Exploratory Study of a Fluxless Aluminum Brazing Process for Beryllium

High peak strengths with considerable overall variations prompt discussion of the parameters affecting joint strength

BY R. J. JUNTZ, W. G. KING, G. TARDIFF, JR. AND E. F. WESTLUND

ABSTRACT. A process for fluxless vacuum brazing of beryllium with aluminum which involves preplacing the aluminum and applying a small pressure (< 1 psi) across the joint during brazing was found to result in very high joint tensile strengths. The peak strengths of nominal 0.0005-in. thick brazes made with nominal 99.999% Al, 1100 Al, and an Al-12% Si alloy below 725 C were found to be within a few thousand psi of the Be base metal yield strengths (33,000 and 40,000 psi). Variability in the joint strengths, however, would limit design stress to about 20,000 psi.

Differences in the degree of alloying across the Be and Al interfaces and in the final joint thicknesses are cited as contributing to the strength variation. The former is affected by variation in oxide film thickness and in the manner in which the Al oxide film breaks up during the pressure brazing process. Some of the data and a qualitative argument suggest that an optimum braze thickness for maximum strength may exist under conditions of base metal yielding. The iron impurity in the 1100 Al brazing material results in a high density of iron-rich particles near the interface in the case of thick (> 0.010 in.) brazes which could degrade the strength of thick brazes. Suggestions for improving the consistency of the process to give higher useful design stress are given.

Introduction

The goal of this effort was to determine if and under what conditions strong joints could be made using aluminum brazing materials without the use of flux. It is noted that flux brazing methods are routinely used commercially for brazing beryllium with aluminum.[1] It was considered, however, that a fluxless method would be advantageous in some applications because the difficulties associated with the use of flux and problems associated with trapped flux such as strength variation and post-braze corrosion could be avoided.

The authors are associated with the Lawrence Livermore Laboratory, University of California, Livermore California.

Experimental Procedure

Early Experience

Early experience had indicated that Al placed on a Be surface and heated to temperatures well in excess of its melting point would not wet and flow on the Be (oxide) surface. This was true regardless of the procedure used to clean the surfaces or the quality of the vacuum. This lack of wetting was assumed to be due to the effect of an aluminum oxide film which prevented contact of the liquid Al with the Be (oxide) surface. Brazing of Be with Al by flow and capillarity in the absence of flux was therefore not considered possible under ordinary circumstances.

By preplacing the Al in the form of a thin shim between the Be surfaces, the need for capillarity to cause spreading and filling of the joint with liquid is avoided. Further, it was found that by applying a low pressure across the joint during brazing some of the liquid extruded out from between the Be surfaces. Metallography of these joints indicated that wetting of the Be by the Al had occurred, and bench tests indicated that the joints were strong. Presumably, the oxide film was broken up during extrusion of the liquid and this allowed wetting to occur.

It was established that a pressure of 0.58 psi applied across the joint containing a 0.003 in. shim of Al resulted in a final braze thickness of about 0.0005 in. and this was considered, on the basis of the Orowan[2] equation, thin enough to assure high strength in the absence of interfacial weakness. The Orowan equation is derived using an elastic-plastic analysis of deformation of a thin ideal rigid-plastic material deformed between rigid anvils. Under the additional assumptions of a Tresca yield criterion and that the shear stress acting along the anvil-braze interface can be given by the yield strength in shear of the braze material, the Orowan equation for predicting braze joint tensile strength takes the form:

$$\sigma_f = \sigma_Y (1 + d/6t) \qquad (1)$$

where σ is the fracture stress of the braze joint, σ is the uniaxial yield strength of the braze metal, d is the diameter and t is the braze metal thickness.

The strengthening predicted by the Orowan equation results because the rigid base metal restrains the braze metal from contracting laterally. This leads to transverse principal stresses which introduce a hydrostatic component of stress into the braze. Since yielding depends on the difference between the principal stresses (e.g., the shear stress), the axial stress required to cause yield (and failure) of the braze metal is increased. The Orowan equation predicts a dramatic increase in fracture strength as braze thickness is reduced because the shear stresses which act at the interface become much more effective in preventing lateral contraction as the braze becomes thinner.

