

**MAGNET**  
**OAK RIDGE NATIONAL LABORATORY**

operated by  
**UNION CARBIDE CORPORATION**  
for the  
**U.S. ATOMIC ENERGY COMMISSION**



ORNL - TM - 413 *sky*

COPY NO. - *24*

DATE - Nov. 8, 1962

PROGRESS REPORT - BRAZING OF CERAMICS

C. W. Fox

ABSTRACT

The inherent properties of ceramic materials make them very attractive for potential use in nuclear reactors as well as other high-temperature corrosive environment applications. To obtain the utmost from the attractive properties of these ceramic materials, suitable joining procedures must be available. Although ceramic-to-ceramic and ceramic-to-metal joints have been produced for many years in specialized industries, a program was undertaken by the Metals and Ceramics Division at the Oak Ridge National Laboratory (ORNL) to develop simplified procedures that would be particularly applicable to high-temperature nuclear reactor uses.

Brazing alloys such as 48 Ti-48 Zr-4 Be (wt %) and 49 Ti-49 Cu-2 Be (wt %) have been found to readily flow on oxide and graphite ceramics. Two demonstration fuel element assemblies were fabricated to illustrate the usefulness of these procedures for nuclear applications. One of these assemblies contained graphite tubes and end caps which were brazed to a molybdenum hanger. The second demonstration fuel element was composed of a compartmented aluminum oxide plate to which aluminum oxide cover plates were brazed.

In addition to these assemblies, assistance was provided to various ORNL experimental groups. A wide variety of ceramic-to-metal joint assemblies was fabricated and included electrical insulation components (magnesium oxide-to-stainless steel) and a synthetic sapphire Hall cell unit.

**NOTICE**

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PROGRESS REPORT - BRAZING OF CERAMICS

INTRODUCTION

The excellent elevated-temperature strength and good resistance to corrosion of ceramic materials (including graphite) make them highly attractive for use in high-temperature reactors of advanced designs. This group of materials also has good resistance to thermal shock, while their major limitation results from their generally poor impact properties.

As the applications for ceramics increase, the need for improved joining procedures to promote their more effective utilization becomes more pressing. Ceramic-to-metal seals have been produced for many years in fields such as the vacuum-tube industry, and there has been a variety of processes proposed and used successfully for making such joints.<sup>1-3</sup> Most of these techniques require that the ceramic be pre-metallized and then joined to the structural metal by soldering or brazing.

The production of ceramic-to-metal assemblies by some of these procedures is a multistep operation which is both time consuming and expensive. Operations of this type tend to be somewhat troublesome where the nature of the work changes frequently as compared to long-run mass-production orders. The premetallizing feature is also undesirable for many nuclear reactor applications since the commonly used intermediate metals, such as manganese, exhibit poor corrosion and oxidation resistance to many of the conventional reactor environments.<sup>4</sup>

---

<sup>1</sup>W. H. Kohl, Materials and Techniques for Electron Tubes, pp 470-518, Reinhold Publishing Corporation, New York, 1960.

<sup>2</sup>G. R. Van Houten, "A Survey of Ceramic-to-Metal Bonding," Bull. Am. Ceram. Soc. 38, 301-07 (June 1959).

<sup>3</sup>H. Bender, "High-Temperature Metal-Ceramic Seals," Ceram. Age 63, 15-24 (April 1954).

<sup>4</sup>G. M. Slaughter et al., "Sodium Corrosion and Oxidation Resistance of High-Temperature Brazing Alloys," Welding J. 36(5), 217s-25s (May 1957).



In view of the many potential benefits which can be obtained from advancements in ceramic brazing technology, a program has been initiated in the Metals and Ceramics Division at ORNL to investigate this field. A primary purpose of the study was to develop simplified procedures for the direct brazing of ceramic fuel elements (including graphite), although development of techniques for constructing a variety of test assemblies containing ceramic components was also recognized as being of major concern. It was highly desirable that the brazing alloys used in fabricating such assemblies would wet and flow on ceramics in much the same manner that conventional alloys flow on stainless steels and other common structural metals without the necessity for intermediate metallizing operations.

## GENERAL CONSIDERATIONS

### Wetting Problems

One of the basic problems in brazing ceramics lies in their poor wetting by conventional brazing alloys and procedures. As mentioned previously, there are several commercial processes that have been used in brazing ceramics to themselves, to dissimilar ceramics, and to metals. The mechanisms involved in producing bonds by all these methods have been categorized into three general groups:<sup>5</sup>

1. Utilization of a molten ceramic wetting a higher melting refractory metal (such as porcelain enamel on metal).
2. Use of a molten metal to wet a higher melting refractory ceramic.
3. Utilization of solid-state reactions whereby the intimacy of contact is provided by pressure, spraying, or painting. Solid-state reactions occur during firing at a temperature slightly below the melting point of either metal or ceramic.

---

<sup>5</sup>Hayne Palmour III, "Review of High Temperature Metal-Ceramic Seals," J. Electrochem. Soc. 102, 160c-64c (July 1955).

The classification of prime interest to the ORNL work is the second category -- that of using a molten metal to wet a ceramic. Certain metals, because of their atomic size and chemical properties, exhibit an affinity for chemical bonding with ceramics. Titanium and zirconium are two common metals with these characteristics. They both have high affinity for oxygen and can also enter into solid solutions with a number of metals and suboxides. Oxides of titanium and zirconium are highly refractory and it has been proposed that, under proper conditions, titanium and zirconium will reduce some of the ceramic oxides and combine with the released oxygen. High vacuum or high-purity reducing or inert-gas atmospheres are necessary for such brazing procedures to be successful.

