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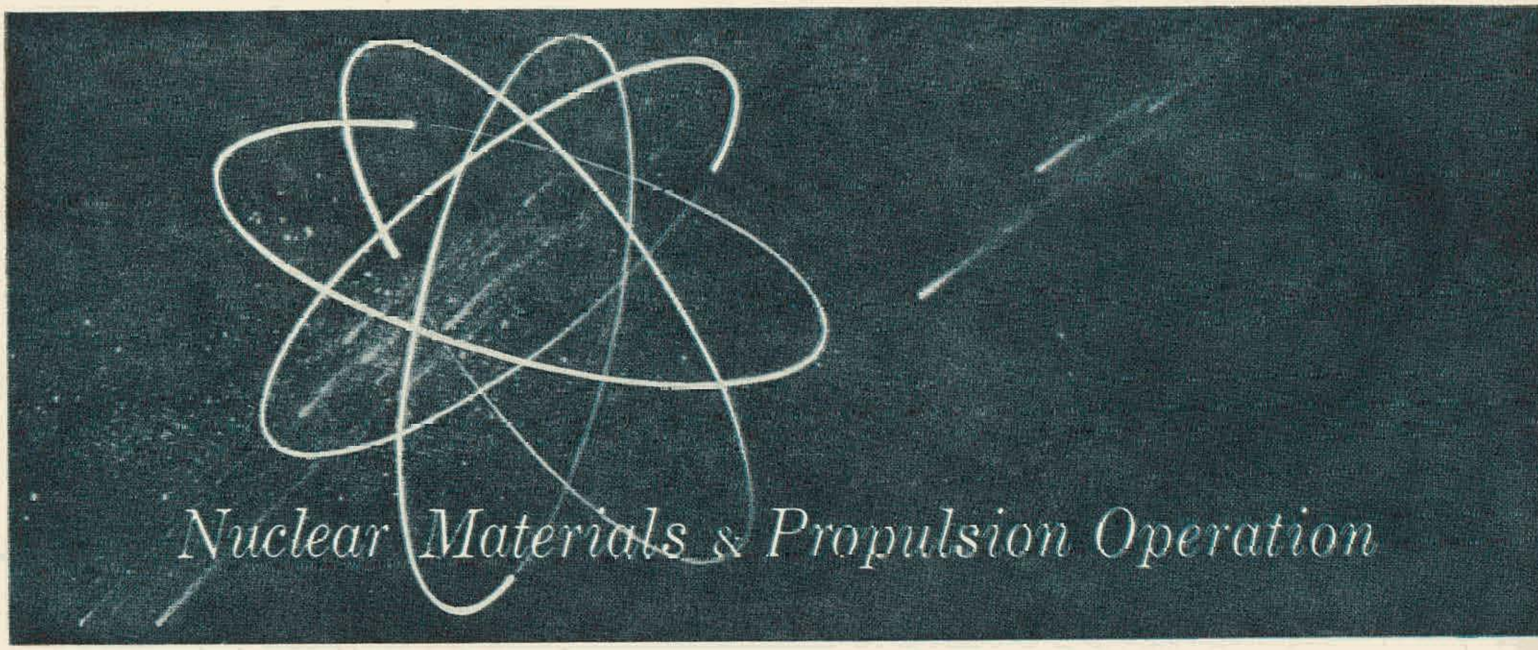

SOLID STATE DIFFUSION BONDING OF REFRACTORY METALS AND ALLOYS

by

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ABSTRACT

Solid-state diffusion bonding of refractory metals by heating in vacuum has been developed for self-bonding Cb to Cb, Mo to Mo, and bi-metal bonding Mo to Ta, etc. Other metals and alloys such as W, Re, Mo, Ta, Cb, V, W-26Re, Mo-50Re, and Ta-10W have also been diffusion bonded. True metallurgical bonds are achieved at the contacting metal interfaces with only sufficient pressure to assure positioning and contact of the areas to be bonded. Grain boundary migration appears to be a major mechanism in forming the bonds. Stress-rupture tests at 4000°F on Mo and 4700°F on Ta-10W alloy were conducted up to 10 hours in hydrogen atmosphere to permit comparison of diffusion bonded joint rupture strength with basic thin sheet properties.

Introduction

The space age requires extreme weight conservation in metallic structures and particularly wherever refractory metals are used. This class of materials has potential applications as thin sheets fabricated into honeycombs, gas diverters, heat-exchangers and other complex components for aircraft, missiles, and space nuclear power reactors. The joining of refractory metals by standard braze alloy techniques reduces high temperature capability due to lower melting point of braze alloy, undesired property changes, and a tendency for braze alloys to vaporize with a resulting joint porosity. Electron beam welding is an acceptable joining method, but is often limited by equipment size, manipulation difficulties, or gas evolution in the weld zone. Solid-state diffusion bonding, as applied to this work without rolling or pressure, avoids some of the preceding limitations and was selected for development as a method of joining thin-sheet refractory metals. In order to evaluate the strength developed by solid-state diffusion bonded joints, close to the expected use temperature, stress-rupture properties were determined on both basic sheet specimens and on diffusion bonded lap joints. Stress-rupture curves were completed for test times to 10 hours at $4000^{o}F$ ($2200^{o}C$) for Mo, and similarly at $4700^{o}F$ ($2600^{o}C$) for Ta-10W alloy. All work within this program was completed on commercially vended sheet.

Solid-State Diffusion Bonding

A preliminary review of solid-state diffusion indicated that removal of surface films (oxides) might eliminate a major barrier to the bonding between contacting metal surfaces. A high vacuum environment for solid-state diffusion bonding of refractory metals was selected to accelerate the removal of the high vapor pressure oxide surface films. Other normal metal-gas reactions (N_2) are also eliminated or neutralized through use of vacuum at elevated temperatures[1]. Oxidation studies of columbium to 2200°F and 5×10^{-3} mm Hg oxygen pressure have been reported[2] elsewhere, and indicate surface oxides tend to dissolve into the metal. Therefore, the solution of surface oxides by the refractory metals might be anticipated in a vacuum, and would assist volatilization reactions in establishing active surfaces for solid-state diffusion bonding. For normal organic and other casual impurities, a pre-treatment by chemical cleaning of the metal surfaces with a 3:1:1 lactic-hydrofluoric-nitric acid mix was also employed in this investigation.

