

# Metallurgical Studies of the Vacuum Brazing of Aluminum

*Structural changes occurring in an Al-Si-Mg alloy during vacuum brazing are studied and supplemented by Auger analyses of the surface which show that it is composed almost entirely of MgO at temperatures above 400 C*

BY W. A. ANDERSON

**ABSTRACT.** Vacuum brazing is replacing flux, dip, and furnace brazing as a method for assembling aluminum heat exchangers. Several sheet products are employed in vacuum brazing, one of which is a composite consisting of an Al-Mn-Mg alloy clad with an Al-Si-Mg brazing alloy. The magnesium in the brazing alloy is released during the brazing cycle and acts as a gettering agent for the removal of oxidizing gases such as oxygen, water vapor, and carbon dioxide in the furnace atmosphere. The magnesium also acts to modify the oxide film on the surface of the brazing sheet, permitting wetting and flow to take place.

To provide more information on the mechanism by which magnesium modifies the surface, a study has been made of the structural changes occurring in an Al-Si-Mg alloy during vacuum brazing. This has been supplemented by Auger analyses of the surface.

Metallographic studies of the brazing alloy showed that initial melting occurs at or slightly below the Al-Si-Mg eutectic temperature of 557 C (1035 F). This is accompanied by rupture of the oxide surface film and exudation of the molten eutectic. On exposure to the vacuum, the molten eutectic loses its magnesium by evaporation and resolidifies. This process is repeated with increasing time and temperature until the entire surface is composed of clean metal. This surface persists to temperatures near that of the Al-Si eutectic (577 C, 1035 F) where significant metal flow and brazing begin.

Auger analysis of the surface showed that it is composed almost entirely of MgO at temperatures above

400 C (752 F). The thickness of the oxide layer varies but is a minimum after formation of the new surface by melting and exudation at the Al-Si-Mg eutectic. Growth of the oxide layer at higher temperatures is governed by the evaporation of magnesium from the brazing alloy and oxidizing conditions in the vacuum environment. Minimum oxide thickness and good vacuums of minimum oxidizing potential are desirable for good vacuum brazing.

## Introduction

Fluxless vacuum brazing, a relatively recent development, is currently employed in the manufacture of products such as oil coolers and the evaporator component of automotive air conditioners. Other applications are being investigated (Fig. 1), and vacuum brazing is expected to increase in popularity and usage as experience is gained with this joining procedure.

Material characteristics as well as processing conditions are important in vacuum brazing. One of the material characteristics affecting performance is the oxide surface on aluminum. Aluminum surfaces normally have self-healing, protective oxide films that are highly resistant to attack by most

natural environments and many chemicals. These films provide good resistance to corrosion and long service life to aluminum products. In brazing, however, such oxide films are undesirable, since they act as barriers to flow, wetting, and joint formation.

To overcome this barrier, vacuum brazing alloys of the aluminum-silicon type generally contain a "promoter," such as magnesium, which performs several important functions. As demonstrated in the work of Terrill et al.,<sup>1</sup> alloy flow and wetting are obtained if the promoting element is capable of reducing aluminum oxide at brazing temperatures and also acts as a gettering agent to remove oxygen and water vapor from the brazing atmosphere. It is significant that promoters function whether incorporated in the brazing alloy or vaporized in the vacuum furnace.

The manner in which the promoting element modifies the oxide barrier to permit flow and wetting is not known. Winterbottom and Gilmour<sup>2</sup> propose that flow and wetting are obtained by a process involving the reduction of the aluminum oxide by magnesium, the formation of a porous oxide and the wicking of molten brazing alloy to the surface. Scamans and Butler<sup>3</sup> have reported the formation of  $MgAl_2O_4$  and MgO by reaction between Mg and  $Al_2O_3$  within the surface film on an Al-Mg alloy in oxidation studies performed in vacuum.

The reduction of  $Al_2O_3$  and the formation of MgO and  $MgAl_2O_4$  do not in themselves account for metal flow and fillet formation, since neither oxide is readily wet by molten aluminum. A further step involving disruption and dispersal of the oxide film is

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*W. A. ANDERSON is a Senior Scientific Associate, Alloy Technology, Alcoa Technical Center, Aluminum Company of America, Alcoa Center, Pennsylvania.*

required. The present investigation was performed to determine whether metallographic studies of the structural changes occurring during brazing would provide information on such a mechanism.