#### Differential Expansion Problems

Another problem in joining ceramics to metals for high-temperature service results from the significant differences in thermal expansion behavior. When the thermal environment of a metal-ceramic assembly is altered, these differences in thermal expansion behavior can lead to high stresses. This condition is often subsequently intensified by thermal gradients that arise as a consequence of thermal diffusivity differences between the metal and ceramic. Ceramics generally possess high elastic moduli and low-relaxation characteristics which prevent relief or redistribution of the stresses. The low tensile strengths of most ceramics may then make them unable to resist fracture under such stresses.

#### Joint Design

The performance of ceramics under compressive loads is very good and should be exploited whenever possible by proper joint design. Another solution to the problem of differing thermal expansion behaviors is to use a low-expansion transition metal, such as molybdenum, adjacent to the ceramic. These transition metals can yield and thereby minimize straining (and fracture) in the brittle ceramic.

## BRAZING ALLOY DEVELOPMENT

The selection of brazing alloys for the initial portions of this ceramic brazing investigation made use of a group of promising experimental alloys already developed at ORNL during the course of other experimental programs. A brazing alloy development program for the joining of refractory metals has been in progress for a number of years, and several hundred different binary, ternary, and quaternary alloys have been formulated during this period.<sup>6</sup> The development of procedures for brazing graphite for advanced molten-salt reactor applications has also been under study at ORNL.<sup>7</sup>

Many of these alloys contain titanium and/or zirconium as major constituents and, as mentioned before, might be expected to bond to oxide ceramics quite readily. In addition, alloys containing strong carbide formers such as molybdenum, tantalum, titanium, and zirconium were found to wet graphite. Alloys with these metals as major constituents should be compatible with many potential reactor environments such as liquid metals and pressurized water.

The suitability of the brazing alloys for joining ceramics can be determined in a general way by metallographic examination of brazed joints. Examples of some high quality brazes obtained with one particularly promising alloy (48 Ti-48 Zr-4 Be, wt %) are shown in the photomicrographs of Figs. 1 and 2. These photomicrographs illustrate good adherence and wetting of the ceramic and show sound, crack-free joints. The brazing has been performed using either resistance or induction heating in a vacuum or inert atmosphere to prevent oxidation of the alloy.

It should be emphasized that the development of a brazing alloy with acceptable wetting and flow characteristics is only a portion of

---

<sup>6</sup>C. W. Fox and R. G. Gilliland, Progress Report on Brazing of Columbium, ORNL CF-61-7-24 (July 5, 1961).

<sup>7</sup>R. G. Donnelly and G. M. Slaughter, "Brazing of Graphite," Welding J 41(5), 461-69 (May 1962).

