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SOLID PHASE WELDING OF TRANSITION MEMBERS FOR RADIOISOTOPE THERMOELECTRIC GENERATORS

J.L. Jellison

MASTER

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Atomic Energy
Commission under Contract AT (29-1)-789

September 1975

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ABSTRACT

This investigation has demonstrated the feasibility of fabricating heat source-thermopile assemblies for radio-isotope thermoelectric generators (RTG) by diffusion bonding techniques. The Au-Ni, Au-Cu, Au-Ag, and Au-Au systems were evaluated. With the 14 MN/m^2 (2000 psi) and 823°K (550°C) limitations imposed on the bonding process so as not to damage the thermopile, bonds of acceptable strengths were only obtained with the Au-Ni and Au-Cu systems. The Au-Ni system was selected for the transition members at the ends of the thermopile, because the Au-Cu system was not compatible for extended times at operating temperatures 673°K ($\sim 400^\circ\text{C}$).

Several solid-liquid interdiffusion (SLID) bonds were made using var-

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ious combinations of gold or silver with germanium, indium, and tin-indium. Although SLID bonds could be made at low pressures ($\sim 3.5 \text{ MN/m}^2$ or 500 psi), the resulting strengths were marginal at 723°K (450°C) for the RTG application.

Procedures and tooling for fabrication of heat source-thermopile assemblies were developed, and two complete RTG assemblies were made by diffusion bonding. One of the assemblies was subjected to system shock and vibration tests and both thermopile and diffusion bonds survived without damage.

ACKNOWLEDGMENTS

W. B. Vine and R. W. Fisher, both SLA Division 5833, conducted most of the parameter diffusion bonding studies. W. B. Vine was assisted by C. Drew (formerly of Division 5833) in bonding experiments involving thermopile and RTG assemblies.

SEM fractographs are the work of C. J. Miglione (formerly of Division 5822). Electron microprobe analyses were performed by G. E. McCorkle (formerly of Division 5822). M. R. Gutierrez, Division 5833, prepared metallographic specimens of bond pairs.

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SOLID PHASE WELDING OF TRANSITION MEMBERS FOR RADIO-ISOTOPE THERMOELECTRIC GENERATORS

INTRODUCTION

A heat conducting transition member is required between the MC 2730 heat source and the thermopile. At the time this study was conducted, solid phase welding was considered as the prime method of fabrication. A pictorial illustration of a diffusion bonded radio-isotopic thermoelectric generator (RTG) assembly is shown in Figure 1. The RTG assembly has been described elsewhere.⁽¹⁾ Due to difficulties in eliminating shorts resulting from pin holes in the insulating glass film over the interconnecting pattern on the thermopile, a mechanical, spring-loaded design was finally selected, rather than the welded transition assembly. The feasibility of joining the heat source to the thermopile by solid phase welding was demonstrated and the results of this study may be of interest for use in future radio-isotope thermoelectric generators. The selection of materials for the thermopile was based on a consideration of the required mechanical and physical properties, together with choice of metal bond pairs on the basis of bondability and material compatibility for extended times (up to ten years) at temperatures in the 623 to 873°K range (350-600°C).

The transition members must provide three functions:

1. Conduct heat to the thermopile,
2. Mechanically support the heat source, and
3. Relieve stresses due to differences in the coefficients of thermal expansion between the heat source and the thermopile so as to prevent damage to the glass-to-metal transition on the hot-side of the thermopile.

FIGURE 1
Pictorial Illustration of Diffusion Bonded RTG Assembly

Objectives

1. Establish bonding parameters for assembly of transition members.
2. Establish bonding parameters for attachment to the pre-assembled transition members to the thermopile and heat source.
3. Develop procedures and tooling for fabrication of heat source-thermopile assemblies.

EXPERIMENTAL PROCEDURES

Welding Parameter Studies

A Gleeble Model 510 thermal-mechanical testing machine was used to study solid phase welding parameters. With the Gleeble, temperature and load can both be programmed as a function of time. Also, both compressive and tensile loads can be programmed in the same test sequence, which permits tensile testing of a bond pair following solid phase welding. Except for a limited number of samples which were saved for metallographic evaluation, test specimens were programmed for tensile testing at 723°K (450°C). Unless otherwise noted, specimens were welded in vacuum, $\sim 13\text{mPa}$. This vacuum was obtained with a turbo-molecular pump.