The Orowan equation has been shown experimentally[3] to lead to a lower estimate of the braze metal thickness required to attain a given strength level in the case of maraging steel brazed with a Ag-Pd alloy for thickness-to-diameter ratios (t/d) >approx. 0.007 in. Assuming the same for Al brazed Be and taking the maximum useful strength as the yield stress of hot-pressed block Be (about 40,000 psi) and using 4000 psi for the yield stress of the Al, the minimum required thickness from Eq. 1 is approx. 0.009 in. at a specimen diameter of 0.5 in. The assumption made above that the maximum effective strength of the joint is limited to the yield strength is based on the idea that constraint is limited by base metal yielding. There is some experimental evidence that base metal yield does indeed limit joint strength.[4]

Having concluded that an adequately thin braze resulted from the particular experimental conditions chosen, we adopted a standard procedure which was used to prepare joints for determining mechanical properties and evaluating process variables and reproducibility.

Standard Procedure

Brazing Process. Hot-pressed block Be cylinders 0.94 in. in diam by 1.0 in. in length were prepared for brazing by handsanding the surfaces to be brazed with 600-grit silicon carbide paper to remove all signs of prior machining. After degreasing in a light solvent, the cylinders were immersed in a 70% H_3Po_4, 25% H_2SO_4, and 5% HNO_3 etching solution for 1 min and rinsed in distilled water.

The Al brazing materials in the form of 0.003-in. thick by 0.94-in. diam shims were cleaned by degreasing in light solvent, immersing in a commercial Al etching solution containing HF and other acids for 1 min, and rinsing in distilled water. The time between cleaning of the materials and insertion into the vacuum chamber was kept under 3 min.

Two Be cylinders with the Al shim placed between them were assembled into a Be clamshell alignment fixture, shown in Fig. 1. The upper cylinder was weighted to produce a pressure across the joint of 0.58 psi (includes the weight of the Be).

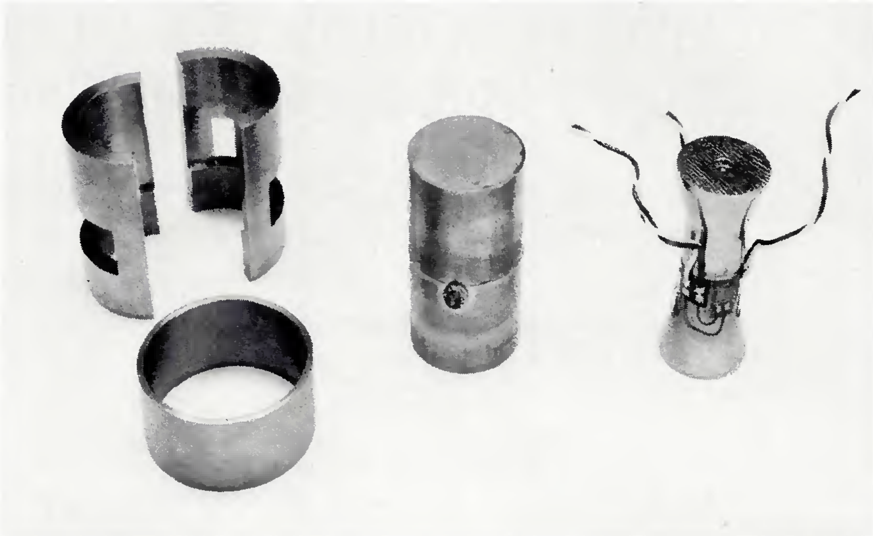


Fig. 1 — Braze fixture, brazed Be cylinders showing Al extrusion, and prepared tensile specimen

The assembly was placed in a radiation shield furnace with a control thermocouple placed in the immediate vicinity of, but not attached to, the Be. After the chamber was evacuated to $<10^{-4}$ mm Hg, the assembly was heated to the brazing temperature, held within 10 C of the brazing temperature for ½ hr and furnace-cooled to a few hundred deg C. After brazing, evidence of Al extrusion out of the joint was observed as a small bead attached to the outer periphery of the joint, as shown in Fig. 1.

Mechanical Property Specimen Preparations

After brazing, a 1.0-in. gage length by 0.5-in. gage diam tensile speci-

Table 1 — Braze Test Results for Batch 1 Beryllium

Braze metal	Braze temp., C	Deviations	Strength, psi	Be strain at fracture, %	Approx. interface failure, %	Approx. joint thickness, in.
999.99% pure Al	680		17,800	0.05	nil	0.00016 — 0.00036
	680		30,900	0.13	nil	0.00016 — 0.0004
	720		21,700	0.08	25	
	720		21,000	0.07	nil	~0 — 0.00012
	720	applied pressure	15,000	0.04	50	
	720	reduced to 0.065 psi	18,700	0.06	25	
1100 Al	680		18,700	0.06	50	
	680		18,600	0.06	50	
	680	starting Al thickness-0.0005 in.	8,100	0.02	50	
	720		27,700	0.10	nil	0.0008
	720		23,800	0.08	25	
	720	surfaces not etched	broke in bench test — very weak		100	
Al-12% Si alloy #718	605	No sign Al-Si melting; broke in bench test			50	
	620		7,700	0.014	50	
	620	held at temp 1 hr	27,100	0.12	25	
	680	low result not explained	7,000	0.01	100	
	680		30,300	0.15	nil	0.0004
	720		33,500	0.45	nil	~0 — 0.00024
	720		21,000	0.07	nil	0.00008 — 0.0004

Note: Unless otherwise stated, the brazing conditions were maintained constant as discussed in text and as follows: Initial Al braze metal thickness, 0.003 in.; applied pressure, 0.58 psi; hold time at braze temperature, ½ hr. Surfaces cleaned as described in text.