Metallographic examination of bonded refractory metal-interfaces attained in this research has supported the thesis that grain boundary migration across the metal contact plane is a major contributing mechanism in establishing the solid-state diffusion bond. Metallurgical bonding by the grain boundary migration mechanism has also been developed by gas autoclaving at high pressures and lower temperatures[3]. High grain boundary migration rates are characteristic of cold worked sheet metals and this is favorable to solid-state bonding. Other investigations have shown that grain boundary migration rates in cold-worked metals can exceed those within annealed metals by a ratio of 1000:1[4]. However, during this investigation several examples of bonding appeared due to the interface contact plane changing to a normal grain boundary without significant boundary migration.

Sound metallurgical bonds have been developed by heating thin sheets (.002" to .030") of W, Re, Mo, Ta, Cb, V, W-26Re, Mo-50Re, and Ta-10W for short periods in high vacuum (10^{-5} mm Hg) and with low contact pressure (0 to 5 psia). Self-bonding (Cb to Cb, etc.) and bi-element bonding (Mo to Ta, etc.) have been shown by ultrasonic testing and metallographic examination to have been established by heating the metals from 2500°-4000°F with only sufficient pressure across the interface to assure necessary contact and positioning. The temperatures required to initiate diffusion bonding between various refractory metals are given in Table I. Metallographic examination indicates that the bonds formed by solid-state diffusion are often indistinguishable from the basic metal structures, as shown for a Cb to Cb bond in Figure 1. The bonds illustrated in Figure 1 were obtained by stacking 3/4" x 3/4" squares of metal in a vacuum furnace, placing a small molybdenum weight on the stack to assure contact of the materials, and heating for one hour at 3000°F in vacuum (10^{-5} mm Hg). Metallographic evidence of diffusion bonded interfaces developed in joining tantalum to molybdenum which in turn is bonded to columbium by heating at 3000°F in 5 x 10^{-5} mm Hg vacuum is shown on Figure 2.

TABLE I

RECOMMENDED OR ESTABLISHED CONDITIONS TO ATTAIN

SOLID-STATE DIFFUSION BONDING OF REFRACTORY METALS

Materials heated one hour at temperature indicated in a vacuum of 5×10^{-5} mm Hg or less.

Bonded Material	W °F	W-26 Re °F	Re °F	Ta °F	Ta-10 W °F	Mo °F	Mo-50 Re °F	Cb °F	V °F
W	3500	3500	3500	3500	4000	3000	4000*	3000	2500
W-26 Re	3500	3500	4000	3500	4000	3000	4000*	3000	2500
Re	3500	4000	4000	4000	3500	3500	4000*	3000	--
Ta	3500	3500	4000	3500	4000	3000	4000*	3000	2500
Ta-10 W	4000	4000	3500	4000	3500	3500	4000*	3000	--
Mo	3000	3000	3500	3000	3500	3000	4000*	3000	2500
Mo-50 Re	4000*	4000*	4000*	4000*	4000*	4000*	4000*	--	--
Cb	3000	3000	3000	3000	3000	3000	--	3000	2500
V	2500	2500	--	2500	--	2500	--	2500	2500

*Only bonding temperature surveyed.

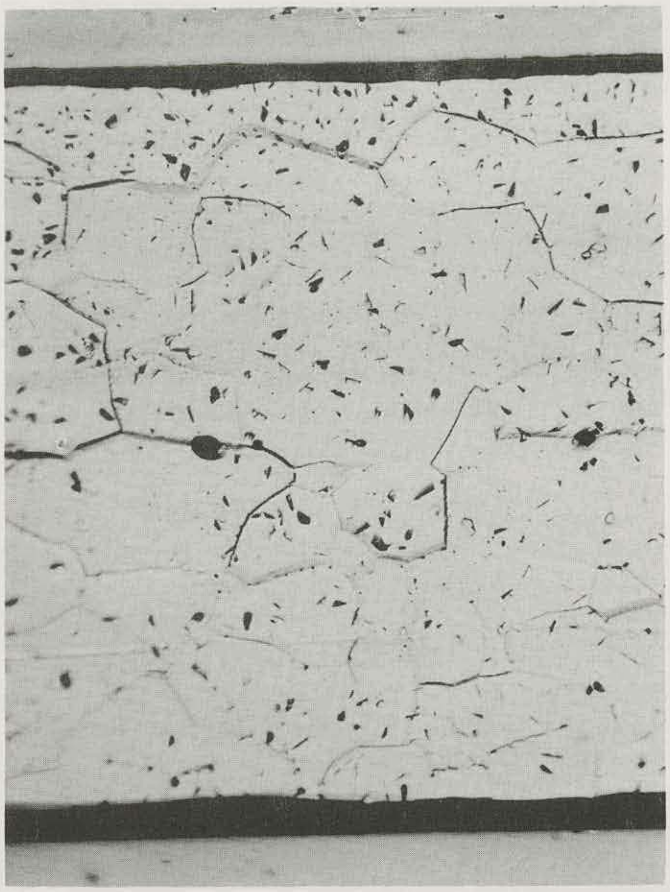

Figure 1 - Photomicrograph showing evidence of the metallurgical bond obtained in joining two thin sheets of Cb through heating for one hour at 3000°F in 4×10^{-5} mm Hg vacuum. Less than 5 psia pressure was applied across the contacting metal interface in the bonding operation. The original interface is marked by two large oxide inclusions purposely selected for orientation. Note crossing of the contact area by grain boundaries occurred during grain boundary migration accompanying grain growth.

