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FINAL REPORT

Customer Ref: 750717
Solar Ref: Sales Order 6-0959-0

1 May 1965 through 1 March 1966

DEVELOPMENT OF BRAZING PROCESSES FOR PYROLYTIC GRAPHITE

SUBMITTED TO

Jet Propulsion Laboratories
4800 Oak Grove Drive
Pasadena, California

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SOLAR RESEARCH LABORATORIES
JPL Contract No. 950717

under NAS 7-100

March 18, 1966

RDR-1453

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I INTRODUCTION

This is the final report on the continuation of a study by Solar Research Laboratories for Jet Propulsion Laboratory on the brazing of pyrolytic graphite. The work reported was performed in the period May 1, 1965 through March 1, 1966. It represents an extension of the work begun on JPL Contract 950717 and reported in Solar Report RDR 1453 covering the period May 19, 1964 through December 31, 1964 (Ref. 1).

Pyrolytic graphite has attractive properties for use in radiation-cooled thrust chambers. These properties include strength at elevated temperatures and anisotropic thermal conduction so that local variations of wall temperature are equalized. However, the anisotropy extends to expansivity such that this varies by a factor of 54 between the principal crystallographic axes. The low expansion in the "a" direction is the principal cause of joining problems. The ability to braze pyrolytic graphite would make possible major weight reductions in attachments between the thrust chamber and the injector. Joints would be required between the thrust chamber and the injector. Joints would be required between pyrolytic graphite and itself, as well as between pyrolytic graphite and ATJ graphite or metals.

As a result of the prior study (Ref. 1) the state-of-the-art at the commencement of the program was such that satisfactory techniques have been developed to join pyrolytic graphite to itself. Joints had a median shear strength of 500 psi at room temperature and essentially the same value at 1500°F with a Gaussian distribution of strength data. Successful joints were made between pyrolytic graphite and ATJ graphite. The difficult problem of pyrolytic graphite-to-metal joints between plates was studied but only partially successful joints were obtained with strengths of 460 psi in shear. Preliminary work with tubes showed a marked difference in stress conditions compared with the flat plates, and led to a recommendation that all future work be performed with tubes.

The problem was changed in several areas when work began on the continuation contract in May, 1965. First, the service temperature requirements had been established to be 2500°F instead of the 1500°F target used in the first study. Second, thermal cycling of joints from room temperature to 2500°F and back to room temperature was established as a criterion. Third, tubes were to be used for much of the evaluation with 2-inch diameter tubes for final testing prior to brazing an injector ring. It became apparent early in the continuation contract that these changes were sufficiently significant so that much of the work accomplished in the first study was of marginal use to help meet these revised goals.

II DEVELOPMENT OF PROCESS FOR BRAZING INJECTORS TO PYROLYTIC GRAPHITE THRUST CHAMBERS

The objective of the continuation program was to develop a process for brazing pyrolytic graphite thrust chambers to injectors and to prepare 3 chambers for test. It was planned to meet this objective by a four-phase program:

1. Braze alloy selection
2. Evaluation of brazing of cylinders
3. Optimization of joint design
4. Preparation of brazed thrust chambers.

Although the contract goals were more than met in terms of number of specimens brazed and other quantitative measurements of accomplishment, determination of the exact problems and the development of solutions cannot be measured quantitatively. It turned out that the statement of work became inadequate when the revised criterion of 2500°F service was applied to joints and a research program had to be started to come up with solutions. As a result, complete optimization of the joint design was not possible and although joints were satisfactory on 2 inch pyrolytic graphite tubes from one supplier, some cracks appeared when the same joints were made on pyrolytic graphite thrust chambers of the same diameter but made by another supplier.

2.1 DISCUSSION OF THE PROBLEM

Previous work at Solar had shown that there was no wetting problem in the brazing of pyrolytic graphite. Flow was somewhat of a problem with metal/pyrolytic graphite joints because of a major difference in the ease with which each of the constituents was wetted. This problem was solved by high titanium braze alloys.

The second problem with pyrolytic graphite is the anisotropy of expansion. In the plane of the sheet, the expansivity is negative at low temperatures and remains less than that of fused silica up to brazing temperatures. On the other hand, the expansion is twice that of steel in a direction normal to the sheet. These gross differences in expansivity between pyrolytic graphite and most metals lead to a rapid build-up of strains, but the low strength of pyrolytic graphite will not allow such strains to be tolerated. The only favorable element in this picture is the low elastic modulus of pyrolytic graphite.

The expansion of a tube is governed by the expansion in a direction parallel with the surface, i.e., in the basal plane of pyrolytic graphite. This expansion controls the change of circumference and hence the radius, while the expansivity of the pyrolytic graphite in a radial direction can only result in thickness changes in the wall. This is one source of major difference in response of different diameter tubes compared with flat plates. Perhaps a bigger difference between flat plates and tubes results from the freedom of the ends of flat plates to move. Some bowing of a flat plate can occur, leading to reduction of the stress levels in the joint. This is illustrated diagramatically in Figure 1.

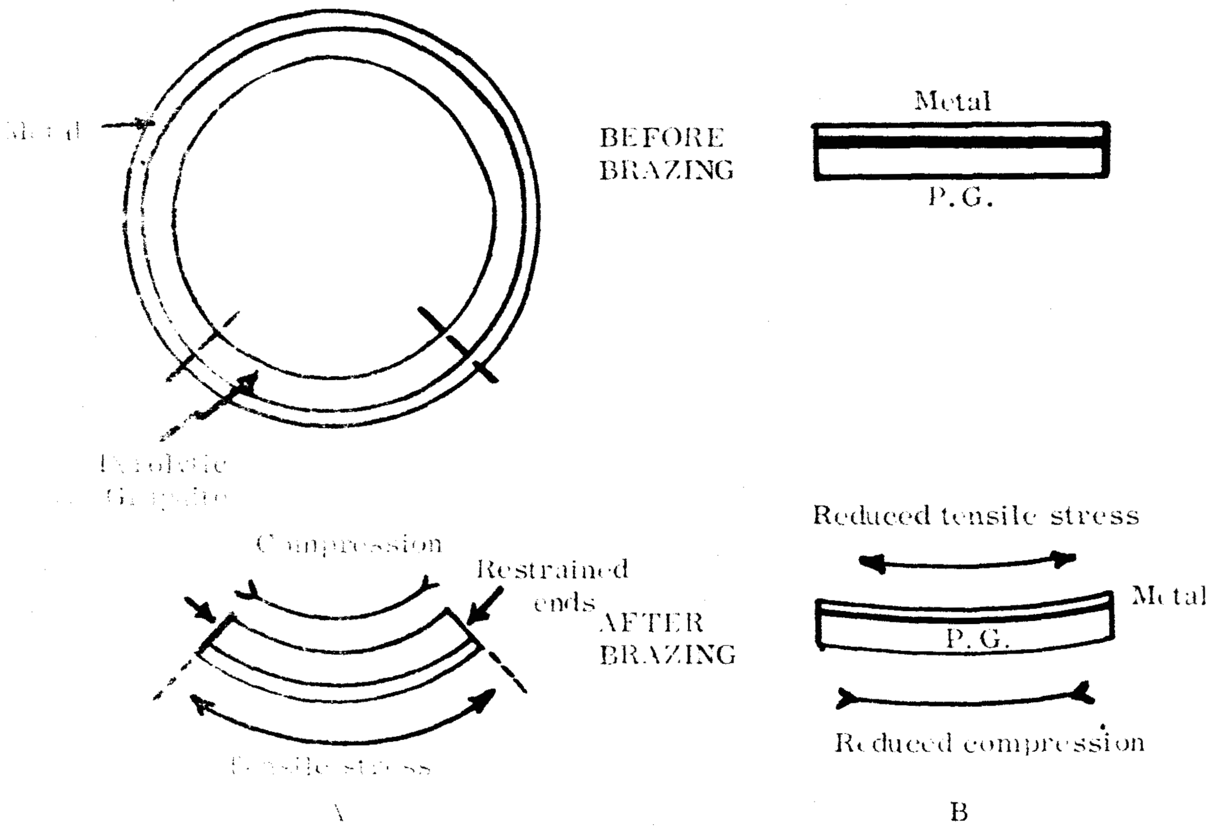


FIG. 1. STRESS CONDITION OF METAL-TO-PYROLYTIC GRAPHITE JOINTS

The melting point requirement of 2500° F led to a revised approach on the problem. Table I compares expansivities of various materials to 2500° F and melting points.

