Zinc Distribution in Vacuum Brazed Alclad Brazing Sheet

With heavy gauges there is sufficient retained zinc in the cladding to provide galvanic protection to the core and, in the case of light gauge materials, increasing the zinc content of 7072 from 1% to 3% provides sufficient zinc to the post-braze cladding to give galvanic protection for the core

BY P. McNAMARA AND O. R. SINGLETON

ABSTRACT. Vacuum brazing technology is currently capable of producing aluminum automotive heat exchangers such as radiators and heater cores. The possible use of 7072 claddings on the surfaces exposed to the coolant to provide additional corrosion protection is of considerable interest. This paper describes the effect of typical vacuum brazing cycles on the distribution of zinc in 7072 clad vacuum brazing sheet.

For heavier gauges (0.05 in. or 1.3 mm), there is sufficient retained zinc in the post-braze composite. For lighter gauges—0.02 in. (0.5 mm) or less—nominal composition 7072 does not provide adequate retained zinc; however, if the initial zinc concentration is increased to 3% there is sufficient retained zinc so that the cladding is significantly more anodic than the core.

Introduction

At the present time there are a number of techniques either in commercial use or development for the production of aluminum automotive radiators and/or heater cores. These techniques include mechanical joining and fluxless brazing in either inert gas or vacuum. Indeed, a number of European automobiles are already equipped with aluminum radiators and heater cores and have performed satisfactorily for a number of years.

There appears to be good agreement that in a properly maintained, properly inhibited antifreeze solution, aluminum will perform satisfactorily. On the other hand, there is almost universal agreement that maintenance of the automobile coolant system is far from adequate in most instances. Because of this, there is increased interest in this country in the use of claddings on the side of the metal exposed to the coolant to provide additional corrosion protection.

The use of Alclad products to resist corrosion has been well established. Alclad products are composite in type consisting of an aluminum alloy core to which are metallurgically bonded protective claddings. The cladding alloy is of such a composition as to provide a surface that has inherent high resistance to corrosion and is also sufficiently anodic to the core alloy to afford electrochemical protection in most corrosive environments. Consequently, any spot of attack will penetrate only as far as the core alloy (or diffusion zone) where further progress is stopped by cathodic protection, i.e., the cladding is preferentially sacrificed to protect the core. The cladding generally used is alloy 7072 which contains 1% zinc and has a solution potential of −0.96 V (.1N Calomel scale) which is at least 100 MV more anodic than typical core alloys such as 3003 and 6951.

The benefits of Alclad 3003 to automobile radiators is described in Union Carbide bulletin #F3919−3M 86-0071. A photomicrograph in this bulletin shows that in a circulating system with a 22% marginally inhibited glycol, the bare 3003 is subject to deep pitting corrosion, while for the Alclad 3003 the core is essentially unattacked.

The vacuum brazing cycle involves heating the material to a high temperature of 1100F (593 C) for finite time periods in a vacuum of 10^{-4} torr. For this reason, the possible use of 7072 claddings in this application raises a number of questions which must be answered. These include:

1. Will the post-braze 7072 cladding retain enough zinc to provide galvanic protection for the core?
2. Will the zinc diffusion into the core result in zinc rich areas such as grain boundaries which would be anodic and promote intergranular corrosion of the core?

Preliminary to Investigation

Zinc Losses During Vacuum Brazing

The 7072 cladding contains a nominal concentration of 1% zinc. During the vacuum brazing cycle zinc losses can occur by sublimation into the vacuum and by diffusion into the core.

The possible zinc distributions in the post-braze composites are shown in Fig. 1. Here one can see that zinc loss can occur both by sublimation into the environment and diffusion into the core. It should be noted that, in the case where both sublimation and diffusion occur, there is a sub-

Paper published by permission of the Society of Automotive Engineers following presentation at the SAE 1978 Congress and Exposition held in Detroit, Michigan, during February 27 to March 3, 1978.

P. McNAMARA and O. R. SINGLETON are with the Metallurgical Research Division of Reynolds Metals Company, Richmond, Virginia.

