Grain Boundary Penetration During Brazing of Aluminum

Copper in the core of brazing sheet with an Al-Si clad may lead to grain boundary penetration of the core

BY D. J. SCHMATZ

ABSTRACT. A tendency for grain boundary penetration of the aluminum-silicon braze clad into its underlying core has been noted after brazing aluminum radiators under vacuum with 6951 aluminum alloy as the core alloy. A study of this phenomenon was made comparing penetration susceptibility of several aluminum alloy types: 6951, 6061, 6063, 3003, 3004 and 3105. Only the 6951 and 6061 alloys exhibited a tendency for excessive grain boundary penetration.

Electron microprobe analysis of the penetration region indicated that magnesium and copper from the core diffused to the liquid and that silicon diffused from the liquid into the core. The copper enrichment of the Al-Si liquid was locally sufficient to lower the melting point and increase the solubility of aluminum. Preferential melting occurred at the grain boundaries. Alloys in which the copper content was less than 0.4% or in which the manganese was above 0.5% exhibited an insignificant amount of penetration. Manganese-aluminum particles appeared to retard liquid penetration.

Introduction

Aluminum alloys used for brazing under vacuum generally consist of sheet with a low melting point component roll welded onto a higher melting point core alloy. For brazing with a flux, the clad of the brazing sheet commonly consists of an aluminum-silicon alloy containing 7–11% Si. An addition of magnesium at a level of 1.5 to 2.5% is made to the clad alloy for brazing under vacuum.

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Table 1—Aluminum Alloy Compositions, %[a]

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn
6951	.2-.5	.8	.15-.4	.1	.4-.8		.2
6061	.4-.8	.7	.15-.4	.15	.8-1.2	.04-.35	.25
6063	.2-.6	.35	.1	.1	.45-.9	.1	.1
3003	.6	.7	.05-.2	1-1.5	—	—	.1
3004	.3	.7	.25	1-1.5	.8-1.3	—	.25
3105	.6	.7	.3	.3-.8	.2-.8	.2	.4

(a) Maximum percentages and percent ranges

During brazing, the thin layer of clad melts, and depending on the brazing temperature and time, some of the core material will dissolve in the liquid. When this occurs uniformly, it is called erosion or solutioning. When it occurs preferentially at grain boundaries, it is commonly called "silicon grain boundary penetration."* Grain boundary penetration could have a significant effect on the corrosion resistance of brazed components, since rapid corrosion can occur at the silicon-aluminum interfaces when particles of silicon form at grain boundaries.

Metallographic examination of the joints in vacuum brazed prototype radiators indicated a tendency for grain boundary penetration to occur in 6951 alloy but not in 3105 alloy. A study was undertaken to determine the variables affecting the susceptibility of a number of alloys to silicon grain boundary penetration.

Alloys and Sample Configuration

The compositions of the alloys studied are listed in Table 1. The sample configuration consisted of a simulated fin-tube arrangement shown in Fig. 1, using either 6951 or 3003 fins and a brazing sheet of the alloy being studied. The composition of the cladding on the brazing sheet was Al-9.5Si-1.5Mg-.08Bi and was about 7.5% of the total sheet thickness which was generally 0.050 in. (1.3 mm). In the case of the 6061 alloy, a clad brazing sheet was not available, so the 6061 was brazed to a 3003 alloy containing a braze clad.

Samples were brazed in a vacuum of about 25 μm at various temperatures within the range of 582°C (1080°F) to 610°C (1130°F) for times ranging from 5 to 10 minutes (min).

Results

The brazed samples were sectioned and examined metallographically for liquid penetration. Only the 6951 and 6061 alloy cores showed significant amounts of grain boundary penetration. The other alloy cores exhibited only moderate wetting of the grain boundaries. A typical example of the penetration observed in 6951 and 6061 is shown in Fig. 2. In contrast, the limited penetration observed in 3003 is shown in Fig. 3.

Figure 2 shows that as penetration occurs, the grain size increases with each

*This terminology may be a misnomer, since the molten brazing filler metal, not silicon, acts to wet an existing grain boundary.