TABLE I

EXPANSIVITIES OF MATERIALS TO 2500° F

Material		Expansion, %	Melting Point, ° F
Pyrolytic graphite	(a direction)	0.15	—
	(c direction)	2.6	—
Silicon		0.5	2605
Molybdenum		0.68	4760
Tantalum		0.9	5425
90Ta-10W		0.85	5500

Silicon-containing braze alloys were favored in much of the earlier work because of the low expansion of silicon, but the proximity of the melting point to the 2500° F service temperature was not encouraging to meet the objectives of this program. Molybdenum and tantalum were favored for the metallic component, both for strength at 2500° F and for low expansion. Although molybdenum has an advantage in terms of expansion, tantalum has excellent ductility and a lower elastic modulus (27×10^6 psi versus 50×10^6 psi). All of these factors were considered in the selection of a metallic member for the joint, and led to the use of 90Ta-10W alloy because of its formability and lack of embrittlement on recrystallization.

In view of the disparity of expansivities of pyrolytic graphite and metals, successful joints must keep the stress below the fracture stress of the pyrolytic graphite. This requires the joint to have sufficient flexibility so that stresses do not become high. This approach is used extensively in metal-to-ceramic or glass seals such as the Housekeeper seal, where the problems are less acute than in the present problem.

2.2 BRAZE ALLOY EVALUATION

The contract called for the evaluation of the following alloys:

No. 1	85.9Ti-5.6V-8.5Si
2	61.8Ti-30.0V-8.2Si
3	43.0Ti-49.0V-8.0Si
4	43.9Ti-38.0V--10.0Cb-8.1Si
5	37.0Ti-40.9V-14.0Cb-8.1Si

At the completion of the evaluation of these alloys, additional alloys were added to the program for evaluation because none of the above alloys were found to meet the requirements fully. The evaluation procedures are described in the following sections.

2.2.1 Materials and Equipment

Table II gives a list of materials and suppliers. High purity alloying elements for braze alloys were supplied from Solar stocks. The braze alloys were are melted in purified argon to form buttons. These buttons were crushed and graded to provide the required particle sizes.

As with earlier work, brazing was accomplished with a 15KW Lepel induction converter. Excellent thermal transfer in the ab planes of pyrolytic graphite made it unnecessary to use a susceptor sleeve for thermal balance. Direct coupling was found satisfactory. All brazing was done in high purity argon. Room and elevated temperature tensile shear tests were performed with a Hounsfield Tensometer. Figure 2 shows one of the specimen-holding devices. Figure 3 is a typical arrangement for elevated temperature testing of plate specimens.

2.2.2 Preliminary Work

The solidus, liquidus and flow temperatures of the five program braze alloys were determined for a pyrolytic graphite substrate. Results are presented in Table III. Although the solidus temperature of four braze alloys was between 10 and [illegible]°F lower than the 2500°F requirement, it was recognized that by reaction of the parts, some increase of solidus (or remelt) temperature might be expected. Therefore, alloy 1 was dropped from the program, but alloys 2 through 5 were retained in the evaluation. As a further safeguard, the beta titanium alloy Ti-13V-11Cr-3Al was added to the list of braze alloys and is included in Table III. Preliminary

TABLE II

MATERIALS

MATERIAL	SOURCE
Pyrolytic graphite plates	Supertemp Corporation
0.060" x 0.75" x 5"	Santa Fe Springs, California
Pyrolytic graphite tubes	JPL
0.050" wall x 1-1/2" diameter x 2" long	
0.050" wall x 2" diameter x 4" long	JPL
Pyrolytic graphite thrust chambers	JPL
2" diameter	
Tantalum - 10% tungsten	Fansteel
0.012" thick	
0.023" thick	Fansteel
Molybdenum, 0.060", 0.020"	Solar stock
Tantalum, 0.060", 0.020"	Solar stock
T111 tantalum, 0.012"	Solar stock

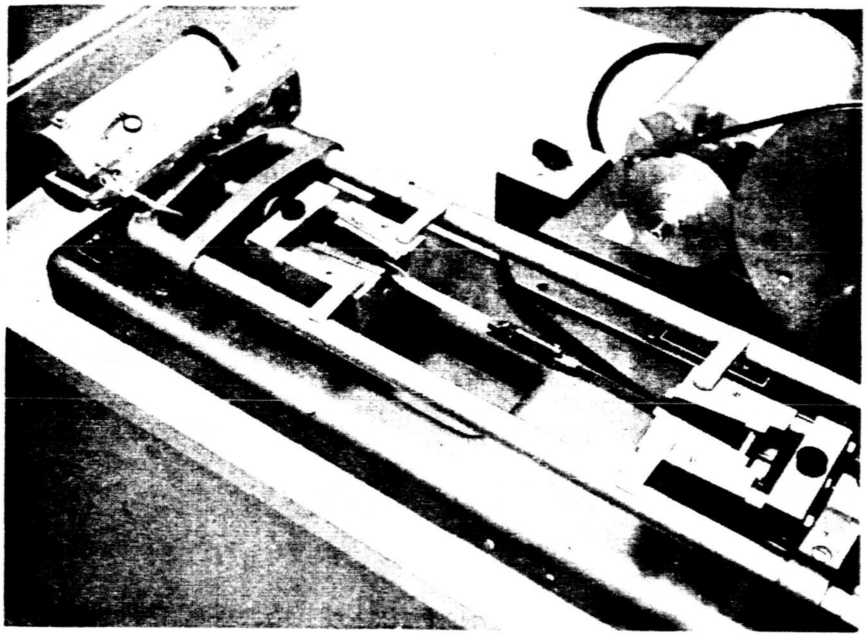


FIGURE 2. HOUNSFIELD TENSOMETER USED FOR ROOM TEMPERATURE LAP SHEAR TESTS

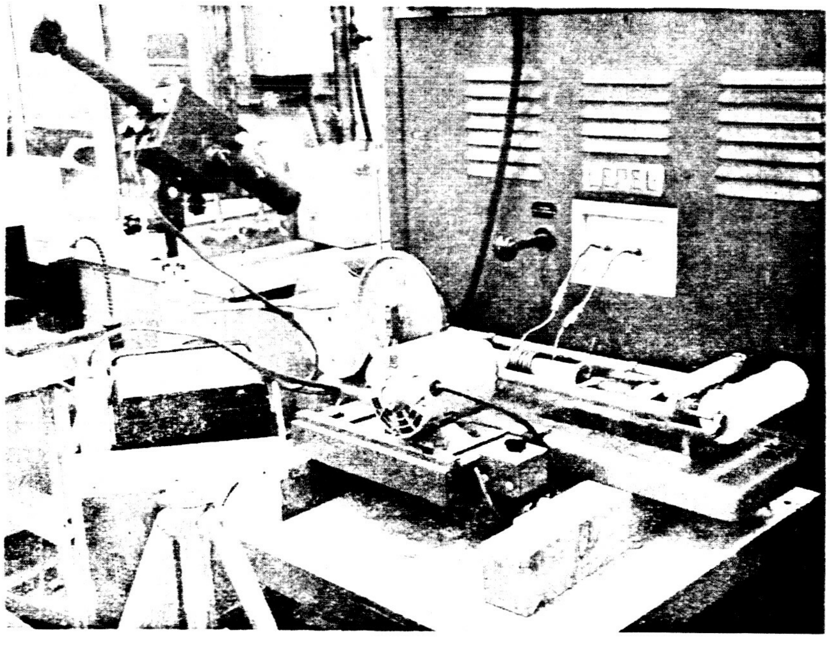


FIGURE 3. ELEVATED TEMPERATURE TESTING OF PLATE BRAZEMENTS

tests with this alloy had not been encouraging for pyrolytic graphite to itself, but it was found to wet graphite and metal equally well.

Single Lap Braze Joints

Single lap specimens were used to evaluate the candidate braze alloys. The pyrolytic graphite plates were prepared by striating the faying surface with 80 grit emery at 45° to the principal axis. Both pure molybdenum and tantalum alloy T-111 plates were used for the metallic members. Anchor holes of 0.035 inch diameter and 0.030 inch depth were drilled in the faying surface of the pyrolytic graphite using the array described in Reference 1. Braze alloy powders were loaded at the fillet area and allowed to flow into the joint during brazing.

Twenty lap specimens were brazed with the five alloys for room temperature strength determinations. Test results are given in Table IV. Shear strengths from 50 to 180 psi were obtained for 14 specimens. The remaining 6 specimens had failed prematurely and could not be tested.