A typical Gleeble specimen assembly is shown in Figure 2. The bond pairs were formed by sandwiching the sheets of other metals (gold, silver, copper) between two 12.7mm diameter rods of nickel (Nickel 200). The bonds obtained with the Gleeble are believed to be somewhat less than optimum because of imprecision in specimen alignment and a pressure hill effect characteristic of compression specimens unrestrained at the circumference which sometimes resulted in an unbonded region near specimen edges. The alignment problem was minimized by use of an improved specimen design which is illustrated in Figure 3. The ends of the rods to which the load was

FIGURE 2

Gleeble Test Specimen Used in Early Series of Tests

FIGURE 3
Modified Gleeble Test Specimen Used in Majority
Test to Improve Specimen Alignment

applied were rounded so as to promote self-alignment of the flat faying surfaces at the opposite end. The ends of the nickel rods were ground to a surface finish of $.4\mu\text{m}$ (16 microinches). Surfaces of the sheets of the other materials were either as-rolled or ground to $.4\mu\text{m}$ (16 microinches). Immediately prior to welding, all parts were processed through a four-step ultrasonic cleaning treatment, which is outlined in Table I.⁽²⁾ Some of the gold sheets received special cleaning treatments which are described later.

In a Gleeble test, the specimen is resistance heated by passing a current through the specimen itself. For these studies, the temperature was monitored and controlled by a 0.25mm diameter chromel-alumel thermocouple. The thermocouple junction was located 0.3 to 0.6mm from the bond interface.

Welding of RTG Assemblies

Because of the complexity, and the fact that they contained non-metallic materials, RTG assemblies could not be welded in the Gleeble testing machine. Therefore, a special diffusion welding system was constructed for use in the assembly of dummy RTG units.

The closed-end stainless steel tube of the vacuum system shown in Figure 4 was inserted in a tube furnace. The location of the assembly to be welded is indicated in Figure 5a. Pressure was applied by dead-weight loading the upper end of the central rod, which passed through a metal bellows seal. The base of the assembly was supported by the plate at the end of the outer three rods. The fixturing used in joining the heat source to the transition member and the thermocouple to the transition members is shown in Figures 5b and 6. A total of five welds were made in one operation. In Figure 6, the individual parts to be welded are laid in order alongside the fixturing which aligned them during welding. The upper punch and lower support (ident-

TABLE 1

Four-step Ultrasonic Cleaning Treatment*

Step 1

Ultrasonically clean for two minutes in trichlorethylene.
Blow dry with dry nitrogen.

Step 2

Ultrasonically clean for two minutes in detergent solution:

80 vol% isopropyl alcohol
20 vol% distilled water
0.2 vol% Renex 690 (wetting agent)
0.005 vol% Span 80 (detergent)

Shake off excess.

Step 3

Ultrasonically clean for two minutes in distilled water.
Blow dry with dry nitrogen.

Step 4

Ultrasonically clean for two minutes in isopropyl alcohol.
Blow dry with dry nitrogen.

*Adapted from SC-M-70-303, "A Survey of Contamination," prepared by Spectroscopy Division 5525, March 1971.

FIGURE 4
Vacuum System Used in Diffusion Welding of RTG Assemblies

FIGURE 5a

Complete Assembly and Fixturing Ready for Joining
Thermopile to Heat Source (overall view)

FIGURE 5b

Complete Assembly and Fixturing Ready for Joining
Heat Source to Thermopile (detail of welding assembly)

FIGURE 6
Assembly and Fixturing Used in Welding
Heat Source to Thermopile

ified in Figure 6) both had 6.35mm diameter hemispherical surfaces which, when assembled, were supported by mating hemispherical sockets located at the end of the load-application rod and the lower support plate (see Figures 5a and 5b). Application of the load through the hemispherical bearing surfaces was effective in promoting self-alignment of the assemblies to be welded.

Figure 7 is a photograph of the fixturing used in welding the cold-side transition member to the copper pedestal of the flexible support. A previously welded heat source-thermopile assembly is shown lying in one-half of the split die. The flexible support shown, including pedestal and ring, had also been assembled by diffusion welding. These parts are also shown in Figure 8. Figure 9 shows the assembly with the outer split die closed and ready for insertion in the welding chamber.

Two thermocouples were welded to the outside die wall of each assembly: one for controlling the temperature of the chamber, and the other for producing a temperature-time chart record of each welding run. The RTG assemblies were welded in a vacuum of $\sim 6\text{mP}$ obtained by means of a liquid nitrogen cold-trapped diffusion pump.

