

XLIV.

## *Applications of Solid-Phase Bonding to Refractory Metals*

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### *Synopsis*

*The refractory metals possess special fabrication problems because of their high melting points and poor oxidation resistance. Modifications of standard primary and secondary working techniques, welding, and brazing have been found suitable to some but not all of the refractory metal alloys being considered. Experiments conducted at the Battelle-Columbus Laboratories have shown that many fabrication problems can be overcome by the application of the gas-pressure-bonding process to refractory metals and their alloys.*

*The gas-pressure-bonding process has been used for both solid-phase joining and powder-metallurgical applications. In this paper, techniques are discussed for solid-phase bonding columbium, molybdenum, tantalum, rhenium, tungsten, and their alloys to themselves and to other refractory metals. Bonding parameters, surface preparations, and microstructural interpretation of the resulting bonds are discussed. Examples are presented of practical applications of this joining process to refractory metal structures. An analysis of the relative advantages and limitations of the solid-phase-bonding technique is also presented.*

### *Introduction*

The primary property of refractory metals which makes them useful is their structural strength at very high temperatures. This provides construction materials for such applications as furnaces, reactors, aircraft, missiles, and chemical processing equipment.

However, to be successfully employed in structural applications, it is necessary to have available satisfactory joining methods which will permit full utilization of the high-temperature capabilities that refractory metals possess.

A number of properties common to these materials complicate joining them to themselves and to other materials. These include poor oxidation resistance, high ductile-brittle transition temperatures, sensitivity to interstitial elements, and tendency to form compounds when in contact with more common materials. Because of these properties, it is necessary to control atmospheres, grain size, and the use of foreign materials if severe degradation of base metal properties is to be avoided. In spite of these limitations, varying degrees of success have been achieved by welding, braz-

ing, and solid-state bonding<sup>1</sup>. Generally, welding results in a large increase in grain size with a corresponding loss in strength and ductility and increase in transition temperature. Brazing severely limits service temperature because of remelting, base metal erosion, and incipient joint weakness.

Some of the problems associated with joints formed in the liquid state can be overcome by solid-state bonding. In this approach to joining, the bond is made by diffusion of atoms from one side of the interface to the other. In many instances, the resulting joint will have properties identical to the base materials. Examples of solid-state-bonding processes include roll bonding, coextrusion, resistance bonding, platen bonding, friction bonding, and gas-pressure bonding. Some work has been done in joining refractory metals by each of these processes<sup>2-6</sup>. This paper will deal with studies at Battelle-Columbus Laboratories on the application of the gas-pressure-bonding process to various refractory metal combinations.

### *Gas-Pressure-Bonding Process*

Discussions of the gas-pressure-bonding process have been presented elsewhere in the literature<sup>7,8</sup>; however, a brief discussion is warranted at this time to provide the reader with sufficient background to understand some of the information which will follow.

The gas-pressure-bonding technique basically is an idealized hot pressing operation performed in a high-pressure, cold-wall autoclave in which the deforming force is applied by a high pressure of an inert gas at elevated temperature. Insulating material is located between the wire-wound resistance heater and the inside wall and closures of the autoclave to prevent appreciable heating of the cold-wall vessel. To prepare assemblies for bonding, the cleaned components are assembled into a thin metal container of the desired geometry which is then evacuated and sealed. The sealed assemblies are then placed in the heater inside the autoclave, and the temperature and pressure required for bonding are applied. At temperature the high gas pressure in the system is uniformly transmitted through the very plastic container walls from all directions to the bond interfaces. The components to be joined are thus locally deformed at contact points into complete contact and are solid-state bonded together by diffusion. The conditions required depend, of course, on the materials being processed; for refractory-metals temperatures of approximately 1600° C. and pressures between 10,000 and 30,000 psi are typical. The application of pressure and temperature can be programmed to accommodate the specific properties of particular metal combination.

### *Important Parametric Considerations*

In solid-state bonding by the gas-pressure-bonding process, the following parameters are of importance: surface preparation, bonding temperature, pressure, and time. Surface preparation is the term used to describe the treatment employed to prepare the faying surfaces prior to bonding. This

treatment includes the machining operations, secondary finishing operations such as grinding, polishing, etc., chemical treatment, thermal treatments, and cleaning operations. The importance of surface preparation in gas-pressure bonding cannot be overemphasized. The presence of contamination in the form of dirt, oxide films, etc., can prevent diffusion across the interfaces and result in poor bonding. Since only microdeformation occurs in gas-pressure bonding, there is no opportunity to break-up and disperse the contamination during the bonding process. It therefore must be removed prior to assembly of the components for bonding. The optimum surface preparation varies with different materials and few generalizations can be made regarding the best techniques. It is safe to say, however, that all possible steps must be taken to provide the cleanest surface for bonding. Surface roughness is also important since the rougher the surface, the more difficult it is to move the surfaces into complete intimate contact. This means that attention must be given to the type of machining operation used to finish the geometries to final dimensions. Naturally, grinding operations produce smoother surfaces than other machining operations; however, grinding grit tends to be embedded in the surface and sometimes interferes with bonding if not removed by a subsequent etching operation. Hence, it is apparent that all surface-finishing operations must be carefully evaluated and integrated to insure a surface suitable for diffusion bonding.

The actual bonding parameters of temperature, pressure, and time are all interrelated. Since diffusion phenomena are controlled by both time and temperature, this importance is rather obvious. Also, as in any heat treatment, they control the final grain size, base-metal properties, and potential contamination from the surrounding environment. Sufficient pressure must be available to move the surfaces into intimate contact. The higher the temperature or the longer the time, the lower the pressure which must be applied since creep is the primary method of macrovoid closure. Lower pressures are more economically achieved and therefore pressure should be minimized where possible. Therefore, one must establish the correct combination of these parameters which will yield the best bonding with a minimum of grain growth and base-metal property change.