TABLE III

PROPERTIES OF CANDIDATE BRAZE ALLOYS

Alloy No.	Solidus °F	Liquidus °F	Wetting and Flow	Braze Temperature
1	2425	2460	Very Good	2560-2750
2	2475	2500	Very Good	2600-2800
3	2480	2535	Good	2625-2800
4	2490	2550	Good	2650-2800
5	2610	2630	Fair	2700-2850
Ti-13V-11Cr-3Al	2760	2800	Excellent	2850-2900

TABLE IV

SINGLE LAP JOINT STRENGTHS FOR P.G. METAL BRAZEMENTS AT ROOM TEMPERATURE

Specimen	Br Alloy	Base Metal	Braze Temp.	psi Shear	Remarks
1	No. 2	Mo .020"	2800	0	Delamination
2	2	Mo "	2700	0	"
3	5	Mo "	2750	20	Pre-tinned
4	5	Mo "	2800	0	Broke handling
5	5	Mo "	2750	50	
6	2	Mo "	2800	50	
7	2	Mo "	2700	60	
8	3	T111 .012"	2750	80	Pre-tinned
10	5	T111 "	2750	120	
11	3	Mo. .020"	2750	180	
12	4	Mo "	2800	60	
14	5	Mo "	2750	100	
15	3	Mo "	2750	0	
16	2	Mo "	2750	0	
17	beta Ti	Mo "	3000	50	
20	beta Ti	T111 .012"	2900	150	
22	2	T111 "	2800	0	Delamination
26	3	T111 "	2800	125	
27	2	T111 "	2750	125	
28	3	T111 "	2750	110	

Analysis of 20 specimens disclosed that all had been poorly anchored. Data from plate braze tests (Ref. 1) disclosed that inadequate anchoring impaired joint strength. At this time a study was made of methods whereby maximum filling of anchor holes could be achieved. Although four different methods to improve anchoring were studied, no satisfactory solution was found. A summary of results is presented in Table V. None of the methods tested presented significant improvement. Because the capillary powder load (No. 3) did indicate slightly better results over the standard braze procedure, the remaining plate samples were brazed using this method.

Table VI presents data for brazed joints between pyrolytic graphite plates and 0.012 inch 90Ta-10W alloy using braze procedure No. 3 (Table V). Seventy-five specimens were made to evaluate strength at room and elevated temperatures. Several premature failures occurred and only in the case of four specimens was the shear strength above the target of 200 psi. Analysis of the tested coupons indicated there were 2 conditions possibly contributing to the low values:

- High residual stress at the joint caused by mismatch differential
- Additional joint stress from non-uniform loading during testing

No studies were made at the time to minimize residual stress at the joint. However, a check was made on possible non-uniform loading by testing additional single lap specimens in tension. The results listed in Table VI under Tension Shear Strength at Room Temperature show an increase in joint strength for alloys 2, 3 and 4, but little effect for beta titanium.

The elevated temperature tensile test results presented in Table VI were obtained from single lap specimens brazed with alloys 2, 3, 4, and 5. A typical arrangement for testing is shown in Figure 3. The tensile shear strengths at 2500° F were lower than the room temperature strengths but still below the 200 psi target. It is interesting to note that the alloys 2, 3 and 4 which had solidus temperatures a little below 2500° F (see Table III) retained fair strengths at 2500° F, confirming that some interaction was occurring. However, a decision was made at this time to drop alloy 5 from the program. It had been retained in spite of poor wetting and flow because it had the highest solidus temperature of all of the silicon-containing alloys (2610° F).

TABLE V

EVALUATION OF METHODS TO INCREASE ANCHORING

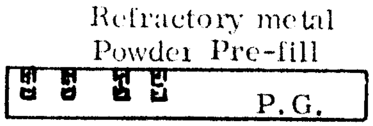
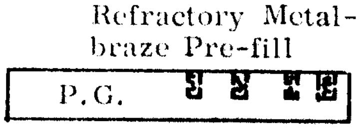
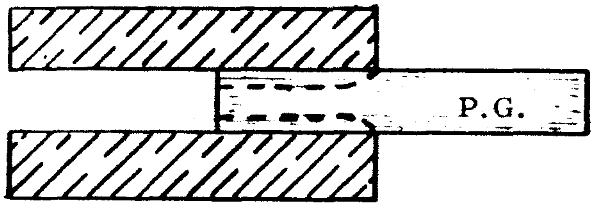
	APPROACH	DESIGN	RESULTS
1	Bevel edge of P.G. to minimize fillet size		Effective anchoring = 40% Shear strength 180 psi without premature failures.
2.	Pre-tinning of P.G. faying surface with titanium approx. 0.0025 inches thick.		Effective anchoring = 35%.
3.	Pre-fill of anchor holes with refractory metal powder 80-100 mesh (Mo, Cr, W).		Effective anchoring = 55%
4.	Pre-fill of anchor holes with 50/50 mixture of braze powder and refractory metal powder.		Effective anchoring = 25%

TABLE VI

JOINT STRENGTHS OF P.G. - TANTALUM BRAZEMENTS

Test Number	BRAZE ALLOY				
	#2	#3	#4	#5	Beta - Ti
	Compressive shear strength at mm temperature, psi (single lap)				
1	125	145	100	—	120
2	110	110	130	—	130
3	154	125	140	—	150
4	190	125	150	—	320
5	—	—	180	—	—
Average	145	126	140	—	180
	Tension shear strength at room temperature, psi (single lap)				
1	280	264	200	—	135
2	—	—	—	—	150
	Tension shear strength at 2500° F, psi (single lap)				
1	139	84	146	90	—
2	171	142	168	125 (2550° F)	—
3	—	—	—	190 (2000° F)	—
	Tension shear strength at 2500° F, psi (double lap)				
1	20	97	107	—	75
2	51	—	36	—	—
3	—	—	81	—	—

Double lap specimens were made with the pyrolytic graphite between two tantalum alloy coupons. Joint strengths (Table VI) were very poor. This is believed to be due to the inability of the joint to relieve stress by bowing so that damage to the pyrolytic graphite may have occurred on cooling. Figure 4 shows how the stress condition is affected by the joint design.



Dotted lines show probable stress patterns

Fig. 4. Stress in Double Lap Brazement

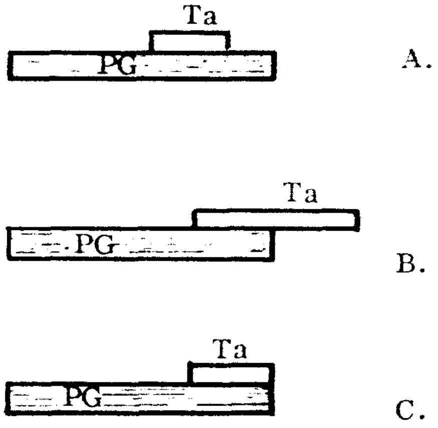


Fig. 5. Modified Single Lap Joints

2.2.3 Modified Lap Joint Specimens

A study was made of various joint configurations to develop reproducible and accurate test results. A single lap type joint was preferred since it is readily adapted for room and elevated temperature testing. Three modified single lap type joints are shown in Figure 5 and were evaluated using beta titanium braze alloy. Test results are shown in Table VII.

These strengths were considerably above the previous strengths although the tantalum alloy was 0.060 inch thick and markedly reduced the bowing possible to relieve differential expansion strains. Joint design B came closest to the design of the original single lap joints, and exhibited by far the lowest strengths. Another factor that may be important is that the strongest joints are obtained with designs A and C where the edge grain of the pyrolytic graphite is not exposed to the braze alloy.

TABLE VII

EVALUATION OF MODIFIED LAP JOINTS

.06 PG - .060" 90Ta-10W Braze Alloy - Ti

Compressive Shear Loading at R.T.

Spec. No.	Cycles to 2500°F	Shear Stress
	Joint Design "A"	
629A	0	733
520B	5	686
	Joint Design "B"	
618B	0	468
618C	5	256
	Joint Design "C"	
622A	0	730
621A	5	590

Design A was used in an additional evaluation of braze alloys 2, 3, 4 and beta titanium. Room temperature strengths of joint determined in compressive shear are shown for beta titanium in Figure 6. The distribution of strength data as brazed is approximately Gaussian with an average strength of 770 psi. After 3 cycles to 2500°F the strength fell to 725 psi (single value) and to 650 psi (2 results) after five cycles. Figure 7 shows the effect of cycling on the other braze alloys compared with the line for beta titanium. Before making any decision on the elimination of braze alloys, remelt temperatures were determined under 30 lbs. load for these joints. The stress varied from 60-90 psi because of variations of area, but this could not be correlated with the stress. Temperature was raised until failure occurred leading to the results in Figure 8.