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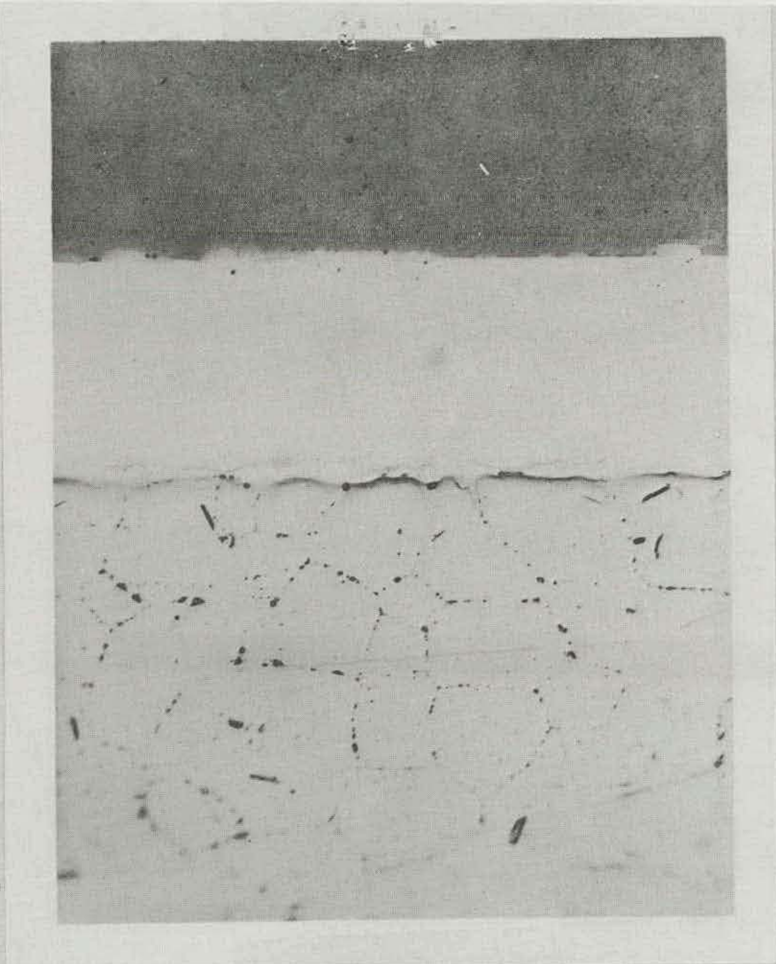

Figure 2 - Metallographic cross-section showing bonded contact interfaces between different refractory metals as joined by heating one hour at 3000°F, 5×10^{-5} mm Hg vacuum, less than 5 psia pressure. Distinct metallic diffusion zones observable at each interface are evidence of metallurgical bonding.

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Emphasis has been directed throughout this program toward establishing large contact areas for diffusion bonding, and with proper mechanical fit-up the weight of the material generally provides required pressure. However, in joining complex components cover sheets are used to assist in assuring contact, and diminish surface separations due to thermal distortion in heating the work.

<u>Evaluation of Solid-State Diffusion Bonds</u>

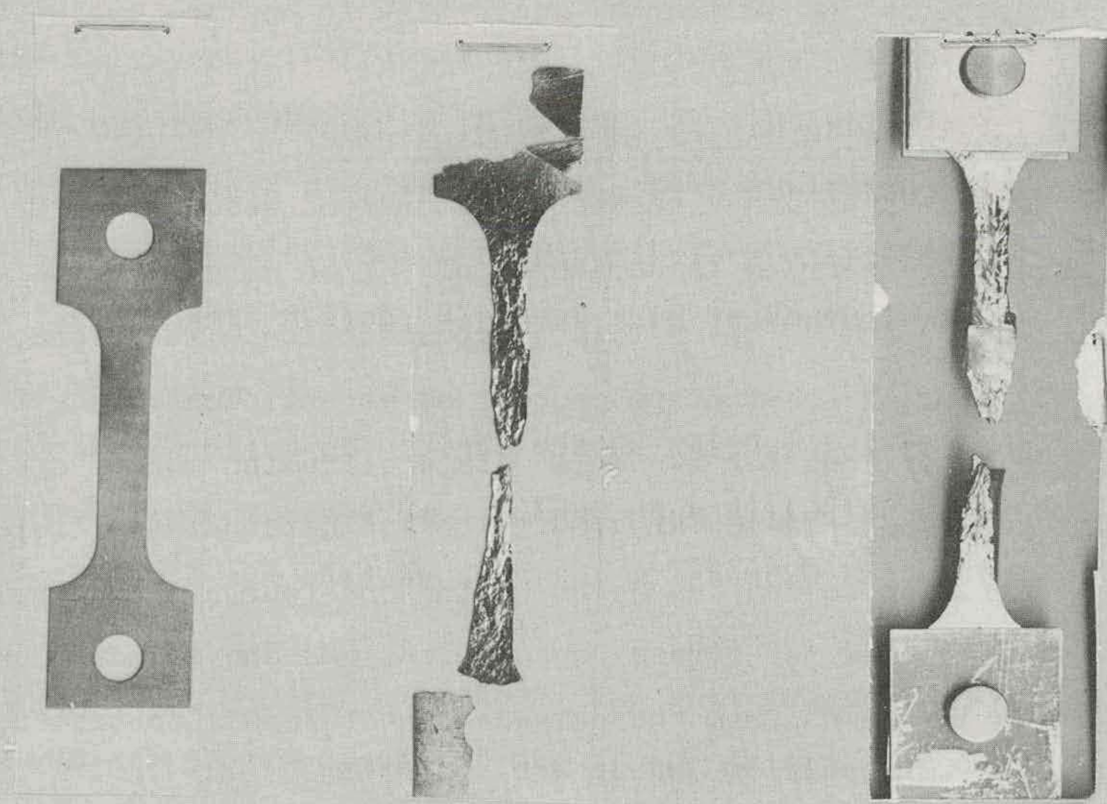
Advanced space power nuclear reactors and associated structure anticipate service temperatures of 75% to more than 90% of the melting point of the metals of construction. Therefore, the ten (10) hour stress-rupture properties at anticipated use temperatures were determined for two solid state diffusion bonded systems, Mo at 4000°F and Ta-10W at 4700°F, to evaluate joint efficiencies. A diffusion bonded lap joint having one-fourth inch overlap distance was assembled for stress-rupture testing, and standard unjoined sheet specimens from the original sheet were also tested as control data points. Standard sheet and diffusion bond test pieces, before and after testing, are shown in Figure 3. Note that the failure in the lap joint specimen is outside the bond area. Failure in the base metal was anticipated because the contact area of the diffusion bond measures 1/4" x 1/4" whereas the sheet cross-section adjacent the bond measured .020" x 1/4".

Stress-rupture tests were conducted in a furnace designed for either tensile or stress-rupture testing in hydrogen, vacuum, or inert gas atmosphere. All rupture tests reported herein were conducted in hydrogen except for heating and cooling the Ta-10W

Figure 3

Tantalum - 10 w/o Tungsten

4700°F Stress-Rupture Test Specimens



Lap Joint Area

Machined Sheet Specimen	Sheet Specimen After Rupture Test	Diffusion Bonded Specimen After Rupture Test

Material was tested at 4700°F in hydrogen. Heated and cooled from 2400°F in argon with hydrogen atmosphere at high temperatures. Test shackles and pins on specimen at right. Fractures at ends of center specimen due to pin and shackle removal. Note lack of deformation in lap-joint (double thickness area) of diffusion bonded specimen at gauge center.