EXPERIMENTAL RESULTS

Parametric Studies

On the basis of the materials which were to be used in the transition members, the Au-Ni system was selected as the prime system for diffusion bonding. However, Au-Ag and Au-Cu bond pairs were also investigated since they had the potential of reducing the pressures and temperatures required during bonding to the thermopile. In addition, diffusion brazing techniques (also termed solid liquid interdiffusion) were evaluated using various com-

FIGURE 7
Parts and Fixturing Used in Joining
Flexible Support to Thermopile

FIGURE 8
Flexible Support and Pedestal

FIGURE 9
Complete Assembly and Fixturing Ready for
Joining Flexible Support to Thermopile

binations of tin, indium and germanium with gold or silver.

It should be recognized that the parameters for bonding the transition members to the thermopile are restricted by the properties of the thermopile and the thermopile tungsten interconnects. The glass used in construction of the thermopile softens and degradation of the tungsten contacts becomes severe at temperatures above about 650°C. Consequently, the bonding studies were restricted to temperatures below 600°C. The maximum permissible pressure was not well established, but was somewhat arbitrarily set at 14MN/m² (2000 psi), although a number of experiments involved higher pressures. There was some concern that even 14MN/m² (2000 psi) was excessive for the tungsten interconnect pattern. Consequently, bonding studies were extended to pressures as low as 3.5MN/m² (500 psi). Low pressures were the primary impetus for the diffusion brazing studies.

Au-Ni

The results of the Au-Ni bonding studies are summarized in Figures 10 and 11. The data for each individual test are given in Table 2. These studies employed wrought gold and nickel and were conducted in vacuum. On the basis of these studies, the maximum permissible bonding parameters (14MN/m² or 2000 psi at 550°C) were selected for bonding the transition members with the Au-Ni system. The average strength (load divided by total cross-sectional area) of 61MN/m² (8750 psi) obtained for bonds made at these parameters was considerable below the maximum achievable for the Au-Ni system (~105MN/m² or 15,000 psi). However, as seen in Figure 10, for a bonding temperature of 550°C, a bonding pressure of 14MN/m² (2000 psi) is in the range where the slope of the strength versus bonding pressure curve is beginning to decrease. Consequently, further increases in bonding pressure of several thousand

FIGURE 10

Influence of Bonding Pressure on Diffusion Bonding of Au-Ni

FIGURE 11

Influence of Bonding Temperature on Diffusion Bonding of Au-Ni

TABLE 2

Results of Gold-Nickel Diffusion Bonding Studies						
Sample No.	Type of Material*		Bonding Parameters			Tensile
	Gold	Nickel	Temp. °C	Pressure psi	Time hrs.	Strength psi
1	RW	GW	480	10,000	2	17,500
3	RW	GW	560	5,250	1	13,500
4	RW	GW	570	1,500	2	6,500
5	RW	GW	455	1,750	2	3,000
11	RW	GW	570	2,500	2	15,500
12	RW	GW	510	2,000	2	10,000
13	RW	GW	455	2,000	2	6,750
14	RW	GW	565	1,750	2	10,750
15	RW	GW	490	1,750	2	8,250
16	RW	GW	450	1,500	2	2,750
17	RW	GW	500	2,000	5	8,250
18	RW	GW	545	1,750	5	13,250
39	PE	GW	570	3,000	5	1,750
45	RW	PE	560	5,750	2	15,250
72	RW	GW	570	3,000	2	7,750
73	RW	GW	500	2,500	2	2,500
74	RW	GW	560	3,500	2	9,500
75	RW	GW	560	2,250	2	5,750
76	RW	GW	560	2,250	2	8,250
77	RW	GW	570	2,250	2	6,750
78	RW	GW	565	2,750	2	10,500
79	RW	GW	510	3,500	2	9,500
80	RW	GW	565	4,500	2	9,000
81	RW	GW	550	2,250	5	10,500
82	RW	GW	560	5,500	2	9,500
83	RW	GW	570	2,500	5	9,000
85	RW	GW	470	4,500	2	4,250
86	RW	GW	505	5,500	2	7,000
87	PE	GW	560	2,500	5	2,750
88	PV	GW	560	2,750	5	2,250
89	RW	GW	570	2,750	5	9,000
90	RW	MW	570	3,000	5	9,000
91	RW	PE	570	2,750	5	10,000
92	PE	PE	560	2,750	5	1,250
94	PE	GW	570	2,250	5	>2,500
99	PE	GW	570	2,500	5	2,500
104	RW	GW	505	10,000	2	12,500
105	RW	GW	460	10,000	2	7,750
107	RW	GW	510	5,000	2	8,250
108	RW	GW	580	5,750	2	15,500
109	RW	GW	465	3,200	2	5,250

Table 2 Continued.....

