234
11/28/77
LA-6928-MS

Informal Report

LA. 1613
UC-25

Issued: November 1977

Graphite-to-Metal Bonding Techniques

Lloyd O. Lindquist
Richard Mah

MASTER

los alamos
scientific laboratory

of the University of California

LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

GRAPHITE-TO-METAL BONDING TECHNIQUES

by

Lloyd O. Lindquist and Richard Mah

ABSTRACT

We report the results of various bonding methods to join graphite to different metals. Graphite/metal bonds were tested for thermal flux limits and thermal flux cycling lifetimes. The most successful bond transferred a heat flux of 6.50 MW/m^2 in more than 500 thermal cycles. This bond was between pyrolytic graphite and copper with Ti-Cu-Sil as the bonding agent.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed. It represents that its use would infringe privately owned rights.

I. SUMMARY

Physical and thermal bonding techniques to mate pyrolytic graphite to copper were tested for suitability in extracting high heat flux loads through the bonds. The most successful bonds were titanium-copper-silver and titanium-copper-nickel braze alloys. Their heat flux capabilities were $\sim 6 \text{ MW/m}^2$, and they appeared to withstand indefinite heat cycling at maximum heat flux.

II. INTRODUCTION

At the Clinton P. Anderson Meson Physics Facility (LAMPF) at the present time, all Line A pion production targets are radiatively cooled. As beam currents rise from present levels ($\sim 300 \mu\text{A}$) in Line A, the surface temperature levels of the graphite targets will exceed 2300 K. At temperatures above 2300 K, graphite begins to evaporate at unacceptable rates (shown in Fig. 1). The A-5 bar proton target in its present configuration will approach this temperature at $300 \mu\text{A}$, with an 800-MeV proton beam. Rotating target wheels of the present design installed at A-1 and A-2 will not exceed 1500 K for 800-MeV proton currents of 1 mA. If the target wheels are not spinning, then they too will experience higher temperatures, $> 2300 \text{ K}$ (see Fig. 2).

The thrust of this investigation has been to develop a metal-graphite interface to transfer heat from the graphite to a coolant, pumped adjacent to the metal. We are initially working with pyrographite, since the maximum pion production per centimeter of material minimizes the dose time for experiments. Pyrographite is the most dense form of graphite, and therefore has maximum pion production per centimeter of material. Some compelling reasons for selecting this material are the low-Z, the high thermal conductivity, the high strength at elevated temperatures, and the high melting point (3500°C).

Fig. 1.

Graphite evaporation rate vs temperature of graphite surface.

Fig. 2.

A-2 stationary target (ATJ graphite), temperature vs proton current ($\rho = 1.7 \text{ g/cm}^3$).

A. Bonding Techniques

We have investigated in parallel several types of thermal bonding approaches. To date, we have made bonds between a metal 6.35-mm-diam (nominal) tube and a graphite cylinder with a hole drilled for the tube (shown in Fig. 3).

The first type of bond tested was polyfurfuryl alcohol (Varcum) graphitized in the space between a copper tube and pyrographite cylinder. The graphitization process bonds the pyrographite to the Varcum. The bonding of the Varcum to the pyrographite occurs while the assembly is held at 200°C for 60 h to achieve graphitization. The copper tube does not react chemically with the Varcum. Varcum merely fills the voids between the pyrographite and the copper tube, and may even mechanically prestress the copper tube during graphitization. This could explain the thermal flux capability of the bond (described later in this report). Two hybrid Varcum compounds were prepared in an attempt to improve on the thermal conductivity of an ordinary Varcum bond. One compound was composed of a heterogeneous mixture of fine aluminum chips and graphitized polyfurfuryl alcohol (Varcum) in the fabricated form. The assemblies that were fabricated using the hybrid compounds are described in Fig. 3.

Fig. 3
Sample for testing graphite-to-copper bonding techniques in an induction heating assembly.

The second hybrid compound used fine copper chips instead of the aluminum chips, in order to improve the thermal conductivity of the heterogeneous mixture as well as to increase the maximum operating temperature of the bond. Copper melts at 1083°C; aluminum melts at 660°C. If the bond exceeds the melting point temperature of the aluminum, it will melt out of the graphitic matrix.

The Varcum preparation technique, compositions, and fabrication procedures are described in Appendix A.

A second method of bonding graphite to metal was electroplating copper to the interior of the graphite hole, then brazing the tube to the copper-plated graphite in a conventional vacuum-brazing furnace with BT (copper-silver) brazing alloy. The electroplating operation was performed with standard copper solutions at normal plating rates for metals, to a thickness of 127 μm . No special techniques were used in the brazing operation. The braze occurred between the plated copper present on the graphite and the copper tube. This technique was attempted since the mechanical roughness of the graphite surface contributes to a mechanical bond; also, the van der Waals forces (between the plated copper atoms and the carbon atoms) added to the strength of the bond as well as to the thermal conductivity. The brazing history is outlined in Appendix B.