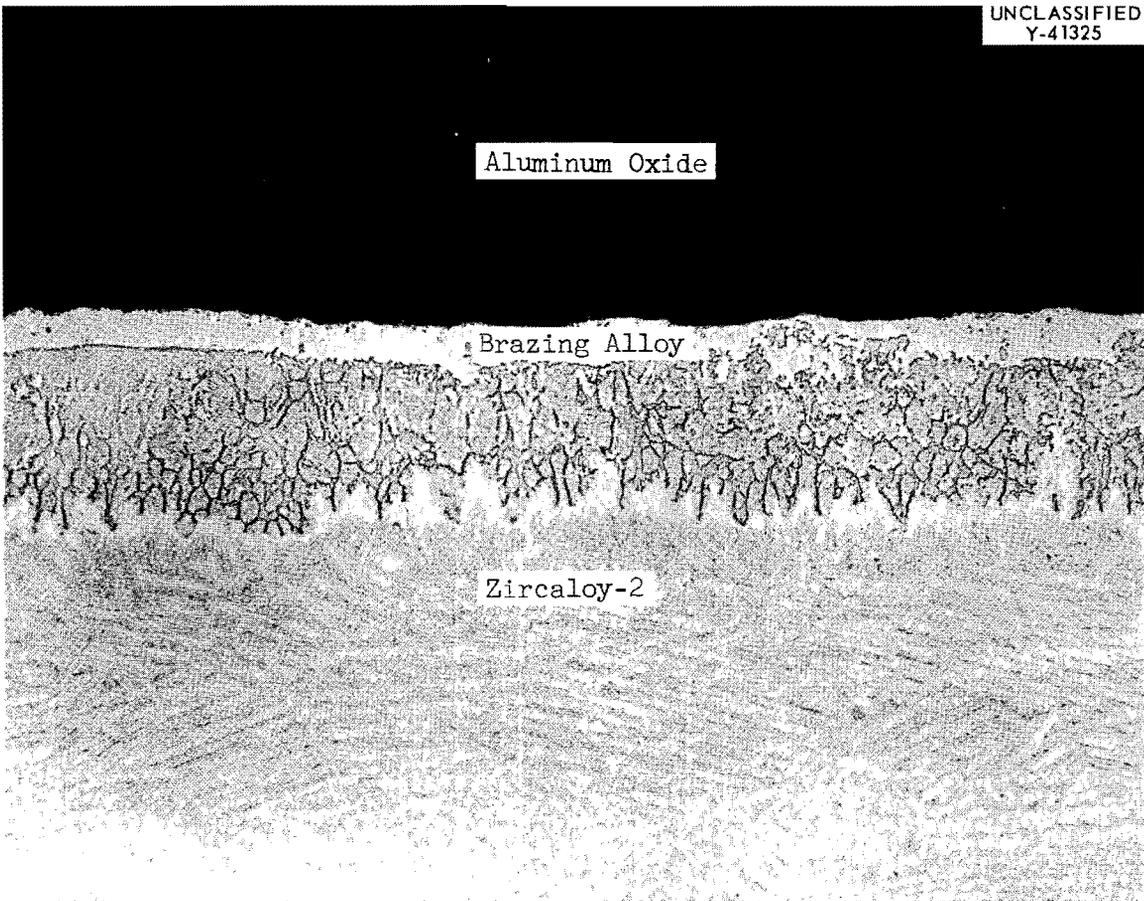


Fig. 1. Photomicrograph of Aluminum Oxide-to-Zircaloy-2 Joint Vacuum Brazed with 48 Ti-48 Zr-4 Be (wt %) at 1060°C for 10 min. Excellent bonding can be seen. As-polished. 200X.

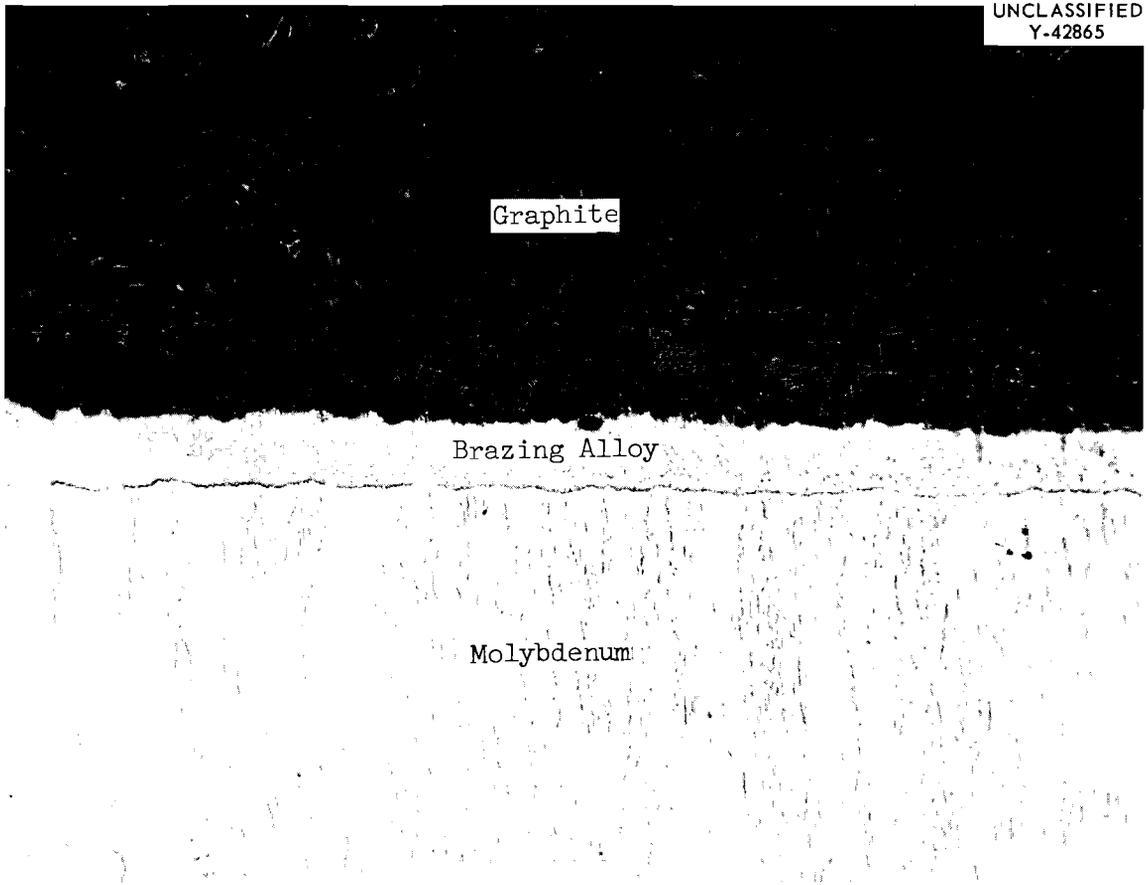


Fig. 2. Photomicrograph of Graphite-to-Molybdenum Joint  
Vacuum Brazed with 48 Ti-48 Zr-4 Be (wt %) at 1060°C for 10 min.  
A very sound bond is evident. As-polished. 100X.

the solution of the problem of joining ceramics to metals. The thermal expansion differences make it mandatory that considerable attention be given also to joint design and materials combinations.

#### FUEL ELEMENT APPLICATIONS

In order to illustrate the potential value of ceramic brazing, two experimental fuel element assemblies were designed and fabricated.