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alloy from room temperature to 2400°F in argon. Temperatures are developed by heating tungsten resistors in the furnace. A small closed-end tube of the material being tested (drilled with a small black body hole) was attached to each test piece and positioned at the center of the test section to permit optical temperature measurement. The optical temperature measuring system was calibrated by several techniques one of which was determining the melting point of columbium to be 4480°F with optical sight glass corrections. This compares directly with published values of 4474 ±18°F as the melting point of columbium. The stress rupture test furnace with optical sighting tube is shown in Figure 4.

Molybdenum sheet, .010" thick, was selected for stress-rupture testing at 4000°F (2200°C). A four hour diffusion bonding treatment at 3500°F was used to join the molybdenum test pieces. The recently developed tantalum - 10 w/o tungsten alloy was also tested as .020" sheet at 4700°F (2600°C) for this program. These test temperatures are in excess of 85% of the melting temperature of each material. The stress-rupture test results are given in Table II, and the stress-curves for Mo are shown in Figure 5 and in Figure 6, for Ta-10W alloy.

The molybdenum stress-rupture test specimens, both control and lap joints, developed elongations to 30.5% at 4000°F. No ruptures were experienced through the diffusion bonded joints. As shown by Figure 5, the stress-rupture life of a diffusion bonded test piece was somewhat shorter than that of basic sheet molybdenum. The fractures in the molybdenum test pieces during the stress-rupture tests usually were located immediately

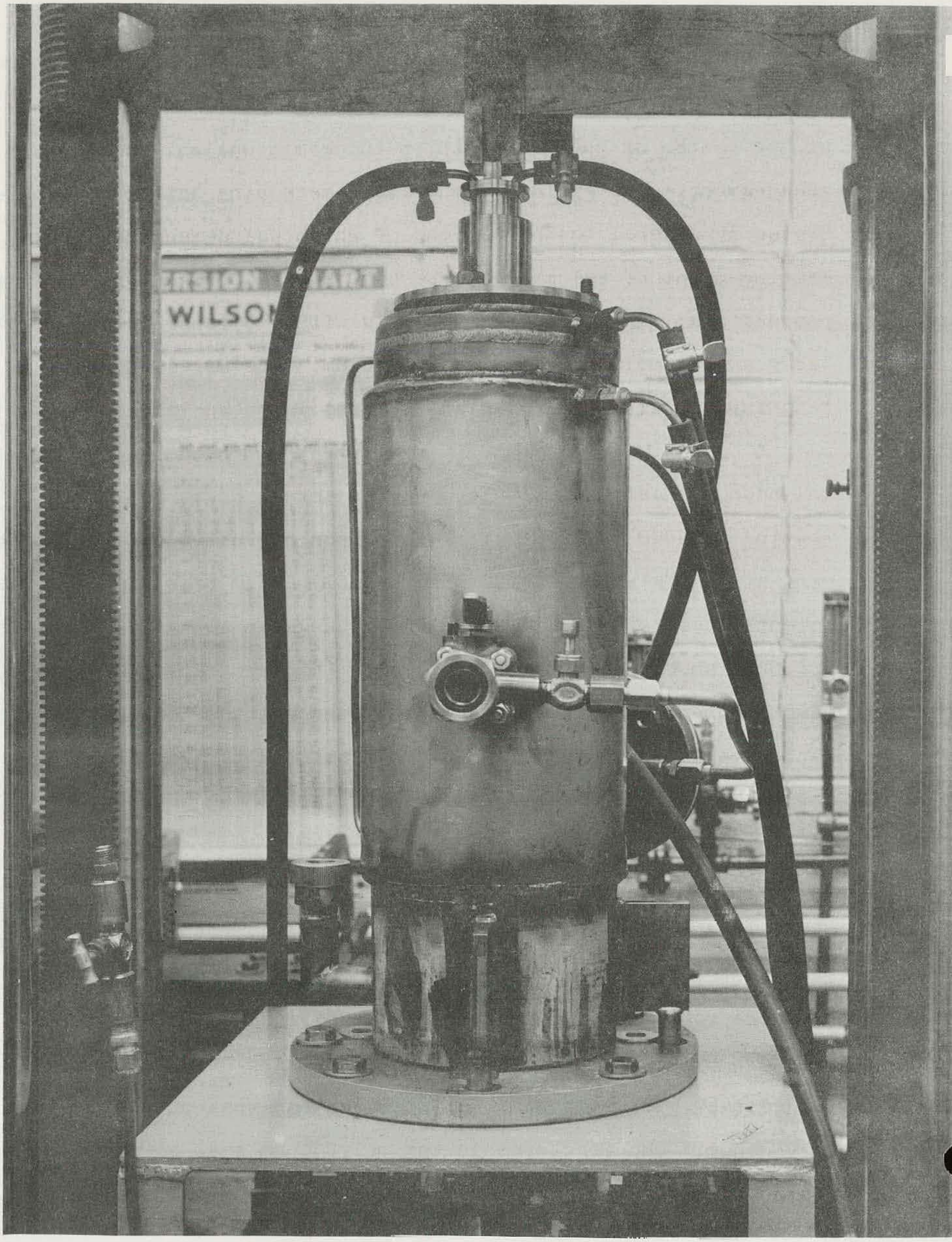

Fig. 4 - Stress rupture furnace (P62-3-15A)