<u>Sample No.</u>	<u>Type of Material*</u>		<u>Bonding Parameters</u>			<u>Tensile</u>
	<u>Gold</u>	<u>Nickel</u>	<u>Temp. °C</u>	<u>Pressure</u> <u>psi</u>	<u>Time</u> <u>hrs.</u>	<u>Strength</u> <u>psi</u>
110	RW	GW	510	3,250	2	6,000
111	RW	GW	560	3,250	2	9,500
112	RW	GW	510	2,200	2	6,750
113	RW	GW	570	2,300	2	9,750
114	RW	GW	570	1,200	2	7,250
124	RW	GW	550	10,250	2	15,000
125	RW	GW	550	1,000	2	3,250
126	RW	GW	550	1,500	2	7,500
127	RW	GW	550	2,125	2	8,250
128	RW	GW	550	3,050	2	10,500
129	RW	GW	550	4,950	2	10,500
130	RW	GW	525	1,500	2	5,250
131	RW	GW	520	2,000	2	7,250
132	RW	GW	525	3,000	2	7,500
134	RW	GW	525	5,075	2	12,000
135	RW	GW	550	2,000	2	8,750
136	RW	GW	550	2,000	2	9,750
137	RW	GW	545	2,000	2	7,000
138	RW	GW	550	2,000	2	7,000
139	RW	GW	550	2,000	5	8,750
140	RW	GW	550	2,125	5	10,250
141	RW	GW	550	2,000	5	7,000
142	RW	GW	550	2,000	5	9,250
143	RW	GW	550	1,500	5	5,750
144	RW	GW	550	1,500	5	8,750
145	RW	GW	550	1,500	5	5,500
146	RW	GW	550	1,500	5	8,000
147	RW	GW	550	1,500	5	8,250
150	RW	GW	500	4,000	2	10,250
151	RW	GW	500	3,000	2	6,000
154	RW	GW	500	5,500	2	9,750
155	RW	GW	500	5,500	2	9,750
156	RW	GW	500	3,000	2	8,750
157	RW	GW	500	4,000	2	9,125
158	RW	GW	450	5,500	2	8,300

*Surface condition and type of material designated by two letter code as follows:

<u>Surface Finish</u>	<u>Type of Material</u>
As-rolled - R	W - wrought
As-plated - P	E - electroplated
Ground - G	V - vapor deposited
Machined - M	

for example: RW indicates as-rolled wrought material

pounds per square inch only result in modest increases in bond strength.

Only wrought gold and nickel were used in the Au-Ni parametric study, whereas electroplated gold and nickel were considered for the RTG transition members. Therefore, additional Gleeble experiments were conducted to determine the bondability of gold platings (baths Sel-Rex BDT 200 and Temperex HD, and nickel plated tungsten at 14MN/m^2 (2000 psi) and 550°C).

Bonds to nickel plated tungsten were comparable to those to wrought nickel rods. The strength of Au-Ni bonds was found to be much less, however, when gold plating (0.12mm or 0.010 inches) was used ($7 - 17.5\text{MN/m}^2$ at 450°C vs $> 49\text{MN/m}^2$ or 1000 - 2500 psi at 450°C vs > 7000 psi). Also, fracture in the plated specimens tended to follow near the Au-Ni interface, whereas fracture generally occurred within the gold sheet in the case of wrought Au-Ni bond pairs. A SEM fractograph of a gold plated specimen is shown in Figure 12. Although the dominant failure mode is ductile rupture, the cellular structure of the plating is seen distinctly. Why the bonds to plated gold are weak is not understood, but may be related to impurities. As-deposited gold from the BDT-200 bath was found to 99.87% pure. The principal impurity in BDT-200 is arsenic. Concentrations of arsenic were identified on the fracture surface of a BDT-200 diffusion bonded sample by the electron microprobe. The Temperex HD bath is purer (99.99% gold) than BDT-200 regarding metallic impurities, but contains organic impurities. The as-plated deposit from the HD bath is characteristically more stress free than that from BDT-200 plating ($14 - 17.5\text{MN/m}^2$ vs $17 - 14\text{MN/m}^2$ or 2000 - 2500 psi vs 1000 - 2000 psi) and much weaker than bonds to wrought gold. The role of organic impurities in the diffusion bonding of plated gold to nickel is not known.