## Procedure

A three-layer composite brazing sheet of commercial fabrication was employed in the present investigation. The sheet had a cladding of a brazing alloy containing 9.7% Si, 1.5% Mg, 0.1% Bi, and a core of an alloy containing 0.5% Mn and 0.4% Mg. The cladding thickness was equal to 12% of the sheet thickness, which was approximately 3 mm (0.12 in.). Thermal analysis of an Al-Si-Mg brazing alloy of this composition showed a ternary eutectic at 557 C (1035 F) and a liquidus temperature of 595 C (1103 F).

Samples 20 mm (0.79 in.) square were sawed from the brazing sheet and given a metallographic polish on one surface. The samples were then heated in a tubular vacuum furnace at various temperatures and several pressures. A 50 mm Vycor tube was employed as the vacuum chamber and

was joined to a 102 mm (4 in.) vacuum diffusion pump. The vacuum chamber was enclosed in a circular, close-fitting, resistance-type furnace, which was controlled by a thermocouple in a dummy specimen within the vacuum chamber. The samples were supported on a Vycor plate during the simulated brazing treatments with the polished surfaces outward.

Samples were heated for 4 min at temperatures ranging from 345 to 600 C (653 to 1112 F) in vacuums of  $5 \times 10^{-5}$  and  $10^{-3}$  torr (6.7 and 133 mPa). Heating rates were approximately 30 C/min (64 F/min), and samples were cooled with the furnace removed to 350 C (662 F), or below, before releasing the vacuum.

After vacuum heating, the polished surface of the sample was examined metallographically for changes in the structure of the brazing alloy. Auger surface analysis was performed on selected samples.

## Results

### Metallographic Examinations

Both optical and electron microscopy were employed in studies of the

structural changes occurring during simulated vacuum brazing. From these studies, information was obtained as to the role of alloy composition and structure on the brazing mechanism.

Examination of the brazing alloy prior to heating showed an aluminum matrix containing uniformly distributed particles of Si and  $Mg_2Si$ . This structure persisted to about 510 C (950 F). At this temperature, the beginnings of grain boundary grooving were detected at the surface of the brazing alloy—Fig. 2. As the temperature increased to approximately 550 C (1022 F), thermal grooving became very pronounced (Fig. 3), indicating greatly increased diffusion and possible loss of magnesium to the vacuum environment.

On heating specimens to 560 C (1040 F), slightly above the Al-Si-Mg eutectic, partial melting occurred and the surfaces of the samples assumed the appearance shown in Fig. 4. Cross sections through the specimens showed solution of  $Mg_2Si$  and surface roughening with a peak-to-valley height of 0.01–0.02 mm (0.0004–0.0008 in.). The amount of melting could not be determined, but it appeared to be of the order of 25 to 30% as would be expected from phase relationships for the Al-Si-Mg system.

On heating samples to 580 C (1076 F), melting increased and significant liquid flow occurred. Structural studies of the resolidified metal showed silicon but no  $Mg_2Si$ , indicating loss of magnesium to the vacuum environment.

To obtain further information on the evolution of magnesium from the brazing alloy, samples were heated in a vacuum microbalance system capable of detecting weight changes to 0.1 mg. Results of such measurements are presented in Fig. 5 and show a rapid loss of weight beginning at approximately 560 C (1040 F), in reasonable agreement with the temperature of the Al-Si-Mg eutectic and the melting observed in metallographic studies of the above samples. Weight loss continued up to the brazing temperature, indicating continuous evolution of magnesium to the vacuum chamber.

Samples were also examined on the scanning electron microscope to obtain more detail on the structural changes occurring during vacuum heating of the brazing alloy. Typical structures observed under different conditions of heating are shown in Figs. 6 through 11.