TABLE II

Stress Rupture Data At 4000° And 4700°F For Ta-10W And Mo

Material Tested	Test Temp., °F	Type of* Specimen	Stress, psi	Rupture Time, hours	% Elongation in 1" Gauge Length
Ta-10W	4700	Sheet	1000	1.35	110.0
Ta-10W	4700	Sheet	1000	1.58	129.0
Ta-10W	4700	Diff.Bond	1000	1.17	
Ta-10W	4700	Diff.Bond	1000	1.53	88.0
Ta-10W	4700	Sheet	750	3.70	100.0
Ta-10W	4700	Sheet	750	4.0	150.0
Ta-10W	4700	Diff.Bond	750	3.89	79.5
Ta-10W	4700	Sheet	600	9.20	136.0
Ta-10W	4700	Sheet	600	8.1	109.0
Ta-10W	4700	Diff.Bond	600	7.87	99.6
Mo	4000	Sheet	1000	1.73	19.0
Mo	4000	Diff.Bond	1000	1.33	11.0
Mo	4000	Sheet	750	3.83	19.0
Mo	4000	Diff.Bond	750	3.2	17.0
Mo	4000	Diff.Bond	750	2.55	5.0
Mo	4000	Sheet	600	5.32	28.0
Mo	4000	Sheet	600	5.05	30.5
Mo	4000	Diff.Bond	600	4.46	6.5
Mo	4000	Sheet	500	8.40	29.5

*Ta-10W Sheet .020" thick; Mo sheet .010" thick.
Diffusion bonds: - Ta-10W - 4 hrs @ 4000°F
Mo - 4 hrs @ 3500°F

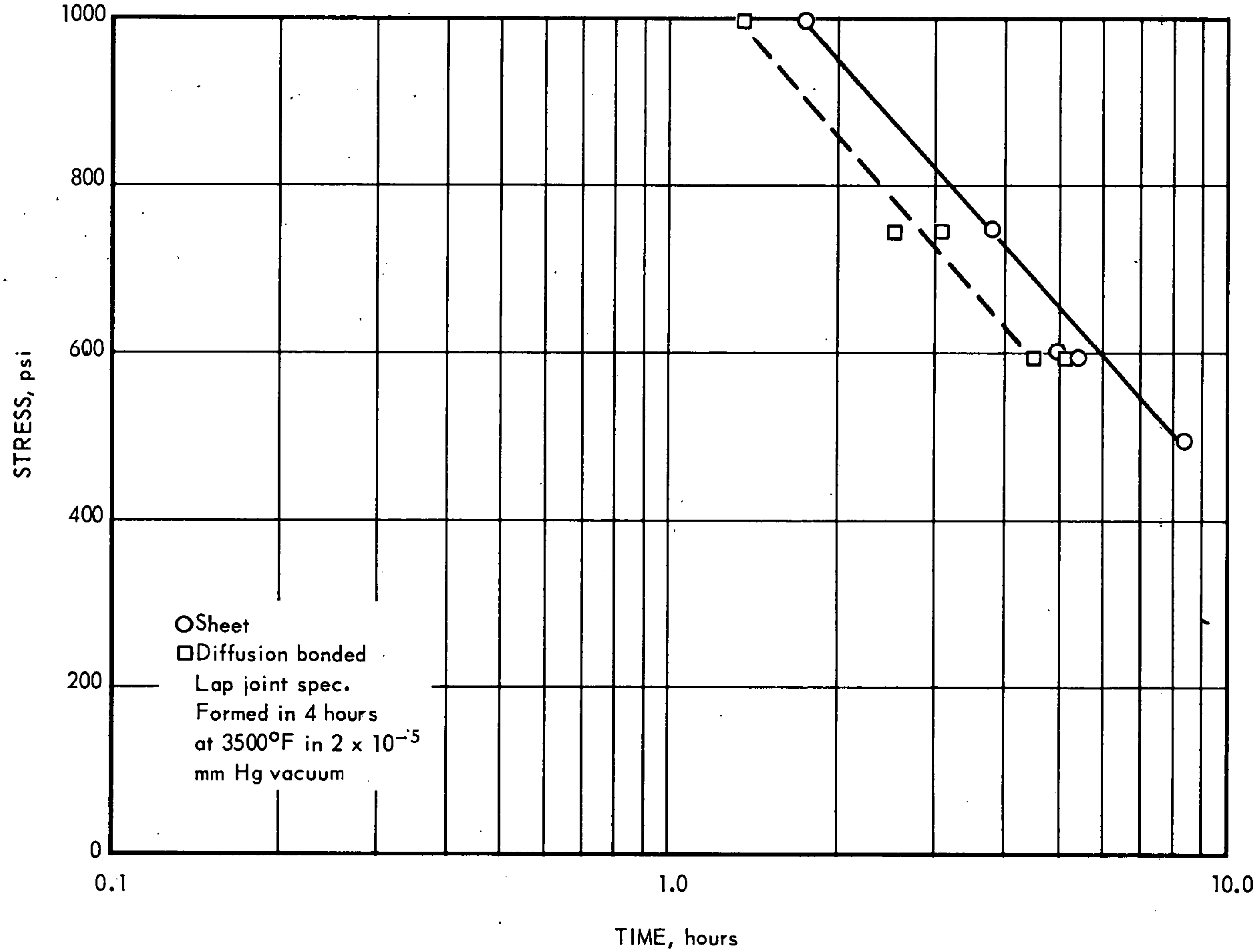

Fig. 5 – Comparison of stress rupture life for Mo sheet (0.010 in.) and diffusion bonded Mo lap joints at 4000°F (H_2)