##### Graphite-Molybdenum Assembly

The first experimental assembly contained graphite tubes joined to a low-expansion molybdenum hanger. Such an assembly is similar to many of the present tubular fuel element designs utilizing metal hangers or "spiders" to hold the individual capsules. The component parts are shown in Fig. 3, while Fig. 4 shows the completed brazed assembly. The end caps were machined from a block of conventional nuclear grade graphite (AGOT), while the tubing is a low porosity, high density grade graphite. Metallographic examination revealed that brazing of the end caps to the tubes, as well as the tubes and end caps to the molybdenum hanger, could be successfully accomplished in one operation. The 49 Ti-49 Cu-2 Be (wt %) experimental brazing alloy readily wet and flowed on all mating surfaces and exhibited good filleting. The assembly was vacuum brazed ( $1 \times 10^{-5}$  torr) one end at a time at 980°C for 5 min, the tube axes being in the vertical position during brazing. The brazing alloy was applied in powder form in the cavity formed by the tube and molybdenum hanger when oriented in the vertical position. The end caps were then set on the preplaced brazing alloy and a metal weight was placed on the end caps to assure that they settled correctly when the brazing alloy became molten. To produce a sound braze joint, it was found necessary to maintain a maximum joint clearance of 0.005 in. on the diameter (preferably 0.003 in.). It is also necessary to have a reasonably smooth surface finish on the graphite after machining in order to maintain uniform joint clearance and assure good capillary flow of the brazing alloy. The joint design and the assembly itself were both kept very simple in order to demonstrate feasibility. They do not reflect an analysis of nuclear requirements or potential stresses in the system.

UNCLASSIFIED  
Y-40854

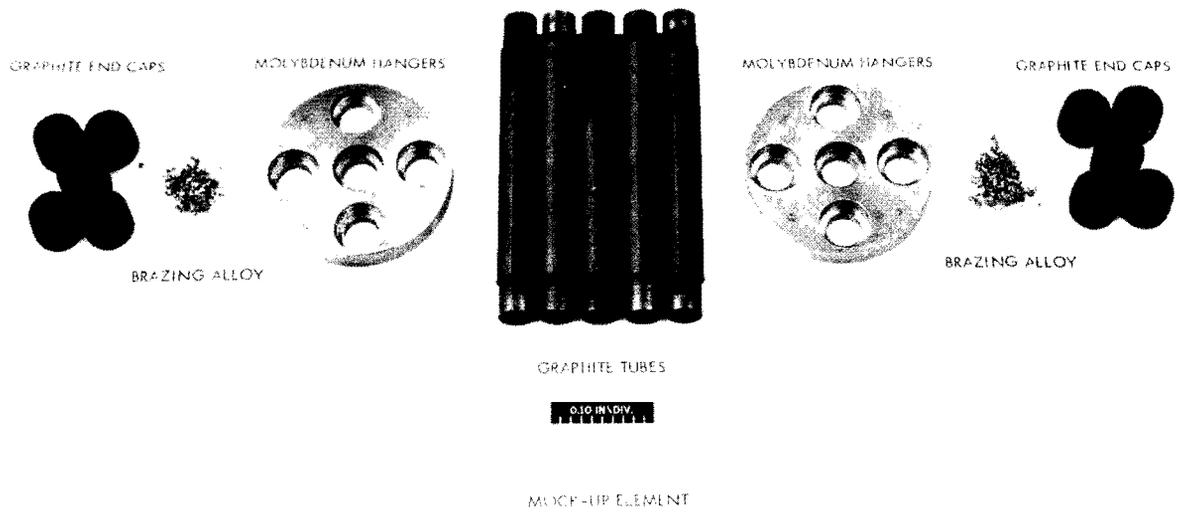


Fig. 3. Components of Demonstration Graphite-Molybdenum Fuel Element.

UNCLASSIFIED  
Y-42526

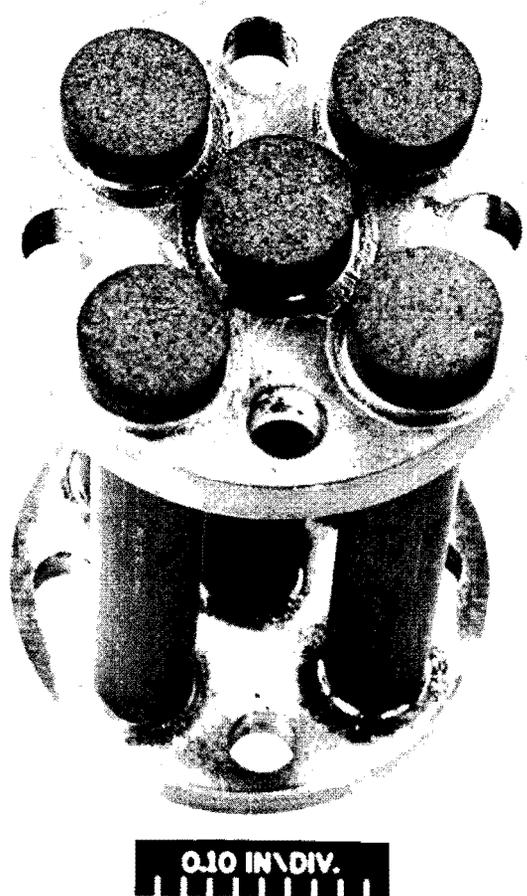


Fig. 4. Completed Demonstration Graphite-Molybdenum Fuel Element Assembly, Vacuum Brazed with 49 Ti-49 Cu-2 Be (wt %) Alloy at 980°C for 5 min. Excellent flow of the alloy is evident.

