

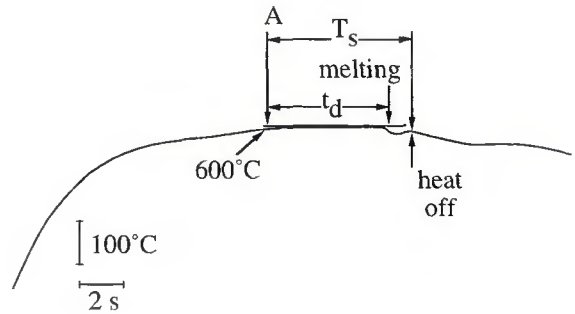


Fig. 9 — Typical evolution of surface temperature during heating. The filler metal was formed after a delay (t_d) of several seconds at 600°C and was characterized by a sudden drop in surface temperature. The furnace lamps were turned off at a preselected time T_s after the selected steady-state temperature (point A) was reached, $t_f = (T_s - t_d)$.

The typical evolution of surface temperature during heating is illustrated in Fig. 9. The temperature reached a steady-state value of 600°C in ~12 s. Formation of Al-Si eutectic liquid occurred after a delay (t_d) of several seconds at 600°C and was characterized by a sudden but temporary drop in surface temperature caused by extraction of the latent heat of melting from the heat bath. The delay t_d stems from the finite time required both for the flux to melt and for surface oxide films to dissolve into the liquid flux (Ref. 17). The furnace lamps were turned off at a preselected time T_s after initial attainment of the selected steady-state temperature (location A in Fig. 9). The interval during which liquid metal was produced was given as $(T_s - t_d)$.

An example of metallurgical cross-section obtained after a typical experiment is illustrated in Fig. 10. The width of the solidified filler metal band formed during the heating time $t_f = (T_s - t_d)$ of 1 s is ~90 μm. Note that several Si particles

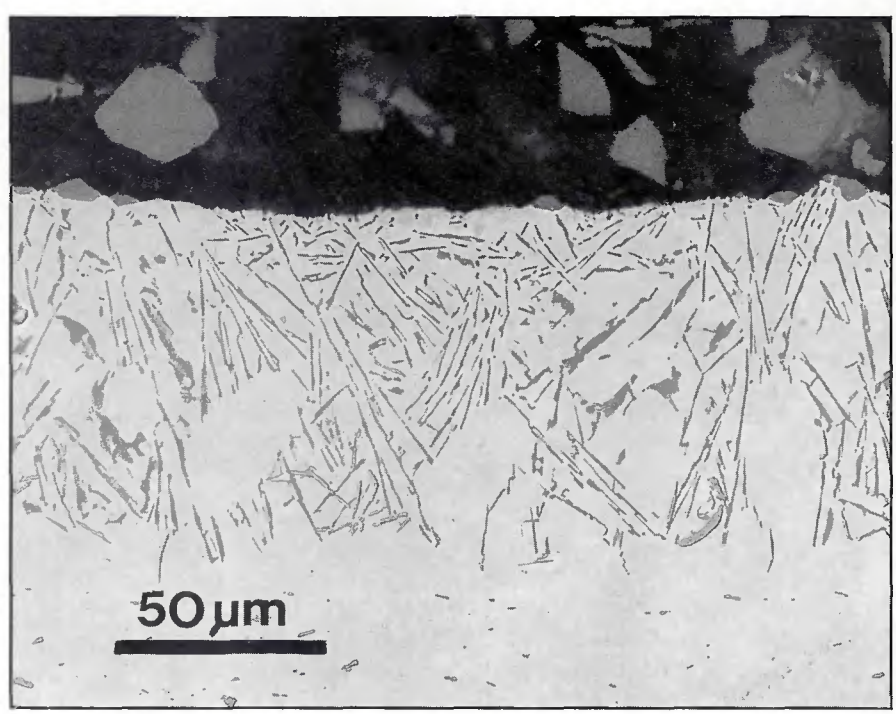


Fig. 10 — Metallurgical cross-section after filler metal had formed during a heating time t_f of ~1 s in the RTA furnace. Note that several Si particles remain undissolved above the aluminum surface.