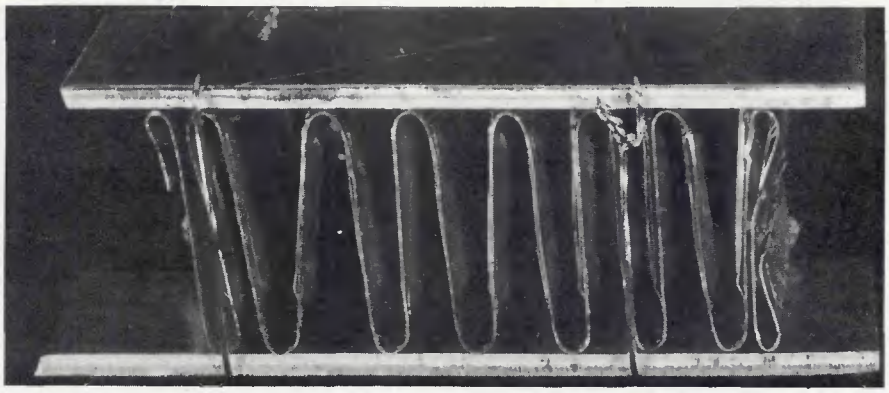

Fig. 1—Sample configuration consisting of fins and flat sheets of clad brazing sheet/base metal combination. The core under the cladding of each flat sheet is the alloy being investigated. X2.5 (reduced 11% on reproduction)

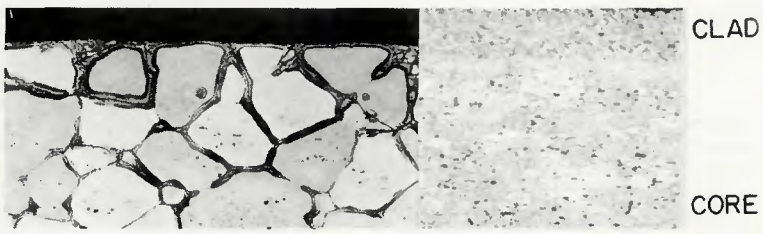

Fig. 2—Typical example of severe liquid penetration observed in either 6951 or 6061 aluminum alloys. Example consists of 6951 brazed in vacuum at 610°C (1130°F) for 10 min; right inset shows original unbrazed clad and core. Keller's reagent; X100 (reduced 25% on reproduction)

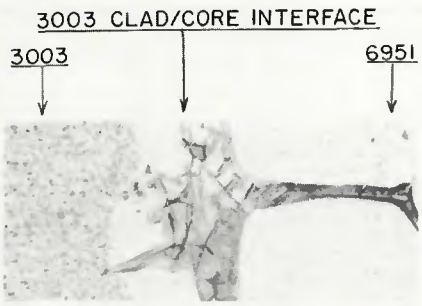

Fig. 3—Liquid penetration into 3003 aluminum alloy (left), contrasted to 6951 (right). Braze cladding was on 3003 core; 6951 was not clad. Original clad/core interface indicated. Keller's reagent; X300 (reduced 40% on reproduction)

grain encompassed by a liquid film. The grain growth appears to be caused by a mechanism similar to that observed during liquid phase sintering. Besides grain growth, less precipitate is observed in the large grains than in the core. The liquid penetration extends along grain boundaries up to the fine grained region of the core. The inset in Fig. 2 shows the original structure and fine grains that were present prior to heating the sample to the brazing temperature.

Electron microprobe analysis of the alloys exhibiting penetration was used to determine the concentration of the various elements within the original core, the penetration region and the prior liquid