#### *Refractory Metal Bonds*

Numerous refractory metal combinations have been successfully joined by gas-pressure bonding. However, all systems and combinations have not been optimized. Detailed discussions of experiments conducted on each system would yield a manuscript far too large to be useful to most readers. For this reason, the discussions which follow will concentrate on satisfactory bonding procedures and the resulting microstructures.

#### *Columbium to Columbium*

Bonding parameters of 1150° to 1325° C. and 10,000 psi for 3 hrs. yield high-integrity solid-phase bonds with columbium. Etching in a nitric-hydro-

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fluoric acid solution produced satisfactory bonding surfaces. The structure and chemical, mechanical, and physical properties of the bond area are consistent with those of the parent metal. Fig. 1 shows a typical solid-phase bond in this system.

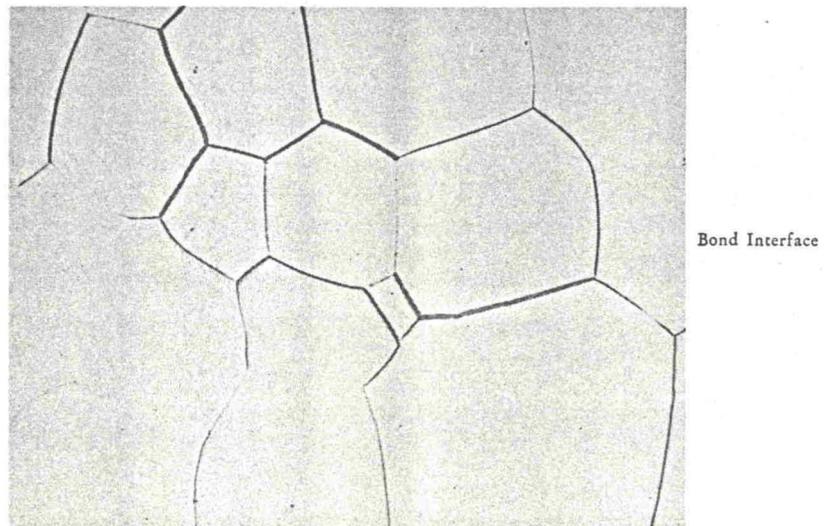


Fig. 1. Columbium self bond.  $\times 100$ .

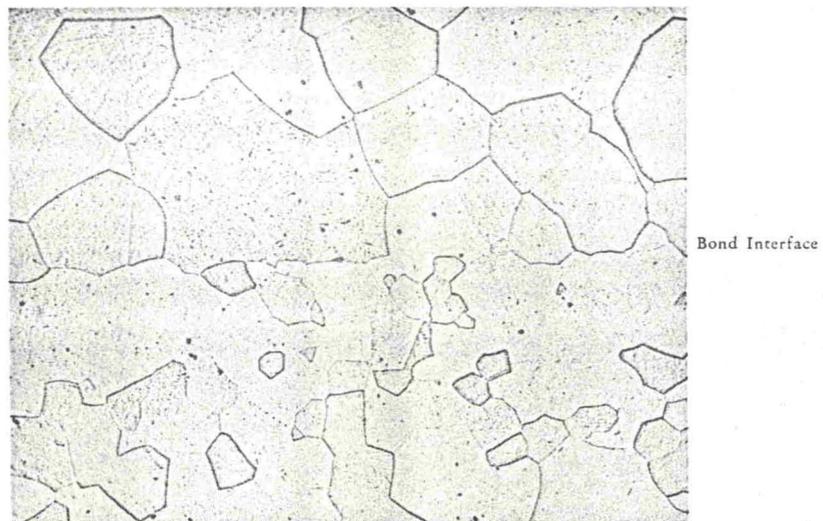


Fig. 2. Columbium-6 w/o vanadium alloy self bond.  $\times 100$ .

Columbium-6 w/o Vanadium to Columbium-6 w/o Vanadium

Excellent bonding was achieved in this system at 1250° C. and 10,000 psi for 3 hrs. as shown in Fig. 2. Etching in a nitric-hydrofluoric acid solution is a satisfactory surface preparation. Base metal properties were achieved.

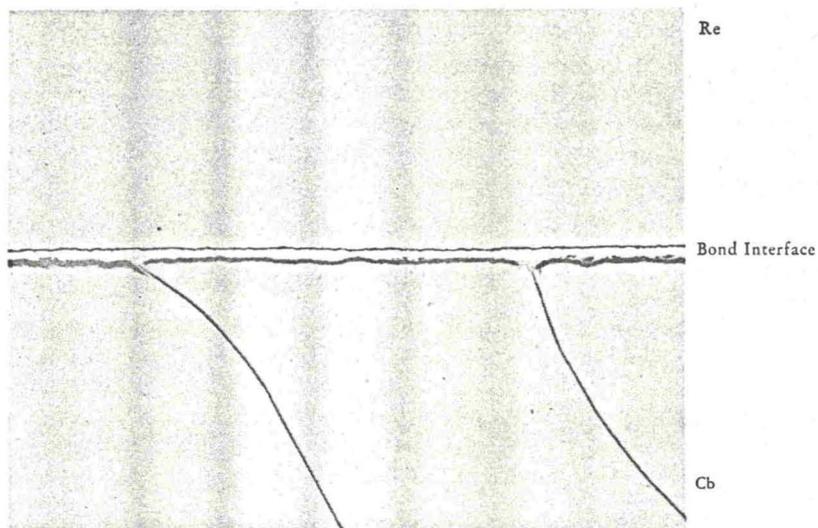


Fig. 3. Bond between columbium and rhenium.  $\times 500$ .