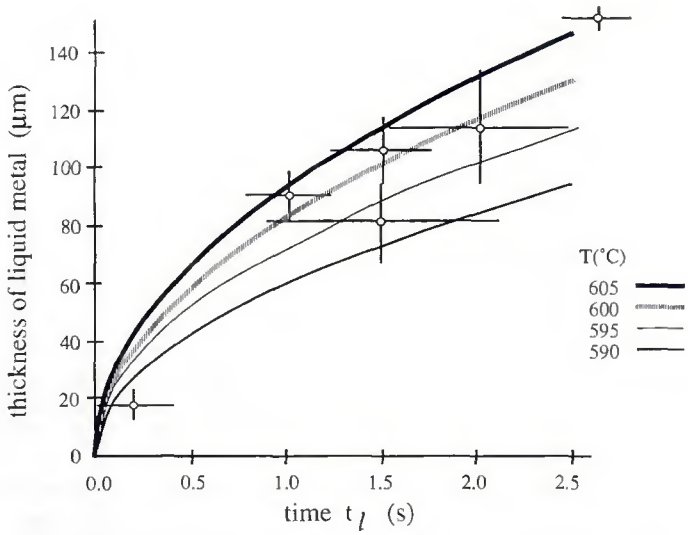


Fig. 11 — Measured dependence of filler metal thickness on t_l following solidification. The curves represent calculated values.

remain undissolved above the aluminum surface. The results of measurements of the dependence of the interdiffusion bandwidth on t_l are plotted in Fig. 11. The error bar associated with each measured value of t represents the maximum estimated deviation of t_l from the mean value of several measurements. The large estimated uncertainty stems from uncertainties about both the onset of filler metal formation and the juncture at which liquid formation ends. Nevertheless, the data of Fig. 11 indicate that the rate of filler metal formation is large at 600°C. The solid curves show the results of calculations carried out in accordance with the analysis discussed below.

Analysis of the Filler Metal Formation Process

The analysis presented below focuses on the mechanism of filler metal formation for the case in which Si is the intermediary brazing material. The model used for the analysis considers interdiffusion in a conventional planar Al/Si binary couple and is similar to previous models developed by various authors for transient liquid phase bonding (Refs. 18, 19). The model is tantamount to assuming that Si particles diffuse collectively as a coherent layer at a plane interface with aluminum. The model thus ignores any effects of the presence of molten flux or thermal convection currents. Any effects of Al alloying additions on Si diffusion rates are also ignored. The aim of the analysis is to calculate the filler metal generation rates expected on the basis of Al-Si interdiffusion alone. A comparison of the calculated rates with the corresponding experimental data would then provide insights into the major factors controlling filler generation in practice.

Consider the Al-Si binary phase diagram shown in Fig. 12A. Under equilibrium conditions, a thin layer of liquid is formed at the Al/Si interface as soon as sufficient Si and Al have interdiffused at a temperature above 577°C (say 600°C) to reach the concentration denoted as $C_{\alpha l}$. The formation of liquid quickly leads to the establishment of equilibrium between the solid α-Al solution and the Si layer with an intermediate liquid of composition ranging from $C_{l\alpha}$ and C_l as illustrated in Fig. 12B. As shown by other workers (Refs. 18, 19), the Si dissolution stage can be treated as a moving boundary problem in which Fick's law is applied to the liquid and solid phases. The equations governing the diffusion process are

$$\frac{\partial X_\alpha}{\partial t} = D_\alpha \frac{\partial^2 X_\alpha}{\partial x^2} \quad (1)$$

$$\frac{\partial X_\ell}{\partial t} = D_\ell \frac{\partial^2 X_\ell}{\partial x^2} \quad (2)$$

where X_α and X_ℓ represent the Si concentrations respectively in the solid α-Al and the liquid phase in the diffusion couple, and D_α and D_ℓ are the diffusion coefficients of Si respectively in α-Al and the liquid Al-Si alloy of near-eutectic composition, at the brazing temperature. The solutions of Equations 1 and 2 are given as (Ref. 18)

$$X_\alpha = A + B\ erf\left(x / \sqrt{4D_\alpha t}\right) \quad (3)$$

and

$$X_\ell = C + D\ erf\left(x / \sqrt{4D_\ell}\right. \quad (4)$$

where A, B, C and D are constants to be evaluated from the boundary conditions of the problem. From Equations 3 and 4, the conditions that x = 0 at t = 0 and that the Si concentrations at the moving boundaries remain constant, immediately identify the location of the α-alu-