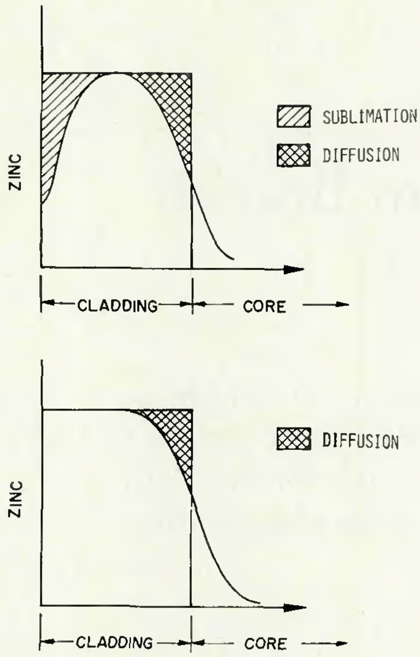

Fig. 1—Schematic of possible post-braze zinc distribution in 7072 clad brazing sheet

surface region which would be anodic to the surface.

Materials

The materials chosen for this investigation were typical of materials which would be used in radiator construction and were:

1. 0.05 in. (1.3 mm) 3003 clad one side 10% with X4104 and the other side clad 7½% with standard 7072 (1% zinc).
2. 0.05 in. (1.3 mm) 6951 clad one side 10% with X4104 and the other side 7½% with standard 7072 (1% zinc). This would be used for the header portion of the radiator.
3. 0.017 in. (0.43 mm) 3105 type alloy clad one side 15% with X4104 and the other side clad 7½% with 7072 containing 1, 2 or 3% zinc.

Table 1—Composition of Alclad Vacuum Sheets Used in This Study

	Nominal composition, %				
Component	Si	Cu	Mg	Mn	Bi
Brazing clad ×4104	9.7		1.5		0.1
Core 3003		0.12		1.2	
Core 3105[a]			0.4	0.4	
Core 6951	0.3	0.25	0.6		

[a] Type alloy.

The nominal compositions of the various alloys are shown in Table 1.

Experimental

Brazing Test

The above materials were subjected to simulated vacuum brazing cycles which would be typical of a production operation. The maximum temperature was 1100 F (593 C) with a time of 7 min above 1000 F (538 C). The samples, usually 3 × 6 in. (76 × 152 mm) × thickness, were hung vertically.

In some instances the samples were contained in a rectangular box (still suspended vertically) to simulate the atmosphere in the interior of an assembly. In the case of the heavy gauge material, an assembly consisting of six 3½ × 5¼ in. (89 × 133 mm) plates separated by 3003 rings and spacer bars was also brazed.

A schematic of the interior of a typical Material Evaluation Assembly (MEA) is shown in Fig. 2.

Zinc Distribution

Cross sections of the material before and after the simulated brazing cycle were mounted and polished. These mounts were then inserted in the electron microprobe, and the zinc distribution was determined by moving the samples at a controlled rate under the beam with the direction of movement being normal to the cladding core interface.

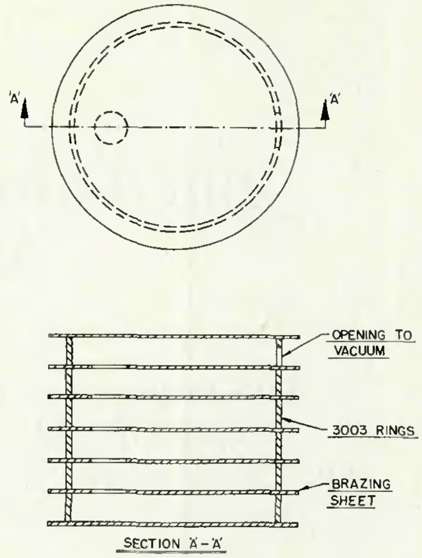

Fig. 2—Schematic of interior surface of typical material evaluation assembly

The electron microprobe zinc signal was calibrated using aluminum zinc standards with zinc levels of 0.5, 0.8, 1.2 and 1.9%.

Potential Measurements

Solution potential measurements were made in a 1N sodium chloride 0.3% hydrogen peroxide solution using a saturated Calomel electrode as the standard. All potential values were corrected to the .1N Calomel scale by subtracting 85 millivolts from the saturated Calomel value.

A 7072 standard and a pure zinc standard were included in all potential measurements.