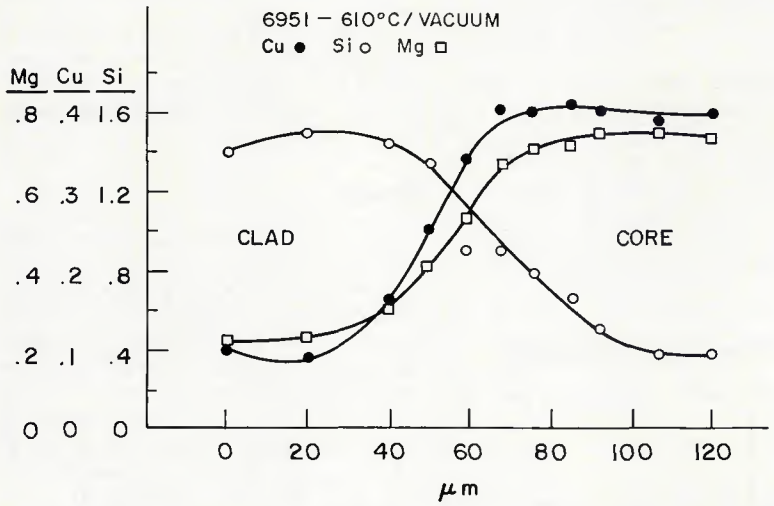

Fig. 4—Concentration-penetration plot for Cu, Si and Mg across penetration interface in 6951 alloy. Brazed in vacuum at 610°C (1130°F)

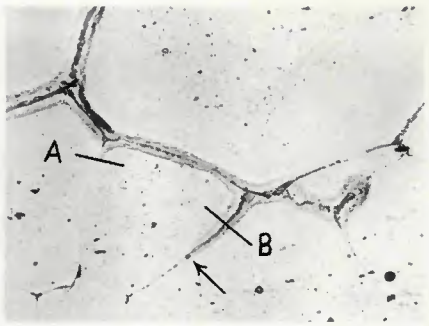

Fig. 5—Liquid penetration alloy in 6951. Area A is precipitate-free at the end of the liquid region (see analysis in Fig. 6); area B is through-precipitate region (see analysis in Fig. 7). Arrow indicates type of particle which typically is iron-rich. Keller's reagent; X500 (reduced 50% on reproduction)

regions. A concentration-penetration plot of Si, Mg, and Cu through a grain in the penetration region into the core is shown in Fig. 4. Here silicon has diffused from the liquid into the core, and the magnesium and copper levels in the penetration region are lower than in the core; the silicon level in the penetration region is at about the solubility level of silicon in aluminum for the temperature used.

The areas that were liquid at the brazing temperature consisted of a single or group of particles near the center of the prior liquid region, as shown in Fig. 5. Microprobe analysis across a number of these prior liquid regions showed that the particle-free region or the leading edge of the liquid (area A in Fig. 5) was significantly enriched in copper. Analysis of areas such as B in Fig. 5, through particles, indicated that the composition of the particles varied from pure silicon or Mg_2Si to very complex combinations of Al, Si, Mg and Cu. Two microprobe traces of prior liquid regions (typified by areas A and B in Fig. 5) are shown in Figs. 6 and 7 to illustrate the variations observed.

Apparently the copper and magnesium from the core diffuse to and enrich the liquid Al-Si region, and silicon diffuses from the liquid into the core. On solidification of the liquid in the boundaries, various complex phases are formed.

In a majority of cases, a precipitate containing iron was found at the end of a liquid region, as shown by the arrow in Fig. 5. These particles were of about the same composition as iron particles found in the core, *i.e.*, they were either Al(Cu,Fe) or Al(Fe,Si). When a particle was not found at the end of the liquid region, some particles within the prior liquid contained relatively high iron contents; this indicated that the particles had been dissolved and reprecipitated or circumvented by the liquid.

The small general precipitates in the core were too small to determine their individual compositions; however, the general analysis indicated that they were Mg_2Si and $CuAl_2$. At the brazing temperature, these precipitates are in solution

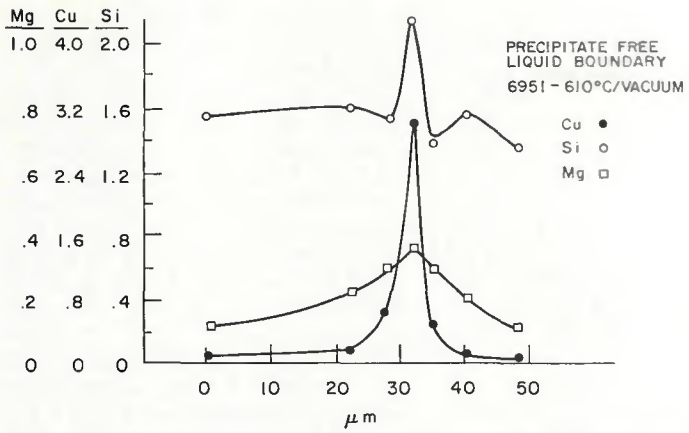

Fig. 6 — Copper, silicon and magnesium concentrations in precipitate-free liquid boundary in 6951 alloy. Brazed in vacuum at 610°C (1130°F)