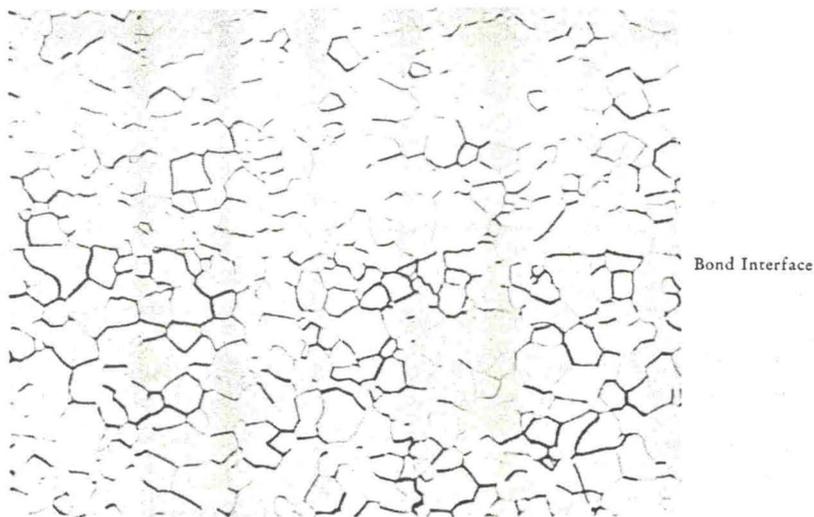


Fig. 4. Molybdenum self bond.  $\times 100$ .

#### Columbium-Rhenium

Fig. 3 shows the bond formed between columbium and rhenium after 3 hrs. at 1600° C. and 10,000 psi. The columbium surface was prepared by etching in nitrichydrofluoric acid. The rhenium surface was cleaned by firing in dry hydrogen at 1100° C. Properties of the bond were strong but somewhat brittle which is attributed to the X-phase in this system.

#### Molybdenum-to-Molybdenum

Bonding of molybdenum to itself can be accomplished at 1450° C. and 10,000 psi for 3 hrs. High-strength bonds are achieved; however, some loss in room temperature-ductility occurs due to the recrystallization of the base material during bonding. Fig. 4 shows a typical bond between molybdenum surfaces which were etched in nitric acid.

#### Molybdenum-to-Titanium

Excellent quality bonds can be achieved between molybdenum and titanium as shown in Fig. 5. This specimen was bonded at 925° C. and 10,000 psi for 2 hrs. These bonds possess good mechanical properties. By using a very thin (< 1 micron) film of titanium on molybdenum surfaces, it is possible to join molybdenum to itself below its recrystallization temperature. This approach is quite useful in many diffusion-bonding applications where the temperature of processing must be limited for metallurgical reasons.

#### Molybdenum-to-Rhenium

Complete bonding of molybdenum to rhenium has been achieved by processing at 1600° C. and 10,000 psi for 3 hrs. Fig. 6 shows the interface

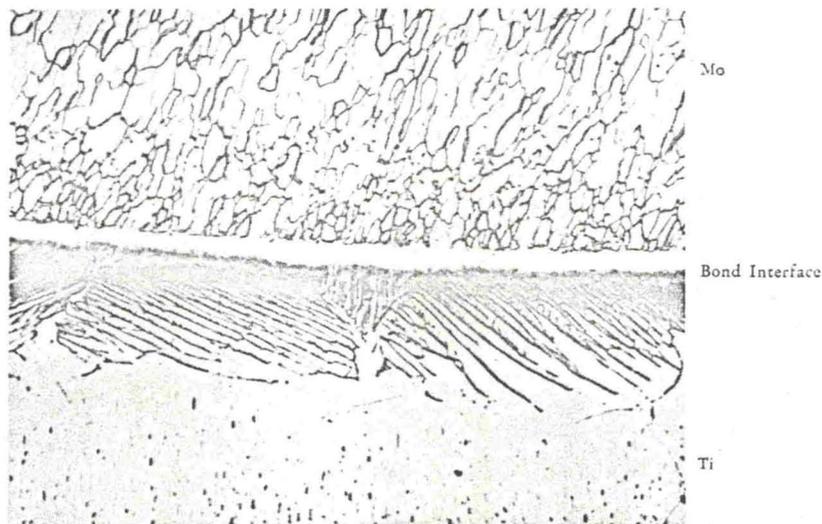


Fig. 5. Bond between molybdenum and titanium.  $\times 500$ .

formed in a composite diffusion couple. The bond formed is quite brittle due to the presence of  $\sigma$  and X-phases. Use of this bond would be limited primarily to compression-type loadings.

#### Molybdenum-to-Tungsten

The lower interface in Fig. 6 shows the bond between tungsten and molybdenum at 1600° C. and 10,000 psi for 3 hrs. This bond is rather weak and can be separated in mechanical testing. Higher temperatures appear necessary to enhance the bonding. However, it has been observed in our experiments that a pronounced Kirkendall effect exists in this system and the creation of voids in the molybdenum occurs at a very rapid rate as the temperature of processing is increased. Application of higher pressures should overcome this problem.