As shown in Fig. 6, samples heated at 550 C (1022 F) and  $10^{-3}$  torr (133 mPa) displayed not only thermal grooving, but also fissuring within the grains, possibly as a result of magnesium evolution. At a temperature of

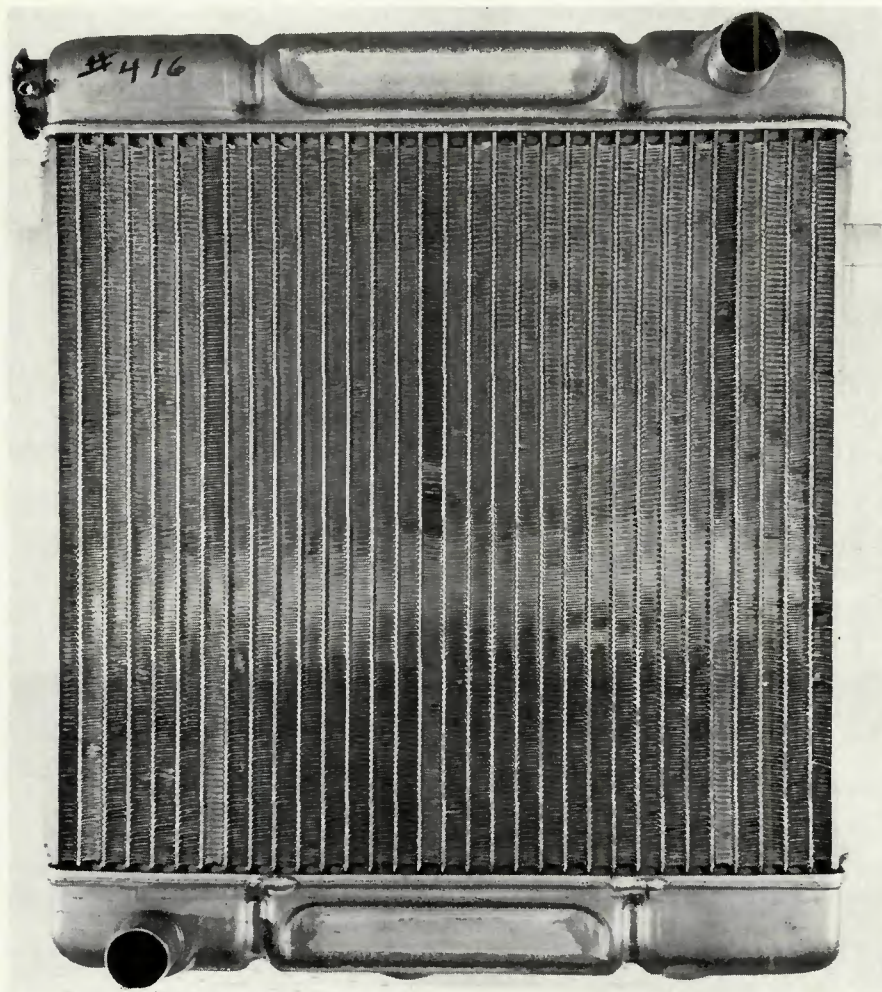


Fig. 1—An experimental aluminum radiator assembled by vacuum brazing



Fig. 2—Unetched surface of brazing alloy after 4 min at 510 C in vacuum.  $\times 500$  (reduced by 33% on reproduction)

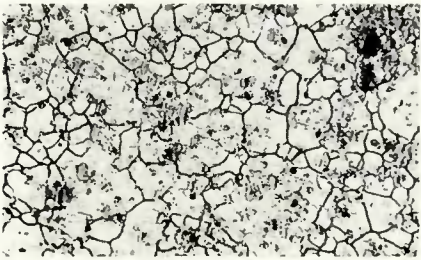


Fig. 3—Unetched surface of brazing alloy showing grain boundary grooving after 4 min at 550 C in a vacuum of  $10^{-3}$  torr (133 mPa).  $\times 500$  (reduced by 33% on reproduction)



Fig. 4—Unetched surface of brazing alloy showing partial melting after 4 min at 560 C in a vacuum of  $10^{-3}$  torr (133 mPa).  $\times 500$  (reduced by 33% on reproduction)

560 C (1040 F) and  $10^{-3}$  torr (133 mPa), the phenomenon shown in Figs. 7 and 8 was observed. Surface topography of this type was also observed in tests at  $5 \times 10^{-5}$  torr (6.7 mPa) and developed more rapidly than at  $10^{-3}$  torr (133 mPa). The lowest temperature of occurrence at  $5 \times 10^{-5}$  torr was about 550 C (1022 F). This temperature also varied with surface condition and was higher for samples with thick, thermal-oxide films.