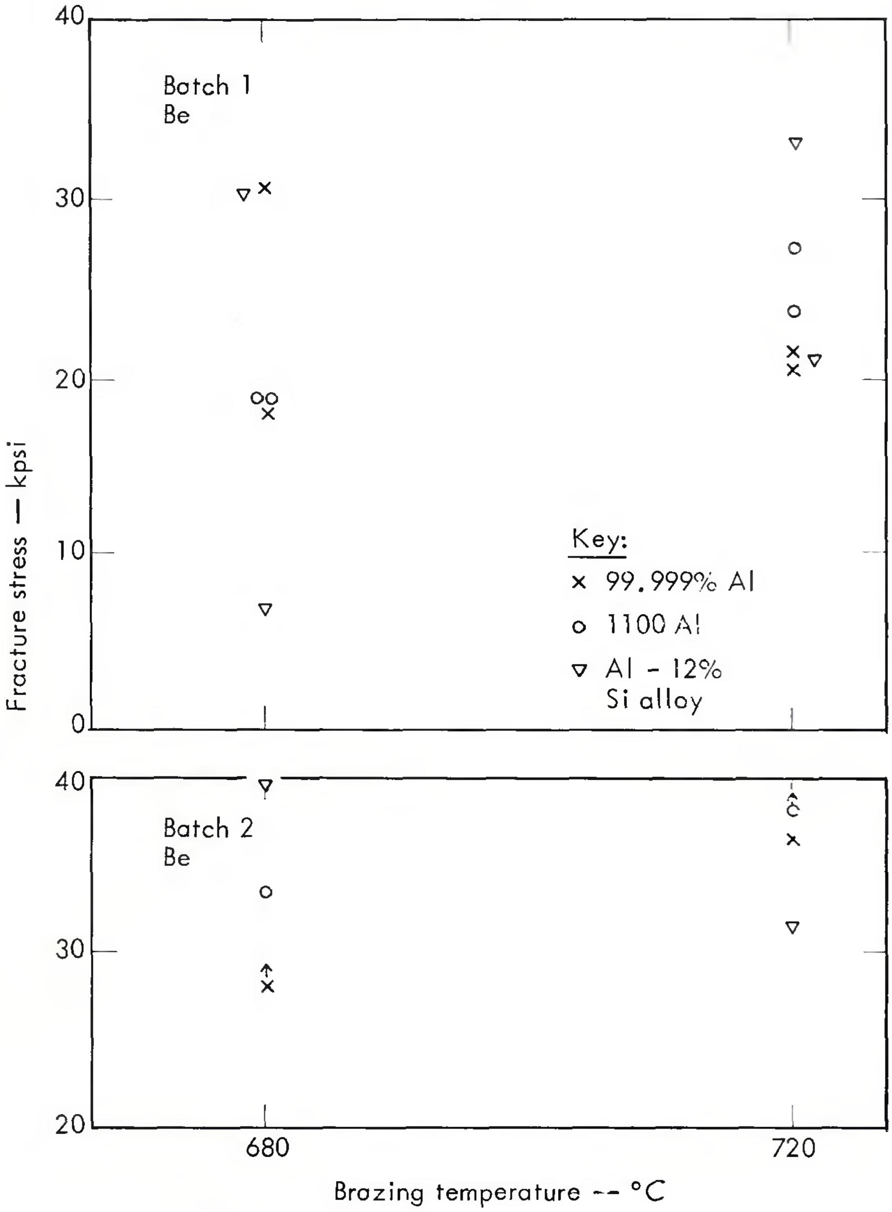


Fig. 2 — Ultimate tensile strengths of Be brazed with Al and Al-Si alloy

men in the configuration shown in Fig. 1 was machined from the brazed cylinder. The first test of an as-machined specimen resulted in fracture in the Be remote from the braze at 27,000 psi. All subsequent specimens were etched to reduce the diameter by a minimum of 0.006 in. to remove surface damage due to machining. In all subsequent tests except one, failure occurred in the braze joint at stresses which ranged up to 39,800 psi.

