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Joining Graphite to Graphite
with Transition Metal Foils

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University of California
LOS ALAMOS • NEW MEXICO

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**Joining Graphite to Graphite
with Transition Metal Foils***

by

Donald J. Sandstrom

*This report is derived from a thesis submitted to the University of New Mexico in partial fulfillment for the degree of Master of Science in the Engineering Science of Materials.

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i

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SUMMARY

A study has been undertaken to determine the relationship of metallic-foil joining and joining parameters to the strength of joints in a high-quality extruded nuclear graphite. The materials chosen for investigation as joining materials on the graphite of interest were considered to be representative of the Group IVA, VA, and VIA transition metals and iron. The parameters used for joining yielded either a fully diffused joint, which was not temperature-limited with respect to service conditions, or a continuous-carbide-interface joint, which was temperature-limited.

The metal chosen from Group IVA for joining was zirconium in the form of 0.0005 in.-thick foil. A series of joining temperatures was investigated: it was shown that a joint having a graphite-carbide-graphite interface was produced until temperatures in excess of the zirconium carbide - carbon eutectic were utilized. The graphite joints made with zirconium possessed the highest strength of all samples tested in room-temperature flexure if the continuous-carbide interface was developed. This high strength is believed to be related to the stability, i.e., the high heat of formation, of the carbide.

Joints made with the Group VA metal, tantalum, possessed a continuous-carbide interface, since it is not practical to exceed the tantalum carbide-carbon eutectic temperature. This series exhibited increasing room-temperature flexure strength with increasing joining temperature. The general strength values were lower than those observed for material joined with the Group IVA foil.

Two metals, molybdenum and tungsten, from Group VIA were evaluated. These metals were chosen because of their relatively low neutron absorption cross sections and also because of their availability in the form of 0.0005-in.-thick foil. Both molybdenum and tungsten have eutectics between the carbide and carbon at temperatures that make the production of a fully diffused joint both feasible and practical. Temperatures which yielded both carbide-interface joints and fully diffused joints were studied. Tests were performed on the various joint types using both room-temperature flexure tests and elevated-temperature tensile tests. The results obtained for this Group indicated that fully diffused joints yielded higher strengths over the range of testing temperatures. Tensile tests were performed on fully diffused joints at temperatures in excess of the joining temperature and these samples possessed strengths comparable to conventional pitch-bonded graphites tested at similar temperatures. In general, the only difference noted between tungsten- and molybdenum-joined material was the temperature required to develop a particular kind of joint structure, i.e., fully diffused or carbide interface.

In addition to the properties developed with these joining materials, it was noted that, in order for significant amounts of graphite to be precipitated out of the carbide single phase field, it is necessary to have a phase boundary which has decreasing carbon solubility with decreasing temperature. This condition has been observed in the molybdenum-carbon system and for this reason a significant amount of well-ordered precipitated flake graphite is observed.

Finally, joints were made with 0.0005-in.-thick foil as the joining medium. A fully diffused joint was produced when temperatures in excess of the iron carbide-carbon eutectic were used. Joints made at

temperatures lower than this value showed almost no strength. This feature was in keeping with the observation that strong carbide-interface joints are produced by carbides that have high negative heats of formation and that iron, bonded graphite which has a positive heat of formation, is comparatively weak.

X-Ray diffraction analysis and metallographic evaluations have been made on all materials joined; they indicate that failure usually occurs at the carbide-graphite interface for a solid-carbide joint. In the case of the fully diffused joint the metallography and X-ray diffraction results show that failure occurs in the precipitated primary graphite.

The conclusions of the study are that fully diffused joints are superior to solid-carbide joints in elevated temperature tests. Also, the strongest solid-carbide joints will be produced with zirconium. Increasing the joining temperature generally results in increased room-temperature flexure strength for a solid-carbide joint.