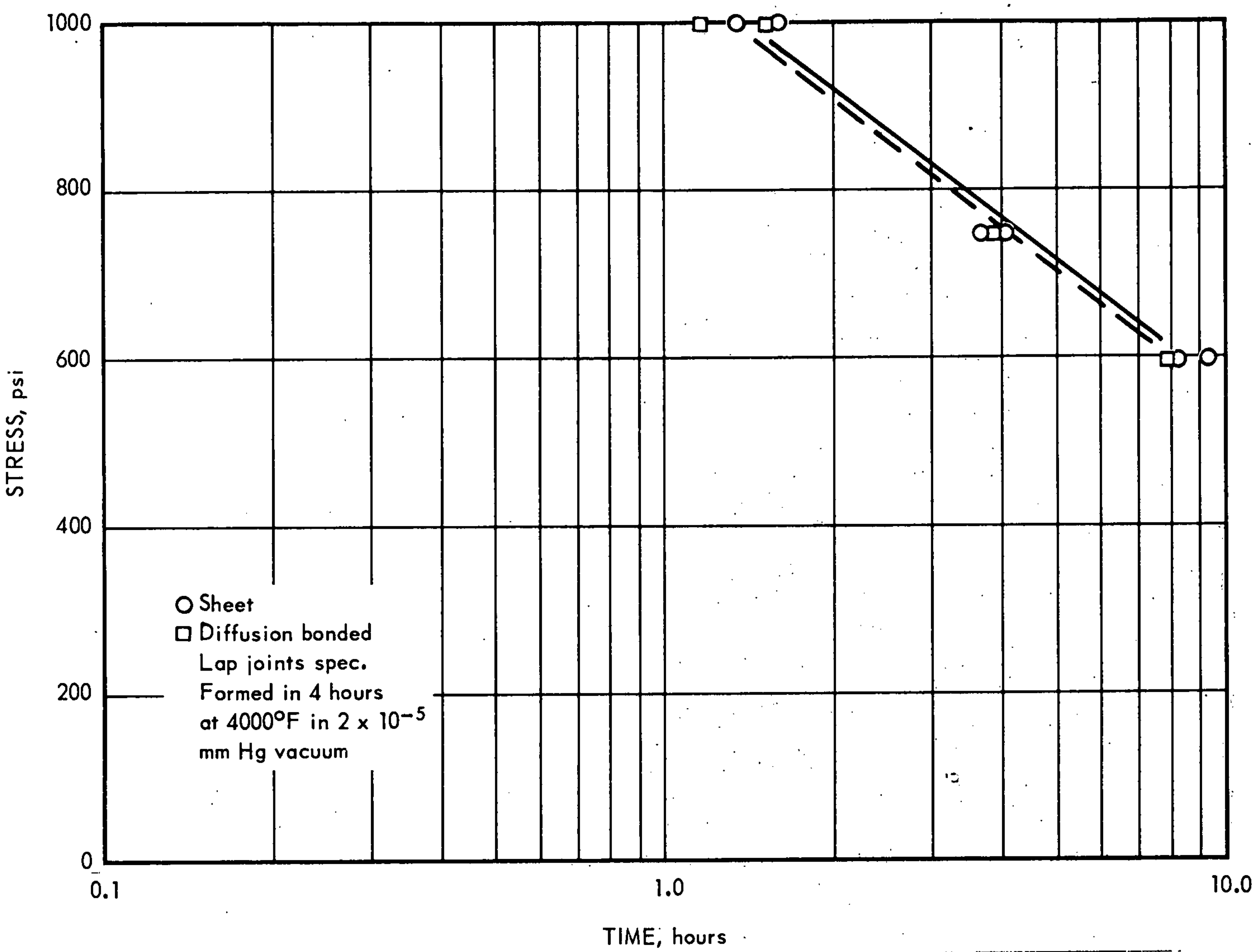

Fig. 6 – Comparison of stress rupture life for Ta – 10W sheet (0.020 in.) and diffusion bonded Ta – 10W lap joints at 4700°F (H_2)

adjacent to the lap-joint, and it is believed that stress-concentrations in conjunction with moderate ductility initiated failure in this area.

Stress-rupture tests on the Ta-10W alloy showed elongation values of 80% to 150% in all tests without undesired joint fractures in the diffusion bonded area of the test specimens. The structure associated with the bond interface in a Ta-10W specimen is shown in Figure 7 after testing at 4700°F.

Temperatures used in solid-state diffusion bonding in this program were not limited by grain growth considerations, but were restricted to 500°F below stress-rupture test temperatures. In the bond-rupture test cycle, large grains were developed as shown in Figure 7 which further illustrates the crossing of the interface contact by grain boundary migration accompanying grain growth.

Potential Applications For Solid State Diffusion Bonding

Several potential applications of solid-state diffusion bonding are under consideration. A multi-layer honeycomb representing a transition from high to lower melting point metals is shown in Figure 8 as one potential application. The multi-layer structure includes a bottom panel of tantalum (M.P. 5450°F) diffusion bonded to a corrugation of molybdenum (M.P. 4750°F); which is joined to a center panel of molybdenum, and in turn is bonded to a top corrugation of columbium with a top surface panel of columbium

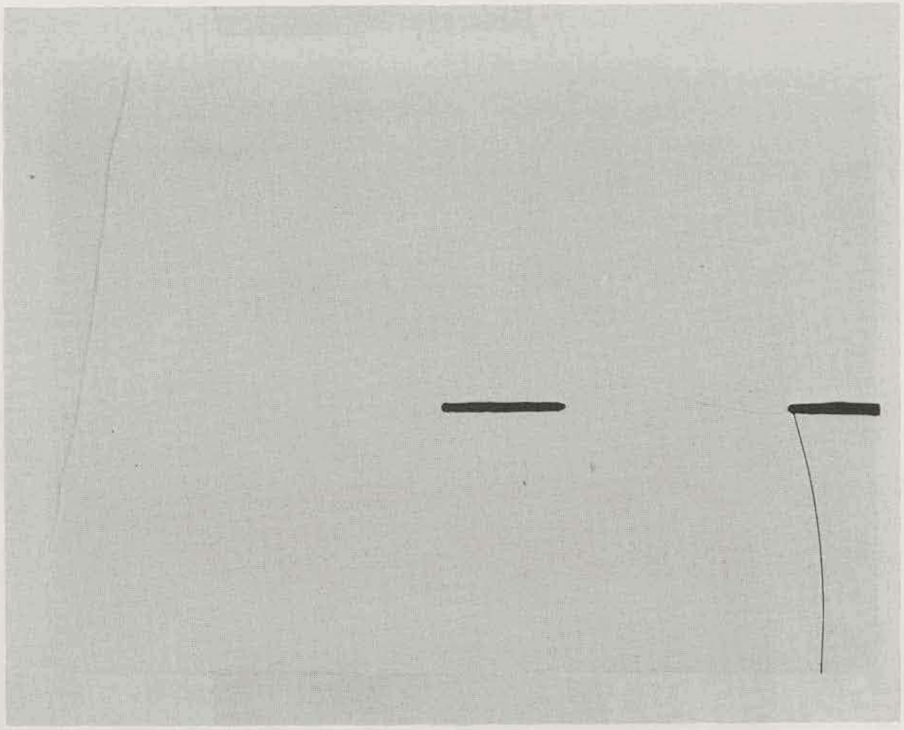

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Figure 7

Joint area of solid-state diffusion bond lap joint in Ta-10W alloy after 8.1 hours stress-rupture test at 4700°F under 600 psia load. Grain growth and grain boundary migration have eliminated the original contact face. Several unbonded areas mark the original contact interface.