DB 87

3000

FIGURE 12

SEM Fractograph of Failure Within Gold
Plating of Au-Ni Diffusion Bond
(BDT-200 electroplate)

Diffusion Bonding Parameters:

temperature - 560°C
pressure - 17.5MN/m² (2500 psi)
time - 5 hours

Au-Cu

Bonding with the Au-Cu system was accomplished at lower temperatures and pressures than with Au-Ni. Good bonds ($\sim 70\text{MN/m}^2$ or 10,000 psi tensile strength or greater) were obtained at pressures as low as 3.6MN/m^2 (545 psi at 550°C) and temperatures as low as 400°C (19MN/m^2 or 2200 psi). Table 3 gives the bond strength of the individual Au-Cu tests. The dependence of bond strength on bonding temperature is shown in Figure 13. Over the temperature range of 400 to 550°C , a slightly inverse dependence on bond strength on bonding temperature was observed, suggesting that higher temperature weakened bonds by formation of Kirkendall porosity or segregation of impurities. Bonds made at 300°C (32 and 35MN/m^2 or 4500 and 5000 psi) were much weaker than those made at 400°C or above; therefore, we conclude that, for the conditions employed, a bonding temperature of $\sim 400^\circ\text{C}$ is nearly optimum for the Au-Cu system.

Specimens made by bonding gold sheet (0.25mm or 0.10 inches) between copper rods were observed to fail by ductile rupture (see Figure 14). However, two specimens made by plating $18\mu\text{m}$ of copper on gold exhibited intergranular fracture (see Figure 15). On the basis of metallographic evaluation and electron microprobe analysis, the fracture appears to follow a line of voids and sulfur-rich segregates near the center of the copper electroplate. The voids can be observed in the photomicrograph shown in Figure 16. A slight amount of porosity was also observed in the vicinity of the diffusion zone of wrought Au-Cu specimens. The porosity may be the result of a Kirkendall diffusion affect. As discussed in Appendix I, the Au-Cu system is inadequate for extended time use at 450°C .

TABLE 3

Results of Gold-Copper Diffusion Bonding Studies						
Sample No.	Type of Material*		Bonding Parameters			Tensile
	Gold	Copper	Temp. °C	Pressure psi	Time hrs.	Strength psi
43	RW	MW	565	2,730	2	13,000
44	RW	MW	495	2,730	2	13,000
46	RW	MW	490	2,275	2	13,000
50	RW	MW	300	5,005	2	5,690
51	RW	MW	560	910	2	13,000
52	RW	MW	300	4,550	5	4,060
53	RW	PE	560	2,250	5	12,000
55	RW	MW	500	1,820	1	11,500
56	RW	MW	450	1,360	2	8,940
58	RW	MW	560	545	2	12,190
59	RW	MW	500	910	2	11,375
60	RW	PE	560	3,250	5	8,500
61	RW	PE	550	2,750	5	
62	RW	MW	450	2,275	2	12,180
63	RW	PE	560	3,000	5	12,750
64	RW	PE	565	3,000	5	9,500
65	RW	MW	405	3,180	2	10,560
68	RW	RW	565	2,750	5	11,250
69	RW	RW	565	2,750	5	10,500
70	RW	RW	565	2,750	5	14,190
118	RW	MW	400	2,730	2	13,360
119	RW	MW	390	3,450	2	14,110
121	RW	MW	450	1,230	2	16,185
122	RW	MW	500	955	2	

*See footnote for Table 2.

FIGURE 13
Influence of Bonding Temperature on Diffusion Bonding of Au-Cu

DB 51

1000X

FIGURE 14

SEM Fractograph of Failure Within Gold
Sheet of Au-Cu Diffusion Bond
(wrought copper)

Diffusion Bonding Parameters:

temperature - 560°C
pressure - 6.4MN/m^2 (910 psi)
time - 2 hours

DB 60

1000X

FIGURE 15

SEM Fractograph of Failure of Au-Cu Diffusion Bond
Which Occurred Near Original Center of Copper Electroplate

Diffusion Bonding Parameters:

temperature - 560°C
pressure - 22.8MN/m² (3250 psi)
time - 5 hours

DB 53

100X

FIGURE 16

Metallographic Cross-section of Au-Cu Diffusion Bond
Made with Electroplated Copper

Au-Ag

Au-Ag bonds (wrought gold and silver) were obtained at somewhat lower pressures (as low as 8MN/m^2 or 1150 psi at 560°C) than required for Au-Ni bonds. However, the strength of the Au-Ag bonds was anomalously low and much weaker than Au-Ni bonds at 450°C ($8.5 - 21\text{MN/m}^2$ or 1250 - 3000 psi vs $>49\text{MN/m}^2$ or 7000 psi). The results of the Au-Ag bonding parameter study are given in Table 4.