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	ii
ACKNOWLEDGEMENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER	
I. INTRODUCTION	1
Statement of Problem	1
Review of the Literature	3
Scope of the Investigation	6
II. MATERIALS, EQUIPMENT, AND JOINING PROCEDURES	7
Graphite	7
Bonding-Elements	8
Equipment Used for Joining	9
Mechanics of Joining	11
Temperature Measurement	14
III. TESTING PROCEDURES	17
Room-Temperature Flexure Testing	17
High-Temperature Tensile Testing	17
Metallography and Electron Microscopy	19
X-Ray Diffraction	21
IV. RESULTS AND DISCUSSION	22
Graphite Properties	22
Molybdenum-Bonded Graphite	25
Tungsten-Bonded Graphite	39
Tantalum-Bonded Graphite	47
Zirconium-Bonded Graphite	52
Iron-Bonded Graphite	56
V. CONCLUSIONS AND RECOMMENDATIONS	63
Conclusions	63
Recommendations	64
APPENDIX	
Diffraction Pattern on Los Alamos Extruded Graphite	66
Phase Diagrams (Figs. 33 - 36)	67
Mechanical Test Data (Tables III - XII)	71
List of References	84

LIST OF TABLES

<u>TABLE</u>	<u>PAGE</u>
I. Chemical Analysis of Bonding Elements.....	9
II. Ratios of Intensities of Diffraction Peaks of Los Alamos Graphite and Randomly Oriented Graphite.....	25
III. Elevated-Temperature Strength of Los Alamos Graphite.....	71
IV. Elevated-Temperature Tensile Strength of ATJ Graphite.....	72
V. Joining Parameters and Room-Temperature Flexure Strength of Graphite Joined with 0.0006-in. Molybdenum Foil..	73
VI. Joining Parameters and Elevated-Temperature Tensile Strength of Graphite Joined with 0.0006-in. Molybdenum Foil.....	74
VII. Joining Parameters and Room-Temperature Strength of Graphite Joined with 0.0005-in. Tungsten Foil.....	76
VIII. Joining Parameters and Elevated-Temperature Tensile Strength of Graphite Joined with 0.0005-in. Tungsten Foil.....	77
IX. Joining Parameters and Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Tantalum Foil....	79
X. Joining Parameters and Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Zirconium Foil...	80
XI. Joining Parameters and Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Iron Foil.....	81
XII. Joining Parameters and Elevated-Temperature Tensile Strength of Graphite Joined with 0.0005-in. Iron Foil.....	82

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	Schematic Drawing of the Induction-Heated Graphite-Joining Device.....	10
2	Graphite-Joining Device.....	12
3	A. Schematic Drawing of a Sample-Alignment Device.....	13
	B. Joined Graphite Samples.....	13
4	Corrected 'Black-Body' and Surface Temperature vs. Observed Surface Temperature.....	16
5	"Thirds-Point" Flexure Testing Device.....	18
6	A. High-Temperature Tensile-Test Furnace in Place in an Instron Tensile Machine.....	20
	B. High-Temperature Tensile Sample in Place in the Furnace.....	20
7	Tensile Strength vs. Temperature for Extruded Los Alamos Graphite.....	23
8	Tensile Strength vs. Temperature for ATJ Graphite.....	24
9	Room-Temperature Flexure Strength of Graphite Joined with 0.0006-in. Mo Foil vs. Joining Temperature.....	27
10	Tensile Strength vs. Temperature for Los Alamos Graphite Bonded to Itself with 0.0006-in. Mo Foil.....	28
11	Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0006-in. Mo at 2150°C.....	30
12	Microstructure Developed in Graphite Joined to Graphite with 0.0006-in. Mo Foil at 2450°C.....	32
13	Microstructure Developed in Graphite Joined to Graphite with 0.0006-in. Mo Foil at 2660°C.....	34
14	Composite Electron Micrographs of "Fully Diffused" and Solid-Carbide-Interface Graphite Joined with Molybdenum.....	36
15	X-Ray Diffraction Patterns of Solid-Carbide-Interface Low-Temperature Graphite Joints Produced with Molybdenum.....	37
16	X-Ray Diffraction Patterns of Partially Diffused and Fully Diffused Carbide-Interface Graphite Joints Produced with Molybdenum.....	38
17	Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. W Foil vs. Joining Temperature.....	41
18	Elevated-Temperature Tensile Strength of Graphite Joined with 0.0005-in. W Foil vs. Testing Temperature.....	42