Fig. 6—Scanning electron micrograph showing grooving of brazing alloy after 4 min at 550 C in a vacuum of  $10^{-3}$  torr (133 mPa).  $\times 2000$  (reduced by 33% on reproduction)

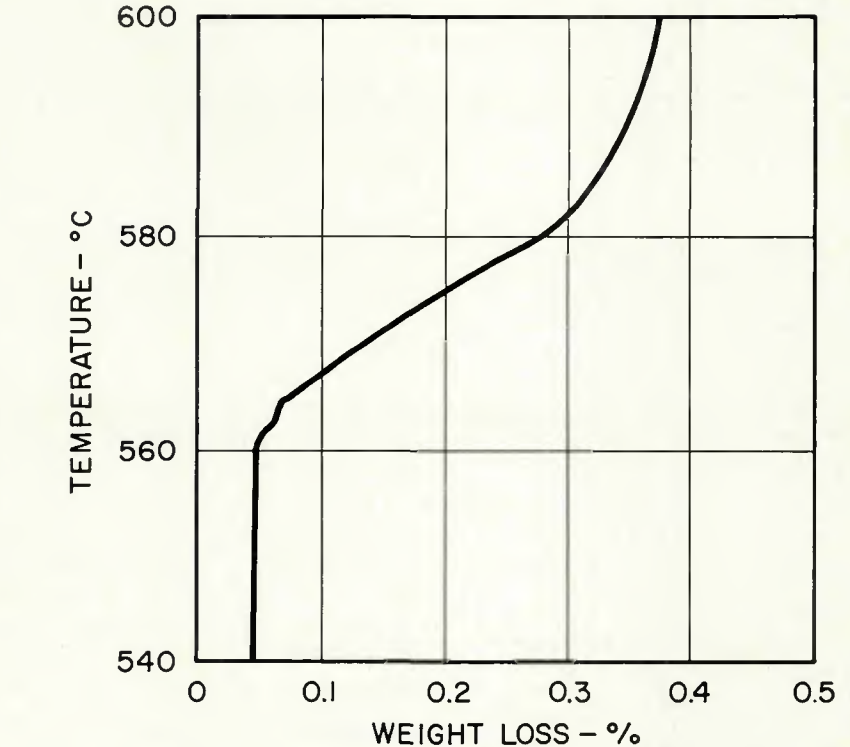


Fig. 5—Weight loss curve for brazing sheet heated in vacuum. Starting vacuum was  $6 \times 10^{-3}$  torr (8 mPa). This increased to  $10^{-4}$  torr (13 mPa) during the early stages of heating and then decreased to  $8.5 \times 10^{-5}$  torr (11 mPa) at 560 C. At this temperature there was a small pressure increase as melting began, followed by a decrease to  $3 \times 10^{-5}$  torr (4 mPa) at 600 C

A study of these surfaces suggested that the phenomenon was one of localized melting resulting in rupture of the oxide film and exudation of a complex Al-Si-Mg eutectic. However, an electron-probe microanalysis of one of the exudates showed only aluminum and silicon. This suggested that the magnesium (and bismuth) was lost to the vacuum environment after formation of the structure shown in Figs. 7 and 8.

Continued holding at 560 C (1040 F) or exposure to higher temperatures produced further transformation of the surface as shown in Fig. 9. Following the initial exudation process, further melting and growth resulted eventually in the creation of a new surface such as is shown in Figs. 10 and 11. A cross section through the specimen at this stage of heating

showed that the originally smooth surface was now roughened and contoured as a result of melting—Fig. 12. This surface structure persisted to temperatures near the Al-Si eutectic (577 C, 1071 F) before flow occurred.

The existence of this structure at such a temperature can be explained by the evaporation of magnesium from the sample. As magnesium is lost from the exudate, the melting temperature of the remaining liquid increases and approaches that of the Al-Si eutectic. The exudate should thus resolidify after forming, preserving the contoured shape shown in the micrographs.