### Compartmented Aluminum Oxide Assembly

A second advanced concept is to make an element completely out of an oxide ceramic, and one possible design is a compartmented ceramic plate to which top and bottom cover plates would be brazed after loading with fuel. An experimental assembly of this design, also vacuum brazed ( $1 \times 10^{-5}$  torr) with the 49 Ti-49 Cu-2 Be (wt %) alloy, is seen in Fig. 5. The compartments of the assembly were produced by spark-discharge machining. As with the case of the previous assembly, this design does not include any specific nuclear considerations in its size or design, but it does illustrate that it may be possible to successfully fabricate and join such an assembly. A photomicrograph of a joint of this type is shown in Fig. 6. The titanium-copper-beryllium alloy flowed well and made a sound, crack-free joint. The brazing conditions for this assembly were 980°C for 10 min. The brazing alloy was applied in granular form and was preplaced on the ledge around the joint. The  $Al_2O_3$  surfaces were ground flat prior to brazing and were held together with molybdenum wire during the brazing cycle.

### SERVICE APPLICATIONS

The joining of ceramics to metals also finds application in a wide variety of other fields. This fact is evidenced by the many and varied requests from ORNL experimental groups for service assistance. In order to indicate the progress made to date and the type of assemblies that it is possible to fabricate, some of these projects will be discussed briefly.

#### Bearing Assembly

A process was developed for brazing a bearing journal of aluminum oxide to a metal inner sleeve. Titanium was selected as the material for the inner sleeve since it has a coefficient of thermal expansion approximating that of alumina and thus minimizes the expansion-differential problem. Of those alloys that were investigated, the most satisfactory was the 49 Ti-49 Cu-2 Be (wt %). The assembly was slowly heated to 1000°C in vacuum, held at temperature for 10 min, and furnace cooled.

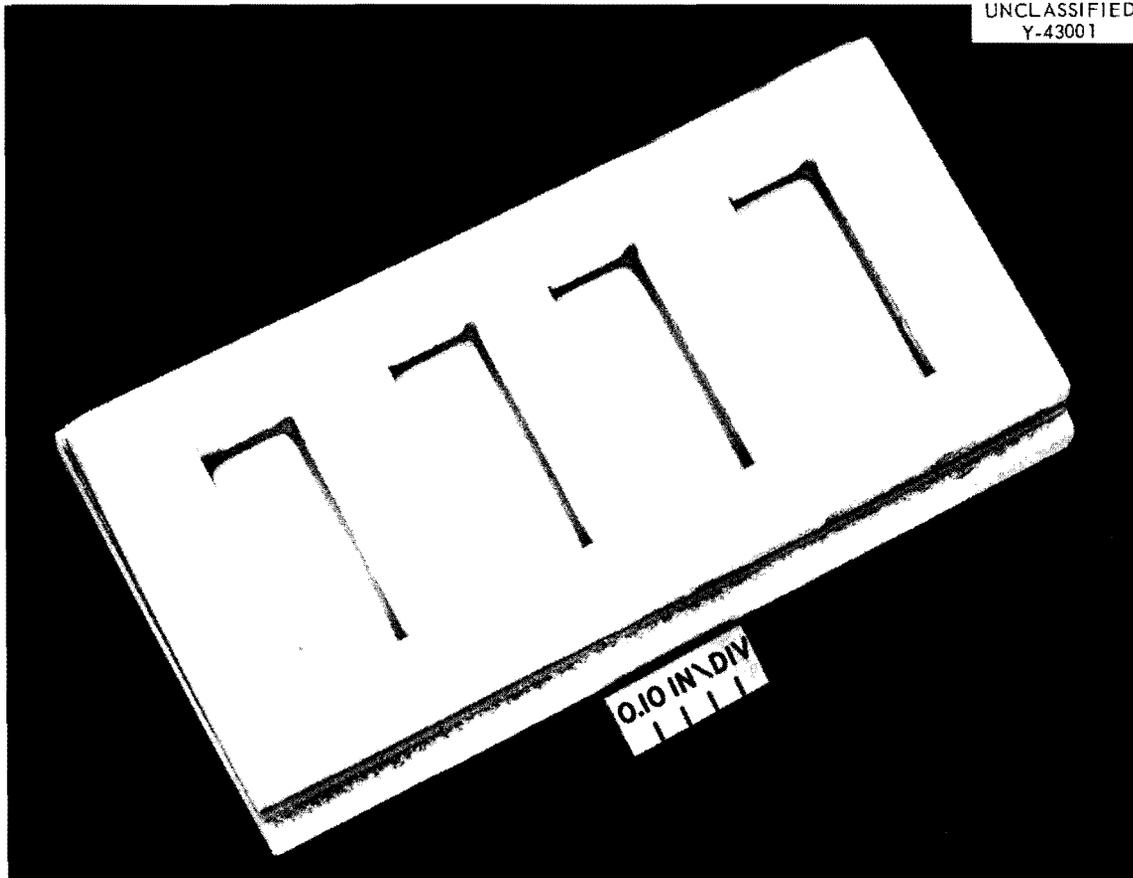


Fig. 5. Demonstration Compartmented Aluminum Oxide Assembly Vacuum Brazed with 49 Ti-49 Cu-2 Be (wt %) Experimental Alloy. The brazing conditions were 980°C for 10 min.