19	Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. W Foil at 2450°C...	44
20	Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. W Foil at 2850°C...	45
21	X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. W Foil at Various Temperatures.	46
22	Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Ta Foil vs. Joining Temperature.....	48
23	Microstructural Characteristics of Graphite Bonded to Graphite with 0.0005-in. Ta Foil at 2450°C and 3000°C.	49
24	X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. Ta Foil at Various Temperatures.	51
25	Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Zr Metal Foil vs. Joining Temperature.....	53
26	Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. Zr Foil at 2350°C..	54
27	Microstructure Developed in Graphite Joined to Graphite with 0.0005-in. Zr Foil at 2750°C and 2850°C.....	56
28	X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. Zr Foil at Various Temperatures	57
29	Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Fe Foil vs. Joining Temperatures.....	59
30	Tensile Strength vs. Temperature for Los Alamos Graphite Bonded to Itself with 0.0005-in. Fe Foil.....	60
31	Microstructures Developed in Graphite Joined to Graphite with 0.0005-in. Fe Foil at Various Temperatures.....	61
32	X-Ray Diffraction Pattern of Los Alamos Extruded Graphite.	66
33	Zirconium-Carbon Phase Diagram.....	67
34	Tantalum-Carbon Phase Diagram.....	68
35	Molybdenum-Carbon Phase Diagram.....	69
36	Tungsten-Carbon Phase Diagram.....	70

CHAPTER I

INTRODUCTION

STATEMENT OF THE PROBLEM

The use of carbon in the form of graphite has been a significant aid in the development and progress of nuclear science and industry. The first pile to achieve a self-sustaining nuclear chain-reaction, CP-1,¹⁴ used graphite as the moderating material. Since the first pile was constructed, a host of nuclear reactors have been assembled with graphite as the moderator material. But in many nuclear applications, those properties of graphite that are most unusual are not pertinent. It is an unusual and attractive high-temperature structural material. Its high-temperature properties coupled with its low neutron absorption cross section make it a leading candidate for moderator or structural material in high-temperature gas-cooled reactors. The reasons why graphite has not been fully exploited as a high-temperature material will, in part, be discussed in the following text.

Carbon, in the form of graphite, has a highly anisotropic nature which can be directly related to its crystallographic structure.¹⁰ The anisotropy manifests itself in electrical, thermal, and mechanical properties that vary widely with crystallographic orientation. In addition to the inherent material properties, the atmospheres of certain high temperature reactors introduce other restrictions to the use of graphite as a structural material. The choice of materials used for joining graphite

to itself must, of necessity, consider the environment to which these joints will be subjected. The importance of developing a fundamental understanding of the mechanism of bonding which occurs during the joining operation cannot be stressed enough.

The choice of the title for this thesis was dictated by the fact that to use the terms "brazing", or "diffusion bonding", would be slightly misleading. In this context, then, it becomes clear that an exact definition of terms, as used here, is needed, and is given below. These terms are not intended for use in the usual metallurgical sense.

Brazing: This term applies to joints which are prepared using a metal foil or powder which is transformed to a continuous solid carbide phase in situ. Such a joint will not be composed of a mixture of graphite and metal carbide. This differs from normal usage in that no melting occurred, but a third material now exists which generally has a lower melting point than the matrix.

Diffusion Bonding: This term applies to joints made with metal foils, or powders, which are transformed to the carbide and subsequently heated to a temperature in excess of the metal carbide-carbon eutectic. This temperature will yield an interfacial-layer joint composed of precipitated primary graphite and isolated metal carbide particles. Since the remelt temperature of such a joint is in excess of the joining temperature, this joint will be called a diffusion bond.

The work described in this thesis was performed to determine the properties of a variety of joints, and to develop a better understanding of the fundamentals of the joining process.

REVIEW OF THE LITERATURE

A search of the literature has shown a significant amount of investigation into the problem of graphite joining. Ando et al¹ and Wade²² have described a technique in which the conventional brazing alloys; i.e., iron and nickel or silver and copper, were alloyed with a strong carbide-former; e.g., titanium, and used to braze graphite to metallic components. This technique produced joints which had a metallic-carbide mixed phase at the joint area. The mechanism of bond formation was not considered by these investigators.

Blet⁵ has described a process for joining graphite to itself with titanium foil as the bond promoter. This process requires that the graphite body be heated to a temperature slightly greater than the melting point of titanium ($1668 \pm 8^\circ\text{C}$). The process yields a joint having a solid-carbide interface with good mechanical properties at room temperature. X-Ray diffractometry and radiographic evaluations were performed on bonded samples. No analysis of the bonding mechanism was proposed in this description of work.