#### Auger Surface Analysis

Selected samples treated in vacuum were subjected to Auger surface analy-

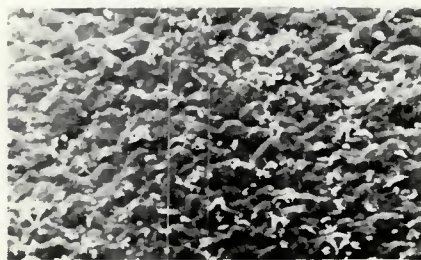


Fig. 7—Scanning electron micrograph showing early stages of melting and exudation at 560 C.  $\times 200$  (reduced by 33% on reproduction)



Fig. 8—Scanning electron micrograph in Fig. 7 at higher magnification.  $\times 1000$  (reduced by 33% on reproduction)

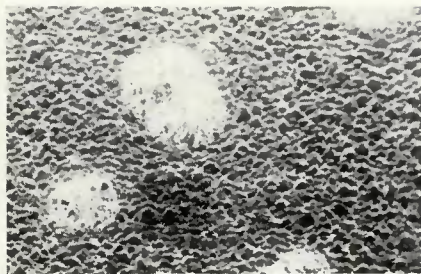


Fig. 9—Scanning electron micrograph showing the growth pattern of new surface by melting process at a temperature a few degrees above the Al-Si-Mg eutectic.  $\times 100$  (reduced by 33% on reproduction)

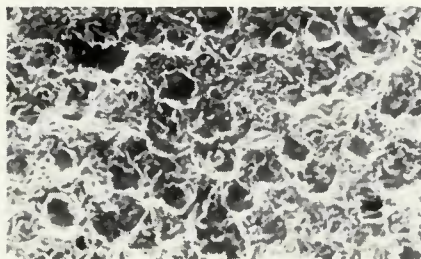


Fig. 10—Scanning electron micrograph showing completely formed new surface.  $\times 400$  (reduced by 33% on reproduction)



Fig. 11—Scanning electron micrograph of Fig. 10 at higher magnification.  $\times 1000$  (reduced by 33% reproduction)

sis. Trace quantities of surface contaminants such as F, Cl, Ca, S, P, N, and Na were present on most samples. Carbon was present also. Suspect sources were surface contamination by carbonaceous compounds and by carbon residuals in the Auger equipment. Because of this and the inherent inaccuracy of carbon measurements by Auger, values for carbon content were disregarded and Auger analysis was based on normalized values for Al, Mg, O, and Si only.

Auger analysis of the as-polished surface of the sheet employed in these tests indicated that there was a Beilby layer of disturbed metal extending perhaps as much as 60 nm (600 Å) into the sample. This layer was of relatively uniform composition and comprised of metallic aluminum, small amounts of aluminum and magnesium oxides and a significant oxygen component, possibly entrained H<sub>2</sub>O or an OH<sup>-</sup> ionic species resulting from wet pol-

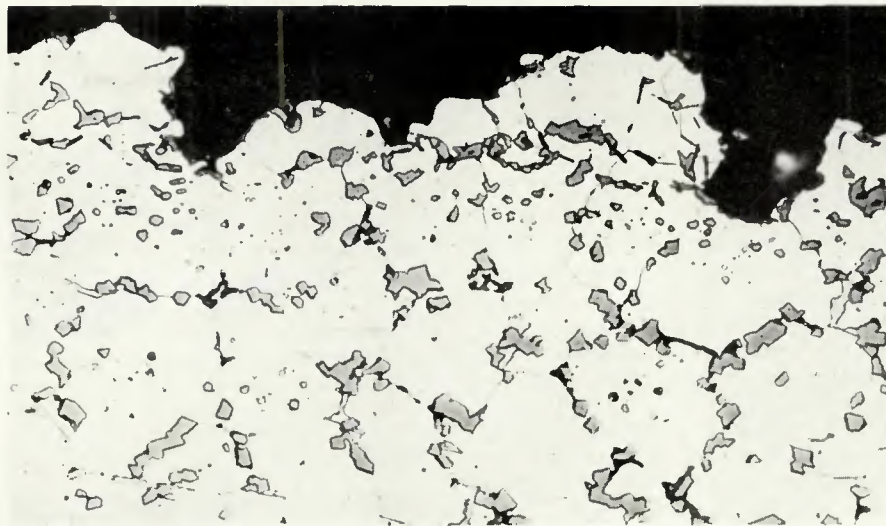


Fig. 12—Optical micrograph showing cross-section through specimen and exudation phenomenon. The structure is composed primarily of silicon particles in an aluminum matrix, plus a small amount of Al-Fe-Si constituent as impurity and a small amount of Mg<sub>2</sub>Si. The Mg<sub>2</sub>Si appears in the body of the alloy as a dark-etching phase, but not in the exudate where magnesium has been evaporated to the vacuum chamber.  $\times 500$  (reduced by 23% on reproduction)