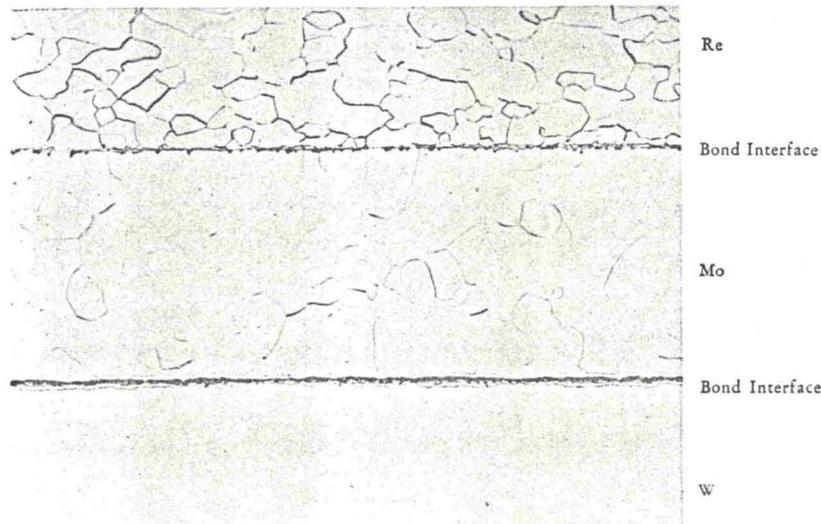


Fig. 6. Bonds between molybdenum and rhenium and molybdenum and tungsten.  $\times 250$ .

#### Molybdenum-50 w/o Rhenium-to-Molybdenum-50 w/o Rhenium

This molybdenum alloy can be very nicely bonded at 1600° C. and 10,000 psi for 3 hrs. as shown in Fig. 7. Excellent mechanical properties are achieved with the bond being both strong and ductile. Surface preparation consists of grinding and polishing with fine alumina grit followed by careful cleaning in hydrogen. Bonded specimens have exhibited good qualities on exposure to service at temperatures to 2200° C.

#### Molybdenum-50 w/o Rhenium-to-Tungsten

Fig. 8 shows the bond between these two materials after pressure bonding at 1600° C. and 10,000 psi for 3 hrs. This bond is mechanically quite strong

but is brittle at room temperature. At higher temperatures, ductility is restored. This couple shows a Kirkendall effect with void formation occurring in the molybdenum-50 w/o rhenium after 1-hr. exposure at 2200° C. This is attributed to depletion of molybdenum from the alloy into the tungsten.

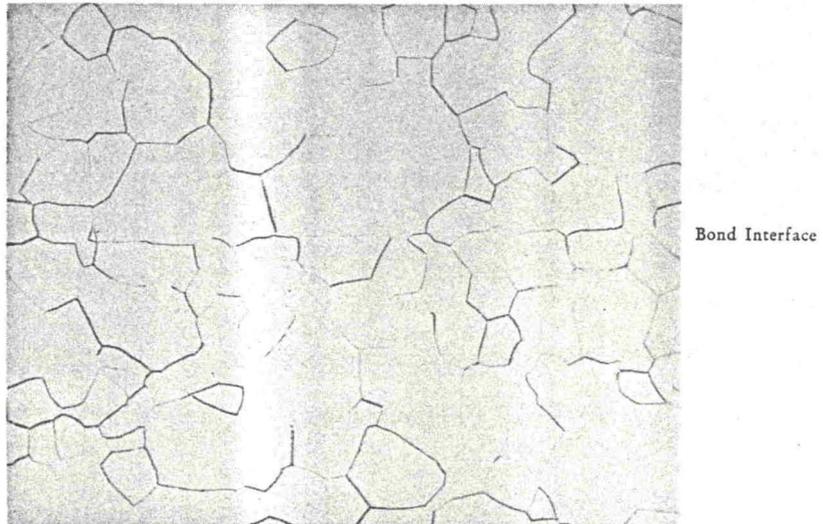


Fig. 7. Molybdenum-50 w/o rhenium self bond.  $\times 250$ .

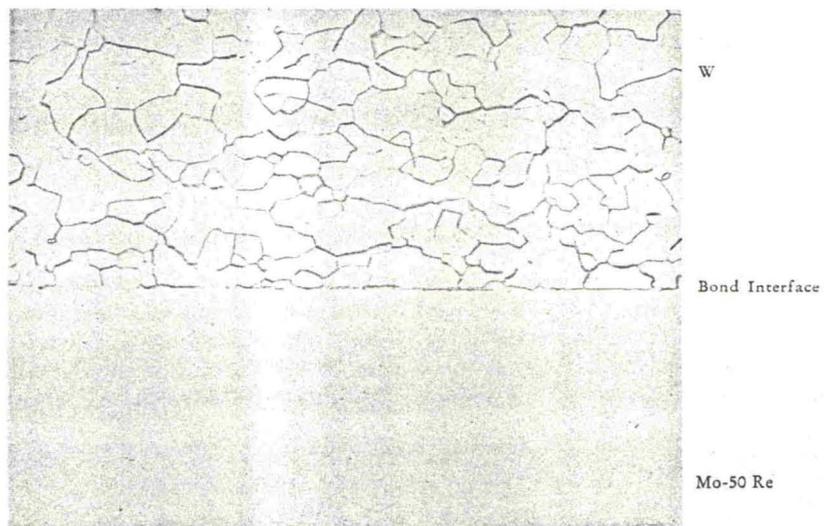


Fig. 8. Molybdenum-50 w/o rhenium bonded to tungsten.  $\times 250$ .

Platinum-30 w/o Iridium-to-Platinum-30 w/o Iridium

Self bonding of platinum-30 w/o iridium alloy is readily accomplished at 1200° C. and 10,000 psi for 3 hrs. The surface-preparation treatment used for the specimen shown in Fig. 9 was an etch in Aqua Regia. Similar results have been achieved with pure platinum and platinum-20 w/o iridium. Excellent strength and ductility are achieved with all of these materials.