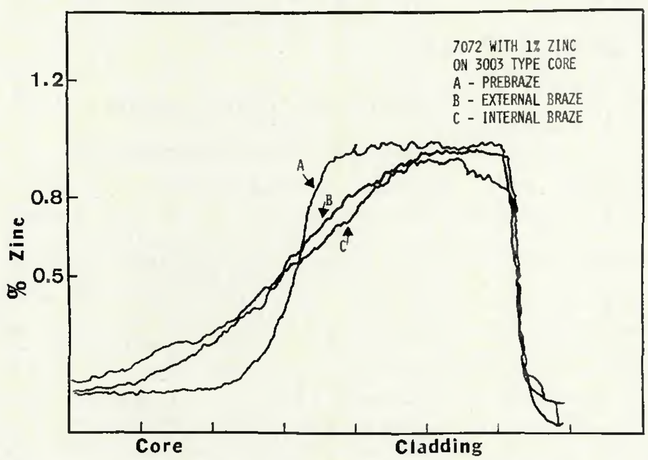

Fig. 3—Typical electron microprobe traces of zinc distribution in 0.05 in. (1.3 mm) gauge, 7072/3003/X4104 composite, pre- and post-braze

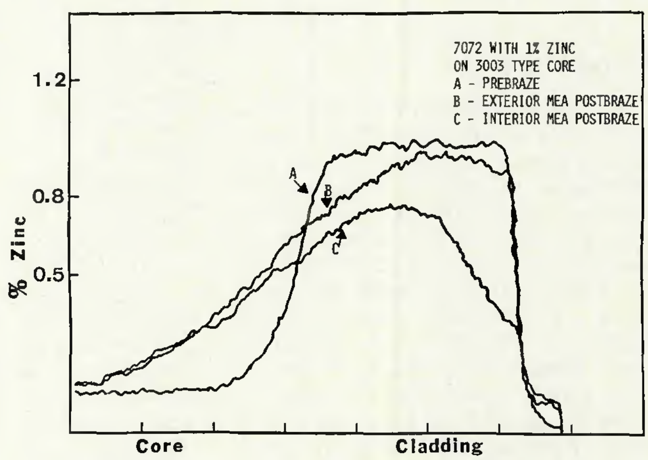

Fig. 4—Typical electron microprobe traces of zinc distribution in 0.05 in. (1.3 mm) gauge, 7072/3003/X4104 composite, pre- and post-braze

Results

0.050 in. Gauge Samples

Typical zinc distributions of pre- and post-braze composites for the 0.05 in. (1.3 mm) material (7072/3003/X4104) are shown in Fig. 3. Examination of the zinc curves shows that the as-produced or pre-braze sample has some minor zinc diffusion into the core as illustrated by the somewhat smaller slope of the zinc profile at the cladding core interface when compared to the slope at the outer surface of the cladding.

For the sample subjected to the simulated external braze, there has been only minor sublimation of zinc from the cladding, but there has been a good deal of zinc diffusion into the core. If this zinc distribution is compared with the pre-braze sample, it appears that the loss of zinc from the cladding is equivalent to the zinc diffusion into the core.

In the case of the sample brazed using a simulated internal atmosphere, there has been more sublimation of zinc from the cladding. This sublimation of zinc is probably due to the interaction of the magnesium vapor from the molten X4104 cladding with the oxide on the 7072 cladding permitting sublimation of zinc.

Figure 4 shows the zinc distribution in samples taken from the brazed Material Evaluation Assembly. Here the zinc distribution of the exterior section is similar to that of the exterior sample shown in Fig. 3. There has been only minor loss of zinc by sublimation, but there has been considerable diffusion of zinc into the core. Again, we can semi-quantitatively see that the amount of zinc which has diffused into the core is approximately equivalent to that depleted from the cladding.

In the case of the interior section of the MEA, it will be noted that the zinc profile shows considerably more loss of zinc by sublimation. Consider that the MEA is a small box with a relatively large volume of X4104 cladding with only a small opening. One can see that there is a considerable vapor pressure of magnesium inside the MEA. This magnesium presumably changes the surface oxide on the 7072 cladding as proposed by Winterbottom,[1] thereby permitting the sublimation of zinc.

The zinc distribution for the interior MEA illustrates that the zinc maximum is considerably sub-surface.

The zinc distributions of the 0.05 in. (1.3 mm) gauge 7072 clad 6951 (7072/6951/X4104) are very similar to those shown in Fig. 3.