Investigators at Aerojet-General⁸ have described a process called diffusion brazing, used for producing bonds between tungsten and graphite components. The conditions required for this bonding were that no recrystallization occur in the tungsten and that the remelt temperature of the joint be greater than the temperature of formation. The best results were obtained using manganese-base alloys with a high concentration of molybdenum as the joining material. It was postulated by the investigators that a liquid phase was formed, but no further considerations of bonding mechanism were described.

The method of graphite joining which is most widely utilized incorporates some type of adhesive as the joining medium. Typically these adhesives are composed of a coal-tar pitch or other high-coking-content resin. Johnson¹³ has described some results obtained by bonding graphite to graphite using furfuryl alcohol as the cement. Leak-tight fully carbonized joints are produced using this technique. The structure of joints of this type is entirely carbonaceous and as such should possess good elevated-temperature strength properties, however, no elevated-temperature properties were reported by this author. The process involving bonding with furfuryl alcohol resin as the cement has been utilized at the Los Alamos Scientific Laboratory for some time. The joints produced by this process in general possess excellent room-temperature properties, but do have some unexplained problems with repeatability of properties.

Investigations of diffusion reactions with graphite and other forms of carbon have been reported by several investigators.^{6, 10, 24} Some of the investigations have described a precipitation mechanism upon which a technique of bond formation may be postulated. The exact details of this postulate are described in the classified literature. This same mechanism appears, in principle, to be operative in certain areas of bonding which will be described in this thesis.

A search of the patent literature has revealed two patents entitled "Joining of Graphite Members" by Morris A. Steinberg.¹⁸ In these patents the investigator described the method of utilizing metal powders or foils as a means of producing graphite-to-graphite joints. The bonding mechanism postulated in the patents is substantiated by this thesis. Steinberg theorized that during the heating cycle the metal is converted to the carbide. The solubility of the carbon in the carbide is greater at

elevated temperatures and upon cooling, some carbon is precipitated from the carbide as graphite. The resultant joint is then characterized as being a graphite-to-graphite joint. This author agrees in principle--but not in detail--with the mechanism described in these patents.

SCOPE OF THE INVESTIGATION

The methods of analysis which have been employed in this investigation include room-temperature flexure testing, high-temperature tensile testing, optical microscopy, electron microscopy, X-ray diffraction, and conventional chemical analysis.

The flexure test is considered to be a good screening test and it has been used to generate most of the data reported here. This test is a comparatively easy one to perform; and because it is a standard test for most brittle materials, it is possible to make direct property comparisons between joints in extruded Los Alamos graphite and unjoined materials.

The high-temperature tensile testing does yield some extremely significant data. Owing to the complexity of testing specimens at temperatures in excess of 2000°C, the number of tests had to be limited. This test was used to illustrate the striking difference in properties between diffusion-bonded and brazed-graphite joints.

The metallographic evaluation was performed using conventional optical microscopy, and electron microscopy in some instances. All the metallographic specimens were cathodically etched. This sample preparation procedure was found to be necessary in order to reveal completely the layer structure of graphite in the joint area.

X-Ray diffraction studies of the fracture surfaces were utilized to determine the type of carbide present, the orientation of the precipitated graphite, and as a check, together with metallography, of the joining temperatures employed. The diffraction data was extremely difficult to analyze; however, it appeared to yield good correlation with phases predicted by the phase diagrams.

CHAPTER II

MATERIALS AND EQUIPMENT

GRAPHITE

Los Alamos extruded graphite was chosen for use in this program because the material is extremely well characterized; i.e., the composition and parameters of manufacture are well known.

Los Alamos graphite differs from the more common commercial and nuclear grade graphites in that the binder material is a polymerized furfuryl alcohol resin. Most commercial graphites are generally composed of petroleum-coke filler with a petroleum-pitch binder. Los Alamos graphite is utilized for its high coking content and the desirable property of retaining dimensional stability through the curing cycle.

The raw material for all of these experiments was produced from a single lot of batch-extruded graphite. The composition of the graphite included a petroleum-coke filler material (designated 1008 by the Great Lakes Carbon Co.), 26 percent by weight partially polymerized furfuryl alcohol resin binder, and 1.25 percent by weight wood flour filler. The density of this material was 1.82 gm/cc after thermal-treatment.