A SEM fractograph of a typical failed Au-Ag bond is shown in Figure 17. The bonds failed by ductile rupture in the silver very near the original faying surfaces. The extremely small microvoids suggest that the low strength may be related to the presence of a large number of void nucleation sites along the plane of fracture. Examination of cross-sections of Au-Ag bonds by SEM and electron microprobe or the fracture surface by electron microprobe yielded no evidence as to the nature of the microvoid nucleation sites. Low strength failures of Ag-Ag diffusion bonds of an earlier investigation were attributed to entrapped gases.⁽³⁾

An alternative explanation of the small microvoid size is that they merely reflect an extremely small amount of plastic deformation during the fracture process.

Au-Au

A number of attempts were also made to produce Au-Au bonds, but the best bond strength was only of the order of 7MN/m^2 (1000 psi) and on the basis of SEM examination, a high percentage of the surface of failed tensile samples appeared not to have been bonded. Au-Au samples were bonded at pressures as high as 70MN/m^2 (10,000 psi) at 550°C . Surface preparations included various combinations of polishing, etching in aqua regia, and vac-

TABLE 4

Results of Gold-Silver Diffusion Bonding Studies

Sample No.	Type of Material*		Bonding Parameters			Tensile
	Gold	Silver	Temp. °C	Pressure psi	Time hrs.	Strength psi
2	RW	RW	570	2,250	2	2,250
7	RW	RW	500	6,000	1	2,250
8	RW	RW	455	2,750	1	1,500
9	RW	RW	510	3,250	2	2,000
23	RW	RW	600	10,000	2	1,750
30	RW	RW	550	1,750	5	2,750
33	RW	RW	490	1,750	5	2,000
34	RW	RW	560	1,500	5	1,500
35	RW	RW	560	1,150	2	3,000
36	RW	RW	550	1,500	5	1,250
93	PE	PE	570	2,500	5	750
97	RW	PE	570	2,250	2	1,250

*See footnote for Table 2.

DB 23

1000X

FIGURE 17

SEM Fractograph of Failure
of Au-Ag Diffusion Bond

Diffusion Bonding Parameters:

temperature - 600°C
pressure - 70MN/m² (10,000 psi)
time - 2 hours

uum annealing (10^{-2} mPa) at high temperature (800 - 1000°C), as well as the four-step ultrasonic cleaning procedure described in Table 1. The difficulties encountered in producing Au-Au bonds are believed to be related to the fact that, when thin gold sheets are sandwiched between rigid members, pressures up to 70MN/m^2 (10,000 psi) are insufficient to produce the interfacial plastic flow needed to disrupt organic surface films. Also, the surface films are much more soluble in copper and nickel than in gold, which is believed to be the explanation as to why Au-Au bonds cannot be made under the same conditions that produce Au-Ni and Au-Cu bonds.

SLID Bonding Systems

Several bonding experiments involving various combinations of germanium, indium, and tin-indium with gold or silver have been completed to evaluate the feasibility of SLID bonding (solid-liquid interdiffusion, also called diffusion brazing). Since the initial diffusion interaction occurs between liquid and solid phases, SLID bonding affords the possibility of bonding at very low pressures (3.5MN/m^2 or 500 psi or less). The results of SLID bonding experiments are summarized in Table 5. The specimens were bonded in a two-step cycle: they are held $\sim 50^\circ\text{C}$ above the eutectic melting point for ~ 15 minutes and then heated over night (~ 15 hours at ~ 500 psi) at 550°C to diffuse the low melting point elements into the base metals (Au or Ag). Although the resulting bonds were not high in strength at 450°C (17.5MN/m^2 or 2500 psi or less), these experiments demonstrate that the low-melting-point eutectic compositions in these systems can be eliminated by diffusion.

TABLE 5

Results of SLID Bonding Experiments			
System	Eutectic Melting Temperature, °C	Tensile Strength at 450°C	
		psi	MN/m ²
Au-In-Sn	~115°C	2000	14
Au-Ge	356°C	2500	17.5
Ag-In	141°C	1000	7
Ag-In-Sn	~115°C	2000	14

RTG Assemblies

Thermopile - Transition Member

A number of metallized thermopiles or dummy thermopiles were diffusion bonded to transition members. The ends of these thermopiles were coated with 2 - 5 mils (50 - 125 μ m) of electron beam evaporated gold (by SLA Division 5834) over the sputtered gold metallization. Early attempts to bond transition members to thermopiles were met with very limited success due to poor adhesion of the insulating glass layer to the thermopile. As a consequence, a number of samples failed at the glass-thermopile interface during disassembly from the diffusion bonding fixtures or during preparation for tensile testing. Division 5834 concluded that the poor glass adhesion was due to inadequate cleaning of the thermopiles prior to glassing. Subsequently, a series of experiments was conducted to evaluate the strength of diffusion bonded interfaces on samples prepared using improved cleaning techniques. A bonded test specimen from this series is shown in Figure 18. The results of these experiments are summarized in Table 6. Since two of these specimens failed at a tensile stress of the order of 35MN/m² (5000 psi) and 7 out of 8 of the specimens failed above 7MN/m² (1000 psi), these studies suggest

FIGURE 18

Test Specimen of Transition Member Bonded to
Si-Ge Dummy Thermopile

NOTE: Upper nickel part has transverse
hole through it so that it can be pinned
to facilitate tensile testing.