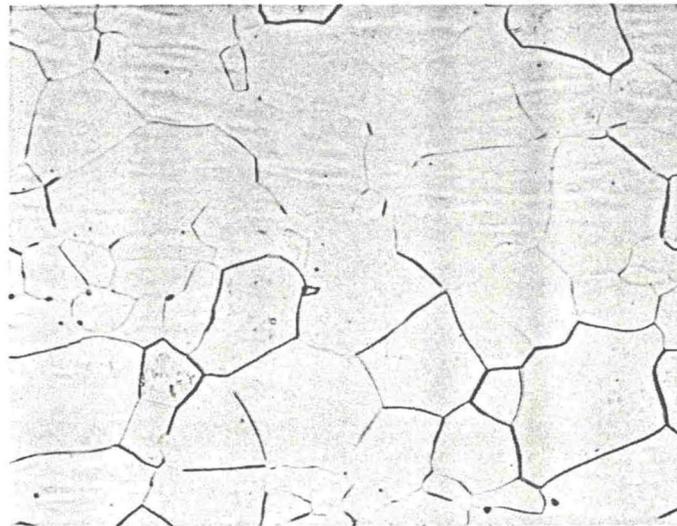


Fig. 9. Platinum-30 w/o iridium self bond.  $\times 500$ .



Fig. 10. Tantalum self bond.  $\times 100$ .

## Tantalum-to-Tantalum

Tantalum surfaces prepared by etching in nitric-hydrofluoric acid solutions can be satisfactorily bonded at 1450° C. and 10,000 psi for 3 hrs. Fig. 10 shows a tantalum self bond possessing parent metal strength and ductility. Care must be exercised to avoid hydrogen pick-up during processing or embrittlement may result.

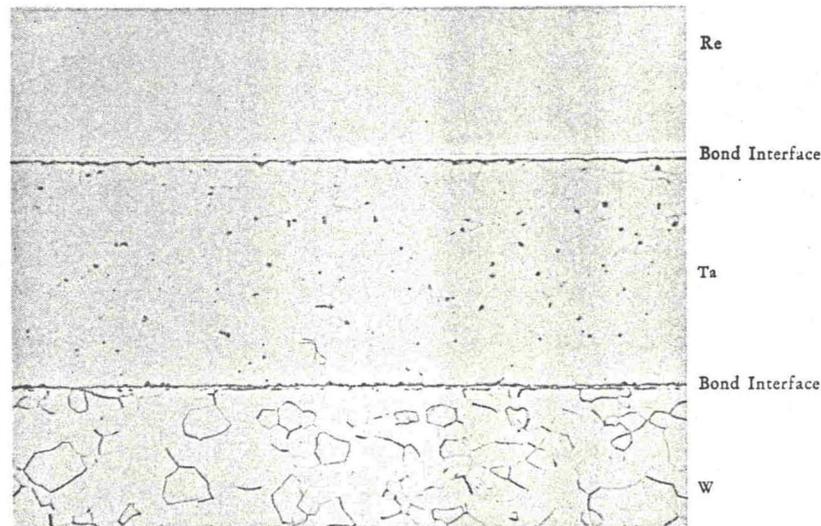


Fig. 11. Bonds between tantalum and rhenium and tantalum and tungsten.  $\times 250$ .

## Tantalum-to-Rhenium

The upper interface shown in Fig. 11 shows the bond formed between tantalum and rhenium at 1600° C. and 10,000 psi for 3 hrs. The bond as formed is strong but very brittle so that crack propagation and fracture along the interface is easily promoted. This brittle behavior is attributed to the X-phase in this system. Exposure at higher temperature only increases the amount of the X-phase and does not help the properties of the joint. No Kirkendall effect has been noted up to 2200° C. in bonded specimens.

## Tantalum-to-Tungsten

Tantalum-to-tungsten appears to be quite similar to the molybdenum-tungsten system in that temperatures above 1600° C. appear required to get high-strength bonds. Fig. 11 also shows a bond formed at 1600° C. and 10,000 psi for 3 hrs. While appearing well bonded, the joint was relatively weak. It is believed that slightly higher bonding temperatures would be

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beneficial. Since only a limited Kirkendall effect was noted in heat treatments up to 2200° C., there does not appear to be an inherent problem in the use of higher bonding temperatures.

**Rhenium-to-Rhenium**

Excellent bonds between rhenium surfaces can be achieved at 1600° C. and 10,000 psi for 3 hrs. A surface preparation of grinding and polishing with alumina grit followed by hydrogen cleaning at 1100° C. has been satisfactory. These bonds have strength and ductility equivalent to the base material. Fig. 12 shows a typical rhenium self-bond. Note the heavy twinning in the microstructure which resulted during preparation of the metallographic specimen.

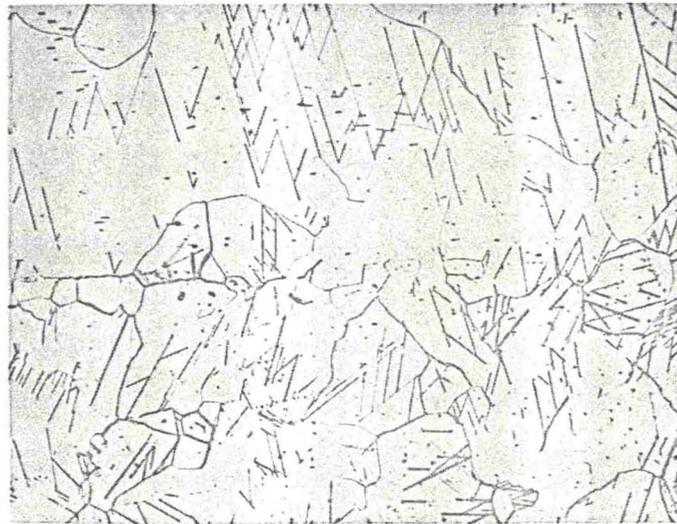


Fig. 12. Rhenium self bond. × 250.