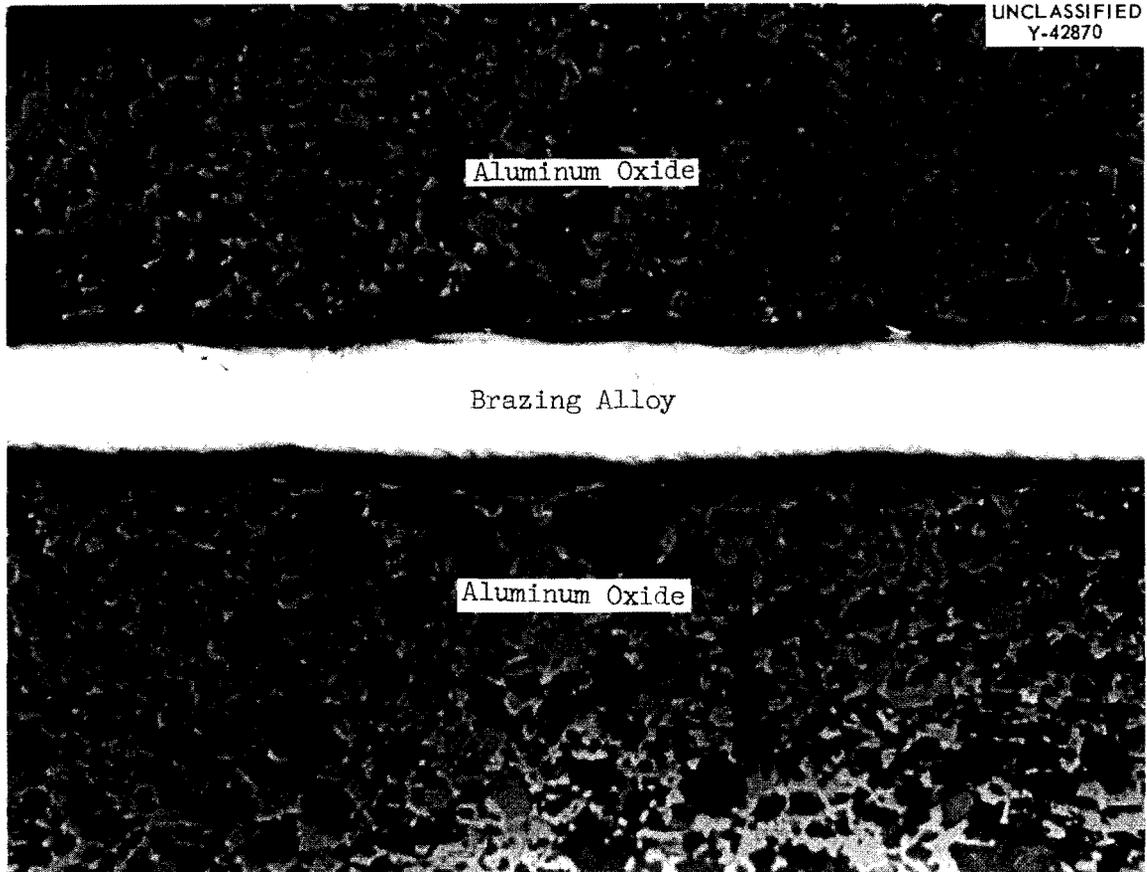


Fig. 6. Photomicrograph of  $Al_2O_3$  Joint Vacuum Brazed with 49 Ti-49 Cu-2 Be (wt %) at  $1000^\circ C$  for 10 min. A high-integrity joint is evident. As-polished. 200X.

A mockup of the assembly is shown in Fig. 7. Thermal cycling of the part from ambient to 300°C did not produce any cracking or visibly affect the joint integrity.

#### Insulation for Electrical Leads

Another application required the fabrication of an in-pile test assembly containing insulated electrical leads. A brazing alloy composition of 48 Ti-48 Zr-4 Be (wt %) was selected since an additional requirement of low-neutron cross section was imposed. Figure 8 shows the completed assembly which was leak-tight and in which the titanium lead-through wires were electrically insulated from the titanium cap by aluminum oxide tubing.

A similar project involved electrically insulating a tantalum wire, which was to act as a resistance heater for a tubular stainless steel fuel capsule, from the fuel capsule. Magnesia (MgO) was used for the insulating material and it can be seen in the end-cap assembly shown in Fig. 9. Molybdenum was introduced into the assembly to act as a buffer material between the ceramic and the stainless steel. Figure 9 shows the end-cap assembly and a portion of the stainless steel fuel capsule to which it was welded.

The sequence of operations was as follows:

1. The molybdenum was vacuum brazed to the stainless steel end cap with pure copper. Brazing conditions - 1100°C for 10 min.
2. Magnesia-to-molybdenum joint vacuum brazed with 49 Ti-49 Cu-2 Be (wt %) at 990°C for 5 min.
3. The tantalum wire was then vacuum brazed to the magnesia insulator with the same alloy (titanium-copper-beryllium) and brazing conditions.
4. The final step in the assembly was tungsten-arc welding of stainless steel end cap to the fueled capsule.

#### Hall Cell Fabrication

The fabrication of a Hall cell involved one of the most interesting and complicated ceramic brazing problems. The components for this assembly represented a wide variety of materials and included synthetic

UNCLASSIFIED  
Y-37707



Fig. 7. Aluminum Oxide-to-Titanium-Bearing Mockup Assembly  
Brazed with 49 Ti-49 Cu-2 Be (wt %). Vacuum brazed at 1000°C for  
10 min.

UNCLASSIFIED  
Y-39934



Fig. 8. Brazed Ceramic-to-Metal Assembly with Titanium Wires Insulated from Titanium Cap by Aluminum Oxide.