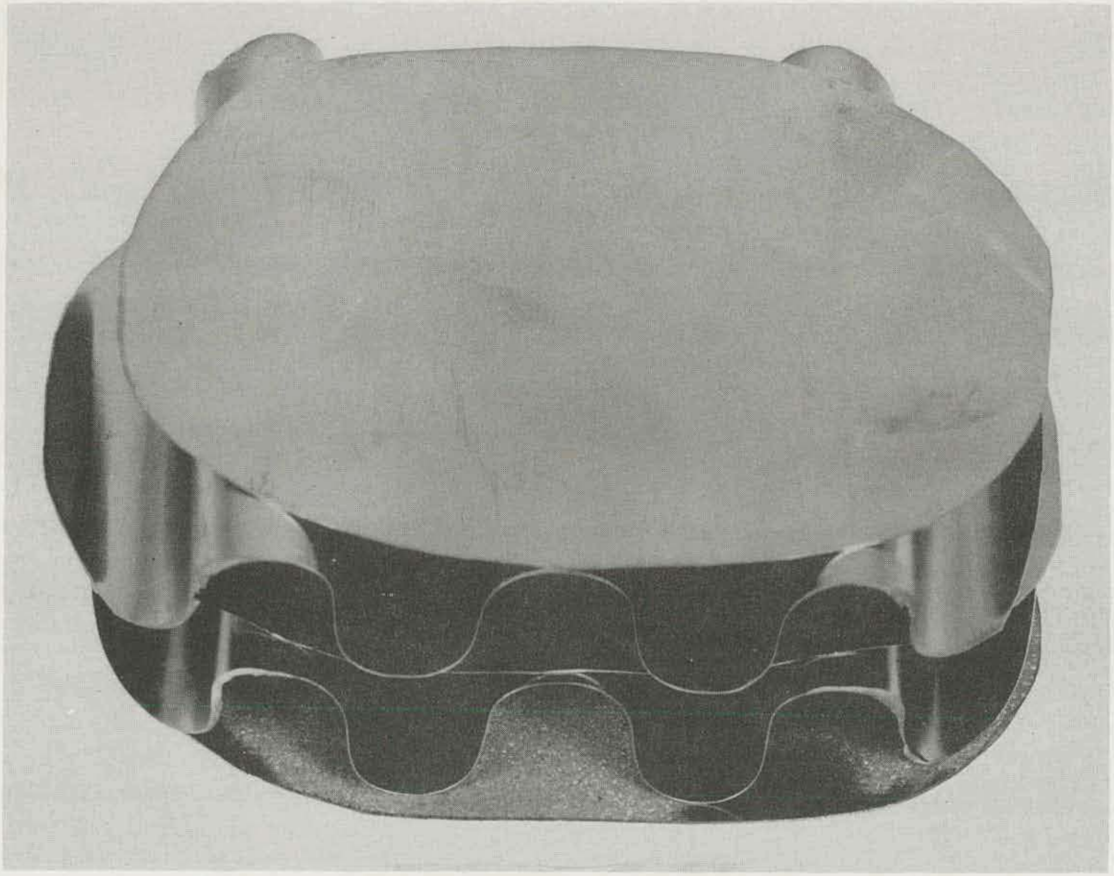

Figure 8 - Multilayer honeycomb representing high to lower melting point transition in materials

Bottom panel sheet is tantalum which is solid-state diffusion bonded to a molybdenum corrugation; center panel is molybdenum; top corrugation is columbium, and top skin panel columbium. All thicknesses .010". Bonded **by** heating 1/2 hour at 3500°F in 5×10^{-4} mm Hg vacuum. No applied loading.

Photo 1 X Neg. P 62-2-27

(M.P. 4474°F). Many similar honeycomb structures have been fabricated of molybdenum, tantalum, and columbium sheets during the development program. Numerous joints have been examined metallographically, and have shown satisfactory bonding with the required initial interface contact properly provided. Explosive forming-coining techniques have been developed to assure required mechanical tolerances, and to provide proper contact for diffusion bonding.

Honeycombs of the type shown in Figure 9 have been made in Ta, Mo, and Cb. After slicing in half, joint cross-sections were examined metallographically. Typical interface bonding in a Cb honeycomb is shown in Figures 10 and 11. Larger areas of bonding have been obtained by surface lapping the contact surfaces of corrugated honeycomb cores, and by a surface precleaning with acids. However, a total overall bond length exceeding the sheet metal thickness has been observed in every bonded joint sectioned for metallographic examination.

Summary

A process has been developed for joining refractory metals and alloys in vacuum at elevated temperatures. Low pressures are used to assure contact between metal interfaces, and this feature enables complex hollow thin shapes to be joined without damage. Diffusion bonding between different metals and alloys has been demonstrated. The removal and dissolution of surface oxide films by the vacuum in heating assists in obtaining metallurgical bonds.