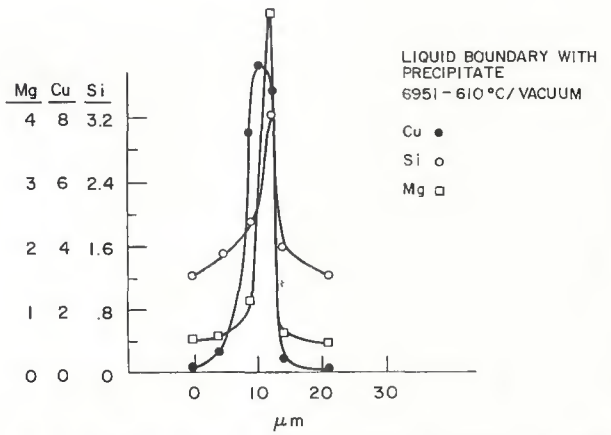

Fig. 7 — Copper, silicon and magnesium concentrations in liquid boundary with precipitate in 6951 alloy. Brazed in vacuum at 610°C (1130°F)

but reform, either as the sample cools or during aging at room temperature. A significantly lower precipitate density exists in the penetration zone because of the low magnesium and copper levels.

A microprobe analysis of high manganese aluminum alloy 3004, in which limited penetration occurred, is shown in Fig. 8. Silicon is high in the penetration region, and magnesium and copper are low; however, particles containing manganese (not shown) were found throughout the core and penetration region. While some liquid was present at the grain boundaries, the penetration was very limited.

An analysis of a liquid region in the 3004 is shown in Fig. 9. A high manganese level is found in the liquid, indicating an interaction of the liquid with the manganese particles in the grain boundaries. Copper and magnesium concentrations in the liquid are only slightly above that of the base metal, indicating limited concentration of these elements in the liquid region of the 3004 compared to 6951 (Fig. 7).

Temperature Dependence

Magnesium and copper apparently diffuse from the core to the liquid regions, and the liquid penetration is never seen to advance further than the transition region. For these reasons, the rate controlling process appears to be the diffusion of these elements in aluminum. Because the liquid moves continuously towards the core, the diffusion distance for copper, magnesium and silicon remains small and the standard diffusion equations are not applicable for determining diffusivities from the concentration-penetration curves. High effective diffusion rates would be expected because of the proximity of the liquid, and the concentration gradients would be predictably steep. Likewise, the temperature dependence of the penetration would be expected to be large because of a synergistic effect between diffusion of these elements and penetration as the temperature increased.

The temperature dependence of the penetration was determined by brazing a series of samples under vacuum for 7.5 min at temperatures varying from 599°C (1110°F) to 610°C (1130°F) and measuring the maximum penetration relative to the original core/braze clad interface. In addition, a series of samples was brazed in nitrogen for the same times and temperatures in order to determine whether there was an effect of restricted magnesium vaporization on the penetration. The nitrogen atmosphere was expected to reduce the vaporization of magnesium from the surface and to increase the average magnesium concentration remaining in the sample. It was reasoned that an effect on penetration might provide an insight into the factors causing and controlling the penetration.

The data for both the vacuum and nitrogen brazed samples are plotted in Fig. 10 as maximum penetration vs. 1/T. The penetration in the samples brazed under vacuum is higher than the samples brazed in nitrogen, but the temperature dependence is about the same. The

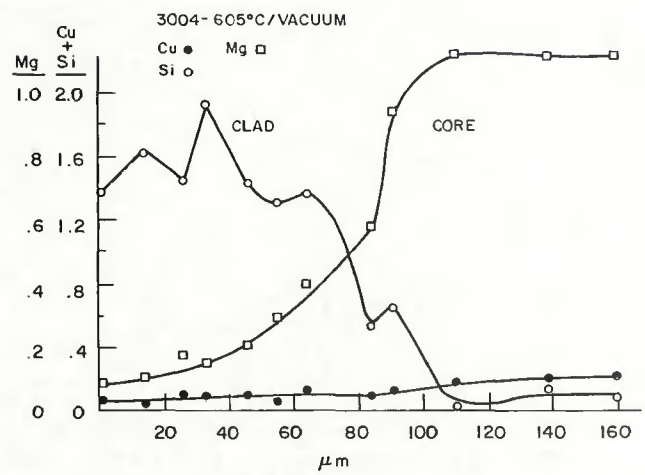

Fig. 8 — Concentration-penetration plot for Cu, Si, and Mg across core/clad interface in 3004 alloy vacuum brazed at 605°C (1120°F). Random manganese-rich particles (not shown) were found in both the clad and core