Two batches of specimens were tested. The Batch 1 specimens were etched in a solution consisting of 70% H_3PO_4. 25% H_2SO_4 and 5% HNO_3, and the Batch 2 specimens were etched in a solution of 5% HF and water and desmutted in a concentrated HNO_3 bath, both at room temperature. Neither of these solutions attacked the Al noticeably. The Batch 1 etch, however, resulted in localized attack at corners and produced some rounding and pitting of the Be in the vicinity of the braze. The Batch 2 etch resulted in a matte finish but removed the Be very uniformly; the Batch 2 etch is therefore considered more desirable.

Mechanical Testing

Three foil strain gages 120 deg apart were attached to each specimen (not spanning the joint) tc facilitate aligning the specimen in the grips prior to loading to failure. The alignment was adjusted until all three gages gave strain indications within 5% of one another at an applied stress of 4000 psi. The strain gaging also provides a measurement of the base metal (Be) strain at failure which can provide insights into the failure mechanism as discussed below.

Results and Discussion

Effects of Braze Material and Temperature on Mechanical Strength

The mechanical property results for all brazes made using the standard procedure are summarized in Table 1 and plotted in Fig. 2. The data of Fig. 2 indicate that very high strengths can be achieved by fluxless brazing of Be with Al. The peak strengths measured for joints in the Batch 1 Be (33,500 psi) and Batch 2 Be (39,800 psi) are similar to the yield strength of the hot-pressed block used which is expected to provide an approximate upper limit to the achievable strength.

The results in Fig. 2 show no consistent differences in strength between the three braze materials investigated. At least one specimen each brazed with 99.999% pure Al, 1100 Al, and 718 alloy (a commercial Al-12% Si brazing alloy) fractured between 30,000 and 34,000 psi in the case of the batch 1 beryllium specimens and between 36,000 and 40,000 psi in the case of the batch 2 beryllium. In addition, there does not seem to be a significant difference in strength between the specimens brazed at 680 and 720 C. Neglecting the one very low result for the batch 1 beryllium the average strength for the brazes made at 680 C is approx. 23,000 psi and for those brazed at 720 C is approx 25,000 psi. For the batch 2 beryllium the average corresponding to brazes made at 680 C is approx. 36,000 psi and for those at 720 C it is approx. 35,000 psi.

A disturbing feature of the data of Fig. 2 is the fairly large range of observed strengths. Neglecting the one very low result for the batch 1 beryllium the strengths vary from 17,000 to 34,000 psi and for the Batch 2 beryllium from 31,000 to 40,000 psi. Design stresses would be limited to the measured minimums or considerably below the maximum achievable strengths. The reasons for the wide range in strengths can be attributed to incomplete wetting or alloying across the interface and variation in braze thickness as discussed in another section.

Effect of Braze Metal Purity

Although the difference in strengths between the specimens brazed with 99.999% Al and 1100 Al was not significant, other information suggests that the effect of purity could be important. Figure 3, for example, shows relatively thick brazes (approx. 0.015 in. thick) made with the two aluminums of different purity. The high concentration of particles seen near the interface in the case of the 1100 Al braze have been determined to be iron-rich by microprobe analysis. The compound is expected to contain Be as it apparently formed by diffusion of Fe from the liquid Al to the interface to react with the Be there.

The presence of a concentrated layer of brittle particles in the braze such as shown in Fig. 3b might be expected to degrade the mechanical strength. The reason that the strengths of the brazes made in the present study were not affected by purity might be that the final braze thickness. and therefore the amount of Fe available to react with the Be, was about a factor of 20 less than that of the brazes shown in Fig. 3. Thus the density of iron-rich particles near the interface in the case of the thin brazes should be far less than that indicated in Fig. 3. This seems to be borne out by the photomicrograph of the thin 1100 Al braze shown in Fig. 4.

Effects of Deviations from Standard Procedure

The effects of various changes in the standard brazing procedure on the fracture strength are given in Table 1. The effect of not etching the Al or Be prior to brazing resulted in a very fragile joint as noted in the table. A light hammer blow was enough to cause the joint to fail. It is expected that the breakup of the heavier oxide film on the unetched Al and/or the diffusion of Al through the oxide film was not as extensive as in the case of the etched surfaces and limited wetting and alloying between the Be and Al.

Reducing the starting Al thickness from 0.003 to 0.0005 in. also resulted in a weak joint, as noted in the table. No apparent extrusion of the liquid occurred during this braze.