On the basis of loss of strength on cycling (Figure 7) and on the remelt temperatures (Figure 8), alloy 2 was dropped from the program. Alloys 3 and 4 in addition to beta titanium were carried forward into the next stage of evaluation on tubes.

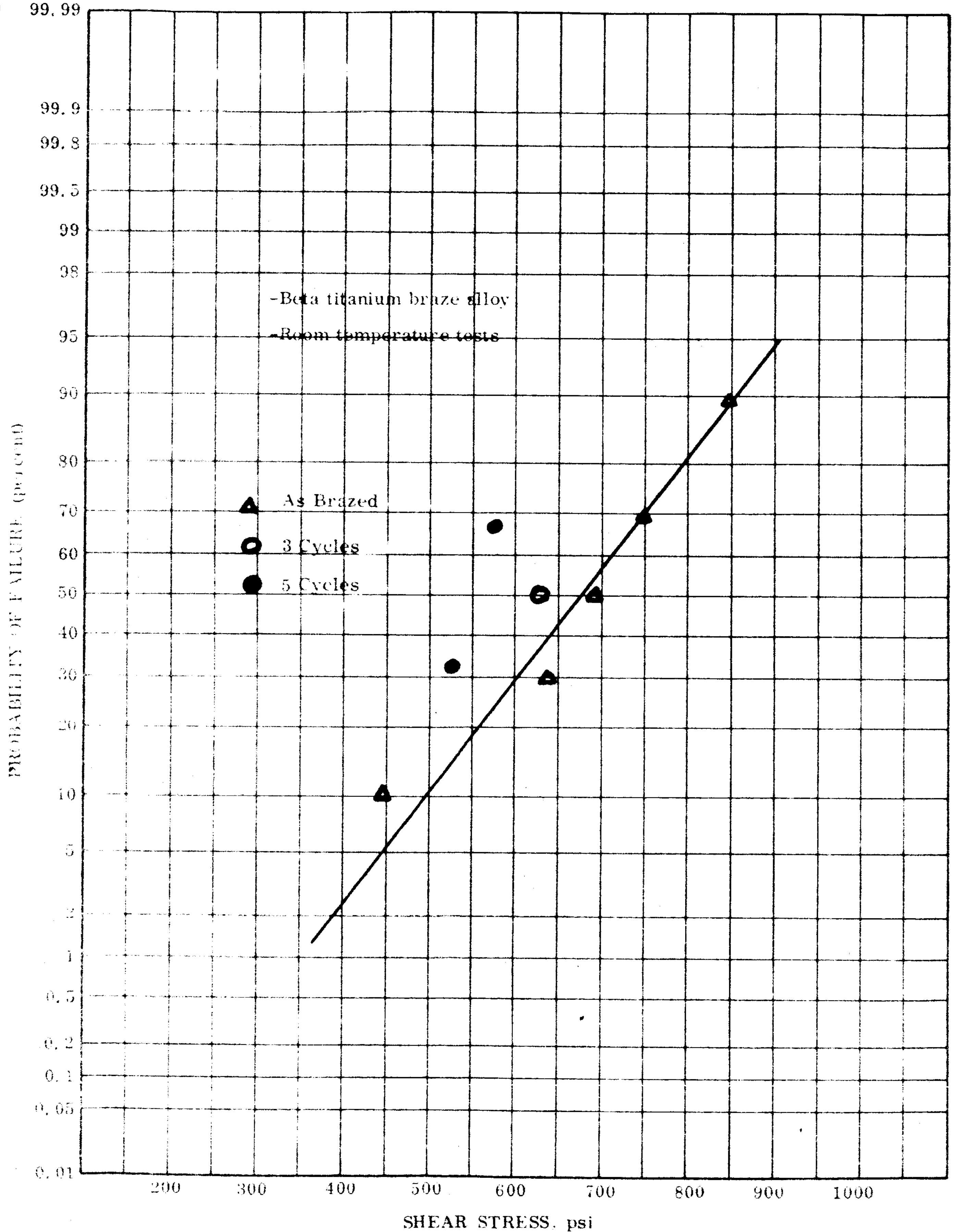
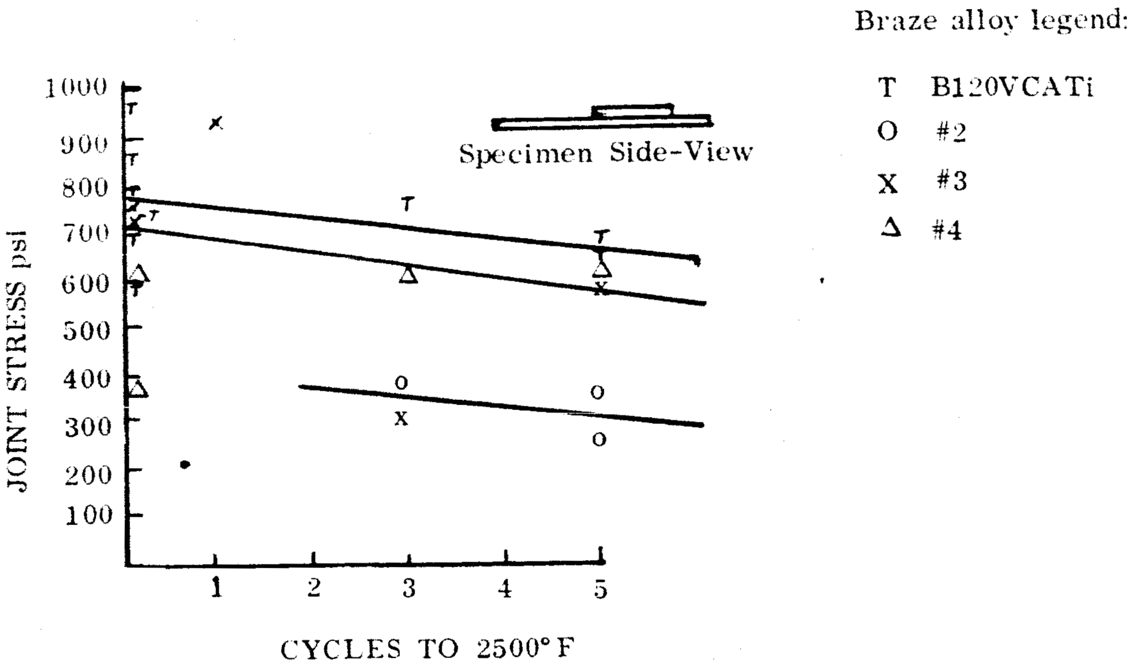


FIGURE 6. SHEAR STRENGTHS FOR PYROLYTIC GRAPHITE - TANTALUM JOINTS



- Compressive shear loading
- 0.060" 90Ta-10W
- Room temperature tests

FIGURE 7. JOINT STRENGTH AFTER THERMAL CYCLING

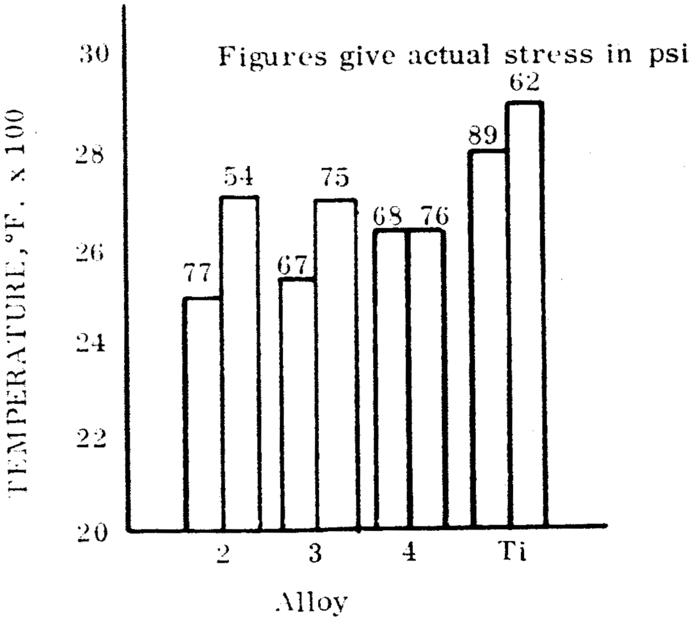


FIGURE 8. REMELT TEMPERATURES UNDER 30 POUNDS LOAD

2.3 EVALUATION OF BRAZING OF CYLINDERS

Braze alloys 3, 4 and beta-titanium were carried forward into this evaluation, conducted initially with 1.5 inch diameter pyrolytic graphite cylinders of 0.055 inch wall. Evaluation of braze alloys alone is not adequate to make a choice on the final selection. It has been shown in the evaluation of braze alloys for flat plates that joint design is, of necessity, evaluated at the same time as the braze alloy. It was found that as the joint requirements become more demanding, the joint design assumes more importance relative to the braze alloy performance.