UNCLASSIFIED  
PHOTO 51459

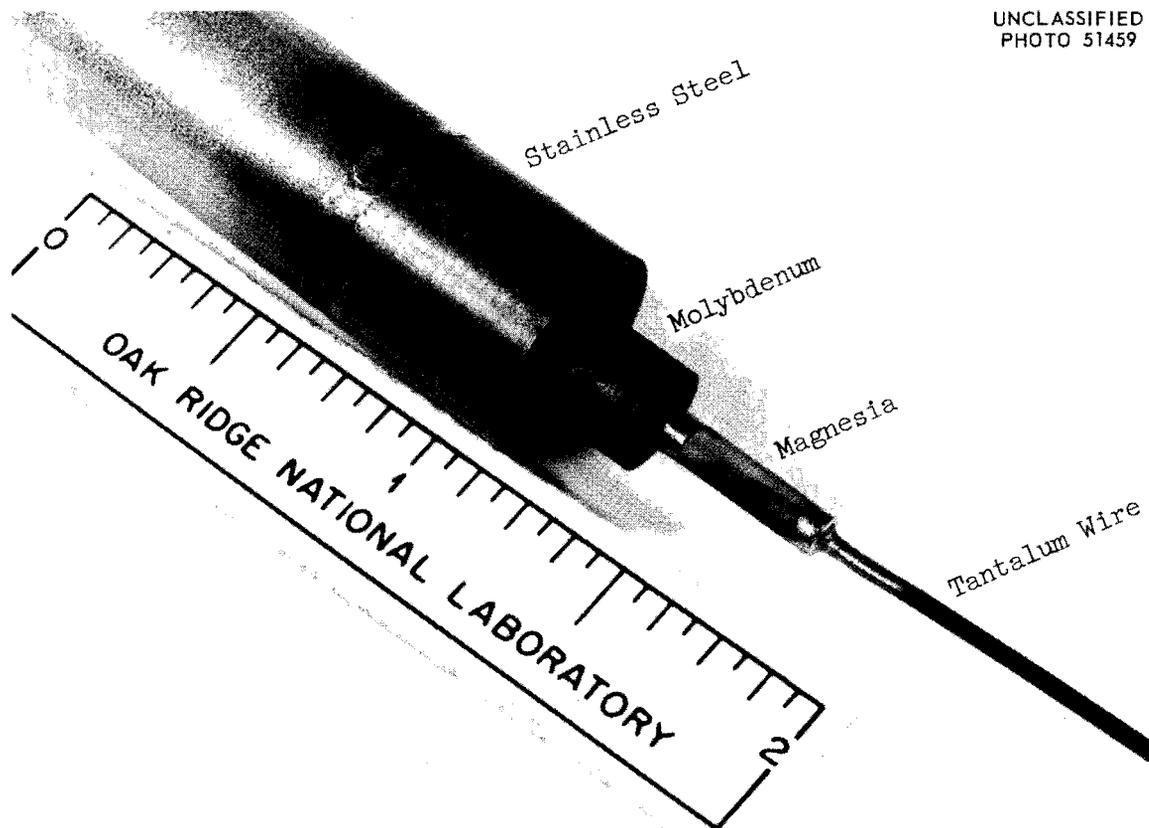


Fig. 9. Brazed End-Cap Assembly Welded to Stainless Steel Capsule. A tantalum wire was insulated from a molybdenum adapter by magnesium oxide.

sapphire, molybdenum, columbium-1% zirconium alloy, zirconium, and stainless steel. Columbium-1% zirconium wires were used as electrodes into the cell and were attached by first brazing the wire to molybdenum adapters. These, in turn, were brazed to the synthetic sapphire. The joint in each case was made with the 48 Ti-48 Zr-4 Be (wt %) experimental brazing alloy. To provide a means of closing the cell after loading, it was necessary to attach a stainless steel flange to the open end. This was accomplished by first brazing a zirconium collar to the synthetic sapphire, and the stainless steel flange was then subsequently brazed to the zirconium. Both joints were brazed in vacuum at 1000°C for 10 min with 95 Zr-5 Be (wt %) alloy. The completed assembly, with the accompanying end closure, is shown in Fig. 10.

#### CONCLUSIONS

Availability of suitable ceramic brazing techniques is an important factor in any advanced program involving ceramics as high-temperature materials. Steps have been taken in this direction through the experimental studies that have been conducted. Brazing alloys such as 48 Ti-48 Zr-4 Be (wt %) and 49 Ti-49 Cu-2 Be (wt %) have been found to readily flow on oxide and graphite ceramics, and have been used to successfully construct demonstration fuel elements and various hardware assemblies.

#### FUTURE WORK

Future work will encompass other ceramics such as beryllium oxide and uranium oxide. Other metal-ceramic joint combinations and other brazing alloy systems will also be investigated. Studies will be continued in an effort to increase the service temperature range of the brazed joints and to provide an even greater reliability for the very stringent service conditions which can be expected.