TABLE 6

Strength of Diffusion Bonded Assemblies Incorporating Si-Ge

Sample Identity	Sample Types	Tensile Strength		Failure Mode
		psi	$\text{N/m}^2 \times 10^{-6}$	
Kovar - 1	Metallized over fused-on glass	2300	16	Kovar-oxide interface
Kovar - 2	Metallized over fused-on glass	2500	17.5	Tungsten transition member delaminated due to previous crack
G-41a*	W coated, glassed, and metallized	1150	8.04	Predominately in SiGe
G-42a*	W coated, sputter	1340	9.36	" "
G-42b*	As above	4700	32.8	" "
G-46a*	Interconnect pattern, glassed, and metallized	535	3.74	" "
G-47a*	Interconnect pattern, sputter cleaned, glassed, and metallized	1040	7.26	" "
G-47b*	As above	5340	37.3	" "

*Dummy thermopile of solid Si-Ge.

that reasonably strong metallized and diffusion bonded interfaces can be made. Since the predominate failure mode in the dummy thermopiles was fracture of the SiGe, the true strength of these interfaces and effect of sputter cleaning was not determined. A thermopile (TP168) was also metallized and diffusion bonded to transition members. This thermopile failed in tension at 595 psi by fracture of the SiGe. The low fracture stress of TP168 as well as the dummy thermopiles is believed to be due to defects such as small cracks in the SiGe.

Lower Flexible Support

The lower flexible support consisted of a woven copper mesh which was bonded to a copper pedestal, which was in turn bonded to the thermopile. The copper mesh mounted between two copper rings and a pedestal are shown in Figure 8. Gold-copper diffusion bonding is employed to assemble the copper mesh, rings, and pedestal. The copper rings and pedestal are electroplated with 0.25mm (0.010 inches) of gold and bonded to the copper mesh at 500°C and 28MN/m² (4000 psi). The resulting assembly was mechanically strong and the densification of copper mesh which was bonded to the pedestal or rings appears sufficient to provide good thermal conductivity (see Figure 19, which is a metallographic cross section of a bonded sample). Samples were bonded with 0.15, 0.20, 0.25mm (0.006, 0.008, and 0.010 inch) diameter wire in order to evaluate flexibility, thermal conductivity, and bondability as a function of wire diameter. Bondability was satisfactory for all three wire sizes, whereas flexibility was judged to be acceptable for 0.15 and 0.20mm wire. Evaluation of the influence of wire size on thermal conductivity was not completed. The 0.20mm diameter wire was selected for subsequent RTG assemblies.

100X

FIGURE 19

Metallographic Cross-section of Au-Cu Diffusion
Bonded Flexible Support Member

Complete RTG Heat Source/Thermopile Assemblies

Two complete RTG assemblies, including simulated heat source, transition members, thermopile, and lower flexible support were made by diffusion bonding. The assembly was accomplished in two operations. First, (see Figures 5 and 6) the heat source, transition members, and thermopile were bonded at 550°C and 14MN/m^2 (2000 psi) for 5 hours (all Au-Ni bonds). During the second bonding step, (see Figures 7 and 9) the lower transition member (terminated with a gold sheet) was bonded to the copper pedestal of the flexible support. Bonding parameters for this operation were 500°C and 14MN/m^2 (2000 psi) for 2 hours. A pictorial illustration of a RTG assembly which shows the positions of heat source, transition members, thermopile, and flexible support is given in Figure 1.

Following diffusion bonding of the RTG assemblies, the ring of the flexible support was soldered to the base plate by the procedure described in Reference 4. The second assembly, DBRTG-1, was subjected to system shock and vibration tests. Radiographs taken of DBRTG-1 following these tests are shown in Figure 20. No evidence that the shock and vibration tests had damaged either the thermopile or any of the diffusion bonds was seen in these radiographs.

DISCUSSION

It is important to recognize that the relationships between bond strengths and bonding parameters obtained in these studies can only be assumed to hold for conditions approximating those under which the experimental data were obtained. In particular, bond pairs of differing surface condition and/or geometry would be expected to behave differently when subjected to otherwise identical bonding conditions.