**Rhenium-Tungsten**

Excellent bond strength can be achieved in this system; however, the bond is very brittle due to the formation of intermetallic compounds. This bond is satisfactory for compression loading applications. Fig. 13 shows a bond which was formed at 1600° C. and 10,000 psi for 3 hrs. and then heat treated at 2200° C. for 1 hr. Note that diffusion is quite sluggish and that no Kirkendall effect is evident under these conditions.

**Rhenium-Zirconium**

Fig. 14 shows a bond formed between rhenium and zirconium at 1100° C. and 10,000 psi for 3 hrs. Note that excessive diffusion has occurred in this case and it would be desirable to decrease both time and temperature of the

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bonding treatment. This interface is not well characterized but does possess at least one hard constituent causing it to be somewhat brittle in nature. Improved properties would be expected if the diffusion zone were more narrow.

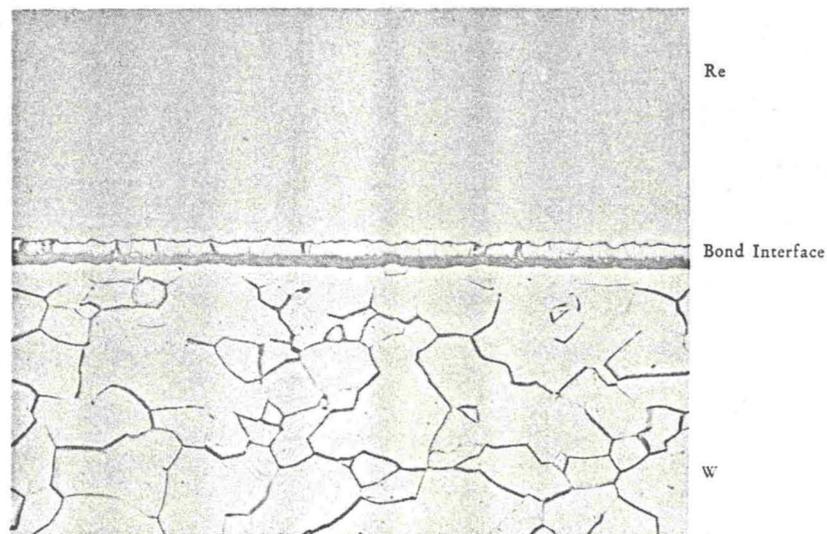


Fig. 13. Bond between rhenium and tungsten.  $\times 250$ .

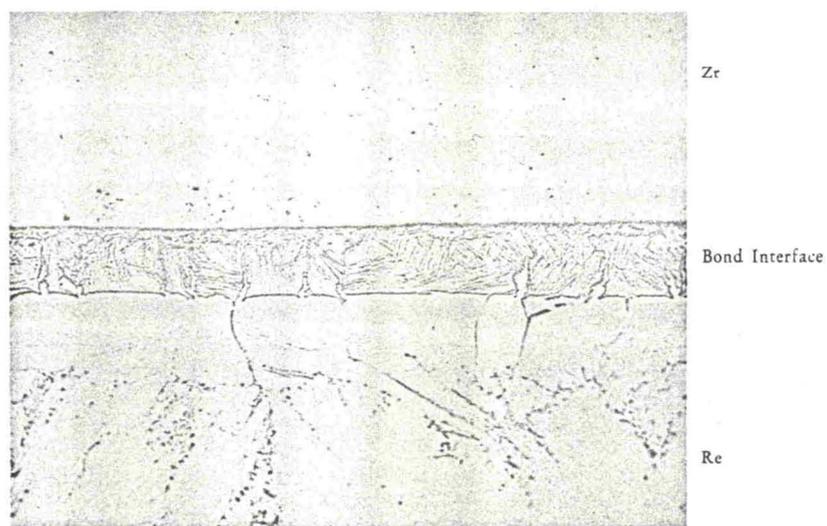


Fig. 14. Bond between rhenium and zirconium.  $\times 250$ .

### Tungsten-Tungsten

Self bonds have been produced in tungsten which have given parent metal strength even to temperatures of 2500° C. Surface preparations should be done so as to produce as smooth a surface as possible. Final cleaning in dry hydrogen at 1100° C. or higher is effective. Fig. 15 shows a bond prepared

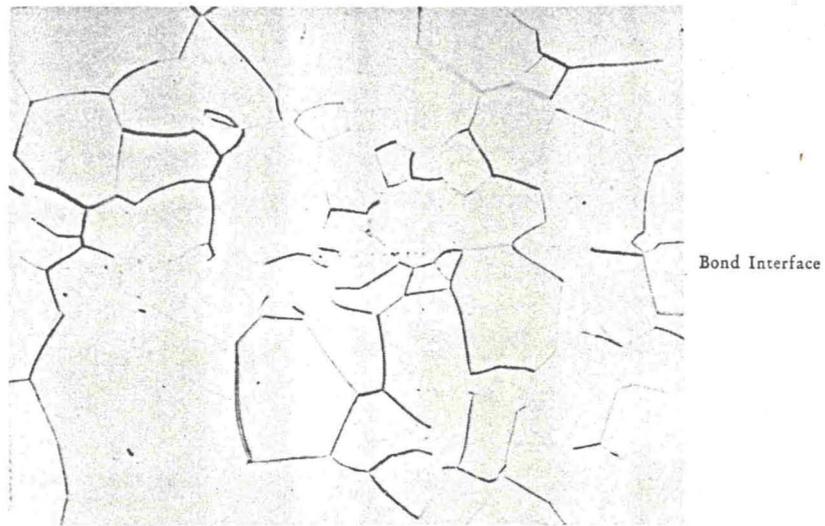


Fig. 15. Tungsten self bond.  $\times 250$ .