Table 2—Solution Potentials for 7072 Cladding (After Simulated Braze Cycle), Measured in 1N NaCl-0.3% H_2O_2 Vs. 0.1N Calomel Electrode at Room Temperature

Alloy	Simulated internal braze	Simulated external braze	Pre-braze
0.50 in. (1.3 mm) 7072/3003/×4104	−0.934	−0.967	−0.970
0.05 in. (1.3 mm) 7072/6951/×4104	−0.920	−0.965	−0.970

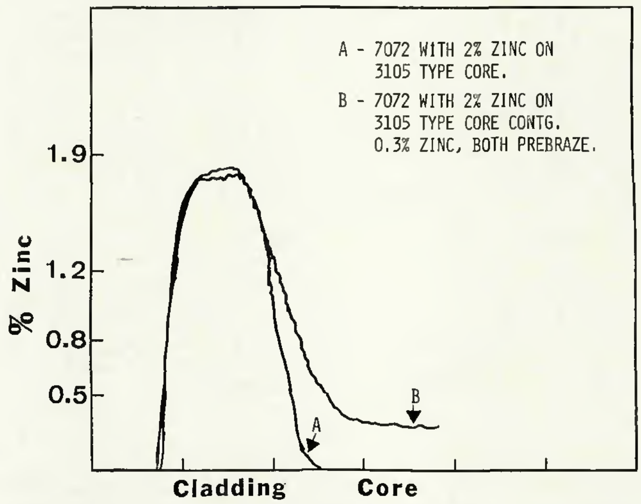

Fig. 6—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072 (2% Zn)/3105/X4104, pre-braze

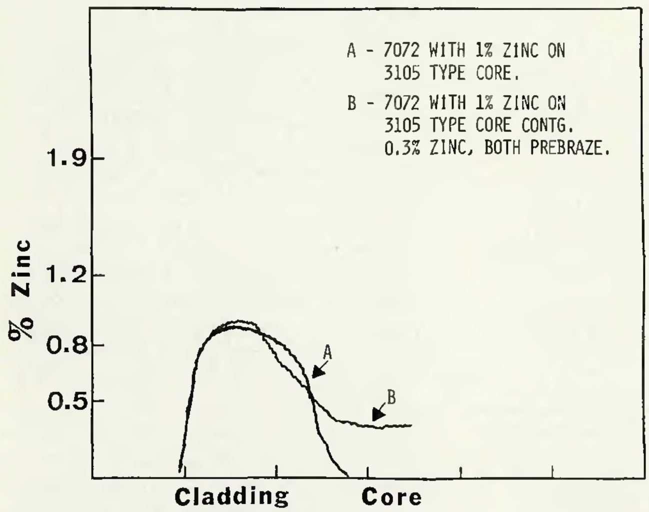

Fig. 5—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072/3105/X4104, pre-braze

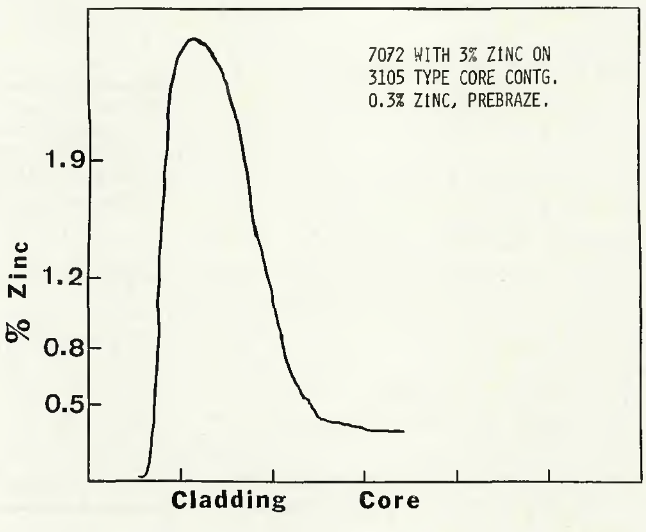

Fig. 7—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072 (3% Zn)/3105/X4104, pre-braze

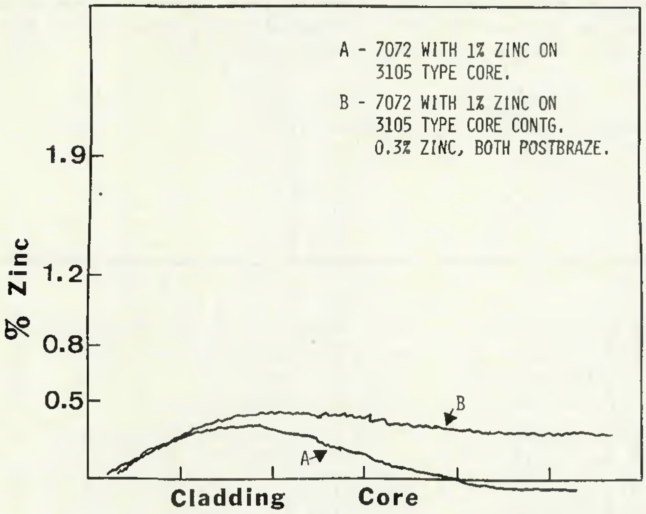

Fig. 8—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072/3105/X4104, post-braze