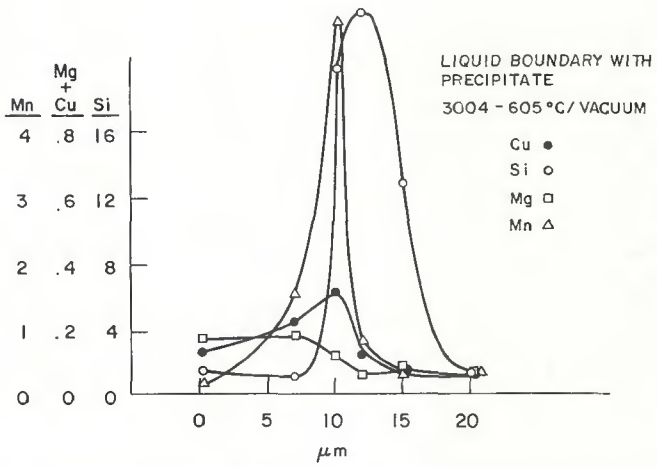

Fig. 9 — Copper, silicon, magnesium and manganese concentrations in liquid boundary with precipitate in 3004 alloy. Brazed in vacuum at 605°C (1120°F)

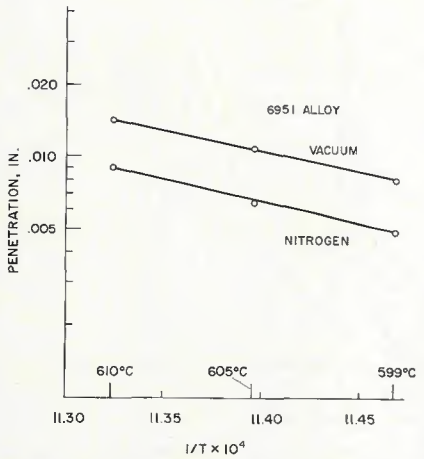

Fig. 10—Liquid penetration vs. 1/T for 6951 alloy brazed under vacuum and in nitrogen

apparent activation energies are 75 kcal/mole for vacuum and 83 kcal/mole for nitrogen.

A concentration-penetration curve for a sample brazed in nitrogen is shown in Fig. 11. Compared to the sample brazed in vacuum (Fig. 4), the magnesium level in the penetration region is higher (0.4% vs 0.2%), and the silicon content is lower (1.1% vs. 1.5%), producing smaller concentration gradients for magnesium and silicon in nitrogen brazed samples. The copper concentration curves are essentially identical in both the vacuum and nitrogen brazed samples.

Discussion

The results of the microprobe analyses of samples in which silicon grain boundary penetration occurs indicate that a number of reactions are occurring simultaneously and that the process is complex:

1. Silicon from the aluminum-silicon-magnesium clad liquid diffuses into the core, raising the silicon concentration in the grains within the penetration region to the solubility limit (approximately 1.5% at 600°C, *i.e.*, 1112°F).

2. The magnesium concentration within the grains in the penetration region is very low (*i.e.*, 0.2%) due to diffusion of magnesium into the liquid. Some high levels of magnesium are found in the liquid grain boundaries as Mg_2Si; however, most of the original magnesium in the brazing filler metal and that which diffuses from the core is lost from the surface by vaporization.**

3. Copper from the core diffuses to the liquid regions enriching the liquid in copper. The grains in the penetration region become quite low in copper (*i.e.*, 0.1%) compared to the initial value of 0.4%.

4. Very frequently, precipitates containing iron are found at the termination of the liquid regions. When manganese is present in the alloy, high concentrations of manganese are found in the liquid regions.