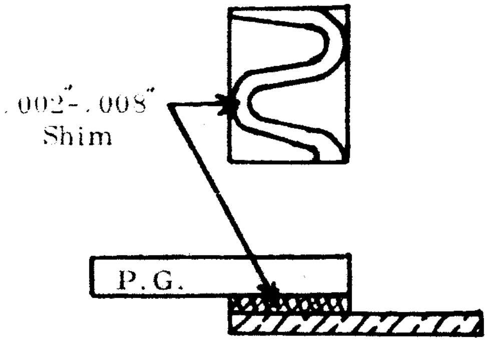
2.3.1 Joint Design

Five basic joint designs were proposed to solve the stress problem, and were included in Solar RDR 1457 dated January 6, 1965. These basic designs are shown in Figure 9 reproduced from RDR 1457, and can be described as:

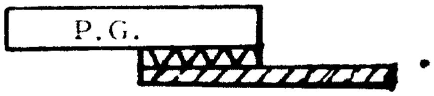
1. Spiral
2. Corrugation
3. Scarf
4. Compression
5. Segmented scarf

The basic concept requires the metal tube to be on the outside. This is because the metal will shrink on to the pyrolytic graphite, placing the wall in compression normal to the basal planes. If the positions were reversed, the graphite would be in tension normal to the basal planes, leading to failure because of the low strength in tension in this direction.

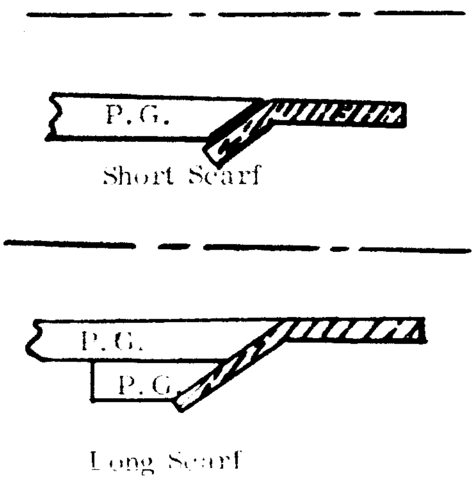
The joint between the metallic member and the pyrolytic graphite must perform two functions. One is to provide a joint able to withstand the pressure within the thrust chamber, and the second is to prevent gas leakage. This dual solution was the basis for the compression joint (type D), where leakage might be tolerated in the joint because a flexible member could be added to provide a gas seal. Type B includes a multiple seal using a flexible foil, and Type E is based on the modified values of expansion coefficient on a scarf, but might require a gas seal. The straight scarf, type C, modifies the axial expansion on the joint line, but not the circumferential. It does provide a joint to all of the basal planes in the graphite so that load transmission should be aided. The spiral type A is based



A. SPIRAL

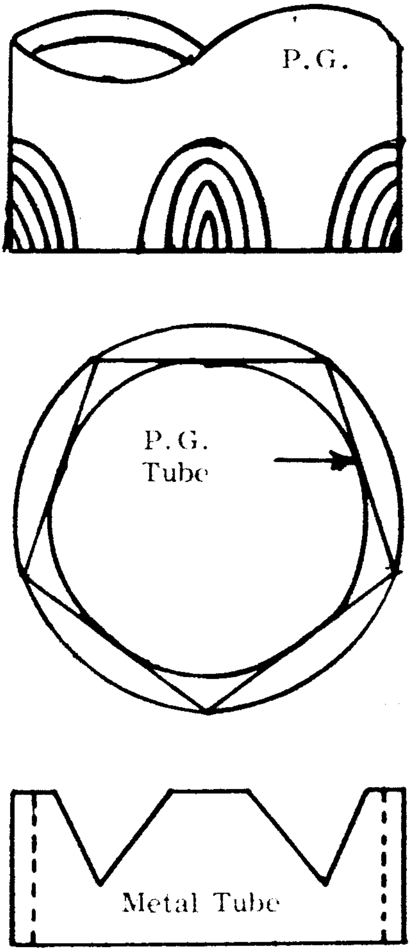


B. CORRUGATION



C. SCARF

D. COMPRESSION



E. SEGMENTED SCARF

FIGURE 9. PROPOSED BASIC JOINT DESIGNS

on some degree of flexibility in the joint, although the spiral must not be so short in the radial direction that it acts as a stiff column.

2.3.2 Evaluation of Joints

Twelve tubes were made by electron beam welding 0.023 inch Ta-10W alloy for evaluation of joint concepts and braze alloys. Additional tubes were made using 0.012 inch T111 alloy.

Joint Design A - Spiral - A tube with 0.023 inch wall was brazed to the pyrolytic graphite using a spiral of 0.005 inch 90Ta-10W alloy. The beta titanium alloy was used for brazing at 3000° F. Incomplete brazing requires a second brazing operation at 2650° F.

The joint was loaded and failed at 152 lbs at room temperature. Figure 10A shows this specimen. This load corresponds to a stress of 540 psi in the wall of the pyrolytic graphite cylinder. Examination of the joint after failure showed that it was incompletely brazed at the spiral-to-graphite interface, although a good braze was achieved at the metal-to-metal interface. Apparently the metal parts expanded together away from the graphite leaving too wide a gap to be filled completely by the braze alloy. This joint design was abandoned, therefore.

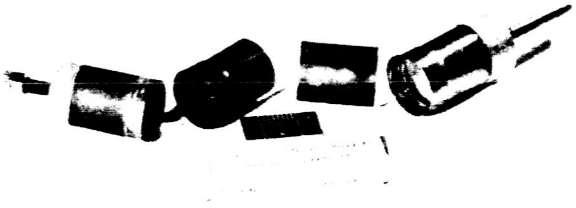
Joint Design B - Corrugation - The corrugated section was made from 0.002 inch 90Ta-10W. A 0.0015 inch foil of beta titanium was preplaced in the joint and brazed at 3000° F for one minute after a net fit-up was achieved at room temperature. The 90Ta-10W tube had a 0.023 inch wall.

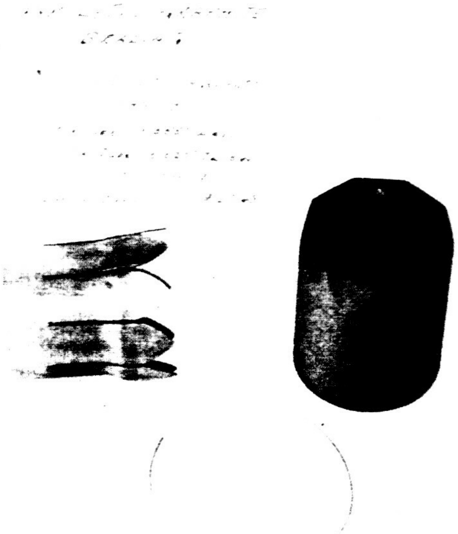
Post braze examination revealed several unjoined areas between the graphite and metal corrugation. The joint failed at 20 lbs load.

A corrugated joint brazed at 2750° F with alloy number 3 showed no improvement in completeness of braze fillet although it failed at 32 lbs load. The unit is seen in Figure 10A.

The poor braze fillets were detected on the metal-to-graphite side of the joint suggesting that expansion of the metal away from graphite was responsible. Because of the expansion disparity no ready solution to this problem could be seen and the joint design was abandoned.

A. Spiral and Corrugated Joints





B. Segmented Scarf Joint Components

C. Scarf and Compression Joints

FIGURE 10. PYROLYTIC GRAPHITE BRAZING, MODIFIED SCARF COMPONENTS BEFORE BRAZING

Joint Design E - Segmented Scarf - The segmented scarf joint is an attempt to reduce residual stress of brazed pyrolytic graphite-metal tube assemblies by reducing the mismatch in the expansion properties of both materials. This design is similar to the scarf joint except that the metal cylinder is segmented and a larger faying surface scarf angle is used.