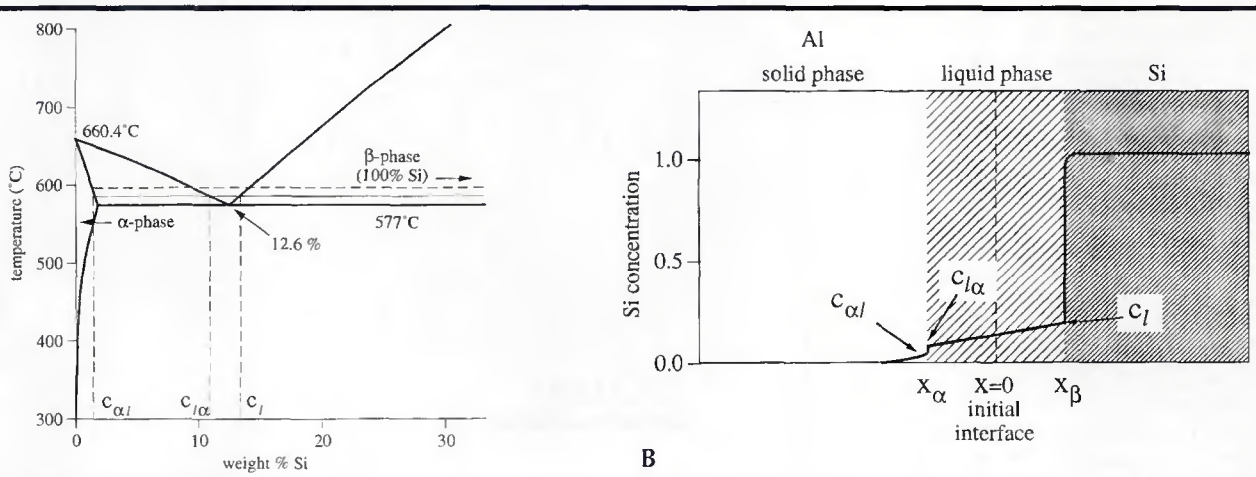


Fig. 12 — A — Al-Si binary phase diagram; B — under equilibrium conditions at the brazing temperature, a layer of liquid is formed with a Si concentration ranging from $c_{l\alpha}$ at the Al/liquid interface, to c_l at the liquid/Si interface.

minum/liquid and liquid/Si interfaces as

$$x_\alpha = A_\alpha \sqrt{4D_\alpha t} \text{ for } x < 0 \quad (5)$$

$$x_\ell = A_\ell \sqrt{4D_\ell t} \text{ for } x > 0 \quad (6)$$

where A_α and A_ℓ are constants to be determined from the boundary conditions of the problem (Ref. 18). It may readily be shown that substitution of Equations 3 to 6 into these boundary conditions leads to the following equations

$$\frac{A_\ell \exp\left(A_\ell^2 - A_\alpha^2 D_\alpha / D_\ell\right)}{|A_\alpha|\sqrt{D_\alpha / D_\ell}} = \frac{c_{\ell\alpha} - c_{\alpha\ell}}{1 - c_\ell} + \frac{c_{\alpha\ell}}{\sqrt{\pi}(1 - c_\ell)} \cdot \frac{\exp(-A_{\alpha\ell})}{|A_\alpha|\left(1 - erf(|A_\alpha|)\right)} \quad (7)$$

$$A_\ell \exp\left(A_\ell^2\right) \left\{erf(A_\ell) + erf\left(|A_\alpha|\sqrt{D_\alpha / D_\ell}\right)\right\} \frac{c_\ell - c_{\ell\alpha}}{\sqrt{\pi}(1 - c_\ell)} \quad (8)$$