The third approach to bonding graphite to metal was to purchase* and test commercial bonding compounds. These carbon-based, thermally conductive compounds were tested and fabrication proceeded according to manufacturers' directions (see Fig. 3). One compound was Grade GC Graphite Cement and the other was a thermal putty compound. The preparation history is found in Appendix B.

A fourth bonding technique attempted to braze the graphite and metal tube directly together (Fig. 3). Two braze alloys, Ti-Cu-Ni and Ti-Cu-Sil,** that have successfully bonded copper and pyrolytic graphite (in the configuration shown in Fig. 3) were used; chemical compositions are shown in Table I. Although these braze materials are referred to as alloys, they are not solid solutions. They are actually sandwiches of three different metal foils rolled together to form what we have called braze alloys. The brazes were made in a conventional vacuum braze furnace, and studies were made to determine the optimal time-at-temperature braze. These studies showed that a temperature of 900°C for 5 min produced the best bond when brazing copper to pyrolytic graphite with Ti-Cu-Sil. When using the Ti-Cu-Ni braze, a temperature of 980°C for 2 min produced the best bond. Bond evaluations were made by macroscopically examining a longitudinal section of the brazed part for braze alloy flow and integrity. Subsequent work using the same variables with the same braze alloys showed that copper could be brazed successfully to ATJ graphite.

In the braze alloy, the titanium reacts with some of the graphite and forms an interface (TiC). The remainder of the braze alloy forms a solid solution with the TiC and the copper tube. Since titanium is a reactive metal, the same property that makes the braze alloys outstanding makes them difficult to work with. If the braze alloys — especially Ti-Cu-Ni — were allowed to react with the copper tube for too long a time, the titanium would produce holes or thinned sections in the wall of the copper tube. Nevertheless, a strong mechanical and thermal bond can be produced if carefully controlled.

Efforts are under way to braze various elemental and alloy tubes to graphite with the same braze alloys (Ti-Cu-Sil and Ti-Cu-Ni). This will widen the selection of materials that can be bonded to both ATJ and pyrolytic graphite. Other elements and alloys will further widen the selection of heat transfer fluids and, therefore, applications. Studies are being made to determine the optimal time-at-temperature conditions for this furnace with tantalum, stainless steel, and molybdenum. Copper and ATJ graphite have also been successfully brazed with Ti-Cu-Ni and Ti-Cu-Sil. The general brazing temperature has been 900°C, with typical vacuum braze times from 1-10 min (see Appendix B for details).

*Dylon Industries, Inc., Cleveland, OH 44162.

**Purchased from Western Gold & Platinum Company, Belmont, CA 94002.

TABLE I
CHEMICAL COMPOSITION
OF BRAZE ALLOYS

	<u>Ti-Cu-Sil</u>	<u>Ti-Cu-Ni</u>
Titanium	4.5	70.0
Copper	26.7	15.0
Silver	68.8	----
Nickel	----	15.0

B. Photographic Examination of Bond

Figures 4 and 5 are photomicrographs of pyrolytic graphite brazed to copper with Ti-Cu-Ni. The magnifications are 100X and 250X, respectively. The lightest section in each photograph is the copper tube; the light gray is the braze zone; and the dark gray is the pyrolytic graphite. There was no evidence of the bond breaking or being discontinuous. Figure 6 shows a broken portion in the brazed joint; the fracture is located in the pyrolytic graphite region. This clearly indicates that the braze joint is stronger than either mating material (copper and pyrolytic graphite). These photographs were taken after the braze joint had experienced more than 200 heat cycles of 6.50 MW/m² heat flux. Clearly, this bond has promise for further development and application.

C. Heat Transfer Testing Techniques

The initial heat deposition method selected was high-frequency induction heating of graphite specimens bonded to various metal tubes (see Fig. 3). The heights of the graphite cylinders varied from 12.7 to 76.2 mm. The outside diameters of the graphite cylinder and the tube were 22.2 and 6.35 mm, respectively.

The specimens were placed in the induction heating apparatus (see Fig. 3). The volume inside the quartz tube was evacuated to pressures of 1×10^{-6} to 5×10^{-4} mm of mercury.

Water flowed through the tube at rates from 1.9-11.36 l/min; inlet and outlet water temperatures of this system were measured to $\pm 1/8$ K.