A braze made using the standard procedure with brazing carried out at 620 C resulted in a very weak joint, but extending the brazing time to 1 hr at 620 C increased the joint strength to 27,100 psi. This is comparable to the highest strength joints made in the Batch 1 Be. This experience suggests that diffusion through an oxide film may limit alloying between the Be and Al at the lower brazing temperatures.

Finally, a braze made at 605 C with the Al-12% Si alloy which melts at 577 C had virtually no strength, and no extrusion of liquid out of the joint was observed. The applied force (F) necessary to enlarge a thin wafer of non-wetting liquid when compressed between two anvils can be given by:

$$F = (2\pi r^2/t)\ \gamma_{LV}$$

where r is the radius of the liquid wafer, t is its thickness, and γ_{LV} is the liquid vapor interface energy. γ_{LV} = approx. 840 dynes/cm for Al at 700 C.

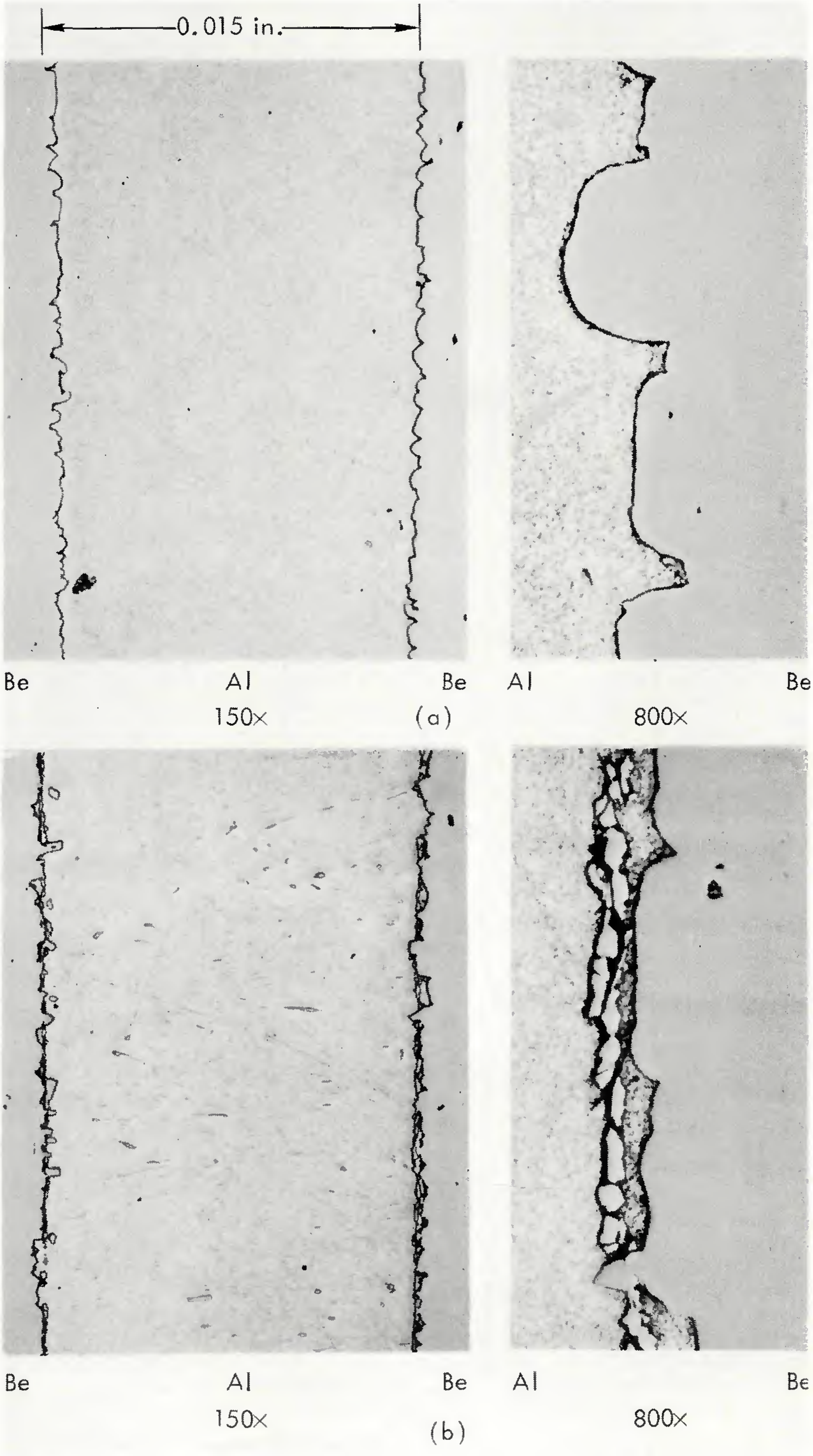


Fig. 3 — Effect of Al purity on microstructure of Be brazed with Al. (a) Braze made with high-purity Al; (b) braze made with 1100 Al. All photos reduced 9%