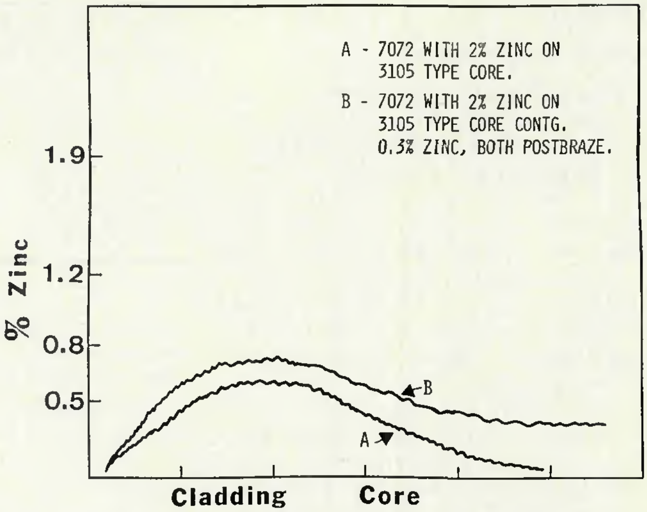

Fig. 9—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072 (2% Zn)/3105/X4104, post-braze

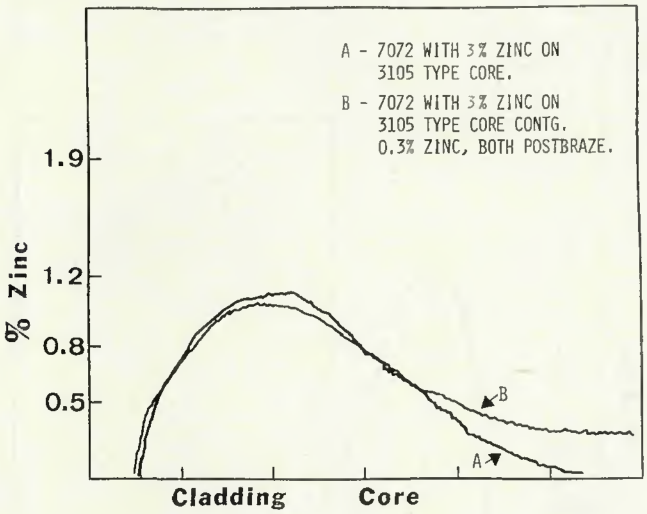

Fig. 10—Typical electron microprobe traces of zinc distribution in 0.017 in. (0.43 mm) gauge, composites of 7072 (3% Zn)/3105/X4104, post-braze

The solution potentials of the post-braze materials are shown in Table 2.

It should be noted that the higher potentials for the simulated internal braze are consistent with the minor zinc sublimation loss found in these samples.

0.017 in. Gauge Samples

Preliminary measurements of standard 7072 cladding on the 0.017 in. (0.43 mm) gauge samples indicated very severe zinc losses during simulated brazing cycles. The program was therefore expanded to examine the effects of increasing the zinc content in the cladding to provide adequate post-braze zinc. It was also rationalized that the addition of 0.3% zinc to the core would reduce the zinc loss by diffusion from the cladding.

The following composites were fabricated into light gauge 0.017 in. (0.43 mm) H-14 sheet to simulate the gauge and temper of material that might be used in radiator tubes; the nominal cladding percentages were 7½% for the 7072 and 15% for the X4104.

1. 7072 with 1% Zn/3105/X4104.
2. 7072 with 1% Zn/3105 with 0.3% Zn/X4104.
3. 7072 with 2% Zn/3105/X4104.
4. 7072 with 2% Zn/3105 with 0.3% Zn/X4104.
5. 7072 with 3% Zn/3105/X4104.
6. 7072 with 3% Zn/3105 with 0.3% Zn/X4104.