5. A nitrogen atmosphere during brazing increases the concentration of magnesium and decreases the concentration of silicon in the penetration zone. The copper concentration is unaltered.

6. The apparent activation energy for liquid penetration measured from the penetration data is 78-83 kcal/mole.

The occurrence of extensive penetration in only certain alloys indicates a strong relationship of penetration to the alloying elements in the core material. Penetration can be caused by either a change in the free energy relationship of the liquid brazing filler metal to the solid or by localized melting preferentially occurring at the grain boundaries.

Certain liquid metals will wet and penetrate grain boundaries of a dissimilar metal and cause liquid metal embrittlement (Ref. 1). Liquid phase sintering of metal powders relies on the wetting of the powder surfaces and penetration of solid contact points by the liquid phase (Ref. 2). Wetting and penetration in these cases are governed by the liquid/solid interfacial energy relationship and the grain boundary energy.

The dihedral angle, θ, made by the liquid with the solid at a grain boundary is related to the interfacial and grain boundary energies by, $\cos\frac{\theta}{2} = \frac{\sigma_{gb}}{2\sigma_{SL}}$. Thus, if $\sigma_{SL} \leq \frac{1}{2}\sigma_{gb}$, $\cos\frac{\theta}{2} = 1$, $\theta = 0$, and complete wetting occurs. In systems in which the dihedral angle is greater than 60 deg, only a small penetration down the boundary will occur (Ref. 3). Large dihedral angles are observed in aluminum alloys such as 3003 and 3004 when brazed with aluminum-silicon clad brazing filler metal—Fig. 3.

For σ_{SL} or σ_{gb} to govern the penetration observed in 6951 and 6061 it would require a unique relationship of the interfacial and grain boundary energies to exist only in certain compositions. The diffusion of magnesium and copper from the core of these alloys to the liquid could locally alter σ_{SL} and possibly σ_{gb} at the penetration/core interface such that penetration would occur. The effect would be very localized and depend on the alteration of the core composition as well as the liquid. This is consistent with the fact that other alloys in contact with 6951, and the liquid during brazing did not show significant penetration—Fig. 3. While an interfacial energy mechanism cannot be ruled out, other evidence (such as the width of the liquid regions and the large temperature dependence of the process) indicates that a more probable mechanism is localized melting at the grain boundary.

At the brazing temperature, the equilibrium liquid composition in the Al-Si-Cu system with about 10% silicon, is approximately Al-10Si-4Cu. Therefore, the liquid will act as a sink for any copper that diffuses to the liquid/solid interface. Similarly, the equilibrium composition of the solid is about Al-1.6Si, and silicon would diffuse from the liquid into the solid core.

The addition of about 3% copper to aluminum-silicon lowers the melting point such that a liquid phase is formed at 548°C (1020°F) in contrast to 577°C (1071°F) for aluminum-silicon (Ref. 4). With a lower melting point, more liquid would be present at the brazing temperature and more aluminum would be taken into solution and the liquid/solid interface would move into the solid.

***Bulk analysis of the cladding after vacuum brazing indicates that a level of only 0.2 to 0.3% Mg remains compared to the initial 1.5% Mg.*