In addition to the characteristics imparted to the finished graphite by its components, other characteristics are affected by the method of forming, such as extrusion.²¹ The milled calcined petroleum coke used as filler material is an irregular acicular particle with one dimension larger than the other two. The extrusion process accentuates the anisotropy of the product by preferentially orienting the long axes of the particles in

the direction of extrusion. The expected large anisotropy of the graphite is confirmed by X-ray diffraction data presented later in the text.

BONDING ELEMENTS

The metals which have been investigated in this study have been selected on the basis of availability, applicability to use in reactors, and usefulness in illustrating the principles of the joining process. The metal foils were discs 0.0005 ± 0.0001 -in. thick. In most cases the foils were obtained by rolling the material to the minimum practical thickness followed by chemical etching to the thickness described.

The metals used, together with pertinent physical data,^{12, 20} are listed below:

Zirconium - Group IVA (See Figure 33)

Melting Point	- $1855^{\circ}\text{C} \pm 15^{\circ}\text{C}$
Zr-ZrC eutectic temperature	- $\sim 1810^{\circ}\text{C}$
Highest melting carbide, $\text{ZrC}_{0.85}$	- $3420^{\circ}\text{C} \pm 20^{\circ}\text{C}$
ZrC+C eutectic temperature	- $2850^{\circ}\text{C} \pm 50^{\circ}\text{C}$

Tantalum - Group VA (See Figure 34)

Melting Point	- 2996°C
Ta-Ta ₂ C eutectic temperature	- $2830^{\circ}\text{C} \pm 25^{\circ}\text{C}$
Highest melting carbide, $\text{TaC}_{0.9}$	- $\sim 4000^{\circ}\text{C}$
TaC+C eutectic melting temperature	- $3400^{\circ}\text{C} \pm 50^{\circ}\text{C}$

Molybdenum - Group VIA (See Figure 35)

Melting Point	- $2620^{\circ}\text{C} \pm 10^{\circ}\text{C}$
Mo-Mo ₂ C eutectic temperature	- $2205^{\circ}\text{C} \pm 3^{\circ}\text{C}$
$\text{MoC}_{(1-x)}^+ \text{C}$ eutectic	- $2580^{\circ}\text{C} \pm 10^{\circ}\text{C}$

Tungsten - Group VIA (See Figure 36)

Melting Point	- 3410°C ±20°C
W+W ₂ C eutectic temperature	- 2710°C ±5°C
W ₂ C congruent melting	- 2776°C ±5°C
WC+C eutectic temperature	- 2776°C ±4°C

Iron - Group VIIA

Melting Point	- 1536.5°C
Fe+L peritectic	- 1493°C
Fe+Fe ₃ C eutectic temperature	- ~ 1150°C

All of the foils were subjected to chemical analysis prior to use. Foils containing greater than 0.5% impurities were rejected. The results of the chemical analysis are given in Table I.

TABLE I
CHEMICAL ANALYSIS OF BONDING ELEMENTS

<u>Metal Foil</u>	<u>Total Impurities (weight percent)</u>	<u>Major Impurities (weight percent)</u>
Zr	0.35%	0.1% Fe, 0.1% Hf
Ta	0.05%	100 ppm Nb
Mo	0.1%	300 ppm W
W	0.08%	0.1% Ta
Fe	0.13%	300 ppm Nb

EQUIPMENT USED FOR JOINING

The technique used in this program for joining all of the graphite is shown schematically in Fig. 1. The power supply was manufactured by Lepel High Frequency Laboratories of New York, New York. The rated output of this generator is 25 KW at a frequency of 450 KC/sec. The power supply was coupled to a multi-turn water-cooled copper coil which acts as the

Fig. 1. Schematic Drawing of the Induction-Heated Graphite Joining Device.

primary in a transformer. The secondary of this transformer is a single turn coil called a current concentrator which induces high-frequency eddy currents in the sample which is centered in the coil. The concentrator is placed inside an envelope of fused silica glass which serves as the atmosphere-retaining barrier during joining.

During all of the joining experiments, an atmosphere of dry argon gas was used to prevent oxidation of the graphite and bonding element. The gas was introduced into the heating chamber near the slot in the concentrator, to continually sweep gas past the area of the mantle through which temperature measurements were made. An axial pressure was applied to all of the samples during joining by a hydraulic piston assembly and a manually operated pump. The temperature of the sample was measured using a Pyro Micro-Optical Pyrometer manufactured by the Pyrometer Instrument Company, Inc., Bergenfield, New Jersey. This pyrometer is the disappearing-filament type and is considered to be a highly reliable, precision temperature-measuring device. The actual joining apparatus is shown in Fig. 2.