One 1.5" diameter segmented scarf cylinder assembly was prepared using a 0.023" gage Ta-10W tube and 0.055" gage pyrolytic graphite tube, Figure 10B. Nine (9) individual scarfs were machined on the pyrolytic graphite tube-end to correspond to the segmented fingers shaped on the metal tube. Faying surfaces were closely mated prior to brazing. B120VCA-Ti braze alloy was used for brazing at 2850° F.

Post-braze inspection revealed the metal tube had expanded sufficiently to cause an increase in overlap from 0.50 inch to 0.75 inch. This condition created a loss in faying surface contact and subsequent loss of bond area. The joint was taken apart, cleaned and reassembled for rebrazing. Fixturing was made to prevent recurrence of slippage. Inspection after rebraze showed 90 to 95% braze. After several days of shelf life, the joint was found to be delaminated; unfavorable residual stress is suspected to cause this condition.

Geometry of the segmented scarf joint is such that some type of sealing is required for the open areas between the segmented fingers. An evaluation was made of an inner liner foil seal. A successful test unit was made using 0.002" gage Ta foil that was brazed to the I.D. surface of a pyrolytic graphite cylinder. Intimate contact was maintained at the faying surfaces by an inner expansion ring of pyrolytic graphite. The unit was brazed at 2890° F with B120VCA-Ti alloy.

The 1.5" diameter segmented scarf joint assembly that had delamination-failed after brazing was prepared for rebraze. The scarf angle was changed to match more closely the pyrolytic graphite-tantalum expansion. The assembly was brazed at 2900° F with B120VCA-Ti filler. Examination after braze revealed that metal tube expansion at the braze temperature had caused 50% loss of faying surface contact. Areas of close pyrolytic graphite-metal contact were well jointed. This unit failed by delamination prior to thermal cycling.

A 2.0" diameter segmented scarf assembly was prepared similar to the

1.5" diameter unit. Ten scarfs were used. The metal tube section was made from 0.012" gage T111 alloy. A 0.002" gage inner liner seal was positioned for brazing "in place" during the initial firing. Brazing was done at 2900°F using B120VCA-Ti alloy. The segmented fingers and inner lines appear to be well joined although some unbonded areas were noted in the scarf joints.

The 2-inch diameter joint was cycled to 2500°F and appeared sound after one cycle. A tensile test at 2500°F resulted in failure at 11 lbs load and revealed a considerable amount of unbonded area.

The greater success with the two-inch diameter joint is believed to be associated with the use of a more flexible metal member (0.012 inch versus 0.023 inch) and with improved tooling procedures in brazing. But the success was not great enough to warrant continued study and this joint design was abandoned.

Joint Design C - Scarf Joint - The scarf joint has the theoretical advantage that load is transmitted to the pyrolytic graphite in its strongest direction. Previous work had shown that load cannot be transferred from the surface of the pyrolytic graphite into the interior because of the weakness normal to the surface. Anchor holes to provide metallic load-transfer members to planes within the thickness of the wall were shown to be a solution to overcome this problem, but are not needed with a scarf joint. Specimens showing this design are shown in Figure 10C.

Table VIII shows some joints made with a scarf angle of approximately 35 degrees. The long scarf consisted of a double thickness wall to the pyrolytic graphite made by brazing two concentric halves of a split pyrolytic graphite tube to the outside of the 1.5 inch pyrolytic graphite tube. It was evident from this work that the joint design is poor because the braze alloy bond line is in peel, and that the residual stress condition is too high. The latter conclusion is supported by the finding that strengths were lower at room temperature than 2500°F, because the differential expansion stress increases as the temperature is decreased. No further work was performed with this design.

Joint Design D - Compression - The compression joint requires two brazements. One is the joint between the two pyrolytic graphite tubes (see Figure 11A), and the second is a joint between the metal tube and the outer pyrolytic graphite ring. The Si-2Ti alloy was identified as the best braze alloy for pyrolytic graphite to itself (Ref. 1) and was used, therefore, to make the first joint. This alloy flowed

TABLE VIII

RESULTS WITH SCARF JOINTS

	BRAZE		
Joint	Alloy	Temp. °F	Results
1.5 inch scarf	beta-Ti	2900	Excellent fillets. Broke in handling
1.5 inch scarf	beta-Ti	2900	Excellent fillets. Cycled 5 times to 2500° F Failed at 66 lbs load (235 psi)
1.5 inch scarf	beta-Ti	2900	Excellent joint. Cycled 5 times to 2500° F Failed at 15 lbs (65 psi) at 2500° F Believed the result of out-of-alignment
1.5 inch scarf	beta-Ti	2900	Good joint. Cycled to 2500° F Failed at 85 lbs (325 psi) at 2500° F
1.5 inch scarf	beta-Ti	2850	Good joint, but alignment poor Cycled 5 times to 2500° F Burst test at room temperature (100 psi)
1.5 inch long scarf	beta-Ti	2850	Joint slippage in braze
1.5 inch long scarf	beta-Ti	2850	Good bond. Cycled 2500° F but separated in cycling
1.5 inch long scarf	beta-Ti	2850	Good bond. Tested at room temperature after cycling. Failed at 40 lbs (125 psi). Incomplete bonding.
2 inch long scarf	beta-Ti	2850	Inadequate braze alloy
2 inch long scarf	beta-Ti	2850	Sound braze. Cycled 5 times. Burst test at room temperature (100 psi) Some misalignment.

at 2700° F. Six tubes were prepared with this braze alloy with braze temperatures as high as 2850° F to attempt to increase the flow temperature by additional interaction. Six 90Ta-10W tubes were brazed to these tubes as shown in Figure 11A. Braze alloy No. 4 (flowing at 2800° F); Si-2Ti; and beta-titanium were used in attempts to attach the metal tube, but no success was achieved. The main problem appeared to be remelting of the initial Si-2Ti braze when brazing the metal-to-pyrolytic graphite joint, even when Si-2Ti was used. No satisfactory joints were obtained and the approach was discontinued.

The same joint design was studied with beta-titanium for both joints. Three tubes were brazed with this alloy and results appeared to be good. One joint was successfully given the five cycles to 2500° F and cooled to room temperature. Therefore, this joint design was chosen for optimization.

2.4 OPTIMIZATION OF JOINT DESIGN

Two selections were made as a result of the work reported in Section 2.3. One was to restrict the development to beta-titanium braze alloy. The second was to optimize the compression joint (design D), Figure 9.

Beta titanium was chosen as the braze alloy for the following reasons:

- Superior remelt temperature to alloys 3 and 4
- Excellent wetting of both graphite and tantalum alloys equal to that of alloys 3 and 4
- Ease of loading because B120VCA wire was used to load instead of powder (alloys 3 and 4)
- Uniformity of braze alloy loading was achieved more readily with a wire than with powder.

Compression design D was chosen for optimization because of good performance in the initial evaluation. Although joint soundness appeared equal for design D and the scarf joint (design C), poor strength of design C was related to the intrinsically poor design where the braze alloy and joint was placed in peel. The compression design is inherently fail-safe. In the event of cracking of the braze alloy or joint, the strength of the coupling would not be reduced. Gas leakage might be a problem, but this could be prevented by an internal foil seal.

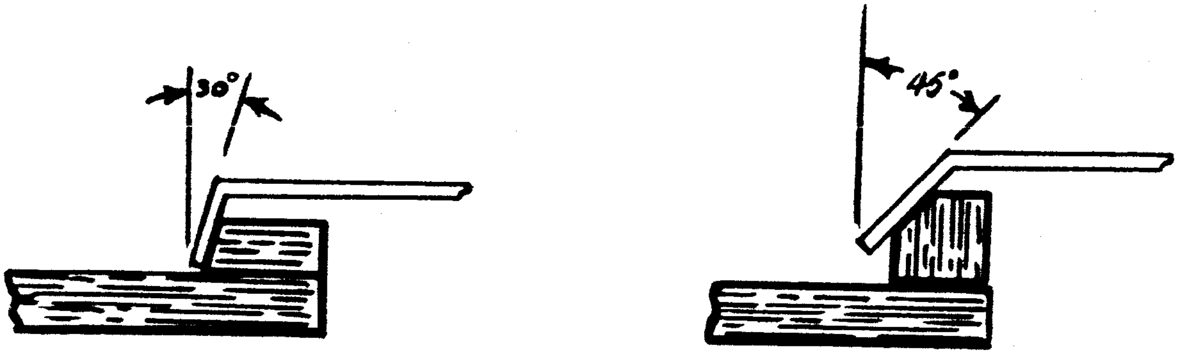
The original design D was not optimum because the outer graphite had a 0.055 inch wall leaving little overlap available for the metal-graphite joint. Hence it was redesigned to use a collar with the opposing orientation of the pyrolytic graphite. The radial expansion of a pyrolytic graphite tube is governed by the change of circumference and hence by the expansion in the ab (basal) planes, although the wall thickness may be influenced by the expansion normal to the basal planes. A collar cut from a thick plate also will have the hole radius controlled by the expansion in the a b (basal) planes. Hence the pair are compatible expansion-wise. The scarf allows an intermediate expansion value of the graphite to be selected to make expansion compatible along the scarf. But nothing can be done to change the circumferential expansions of the two members so that the metallic member will place the graphite in compression on cooldown.