Table 3—Solution Potentials for Post-Braze 7072 Claddings Measured in 1N NaCl-0.3% H_2O_2 Vs. 0.1N Calomel Electrode At Room Temperature—Unbrazed Potentials Included for Comparison

Sample description	Solution potential vs. .1N calomel
(1) 1% Zn unbrazed	–.955
(1) 1% Zn brazed	–.837
(2) 1% Zn unbrazed	–.967
(2) 1% Zn brazed	–.841
(3) 2% Zn brazed	–.849
(4) 2% Zn brazed	–.853
(5) 3% Zn brazed	–.907
(6) 3% Zn brazed	–.904

Typical electron microprobe traces of zinc distribution for samples 1, 2, 3, 4 and 6 are shown in Figs. 5–7. From these traces it is obvious that the zinc levels in the cladding approximate those intended. Again, it should be noted that there has been some diffusion of zinc into the core during fabrication of the composite.

These samples were subjected to simulated brazing cycles in pairs; each pair had equivalent 7072 claddings. These were positioned with the X4104 claddings toward the furnace heaters and the 7072 claddings facing each other. The brazing cycle was controlled so that the samples were at temperatures above 1000 F (538 C) for 7 min and the maximum temperature was 1100 F (593 C).

Representative electron microprobe traces of the post-braze zinc distributions are shown in Figs. 8–10. As can be seen, the maximum levels of zinc in the post-braze claddings were 0.3 to 0.5% for the pre-braze sample with 1% Zn, 0.6 to 0.7 for the pre-braze sample with 2% Zn and 1.0 to 1.1% for the pre-braze sample with 3% Zn.

From the general shape of the post-braze zinc distribution curves, it is obvious that the zinc in the cladding has been depleted both by sublimation into the vacuum and diffusion into the core. It is also obvious that the addition of 0.3% zinc to the core has not significantly changed the retained zinc levels in the cladding.

Solution potentials of the post-braze 7072 surfaces are shown in Table 3.

The solution potentials indicate that only the 3% Zn post-braze has a potential approaching the potential of nominal 7072 (unbrazed samples 1 and 2). This is in agreement with the post-braze zinc distributions.

Discussion

The results in this paper show that heavy gauge brazing sheet (0.05 in. or 1.3 mm 3003 or 6951 clad 7½% with 7072 with a nominal zinc content of 1%) will have sufficient retained zinc after a typical vacuum brazing cycle to afford galvanic protection to the core. This is based on the measured solution potential of the post-braze 7072 cladding surface, and is confirmed by the electron microprobe measurement of the zinc content of the cladding.

For light gauge materials such as would be used in radiator tubes, 7072 claddings with 1% zinc will not have sufficient retained zinc after a typical vacuum cycle to afford galvanic protection to the core. This is again based on the measured solution potential of the cladding which is only marginally anodic to the core. Also, this is confirmed by the electron microprobe measurement of the zinc content of the cladding which is only 0.3%. 7072 with 3% zinc will provide sufficient zinc in the post-braze cladding.

The results also show that for lighter gauge samples there has been considerable loss of zinc by sublimation. On the other hand, for the heavier gauges the sublimation losses have been negligible except in atmospheres containing high partial pressures of magnesium vapor. This difference is probably due to the thicker oxide on the heavy gauge materials preventing the sublimation of zinc.

Conclusions

1. For heavy gauge vacuum brazing sheet (0.05 in. or 1.3 mm clad 7½% with nominal composition 7072), there is sufficient retained zinc in the cladding to provide galvanic protection to the core. The maximum temperature during the brazing cycle was 1100 F (593 C) with 7 min above 1000 F (538 C).

2. For light gauge materials—0.02 in. (0.5 mm) or less clad 7½% with nominal composition 7072—with the same brazing cycle, the retained zinc in the cladding is approximately 0.3% which is only marginally anodic to the core.

3. In the case of the light gauge materials, increasing the zinc content of the 7072 from the nominal 1% to 3% will provide sufficient zinc in the post-braze cladding to provide galvanic protection for the core.

Acknowledgments

The authors wish to express their appreciation to Mr. R. D. Dewey for the electron microprobe data and to Mr. W. H. Ailor for the solution potential data.

Reference

1. Winterbottom, W. L., and Gilmour, G. A., "Vacuum Brazing of Aluminum," *Journal of Vacuum Science Technology*, 13, 1976, pp. 634-643.

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