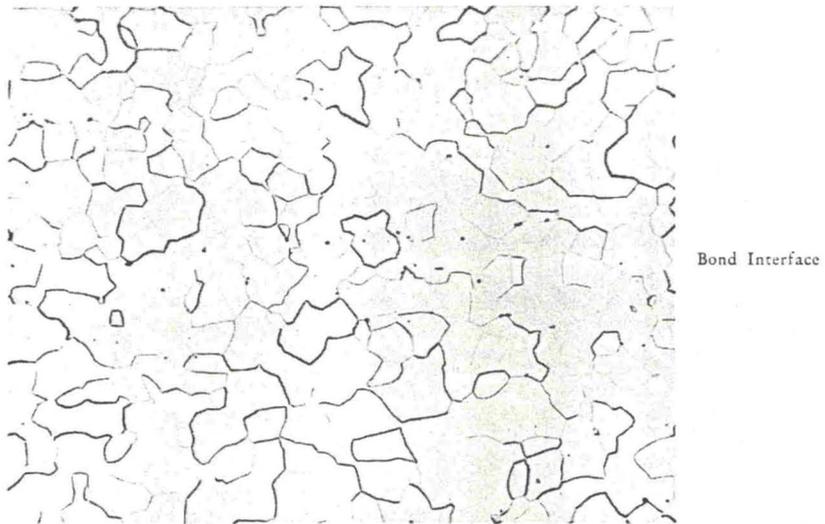


Fig. 16. Tungsten-26 w/o rhenium alloy self bond.  $\times 250$ .

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at 1600° C. and 10,000 psi for 3 hrs. Some small microvoids remain even though complete grain growth across the interface has occurred. Use of pressures of 30,000 psi or higher virtually eliminates microporosity.

### Tungsten-26 w/o Rhenium-to-Tungsten-26 w/o Rhenium

This system lends itself nicely to solid-phase bonding. Fig. 16 shows the high quality of bond achievable at conditions of 1600° C. and 10,000 psi for 3 hrs. Surface preparation consisted of grinding and polishing with alumina grit followed by hydrogen cleaning. Full strength was achieved at the joint. Room-temperature ductility was poor because of the relatively high ductile brittle transition for this material. However, at temperatures above 550° C., the bonds and base metal were quite ductile.

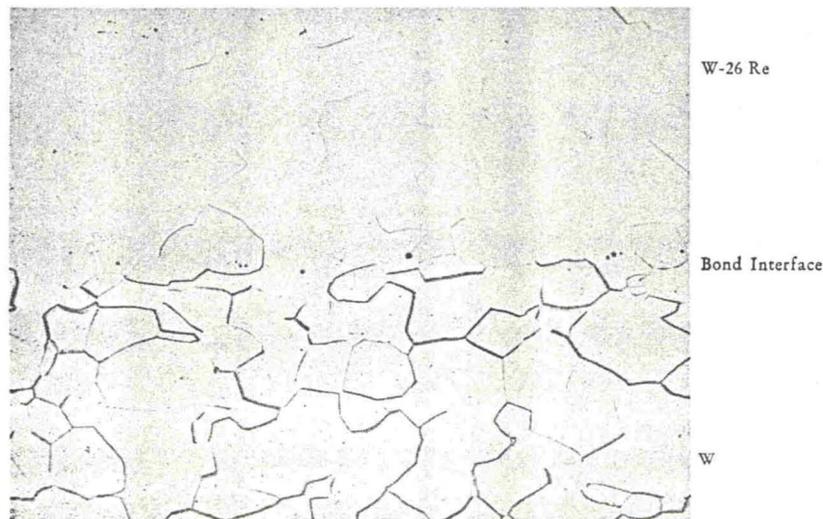


Fig. 17. Bond between tungsten and tungsten-26 rhenium.  $\times 250$ .

### Tungsten to Tungsten-26 Rhenium

Excellent bonding can be achieved between tungsten and tungsten-26 w/o rhenium alloy. Since diffusion dilutes the rhenium content, the brittle sigma phase can be avoided. Fig. 17 shows a bond formed at 1650° C. and 10,000 psi for 3 hrs. Strength of these bonds are excellent and ductility is good if tested above the ductile-brittle transition temperature. Surfaces were prepared by grinding, polishing, and hydrogen cleaning.

### Applications

In the preceding section, bond quality and suitability of solid-phase bonding to various refractory metal combinations was explored. It is not suf-

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efficient, however, to judge the suitability of a joining process on the basis of simplified geometries such as diffusion couples. For this reason, several examples of hardware applications have been chosen to demonstrate the flexibility of the gas-pressure-bonding process for solid-phase bonding.

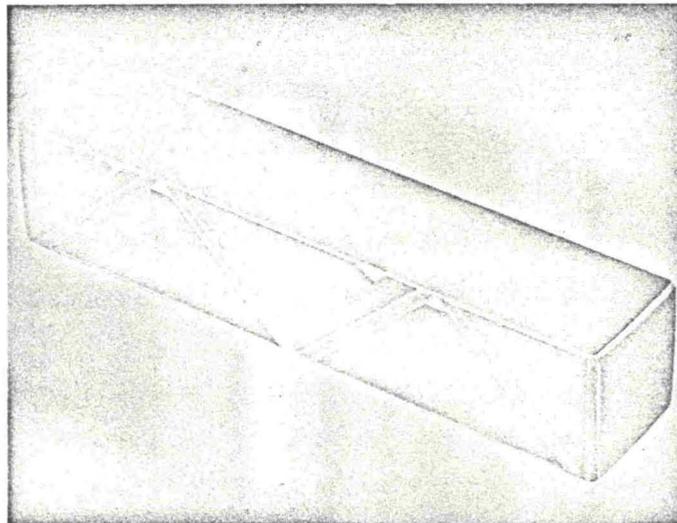


Fig. 18. Truss-supported structure made from columbium.  $\times 1/2$ .