In Equations 7 and 8, $A_\alpha = -|A_\alpha|$; these two simultaneous equations were solved numerically to generate values of A_ℓ and A_α corresponding to the values of D_α, D_ℓ, $C_{\alpha\ell}$, $C_{\ell\alpha}$ and C_ℓ at the selected temperatures. Note that Equations 7 and 8 indicate that the constants A_α and A_ℓ vary with temperature because they depend on the Si concentrations, which in turn depend on the selected brazing temperature as indicated in Table 2. The diffusion constants used in the calculation were $D_\alpha = 2.02 \times 10^{-4} \exp[-136/RT]$ m² s⁻¹ and $D_\ell = 2.08 \times 10^{-7} \exp[-25.7/RT]$ m² s⁻¹, where the activation energies are in kilojoules, obtained respectively from Fujikawa, *et al.* (Ref. 20), and Petrescu (Ref. 21). Note that the variations with temperature of D_α and D_ℓ have little effect on A_α and A_ℓ, because the ratio D_α/D_ℓ is small. At 600°C, the ratio D_α/D_ℓ is ~2.6 x 10^{-4}. The values of $|A_\alpha|$ and A_ℓ calculated from Equations 7 and 8 at temperatures ranging from 590° to 605°C are listed in Table 2.

The dependence on time t of the thickness L of the filler metal layer is given as

$$L = (4t)^{1/2} \left\{ A_\ell (D_\ell)^{1/2} + |A_\alpha| (D_\alpha)^{1/2} \right\} \quad (9)$$

The dependence of L on time, evaluated from Equation 9 at the four temperatures indicated, is shown by the solid curves of Fig. 11. Note the sensitivity of L to brazing temperature. This sensitivity stems largely from the temperature dependence of the ratio $(C_{\ell\beta} - C_{\ell\alpha})/(1 - C_\ell)$ (Ref. 18). Despite the uncertainty in the experimental measurements, there is broad agreement between the calculated and experimental data in Fig. 11. This agreement is surprising in view of the simplifying assumptions in the model.

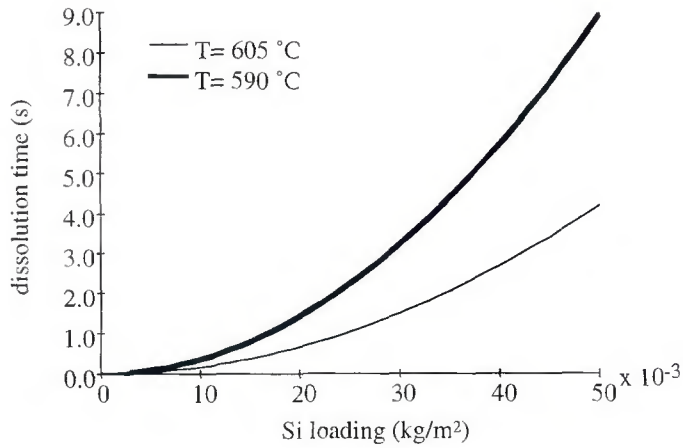


Fig. 13 — Dependence of the time required for complete dissolution of a Si coating as a function of the Si surface coverage corresponding to the coating. The curves were calculated from the planar diffusion-couple model.

The broad agreement between the experimental and calculated data of Fig. 11 suggests that the rate of arrival of Si particles to the aluminum surface is largely unimpeded by the presence of molten flux. The agreement also suggests that the particle arrival rate is considerably larger than the Si dissolution rate so that the particles dissolve essentially as a coherent layer, *i.e.*, as in a true Al/Si diffusion couple. The favorable comparison between experiment and theory indicates that the model may provide useful guidelines on total Si dissolution times. Figure 13 shows the dependence of the time required for complete dissolution of a Si coating as a function of the Si surface coverage (*i.e.*, as a function of the effective coating thickness), calculated on the basis of the planar diffusion-couple model. These data indicate that conversion of Si to filler metal occurs approximately twice as rapidly at 605°C as it does at 590°C, for any Si surface coverage. In many brazing applications where Si coverages range from ~ 10^{-3} to 20 x 10^{-3} kg m⁻², the difference in dissolution times is smaller than 1 s and is thus insignificant in comparison with the total time required for brazing.

As a final note, we point out that filler metal generation rates were also measured with Cu/flux mixes on aluminum at 600°C. The filler formation rates were found to be slightly larger than corresponding values for the Al/Si system, and also agreed with the predictions of the model. For these calculations, the appropriate diffusion coefficients were obtained from Fujikawa and Hirano (Ref. 22) and Ejima, *et al.* (Ref. 23).