The total amount of power deposited in the graphite sample is the sum of the power deposited in the water [volume/minute $\times$ density $\times$ heat capacity $\times$ (T outlet - T inlet)] plus the power dissipated radiatively through the vacuum to the surroundings [power = emissivity $\times \sigma \times$ area $\times$ (T_{surface}⁴ - T_{surroundings}⁴)], where σ = Stephan-Boltzmann constant. There is no opportunity for heat to transfer from the graphite to the surroundings in any other way in our experiment. Heating power to the graphite was controlled by adjusting the amount of power available to the radio frequency oscillator power circuit.

Power transmitted to the graphite load was measured by monitoring the water flow rate through the tube, the $\Delta T = (T \text{ inlet} - T \text{ outlet})$, and the surface temperature of the graphite (measured by an optical pyrometer for temperatures $> 700^\circ\text{C}$).

D. Results of Heat Transfer Studies

Each bonding method was tested to determine maximum heat flux capability through the bond. The results are shown in Table II.

ACKNOWLEDGMENTS

We wish to express our appreciation to the following Los Alamos Scientific Laboratory people for their technical expertise in these tests: Donald E. Hull, high-frequency induction heating; James R. Bradberry, metallography; John Russell, vacuum furnace brazing; and Donald H. Schell, Varcum bonding techniques.

Fig. 4.
Photomicrograph of pyrolytic graphite brazed
to copper with Ti-Cu-Ni; magnification =
100X.

Fig. 5.
Photomicrograph of pyrolytic graphite brazed
to copper with Ti-Cu-Ni; magnification
= 250X.

Fig. 6.
Pyrolytic graphite bonded to copper with Ti-Cu-Ni braze alloy.

TABLE II
RESULTS OF HEAT TRANSFER STUDIES

Material	(W/cm²)
^a Pyrolytic Graphite To Copper/Polyfurfuryl Alcohol With Copper Hybrid	185
^a Pyrolytic Graphite to Copper/Polyfurfuryl Alcohol With Copper Hybrid	625
^a Pyrolytic Graphite to Copper/Copper Electroplated Hole, Then BT Braze to Tube	550
^a Pyrolytic Graphite to Copper/Grade GC Graphite Cement	260
^a Pyrolytic Graphite to Copper/Heat Conducting Compound	130
^b Pyrolytic Graphite to Copper/Ti-Cu-Sil	650
^b Pyrolytic Graphite to Copper/Ti-Cu-Ni	600

^aBonds partially failed.

^bSurvived more than 500 heat flux cycles without failure.

APPENDIX A

VARCUM PREPARATION PROCEDURES

A filled, partially polymerized furfuryl alcohol glue was made with 3.5 g of -400 mesh aluminum powder, stirred thoroughly into 3.5 g of catalyzed Varcum 8251.

Prior to applying the filled glue, the inner diameter of the pyrographite part was coated with unfilled Varcum by brush. This operation was possible because of the short length of the component.

The copper tubing was prepared by sanding the area where the pyrographite would be glued into place and then the roughened area wiped with a coat of unfilled Varcum. The pyrographite part was slipped into place, and rubbed back and forth along the roughened area until only a thin film of Varcum remained on each mating surface. All excess Varcum was wiped off and the Varcum was cured in an oven.

The aluminum glue was then applied to each treated surface. The pyrographite part was slipped back into place, rubbed back and forth over the roughened area until no glue was forced from the joint, and the finished product wiped clean of excess glue; it was then oven-cured for 15 h at 250°C.

The copper-filled glue was prepared in a similar manner. The copper powder used was Cu-36D, with an average particle size of $\sim 1.5 \mu\text{m}$. The powder was reduced in a mixture of AR + H₂ overnight at 280°C. The reduced powder was screened using -400 mesh.

The 46 Wt% copper/54 Wt% catalyzed Varcum 8251 was cured for 60 h at 250°C in the same manner as the aluminum-filled Varcum.

APPENDIX B

HEAT TREATMENT HISTORIES

Ti-Cu-Ni - 76.2- μm foil/6.50-mm hole/6.35-mm tube. Brazed for 20 min at 1283 K.

BT Braze - 127- μm copper plating on pyrographite/102- μm foil/6.71-hole/6.22-mm tube. Brazed 1103 K for 15 min.

Heat Compound - 6.35-mm, scribed approximately one turn per 2.5 cm, the 6.50-mm hole filled with compound. Air-dried for 24 h; 4 h in furnace at 366 K.

Graphite Cement - 6.35-mm tube, scribed approximately one turn per 2.5 cm, the 6.5-mm hole filled with compound. Baked for 4 h in a furnace at 373 K.

BT Braze - 102- μm copper plating on graphite 50.8- μm foil/6.71-mm hole/6.5-mm tube, brazed for 10 min at 1103 K.