Table 1—Approximate Atomic Concentrations of Al, Mg, O and Si at the Surface of Al-Si-Mg Brazing Sheet After Heating in Vacuum

Temperature,		Pressure,		Element, %			
C	F	Torr	Pascal	Al	Mg	O	Si
Metallographic Polish				24.0	7	65.5	3.5
345	650	$5 \times 10^{-5}$	0.0067	19.0	17	58.0	6.0
400	750	$5 \times 10^{-5}$	0.0067	7.0	45	40.0	8.0
510	950	$5 \times 10^{-5}$	0.0067	1.0	49	49.0	1.0
540	1000	$5 \times 10^{-5}$	0.0067	0.5	49	50.0	0.5
550	1020	$5 \times 10^{-5}$	0.0067	6.5	39	53.0	1.5
560	1040	$5 \times 10^{-5}$	0.0067	9.5	34	55.0	1.5
580	1075	$5 \times 10^{-5}$	0.0067	1.0	48	50.0	0.5
600	1110	$5 \times 10^{-5}$	0.0067	1.0	50	48.0	0.5
560	1040	$10^{-3}$	0.133	4.0	43	53.0	0.5
580	1075	$10^{-3}$	0.133	0.5	50	49.0	0.5

ishing with MgO—Table 1.

On heating the sheet in vacuum, the composition of the surface layer changed from one of uniform Al, Mg, O and Si contents to a surface layer with definite concentration gradients. In this layer, magnesium and oxygen were maximums at the surface and aluminum a minimum. Similar relationships are characteristic of commercial sheet employed in vacuum brazing.

A detailed study of the Auger spectra for a sample heated at 345 C (653 F) indicated that the surface was composed almost entirely of oxidized aluminum and magnesium; however, metallic aluminum existed in small amounts to within 5–10 nm (50–100 Å) of the surface.

After heating to 510 or 540 C (950 or 1004 F), the surface of the brazing sheet was composed almost entirely of MgO. At 550–560 C (1022–1040 F), however, a significant aluminum oxide

component reappeared as a result of the eutectic melting and exudation observed in the structural studies of these samples. At yet a higher temperature (580 C, 1076 F), the surface layer reverted again to MgO with only trace amounts of oxidized aluminum.

Data are shown in Table 1 for samples heated at  $5 \times 10^{-5}$  and  $10^{-3}$  torr (6.7 and 133 mPa). A comparison shows that the surfaces of those samples heated at  $10^{-3}$  torr (133 mPa) tended to have more magnesium (MgO) than those heated at  $5 \times 10^{-5}$  torr (6.7 mPa). This suggests more rapid oxidation of the magnesium component of the exudate due to higher partial pressures of oxygen and water vapor in the atmosphere.

Oxide films on samples heated at  $10^{-3}$  torr (133 mPa) also were significantly thicker than those on samples heated at  $5 \times 10^{-5}$  torr (6.7 mPa) based on sputtering times and analyses in the Auger equipment. Of greater signifi-

cance, however, was the observation that the exudation process created a new surface with minimum oxide thickness. Such surfaces are obviously desirable for good wetting and flow in vacuum brazing.

## Discussion

Vacuum brazing with Al-Si-Mg alloys is a complex process involving both chemical and physical transformations. Attention has focused usually on the chemical changes occurring during brazing. As shown in the present investigation, however, physical changes occur in the metal during brazing that contribute significantly to the wetting and flow of the brazing alloy.