Summary and Conclusions

This paper reports on a novel brazing technique for aluminum and show that the technique may be used for joining other metals. The technique uses the *in-situ* formation of filler metal by the eutectic reaction of an intermediary metal powder with the base metal surface. The major requirement on the intermediary metal is that the eutectic temperature be appreciably lower than the melting point of the base metal. The brazing process also requires the use of a flux, preferably a noncorrosive salt such as the potassium fluoroaluminate available as NOCOLOK™ flux (Ref. 6), to remove surface oxide films from the components to be joined. Oxide removal is essential for diffusion of the intermediary metal and the ensuing formation of filler metal. With aluminum, the brazing technique has been shown to be successful using Si, Cu or Ge as intermediary metals. The technique cannot be used for joining aluminum alloys containing Mg in a concentration as small as ~ 0.1 wt-%.

The filler metal generation rates obtained with Si powder are in general

Table 2 — Values of Relevant Constants in the Brazing Process Model

	Temperature (°C)			
	590°	595°	600°	605°
$C_{\alpha l}$	0.013	0.012	0.011	0.010
$C_{l\alpha}$	0.106	0.099	0.091	0.084
C_l	0.135	0.139	0.143	0.146
A_l	0.0456	0.0536	0.0605	0.0667
A_α	20.7	24.8	8.22	32.5

agreement with those calculated on the basis of interdiffusion in a planar Al/Si diffusion couple. This agreement suggests that the presence of molten flux does not interfere significantly with the Si dissolution rate. Examples of brazing of Cu/Cu and Cu/brass joints using mixtures of flux and Si or Ge powders show that the underlying principles of the novel brazing technique are widely applicable. In principle, it should thus be possible to braze a variety of metals using an intermediary element capable of forming a relatively low-temperature eutectic with the base metal. For example, brazing of Ni or Ni-rich alloys may be carried out using Si, Ge, Sm, etc., powders since eutectic reactions with Ni exist at temperatures of ~963°C, 762° and 570°, respectively (Ref. 5). Brazing at these elevated temperatures may be attractive in applications where conventional low-temperature soldering is undesirable, if a suitable flux is available. Similarly, it should be possible to braze other metals, such as refractory materials, using appropriate intermediary powders. The use of a powder mix consisting of two intermediary metals may also be considered for specific applications. In principle, there are no constraints to the combination of base metals and intermediary metals that may be used. In practice, constraints may arise from such factors as the unavailability of a flux capable of stripping surface oxide films at the brazing temperature, the formation of brittle intermetallics, and the cosmetic properties of the joint.

Acknowledgments

All work reported in this paper was carried out while both authors were employed at Alcan International. The authors are grateful to D. Lauzon and to the metallographic and electron optics sections of the Kingston R & D Center of Alcan International Ltd. for providing technical assistance during the course of this work.

References

1. Cooke, W. E., Wright, T. E., and Hirshfield, J. A. 1978. Furnace brazing of aluminum with a non-corrosive flux. SAE Int. Congr., Detroit, Technical Paper Series 780300.

2. Claydon, D. G. W., and Sugihara, A. 1983. Brazing aluminum automotive heat exchanger assemblies using a non-corrosive flux process. SAE Int. Congr., Detroit, Technical Paper Series 830021.

3. Goodremote, C. E., Guntly, L. A., and Costello, N. F. 1988. Compact air cooled air conditioning condenser. SAE Int. Congr., Detroit, Technical Paper Series 880445.

4. Fortin, P. E., Kellerman, W. M., Smith, F. N., Rogers, C. J., and Wheeler, M. J. 1985. Aluminum materials and processes for automotive heat exchanger applications. SAE Int. Congr., Detroit, Technical Paper Series 852228.

5. Ed. Massalski, T. B. 1990. *Binary Alloy Phase Diagrams,* ASM International.

6. Wallace, E. R., and Dewing, E. W. 1976. Joining of metal surfaces. U.S. Patent No. 3,951,328.

7. Niemann, J. T., and Garrett, R. A. 1974. Eutectic bonding of boron-aluminum structural components. *Welding Journal,* Vol. 53, pp. 175–184.

8. Wells, R. R. 1976. Microstructural control of thin-film diffusion-brazed titanium. *Welding Journal,* Vol. 55, pp. 20–27.