Optimization was conducted both on 1.5" and 2" diameter tubes. These were brazed at 2830-2875°F using beta-titanium. The metallic tubes were fabricated from 0.023 inch wall Ta-10W alloy.

Two joints were made to determine brazing parameters, the graphite-to-graphite joint was made prior to the metal-to-graphite joint, joint design D1, Figure 11B. Another joint was brazed in the same way with a larger amount of alloy (1.3 gms) and appeared to be very satisfactory. It withstood five cycles to 2500°F and was so much stronger than any previous joint that the test rig had to be redesigned twice to permit a tensile test at 2500°F. Finally, it failed at 560 lbs at 2500°F after 7 cycles of heating and cooling. This equals a stress of 2340 psi in the wall of the graphite, and a shear stress of 320 psi on the graphite-to-graphite joint. The failure occurred in both the graphite collar and tube.

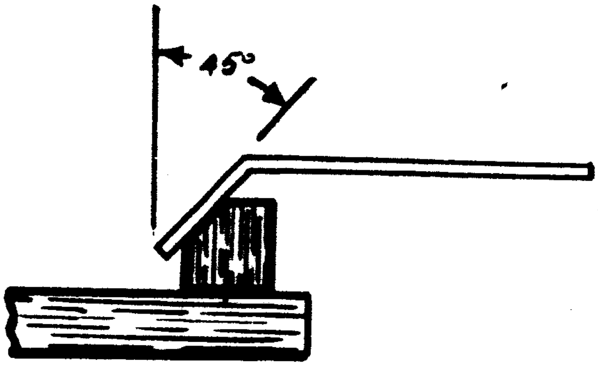
Three more joints were made to establish certain brazing parameters. In one of these the graphite collar-to-pyrolytic graphite tube joint slipped in the braze tooling, leading to damage. Three tungsten wires were inserted through the collar into the tube to avoid this problem and provide strength in braze operation. The anchor holes were used to provide shear strength in service, but could not provide support strength at the brazing temperature.

In section 2.2 it was shown that better strength between pyrolytic graphite plates was obtained when the joint was removed from the exposed end of the plate. This finding was applied to this joint leading to modification D2, Figure 11C.



A. ORIGINAL DESIGN

B. MODIFICATION D1



C. MODIFICATION D2

FIGURE 11. COMPRESSION JOINT DESIGNS

Further optimization of the joint was not possible because of fund limitations. Problems that need study include:

1. Thickness of 90Ta-10W tube
2. Scarf angle
3. Clearance between tube and graphite collar
4. Width of graphite collar
5. Width of faying surface at metal-to-graphite joint
6. Braze alloy firing cycle.

In the absence of information on these points, the design was frozen and applied to thrust chambers.

2.5 APPLICATION TO PYROLYTIC GRAPHITE THRUST CHAMBERS

The compression joint was selected for the pyrolytic graphite thrust chambers although it was recognized by Solar and JPL that optimization had not been completed. Further, it was decided that an adapter ring should be brazed to the chamber ready for electron-beam welding to the injector. There were two reasons for this; one, the injector would not be exposed to the brazing cycle and the risk of possible damage; and second, the injectors were not designed for exposure to the brazing temperature because recrystallization and enbrittlement of the molybdenum would occur and because low temperature braze alloys had been used to assemble the injector.

Chamber 2L. The modified compression design (D2 in Figure 11C) was chosen, and the final dimensions are shown in Figure 12. The clearance C was 0.030 inch for this chamber. The 90Ta-10W tubes were made from 0.023 inch sheet. Chamber 2L was brazed with beta-titanium alloy at 2875° F using a shaped graphite susceptor to localize heating at the joint. The pyrolytic graphite collar was pinned to the chamber by three tungsten wires as shown in Figure 13. All joints appeared excellent after brazing, but a circumferential crack was noted at position (A) Figure 14 (arrow).

Chamber 1L. Clearance distance C was increased to 0.050 inches and approximately 30% less braze alloy was added. This change was made to avoid any excess braze alloy in the annular space between the pyrolytic graphite collar and the tantalum alloy tube. It was reasoned that filling of this gap increases the compressive stresses on the pyrolytic graphite chamber by reducing the flexibility

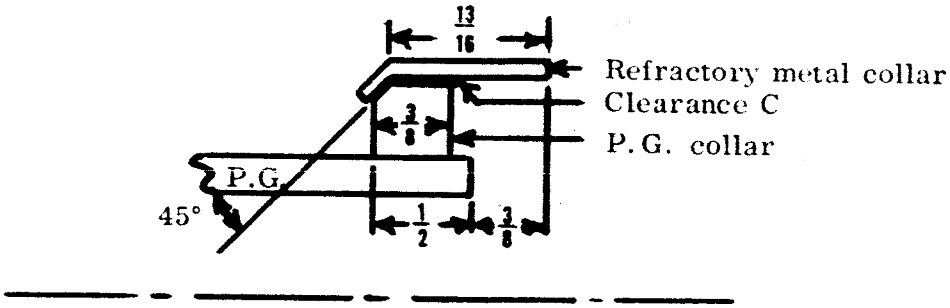


FIGURE 12. DESIGN OF ADAPTOR RING

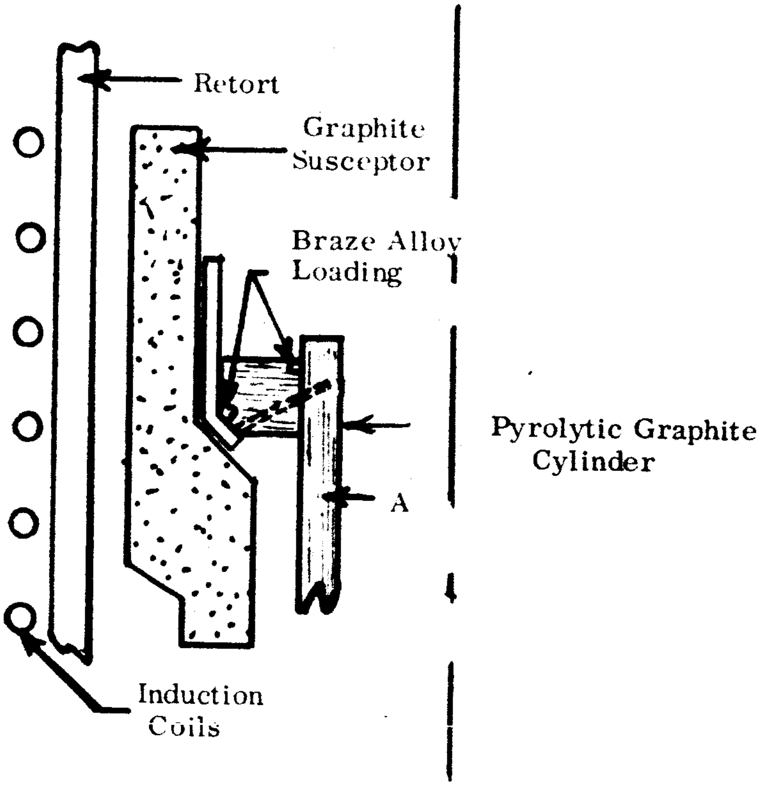


FIGURE 13. SET-UP FOR BRAZING CHAMBER 2L

FIGURE 14. BRAZED THRUST CHAMBERS SHOWING STRESS CRACK

of the outer tantalum tube. An additional minor change was to position the tungsten wires perpendicular to the chamber rather than at an angle.