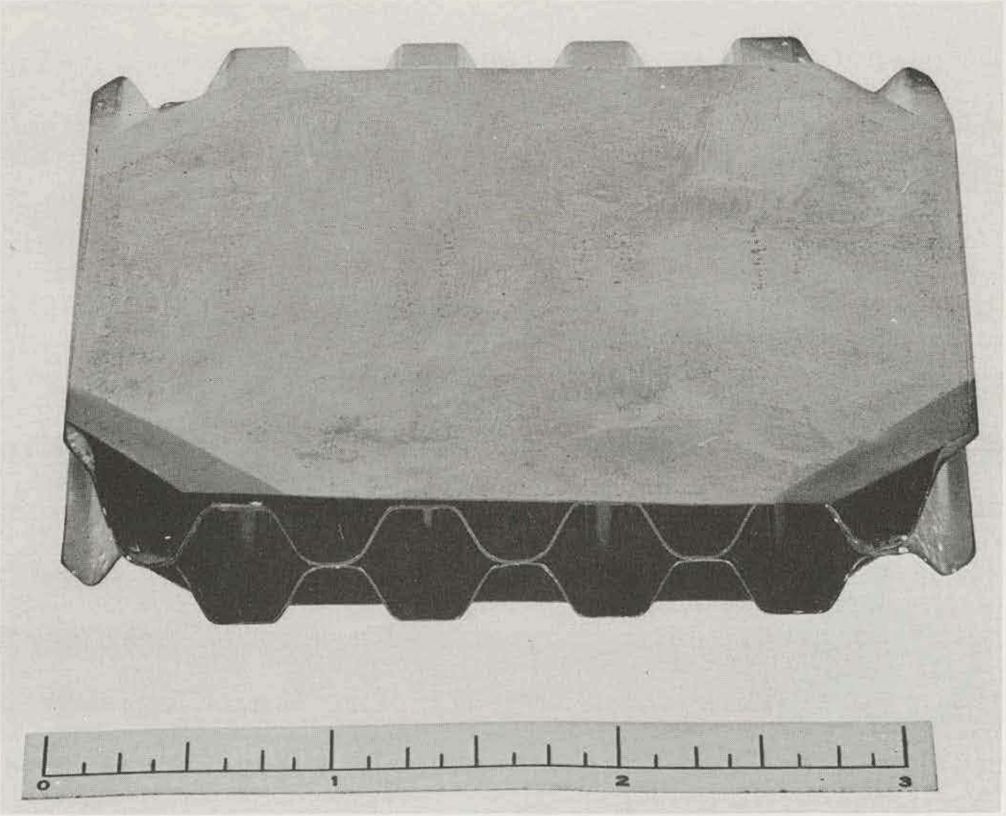

Figure 9

Refractory metal honeycomb assembled by solid-state diffusion bonding in vacuum. A .050" thick tungsten plate was used to assure component contact in heating. The illustrated honeycomb has been produced in tantalum, molybdenum, and columbium.

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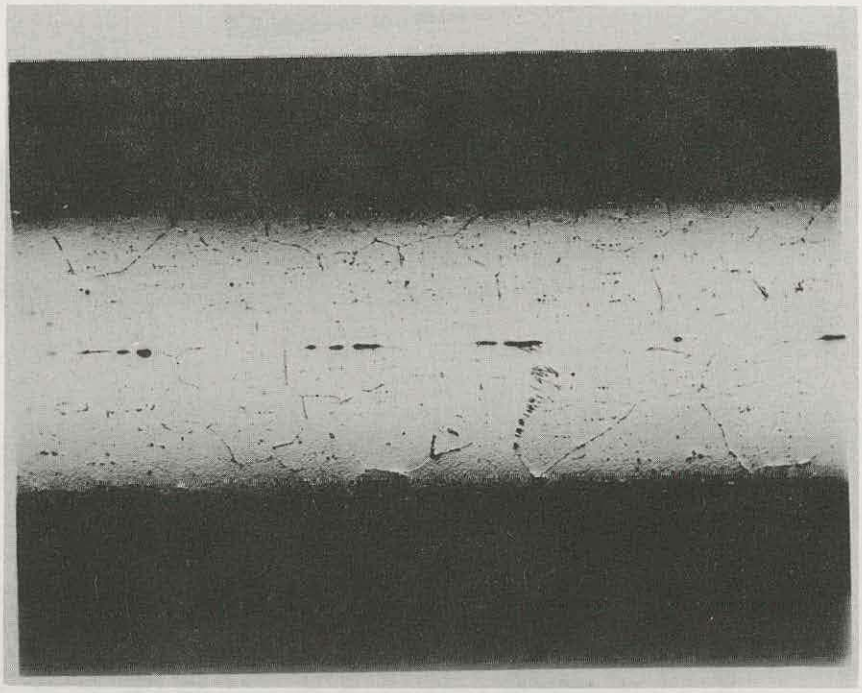

Figure 10

Cross-section through diffusion bonded joint of a corrugated columbium honeycomb core with the top panel as shown in Figure 9. Small non-bonded areas exist along the contact interface, but total bonded area greatly exceeds the total cross-section of the sheet members.

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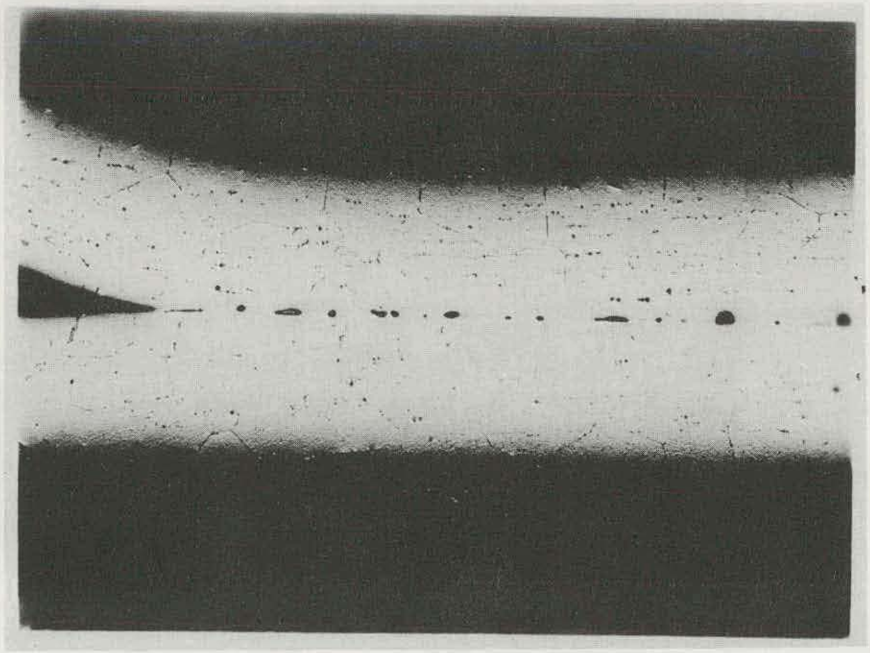

Figure 11

As preceding Figure 9 but cross-section at bottom of honeycomb section showing corrugated core bond with lower surface panel. Etching effects have enlarged apparent size of non-bonded areas.

Etched: Lactic-Nitric-Hydrofluoric Acid Mix

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These bonds have been evaluated through stress-rupture testing and show high joint efficiency.

Conclusions

1. Refractory metals and alloys may be metallurgically bonded by solid-state diffusion initiated upon heating in a vacuum.

2. No low melting or oxide fluxing additons are required to promote bonding in the contacting metal zone. Therefore, changes in physical properties or melting point lowering of the refractory metal are avoided.

3. Stress-rupture tests of diffusion bonded joints in ductile Ta-10W alloy and on less ductile Mo have shown high joint efficiencies at temperatures of 4700°F and 4000°F, respectively.

4. Thin sheet metal of several refractory alloys can be combined into multi-material transition honeycombs and other structures of interest in securing optimum stiffness, corrosion resistance, melting transition, or lowest weight designs.

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