Under the present experimental conditions the force required to enlarge the wafer of liquid (or extrude the liquid) would be approx. 1000 g, whereas only 185 g of force are used in the present tests. The fact that 185 g of force is enough to extrude the liquid at the higher brazing temperatures may suggest that some contact of Al with Be is occurring at the higher temperatures. This would reduce the contact angle and therefore decrease the force necessary to extrude the liquid. Cracks in the oxide film may occur because of thermal expansion of the liquid, and these may provide a mechanism for bringing the liquid into direct contact with the Be (oxide) surface at the higher temperatures.

Effect of Beryllium Base Metal Strength

By plotting the fracture stresses of the brazes versus the strains measured in the Be at the point of fracture, a curve can be developed which should correspond to the stress-strain curve of the Be base metal within the scatter of the various specimens. This was done for both batches of Be in Fig. 5. It is evident from Fig. 5 that the two batches of Be had different strengths, with the Batch 1 Be having a 0.2% offset yield strength of approx. 33,000 psi and the Batch 2 Be having a yield of approx 41,000 psi. The higher average strength of the Batch 2 joints, as indicated in Fig. 2, is then understandable in view of the higher strength of the base metal since the yield stress of the base metal is expected to provide an approximate upper limit to the strength of the brazed joint. In addition, since the pre-yield microstrain is greater for the Batch 1 Be than for the Batch 2 Be at any given stress, it is expected that joints made with the former Be would be more likely to fracture. This is borne out by the data of Fig. 5.

Discussion of the Variability in Braze Strength

There are at least two sources of the variation in braze strength among the data reported in Tables 1 and 2 and plotted in Figs. 2 and 5. These are: (1) the apparent variation in interface strength as judged by the various amounts of interface failure among the specimens, as noted in Table 1 and Fig. 6; and (2) variation in final braze thickness, as noted in Tables 1 and 2 and Fig. 4.

Interface Strength Variation. The cause of the variability in apparent interface strength may be the haphazard way in which the oxide film is broken up during extrusion of the Al braze metal. It is possible to visualize a situation, for example, where a single crack in the film would provide a path of easy extrusion with very little resulting contact between the liquid Al and Be surface. In such situations, good alloying across the interface may rely on diffusion of Al through oxide films. Several approaches are available for improving the extent and reproducibility of Al-Be contact during the brazing process. Brazing under ultrasonic conditions or vapor-depositing titanium on the surfaces to be brazed[5] would provide a physical and chemical method, respectively, of breaking down the oxide film. A simpler method might be to

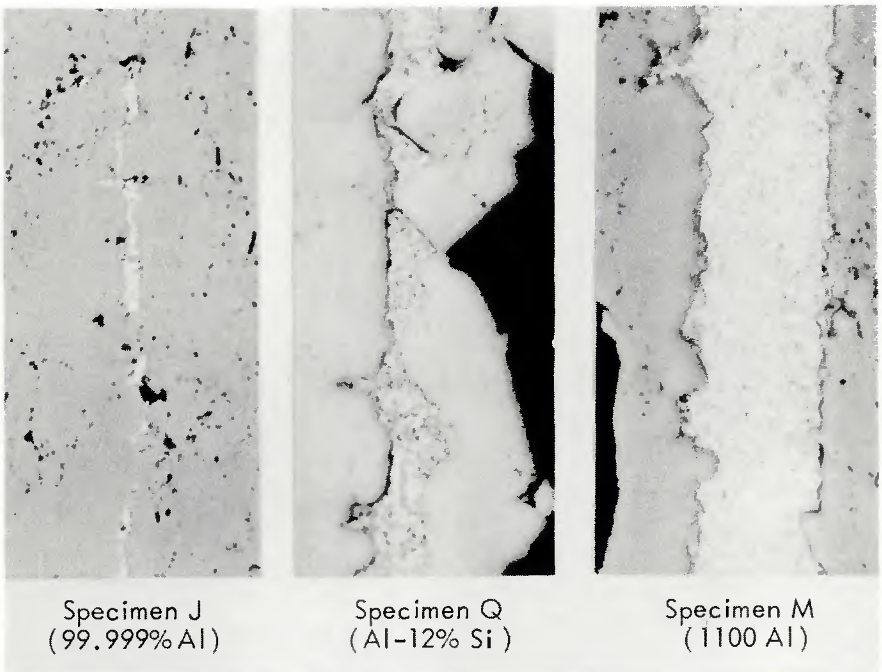


Fig. 4 — Sections through brazed joints after test in cases where fracture was not interface limited. X800, reduced 9%. Specimen J: strength, 21,000 psi; braze thickness, approx. 0.00008 in. Specimen Q: strength, 33,500 psi; braze thickness, approx. 0.00024 in. Specimen M: strength, 27,700 psi; braze thickness, approx. 0.0008 in.

inscribe or press a series of deep concentric circular scores into the Al shim after etching. During the pressure brazing process, the liquid would tend to break away from the film at each score and provide a more consistent means of wetting.