(a) After Shock Test

(b) After Both Shock and Vibration Tests

FIGURE 20
Radiograph of RTG Assembly DBRTG-1 Following
Shock and Vibration Tests

The surface preparation and cleaning procedures used in these studies were selected with the objective that they could be easily implemented with conventional practices and equipment. The four-step ultrasonic cleaning process described in Table 1 is expected to remove most oils, greases, and water soluble contaminants from the surfaces to be bonded. However, surface oxides and adsorbed hydrocarbons would be expected to remain on the sample surfaces. SLA Division 5833 recently studied the effects of d.c. sputtering and ultraviolet light cleaning on the bondability of gold surfaces during thermal compression bonding.⁽⁵⁾ Substantial increases in bond strength were achieved when surfaces were exposed to uV light radiation and ozone, presumably due to removal of adsorbed hydrocarbons prior to bonding. It is possible that if more exotic cleaning techniques were applied to future RTG assemblies, some improvement in bondability would be realized. However, it is doubtful that dissimilar metal bond pairs such as Au-Ni, Au-Cu, and Au-Ag could benefit as markedly from improved cleaning techniques as did the Au-Au system.

Also, other studies⁽⁵⁾ have shown that the bondability of both gold and silver (under conditions of low bulk deformation) can be improved by polishing the bond pairs to achieve optically flat surfaces. High strength diffusion bonds have been obtained at modest temperatures (200-300°C). However, pressures required for bonding in this temperature range have generally been much higher than used in the current study ($70-210 \text{ MN/m}^2$ vs 14 MN/m^2 or 10,000 - 30,000 psi vs ~2,000 psi).

Since bonds of adequate strength were obtained with the Au-Ni system using rather conventional procedures, the evaluation of the bondability of ultra clean, highly polished bond pairs was judged unnecessary. These special surface preparations probably warrant consideration for any future

designs requiring Au-Au bonds.

Finally, it should be noted that the diffusion bonds were performed under conditions of high mechanical restraint. In nearly all instances, thin, ductile layers of gold or silver were sandwiched between relatively thick, rigid layers of tungsten, Si-Ge, or nickel. Consequently, at the highest pressure level investigated, negligible bulk deformation was observed in the bond pairs ($<1\%$). Under conditions of less mechanical restraint, where interfacial shear would become more important in disrupting surface films, lower bonding temperatures could probably be employed.

CONCLUSIONS

1. Of the bond pairs evaluated and without further development, only the Au-Ni system appears satisfactory for use at the hot-side end of the thermopile.
2. The Au-Cu system is acceptable for use at the cold-side end of the thermopile and affords the use of lower bonding pressures and/or temperatures than the Au-Ni system.
3. Although the Au-Ag system permits diffusion bonding at low pressures, anomalously low bond strengths are obtained.
4. On the basis of these studies, development of low pressure, low temperature diffusion bonding processes using the Au-Au system does not appear promising. (However, future evaluation of the bondability of ultra clean, optically flat, gold surfaces may alter this tentative conclusion.)
5. SLID bonding is a feasible process for obtaining metallurgical welds at very low applied pressures. However, for the systems evaluated, the SLID bonds only afforded marginally acceptable strengths at 400°C for

the RTG application.

6. The diffusion bonding approach to assembling a RTG is feasible. (In the present application, however, assembly by diffusion bonding could not be implemented without further development of insulation techniques in order to eliminate pinholes which permit shorts to the interconnection patterns.)

APPENDIX I

Interdiffusion in Au-Cu and Au-Ni Systems

The Au-Cu system was investigated because it afforded lower pressures during bonding to the thermopile. However, we now know that it cannot be considered suitable for the hot shoe side of the thermopile. On the basis of calculations of the interdiffusion of copper and gold made by W. J. Kass, 5834, interdiffusion of Au-Cu would be excessive. Kass's calculations predict that the concentration of copper in gold at a distance of 0.010 inches from the original interface would be in excess of 20 atom % after ten years at 400°C. The effect of higher copper concentrations at the glass-to-metal seal on the thermopile is unknown, but excessive Kirkendall porosity in the region of the original Au-Cu interface would probably result. Similar calculations for the Au-Ni system indicate that the concentration of nickel in gold will drop ~ 0.1 atom % at a distance of 1.1 mils. Kass also calculated that the nickel concentration would drop to this same concentration within a distance of 0.14 mils during diffusion bonding (5 hours at 550°C). On the basis of Kass's calculations, the Au-Ni system appears adequate for the hot shoe bonding.

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