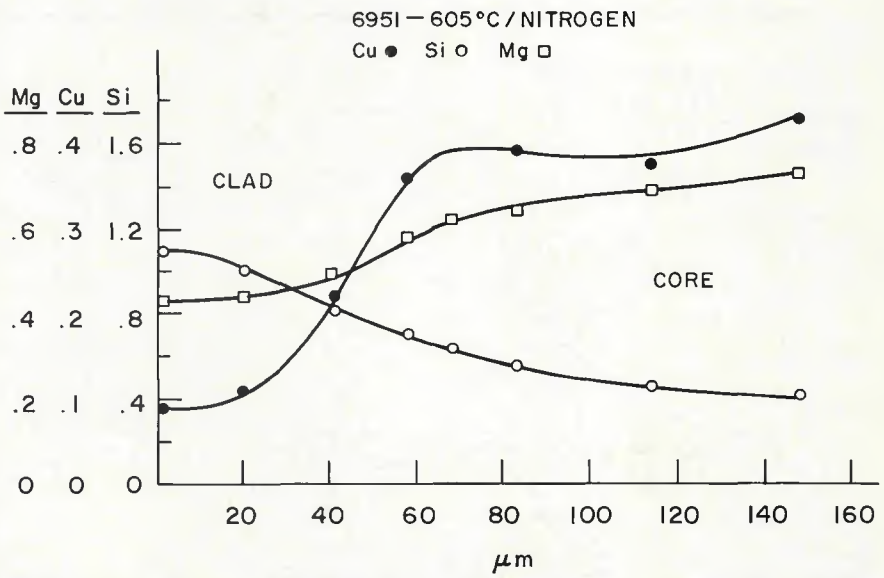

Fig. 11—Concentration-penetration plot for copper, silicon and magnesium across penetration interface in 6951 alloy. Brazed in nitrogen at 605°C (1120°F).

The initial wetting of the surface of an aluminum alloy in contact with Al-Si-Mg liquid is undoubtedly governed by the free energy relationship and as previously discussed, a certain dihederal angle will be established at the grain boundaries. Copper and magnesium will diffuse to the liquid at the surface and the grain boundaries. Since the liquid at the boundaries will extend somewhat into the core, the geometric configuration will lead to more enrichment of copper and magnesium at the boundary than at the surface.

Diffusion into the liquid at the boundary can occur from both grains into the sides of the liquid front. In addition, grain boundary diffusion may occur which would further enhance the concentration at the boundary. The change in composition would lower the melting point and allow more aluminum to go into solution. The liquid would progress down the boundary at a rate dependent on the diffusion of magnesium and/or copper.

Liquid penetration in samples brazed in vacuum at a low temperature appears to stop at the precipitate transition region of the core. At brazing temperature, M_2Si and $CuAl_2$ are soluble in the aluminum. Moreover, the penetration is actually progressing up to where the steep silicon, copper and magnesium concentration gradients occur.

As the temperature increases, the amount of dissolution of aluminum should increase simply due to the temperature change. In addition, the diffusion rates will increase and more copper should diffuse to the liquid, further lowering its melting point. Because the liquid interface continues to move, a short diffusion path is maintained and the penetration will increase more rapidly than predicted from the change in diffusivity with temperature. On this basis, a large increase in penetration would be expected with an increase in temperature and a large temperature dependence would be produced.

Penetration at the higher temperature appears to stop somewhat short of the general precipitate region. Microprobe results indicated iron-rich particles at the ends of the liquid boundaries. It appears that these particles decrease the rate of penetration somewhat, and even greater penetrations might be expected to occur if the iron particles were not present. Manganese in the alloy also inhibits liquid penetration, possibly because of the presence of stable manganese rich particles in the grain boundaries.

The variation in concentrations between samples brazed in vacuum and in nitrogen indicates that there is excess magnesium in the liquid as would be expected in a nitrogen atmosphere; this increases the magnesium level in the grains within the penetration zone and apparently interacts with silicon to decrease its solubility. These two compositional differences apparently reduce the tendency for melting to occur. The lower silicon level in the grains may affect the melting point of the grain boundary region.

Conclusions

The presence of copper in the core of the alloy in which penetration occurs appears to be the main factor governing whether or not penetration occurs. Penetration is a result of copper enrichment of the Al-Si-Mg clad brazing filler metal; copper enrichment lowers the melting point and locally increases the solubility of aluminum. The continual advancement of the liquid interface maintains a small diffusion distance between the copper in the core and the liquid, and produces a high effective diffusion rate.

Copper levels in the 6951 and 6061 alloys were about 0.4%, but only 0.2% in 5005 and 6063. In the manganese-containing alloys such as 3004, the copper was 0.25%; however, there was an abundance of very stable $MnAl_6$ particles, which appeared to restrict penetration.

There are only a few commercial aluminum alloys other than 6951 and 6061 in which extensive penetration might be seen. These are the 6070 and 6262 alloys. The penetration phenomenon has not been observed too extensively because of the limited number of alloy systems in which the copper concentration is in the appropriate range. Silicon penetration has been mentioned in the literature, but not to the extent observed in this study. The extensive penetration seen in these alloys would probably have been attributed to an excessive brazing temperature or time rather than to a compositional effect.

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