9. Timsit, R. S. 1992. Method of brazing aluminum. U.S. Patent No. 5,100,048.

10. Thompson, W. T., and Goad, D. G. W. 1976. Some thermodynamic properties of K_3AlF_6- $KAlF_4$ melts. *Can. J. Chem.* Vol. 154, pp. 3342–3349.

11. Field, D. J., and Steward, N. I. 1987. Mechanistic Aspects of the NOCOLOK flux brazing process. SAE Int. Congr., Detroit, Technical Paper Series 870186.

12. Baldantoni, A., Janeway, B. J., Lauzon, D. C., Purdon, M. J., and Timsit, R. S., 1994. NOCOLOK™ Sil flux — A novel approach for brazing aluminum. SAE Int. Congr., Detroit, Technical Paper Series 940502.

13. Timsit, R. S., and Janeway, B. J. 1993. Aluminum brazing sheet. U.S. Patent No. 5,232,788.

14. Eds. G. Petzow, and G. Effenberg. 1992. *Ternary Alloys,* Vol. 5, ASM International.

15. Tronstad, L., and Veimo, R. 1940. Preliminary researches on the action of water on copper pipes. *J. Inst. Metals,* Vol. 66, pp. 17–32.

16. Singh, R. 1988. Rapid isothermal processing. *J. Appl. Phys.,* Vol. 63, pp. R59–R114.

17. Underhill, R., and Timsit, R. S. To be published.

18. Lesoult, G. 1976. Modeling of the transient phase liquid phase bonding process I. Report of Center for the Joining of Materials, Carnegie-Mellon University, Pittsburgh, Pa.

19. Tuah-Poku, I., Dollars, M., and Massalski, T. B. 1988. A study of the diffusion bonding process applied to a Ag/Cu/Ag sandwich joint. *Met. Trans. A,* Vol. 19A, pp. 675–686.

20. Fujikawa, S. I., Hirano, K. I., and Fukushima, Y. 1978. Diffusion of silicon in aluminum. *Met. Trans. A,* Vol. 9A, pp. 1811–1815.

21. Petrescu, M. 1970. Liquid state atomic mobility of silicon in the unmodified eutectic silumin. *Z. Metallkude,* Vol. 61, pp. 14–18.

22. Fujikawa, S., and Hirano, K. 1989. Impurity-diffusion of copper in aluminum. *Defects and Diffusion Forum,* Vol. 66, pp. 447–452.

23. Ejima, T., Yamamura, T, Uchida, N, Matsuzaki, Y., and Nikaido, M. 1980. Impurity diffusion of fourth period solutes (Fe, Co, Ni, Cu and Ga) and homovalent solutes (In and Tl) into molten aluminum. *Japan Inst. Met.,* Vol. 44, pp. 316–323.

CORRECTION

Figure 1 in "Electromechanical Repair of Turbomachinery Shafts by SAW," by Richard LaFave and Richard Wiegand (April 1994), appeared without labels. The complete figure is shown at right.

In the first paragraph on P. 43 of the same article, reference is made to "12¼-in. (6.4-cm) diameter bolt holes." This should have read, "12 2.5-in. (6.4-cm) diameter bolt holes."

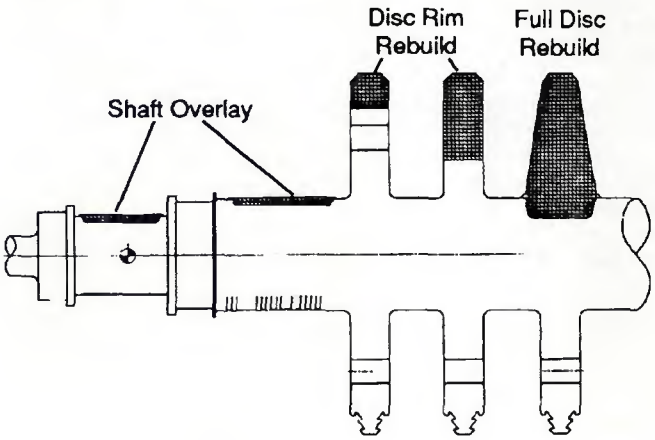


Fig. 1 — Types of repair.