The event of greatest importance is the disruption and dispersion of the oxide film by the expansion and exudation accompanying the melting of an Al-Si-Mg eutectic at a temperature below that of wetting and metal flow. This creates a new surface with minimum oxide and also releases magnesium to the vacuum chamber to getter the atmosphere of oxidizing gases that could produce further oxide build-up and a retardation of the brazing process.

A minimum surface condition must evidently exist for efficient dispersion of the oxide. For example, tests on heavily oxidized specimens of brazing sheet have shown that the new surface formed by exudation is not continuous but has pockets of oxidized metal that could interfere with brazing—Figs. 13 and 14.

It may be speculated that magnesium plays an important role in conditioning the surface oxide to react in the desired manner under the physical forces generated by the melting eutectic. Auger analysis shows that the metal surface changes during brazing as magnesium diffuses from the substrate into the oxide and reacts with



Fig. 13—Scanning electron micrograph of new surface formed on brazing sheet heated at 560 C in a vacuum of  $5 \times 10^{-3}$  torr (6.7 mPa).  $\times 1000$  (reduced by 33% on reproduction)

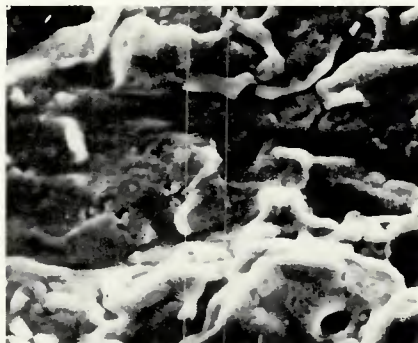


Fig. 14—Scanning electron micrograph of brazing sheet pre-oxidized in air at 535 C then heated in vacuum with sample in Fig. 12. Note poorly developed surface and suggestions of oxidized metal.  $\times 1000$  (reduced by 33% on reproduction)

$\text{Al}_2\text{O}_3$  and oxidizing gases in the atmosphere. These reactions alter the physical character of the surface film on the brazing alloy and undoubtedly influence the dispersion characteristics of the oxide layer during exudation of the Al-Si-Mg eutectic.

## Summary

The structural changes occurring during the heating of an Al-Si-Mg alloy

to the brazing temperature have been followed by optical and electron microscopy. Auger surface analysis has also been performed to provide information on the compositional changes of the oxide on the alloy during heating.

Results show that the magnesium and other elements in the brazing alloy form a low-melting eutectic with aluminum and silicon. When the eutectic temperature is reached, localized melting occurs with rupturing of the oxide film and exudation to the surface. On exposure to the vacuum, the molten eutectic loses its magnesium by evaporation and resolidifies. This process is repeated with increasing time and temperature until the entire surface consists of clean metal. This surface persists to temperatures near that of the Al-Si eutectic (577 C, 1071 F) where significant metal flow and brazing begin.

Auger surface analysis shows that the surface oxide on the brazing alloy is almost entirely  $\text{MgO}$  at temperatures above 400 C (752 F). The film thickness is a minimum after formation of the new surface by exudation at the eutectic temperature. Growth of the film at higher temperatures is governed by furnace conditions and material characteristics. Good brazeability depends on both the physical and chemical effects of magnesium in the brazing alloys.

## References

1. Terrill, J. R., Cochran, C. N., Stokes, J. J., and Haupin, W. E., "Understanding the Mechanisms of Aluminum Brazing," *Welding Journal*, 48, Dec. 1971, pp. 833 to 839.
2. Winterbottom, W. L., and Gilmour, G. A., "Vacuum Brazing of Aluminum," *Journal of Vacuum Science Technology*, 13, 1976, pp. 634-643.
3. Scamans, G. M., and Butler, E. P., "Crystalline Oxide Formation During Al and Al Alloy Oxidation," *Metallurgical Transactions*, 6A, 1975, pp. 2055-2063.

## AWS A5.8-76 Specification For Brazing Filler Metal

This specification prescribes requirements for filler metals which are added when making a braze. The compositions are selected to include those having different brazing properties as well as those having important commercial applications.

Topics covered are: Classification and Acceptance, Manufacture, and Special Filler Metal Grades (including vacuum grade brazing filler metals for vacuum devices). Appendix A: Guide to AWS Classification of Brazing Filler Metals, Appendix B: Marking and Labelling and Appendix C: Metric Equivalents have been added for your convenience.

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