Brazing conditions were unchanged and good brazements were obtained. However, again a circumferential crack appeared extending along an arc of 280°, Figure 14.

It was noted that the quality of the pyrolytic graphite chambers did not seem equal to the quality of the two-inch tubes used in earlier studies. Figure 15 compares the chambers and tubes. More work was done on the two inch tubes, therefore.

Two Inch Cylinder Braze No. 1. This was brazed using the procedures developed for chamber 1L (that is, with reduced quantity of braze alloy). No circumferential crack appeared after brazing so that the difference in response to brazing between 2 inch chambers and tubes appeared to relate to the quality of the pyrolytic graphite. However, after 2 hours standing on the bench, the scarf failed by delamination. Examination revealed inadequate braze area (approximately 80% brazed), indicating that lack of braze alloy was the problem.

Two Inch Cylinder Braze No. 2. Additional braze alloy was used to rebraze the No. 1 cylinder, but the exact amount of braze alloy could not be measured accurately because of the removal of old braze alloy in assembling this unit for rebrazing. This unit formed a circumferential crack after a shelf life of 24 hours.

One and One-half Inch Cylinder Braze No. 3. In an attempt to spread the compression stress, this unit was designed to have a net fit between the titanium and the pyrolytic graphite collar. Figure 16A and 16B are attempts to show the reduction in localized stress by filling the gap with braze alloy along the length of the pyrolytic graphite collar. Figure 16C shows the reduction in peak stress anticipated without a bridging fillet across the gap. The brazed joint showed no cracking or buckling.

Rebraze of Chamber 1L. The original braze was cut off and a new adapter was brazed. The pyrolytic graphite collar was machined to leave a gap of 0.010 to 0.015 inch, but additional alloy was added to fill the gap. The gap was not filled completely with braze alloy. Buckling of the pyrolytic graphite chamber occurred with this procedure, Figure 17.

RE-ORDER No. 66-188

FIGURE 15. COMPARISON OF PYROLYTIC GRAPHITE CHAMBER AND TUBE SURFACES

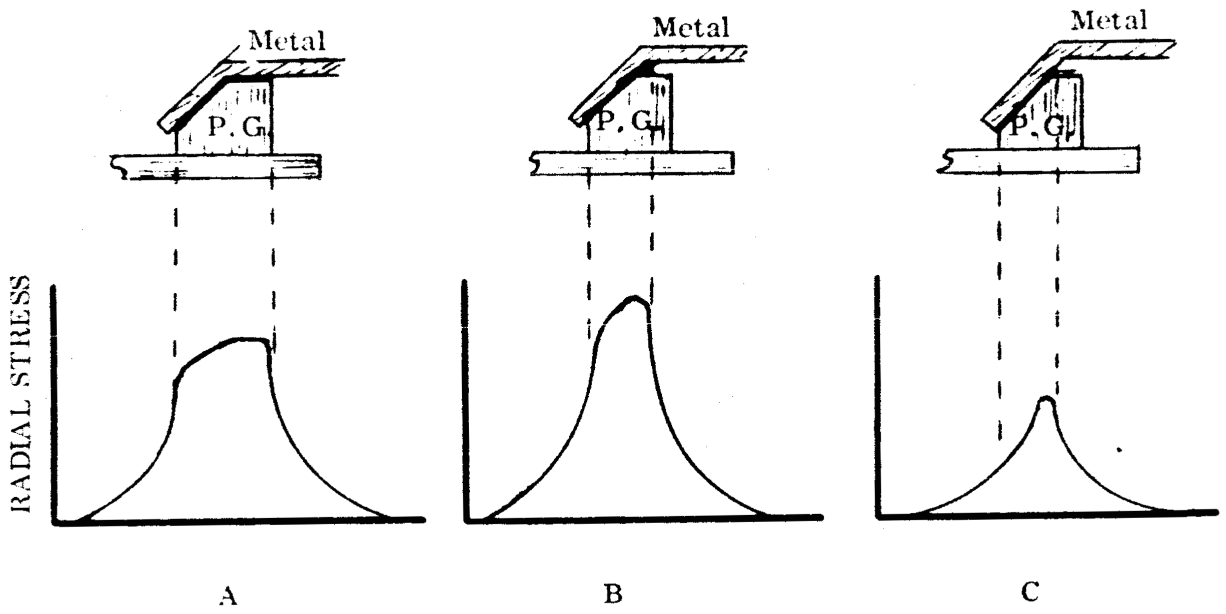


FIGURE 16. SCHEMATIC STRESS PATTERN

Second Rebraze of Chamber 1L. The rebraze was removed and another brazement made. Details of this assemblage were:

Clearance C:	0.050 inch
Tungsten pins:	3 at 120° normal to chamber
Tantalum alloy:	0.012 inch T111.

Similar to #1 cylinder braze mentioned above, this brazement also delaminated several hours after brazing. Inspection revealed a continuous joint for approximately 320° indicating insufficient alloy for complete joining. This unit was not rebrazed.

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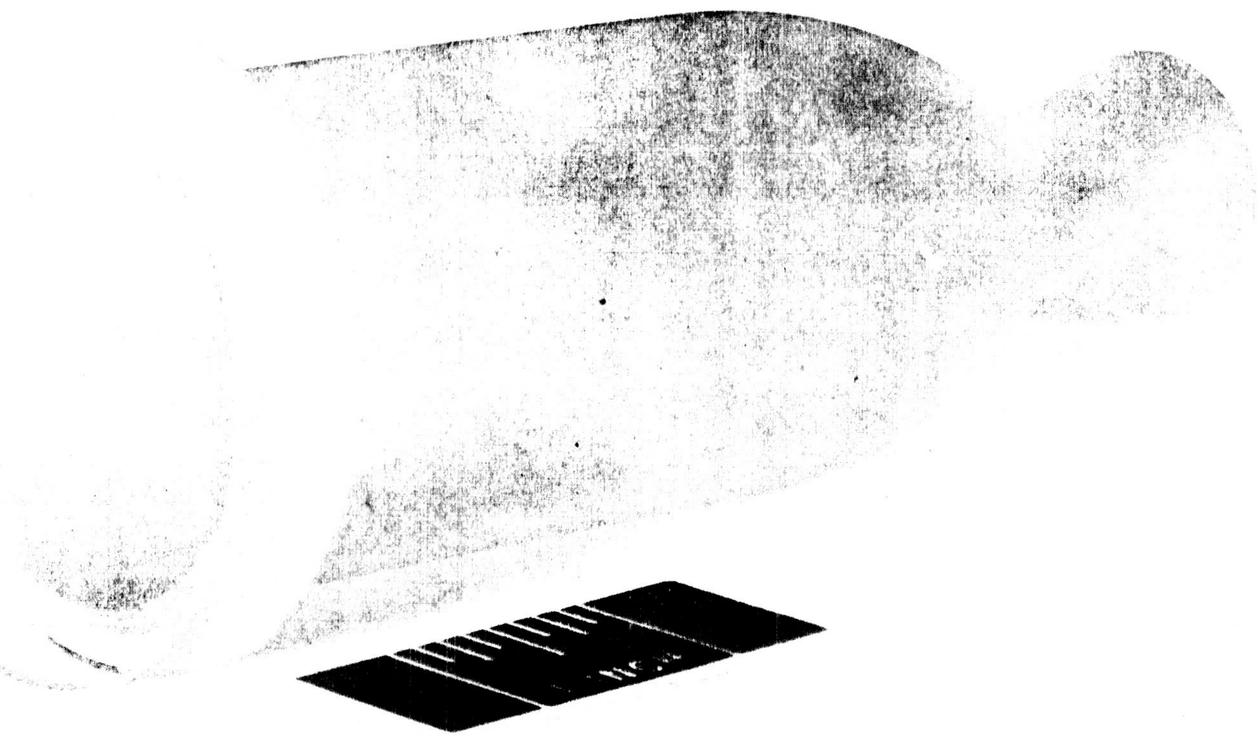

FIGURE 17. THRUST CHAMBER - TANTALUM COLLAR BRAZEMENT SHOWING BUCKLING

III RECOMMENDATIONS FOR FUTURE WORK

Optimization of the compression joint based on design D2 must be made to balance the critical factors of residual stress and joint strength. Factors to be studied must include:

- Thickness of tantalum alloy tube
- Clearance between tantalum tube and pyrolytic graphite collar
- Scarf angle
- Length of scarf
- Width of graphite collar
- Braze alloy firing cycle
- Heat treatment to decrease stress by decreasing zero stress temperature.