UNCLASSIFIED  
PHOTO 57667

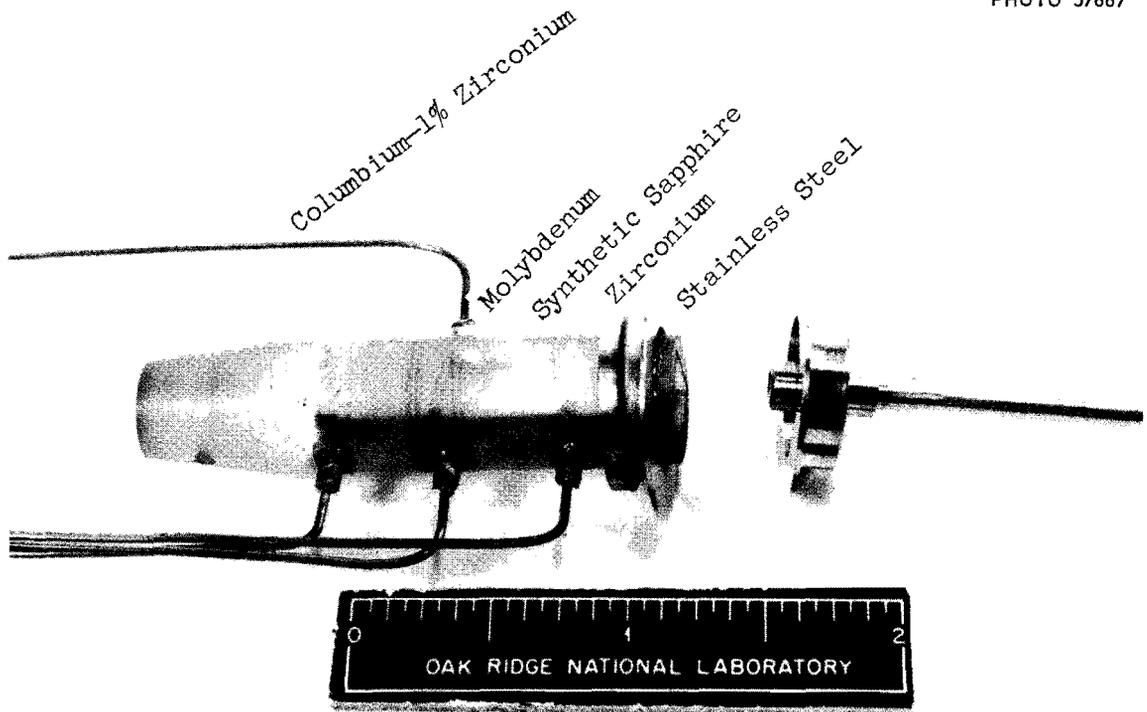


Fig. 10. Synthetic Sapphire Hall Cell Assembly.

ACKNOWLEDGMENT

The author gratefully acknowledges the alloy development work of R. G. Gilliland and the assistance of J. J. Woodhouse and J. D. Hudson of the Welding and Brazing Group in the fabrication of the assemblies, and E. R. Boyd of the Metallography Group for the preparation of metallographic samples and photomicrographs.

DISTRIBUTION

- |        |                            |          |  |
|--------|----------------------------|----------|--|
| 1-2.   | Central Research Library   | 75.      | C. E. Larson   |
| 3.     | Document Reference Section | 76.      | C. F. Leitten, Jr.                                       |
| 4-23.  | Laboratory Records         | 77.      | A. L. Lotts  |
| 24.    | Laboratory Records, RC     | 78.      | H. G. MacPherson   |
| 25.    | ORNL Patent Office         | 79.      | W. D. Manly  |
| 26.    | G. M. Adamson, Jr.         | 80.      | R. W. McClung  |
| 27.    | R. J. Beaver               | 81.      | C. J. McHargue   |
| 28.    | D. S. Billington           | 82.      | A. J. Miller   |
| 29.    | A. L. Boch                 | 83.      | E. C. Miller   |
| 30.    | E. G. Bohlmann             | 84.      | J. P. Murray (K-25)                                      |
| 31.    | B. S. Borie                | 85.      | A. R. Olsen  |
| 32.    | R. B. Briggs               | 86.      | P. Patriarca   |
| 33.    | H. R. Bronstein            | 87.      | J. J. Prislinger   |
| 34.    | R. E. Clausing             | 88.      | H. W. Savage   |
| 35.    | J. H. Coobs                | 89.      | L. D. Schaffer   |
| 36.    | F. L. Culler               | 90.      | J. L. Scott  |
| 37.    | J. E. Cunningham           | 91.      | H. E. Seagren  |
| 38.    | J. H. DeVan                | 92.      | G. M. Slaughter  |
| 39.    | R. G. Donnelly             | 93.      | C. O. Smith  |
| 40.    | D. A. Douglas, Jr.         | 94.      | J. A. Swartout   |
| 41.    | R. M. Farnham              | 95.      | A. Taboada   |
| 42-56. | C. W. Fox                  | 96.      | J. W. Tackett  |
| 57.    | A. P. Fraas                | 97.      | W. C. Thurber  |
| 58.    | E. A. Franco-Ferreira      | 98.      | A. M. Weinberg   |
| 59.    | J. H. Frye, Jr.            | 99.      | J. R. Weir, Jr.  |
| 60.    | R. G. Gilliland            | 100.     | J. C. Wilson   |
| 61.    | A. E. Goldman              | 101.     | C. E. Winters  |
| 62.    | W. R. Grimes               | 102.     | C. H. Wodtke   |
| 63.    | J. P. Hammond              | 103.     | J. Simmons, AEC,<br>Washington                           |
| 64.    | W. O. Harms                | 104-118. | Division of Technical<br>Information Extension<br>(DTIE) |
| 65.    | R. F. Hibbs (Y-12)         | 119.     | Research and<br>Development Division<br>(ORO)            |
| 66-70. | M. R. Hill                 |          |  |
| 71.    | E. E. Hoffman              |          |  |
| 72.    | H. Inouye                  |          |  |
| 73.    | M. T. Kelley               |          |  |
| 74.    | J. A. Lane                 |          |  |