The variation in interfacial strengths could also be associated with variations in oxide film thickness which could result from small variations in the etching procedure, or in the time of exposure to the atmosphere after etching. Surface resistivity could provide a basis for process control if variation in oxide thickness proved to be significant.

Braze Thickness Variation. As noted in Table 1, there were a number of tests where the fracture surface did not exhibit a large amount of interface failure but the braze strength varied considerably (17,800 to 33,500 psi). Measurements of the braze thickness are given in Table 1 for each of these cases. The braze thickness was measured after the test by sectioning through a portion of the fracture plane in which fracture occurred through the Be. In the case of the Batch 2 Be in Table 2, the thicknesses were determined befoɪe testing. In either case, the thicknesses must be considered approximate. In Fig. 5 the braze thicknesses corresponding to the specimens which did not exhibit a significant amount of interface failure are indicated adjacent to their corresponding fracture strength values.

It is not possible to come to any

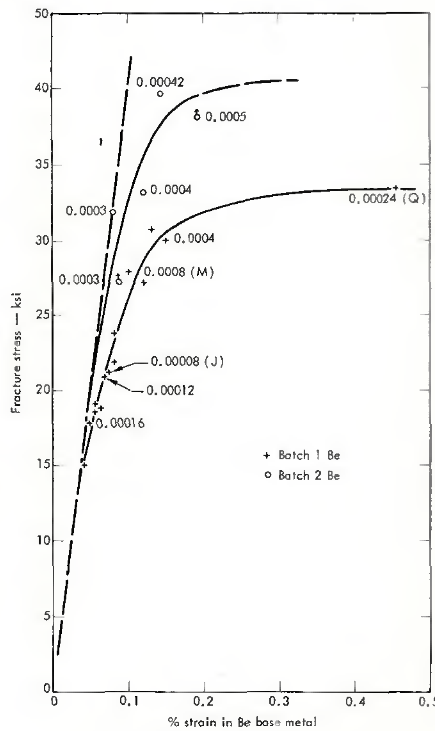
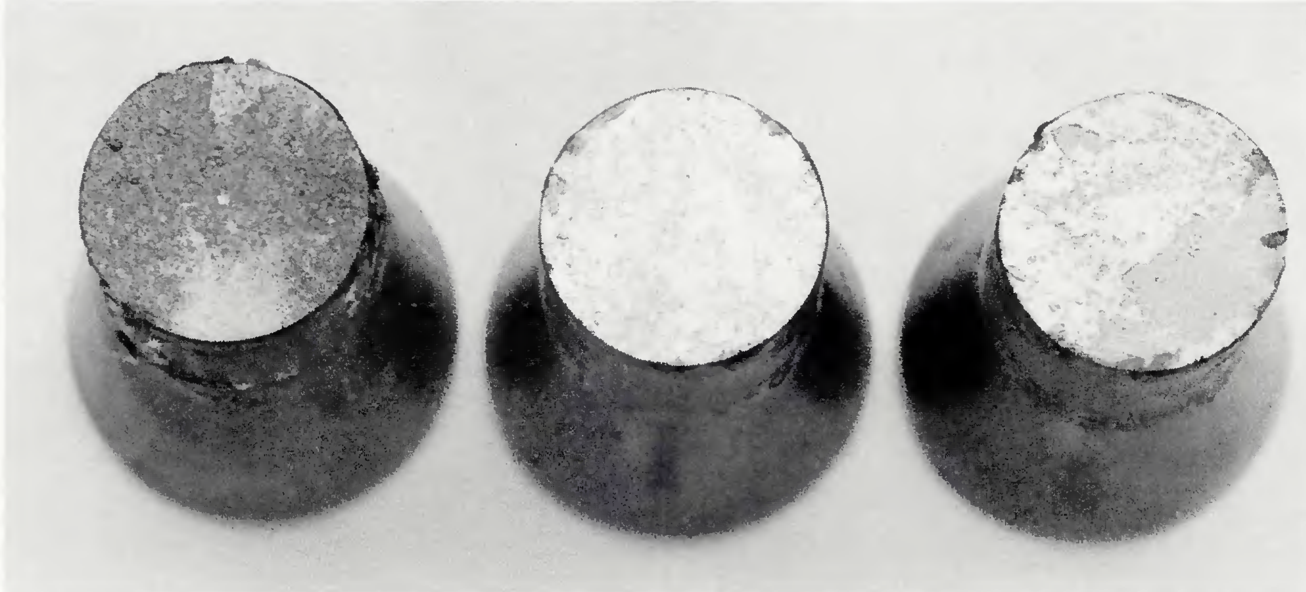