#### Truss-Supported Structure

The truss-supported structure shown in Fig. 18 was fabricated from columbium sheet. All twelve joints in the structure were bonded in one operation by gas-pressure bonding at  $1200^{\circ}\text{C}$ . and 10,000 psi for 3 hrs. Parent metal strength was obtained in all joints.

To prepare this specimen, the eight pieces of columbium were sheared and machined from sheet of appropriate thickness. Low-carbon steel was used as internal tooling to form the triangular cavities between the trusses. The tooling is necessary to prevent collapse of the structure during the gas-pressure-bonding operation. The assembly was canned in a low-carbon steel container, evacuated, sealed, and gas-pressure bonded at the conditions mentioned above. After bonding was completed, the can and tooling were removed by leaching in nitric acid. The columbium is unaffected by nitric acid so this provides a simple and inexpensive method of tooling removal.

#### High-Temperature Heater Component

Fig. 19 shows a component of a high-temperature hydrogen furnace. This component was designed to operate at  $2500^{\circ}\text{C}$ . The specific design requirements necessitated the use of a rhenium tube to be structurally bonded to a heavy tungsten back-up collar. The OD of the rhenium and ID of the

tungsten components were lightly ground and then cleaned in hydrogen. The components were then assembled into proper position and sealed in an evacuated tantalum container. The assembly was then successfully gas-pressure bonded at 1650° C. and 10,000 psi for 3 hrs. After completion of bonding, the tantalum container was removed by mechanical stripping and selective leaching. Visual and ultrasonic inspections of the bond indicated that satisfactory bonding had been achieved. The component was then successfully employed for its intended high-temperature application.

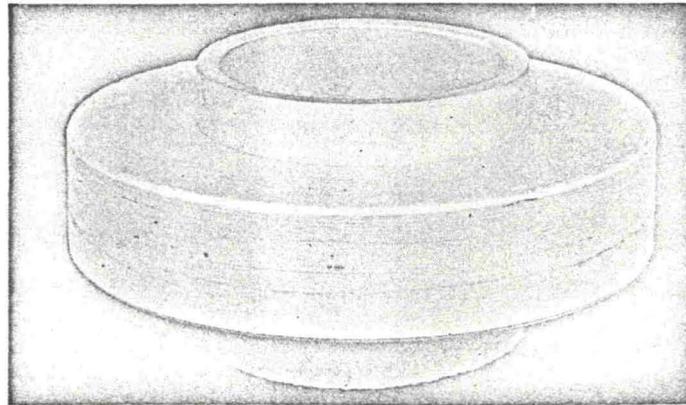


Fig. 19. High-temperature furnace component,  $\times 1/2$ .

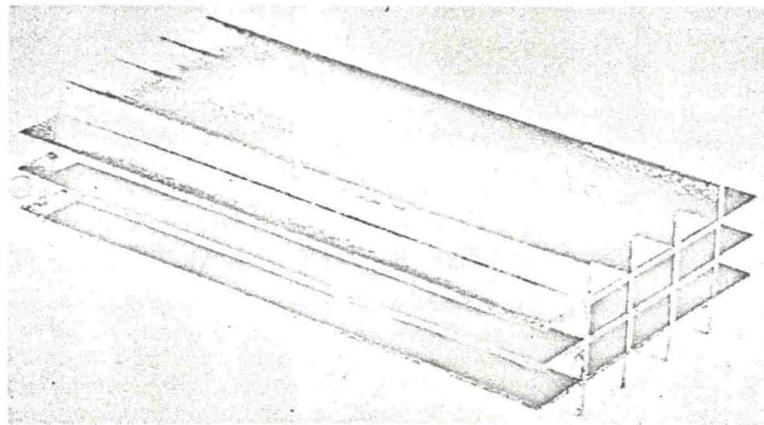


Fig. 20. High-temperature heat exchanger made from tungsten.

#### Tungsten Heat Exchanger

Certain applications in modern technology require heat exchangers to operate at very high temperature. One such application utilizing hydrogen gas as the heating fluid, required the fabrication of the structural heat exchanger shown in Fig. 20.

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The egg-crate design shown was made up from individual strips of pure tungsten. The flow channels were formed by placing molybdenum strips alternately with the tungsten pieces. The molybdenum served the same function as the mild steel in the previous example. The assembly is then canned in molybdenum, evacuated, and sealed. Gas-pressure bonding was conducted at 1600° C. and 10,000 psi for 3 hrs. Removal of the can and tooling was accomplished by leaching in nitric acid which does not attack tungsten. The result was a structure of high integrity which functions as a monolithic body at temperatures in excess of 2000° C.

### Conclusions

Experimental studies at Battelle-Columbus have demonstrated the suitability of solid-phase bonding for applications involving refractory metals. The gas-pressure-bonding process is particularly useful because of the versatility of process due to the omnidirectional application of pressure by the gas. Control of process variables are readily achieved if the process is thoroughly understood in the material system in question. Properties of bonds between similar metals prepared in this manner will be equivalent to those of the base metals. However, in the case of dissimilar materials, attention must be paid to compound formation and Kirkendall effects which may limit the use of joint in high-temperature structural applications.

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