Fig. 5 — Fracture stress of brazed tensile specimens versus strain measured in Be base metal. Arrow denotes fracture initiated in base metal. In all other cases, fracture initiated in joint

definite conclusions about the effect of braze thickness on joint strength because the results given in Table 1 are inconsistent. The data, however, show several instances where the



Specimen H Specimen K Specimen O

Fig. 6 — Fracture surfaces of brazed joints. Specimen H: strength, 30,900 spi; Specimen K: strength, 18,700 psi; Specimen O: strength, 7000 psi.

Table 2 — Braze Test Results for Batch 2 Be

Braze metal	Braze temp., C	Deviations [a]	Strength, psi	Be strain at fracture, %	Approx. joint thickness, in.
99.999% pure Al	680	Batch #2 beryllium	>27,200	0.09	0.0003
	720	Batch #2 beryllium	36,500	no data	—
1100 Al	680	Batch #2 beryllium	33,400	0.12	0.0004
	720	Batch #2 beryllium	>38,200	0.19	0.0005
Al-Si alloy #718	680	Batch #2 beryllium	39,800	0.14	0.00042
	720	Batch #2 beryllium	31,900	0.18	0.0003

(a) Other conditions same as noted in Table 1.

strength was higher for thicker brazes. This is contrary to expectations based upon Orowan's model which predicts lower strength in thicker joints. In the present situation, however, the base metal is plastically deforming and the Orowan model which is based upon a rigid base metal no longer applies. No discussion of the effect of base metal yielding on the dependence of braze joint strength on thickness appears in the literature. Recent developments in understanding[6] the failure of thin brazes, however, provide a qualitative argument which seems to suggest that increases in joint strength might occur with increases in braze thickness in the circumstance of base metal yielding.

Failure of thin brazed joints has been postulated[6] to occur by growth of pre-existing microvoids in the hydrostatic stress environment experienced by the braze. Theory shows that void size increases rapidly with the magnitude of hydrostatic stress. For any given applied stress, the hydrostatic component of stress in the braze metal is greater for a thin braze than for a thick braze (strictly true only for non-strain hardening braze metal). In the circumstance of base metal yielding, the pre-existing microvoids might therefore be expected to grow to the point of failure at a base metal strain less than that required to fail the thicker braze. This implies that the strain to failure of the braze metal decreases with increased hydrostatic stress, and this effect has been experimentally observed in maraging steel brazed with silver.[6].

The above discussion suggests that an optimum thickness for braze joint strength in the circumstance of base metal yielding may exist. This possibility must be checked for any critical strength application, and suggests that joints with fixed thickness will provide more consistent properties.

Acknowledgement

The work for this paper was performed under the auspices of the U.S. Atomic Energy Commission.

References

1. Long. J. and Cremer, G. C., "Beryllium. Brazing and Welding," Paper presented at *Aeronautic and Space Engineering and Manufacturing Meeting,* Los Angeles, Calif., Oct. 7-11, 1968.
2. Orowan, E., Nye, J. F., and Cairns, W. J., M.O.S. Armament Res. Rept., Vol. 16, p. 35, 1945.
3. Saxton, J. J., West, A. J., and Barrett, C. R., "Deformation and Failure of Brazed Joints — Macroscopic Considerations," *Metallurgical Transactions,* Vol. 2, April 1971. p. 999.
4. Saxton, H. J., "The Influence of Cooling Rate and Yield Strength of the Mechanical Behavior of Brazed Joints," Ph.D. thesis SU-DMS-69-T-71, Stanford University, 1969.
5. Weiss, S., Adams, C. M. Jr., "The Promotion of Wetting and Brazing," *Welding Journal Res. Suppl.* Feb. 1967, p. 49-s.
6. West, A. J., Saxton, H. J., Tetleman, A. S., and Barrett, C. R., "Deformation and Failure of Thin Brazed Joints — Microscopic Considerations," *Metallurgical Transactions,* Vol. 2, April 1971, p. 1009.