MECHANICS OF JOINING

A tight-fitting alignment sleeve of high density graphite was used during the initial alignment. Fig. 3A is a conceptual drawing of the alignment technique; photographs of joined samples are shown in Fig. 3B. The pieces were $2\frac{1}{4} \pm \frac{1}{64}$ -in. long, with a $0.749/0.750$ -inch diameter. The ends of the samples were machined perpendicular to their centerline within 0.0005 in. The samples were placed in the alignment sleeve with the metal foil of interest sandwiched between the ends of the sample. The assembly was then placed inside the current concentrator and a slight axial load was applied to the samples. The alignment sleeve was then

Fig. 2. Graphite Joining Device.

A

B

Fig. 3A. Schematic Drawing of a Sample Alignment Device.

Fig. 3B. Joined Graphite Samples.

slid back on the specimen out of the hot zone to permit direct electrical coupling between the sample to be joined and the concentrator. The axial load was then increased to give a pressure of 2000 psi at the joint interface, and the sample was heated to the temperature desired for bonding, typically in 45 seconds. The sample was usually held at temperature for two minutes and fifteen seconds. After the bonding cycle was completed, the generator was turned off and the sample was allowed to cool until it could be handled.

TEMPERATURE MEASUREMENT

Temperatures could be measured only on the surface of the bonded samples. There are several sources of error in such measurements; however, it is the only practical method. The factors which had to be considered in the temperature measurement were:

1. The calibration of the pyrometer;
2. the transmittance of the silica glass mantle;
3. the emissivity of the graphite;
4. the radiation losses to the cold walls of the concentrator.

The pyrometer was calibrated against an NBS tungsten filament lamp that had a known temperature value versus applied current. The pyrometer was adjusted to have a maximum error of 10° at 2600°C . The transmittance of the mantle was determined by measuring the temperature difference obtained by reading a tungsten filament projection lamp in air, and the same lamp placed inside the mantle. The transmittance (τ) of the silica glass was 0.91.

The emissivity of the graphite was not measured because it was assumed that any measurement would be valid only for the sample measured

because of variations in thermal etching, surface finish, or orientation. A value of 0.85 was assumed for the emissivity (ϵ), based upon the accepted range of values (0.80-0.93) published in the literature.¹¹

The variation in temperature across the diameter of the round specimen was measured over a range of temperatures. These measurements were made by drilling a 'black-body' hole in a graphite sample. The hole had a diameter of one-sixteenth of an inch with a depth six times greater than the diameter. This depth-to-diameter ratio was judged sufficient to produce approximately black-body conditions. The temperature on the surface of the sample was observed at a position next to the black-body hole. The corrections applied to the observed temperatures were the transmittance (τ) of the mantle for the black-body hole, and the transmittance (τ) and the emissivity (ϵ) for the surface reading. The corrected values were obtained from the tabulation "Temperature Corrections for Optical Pyrometers Calculated by Planck's Law", compiled by Lee S. Richardson of the Los Alamos Scientific Laboratory.

Fig. 4 is a curve showing the corrected surface and center (black-body) temperatures versus the observed surface temperature. These values show that up to a temperature of approximately 2100°C the corrections applied to the surface temperature measurements yield excellent agreement with the temperature obtained from the 'black-body' specimen. Above the 2100°C temperature the disparity between the surface temperature and the true center temperature increases. The reason for the large positive temperature gradient from the surface to the sample center is attributed to radiation losses from the surface to the cold walls of the current concentrator. The temperature reported in this thesis is the surface temperature corrected to a true temperature at the center of the sample.

Fig. 4. Corrected 'Black Body' and Surface Temperature vs. Observed Surface Temperature.

CHAPTER III

TEST PROCEDURES

ROOM-TEMPERATURE FLEXURE TESTING

The room-temperature strength properties of the bonded material have been determined using the "thirds-point" flexure test. This test is commonly used for determining the mechanical properties of brittle materials. A complete description of the test is given in ASTM-C-78-66.³

The testing device is shown in Fig. 5. The bending load is applied by an Instron Tensile Machine at a loading rate of 0.02 in/min. cross-head travel.

The equation used in the calculation of the modulus rupture is given as follows:

$$\text{Modulus of Rupture (psi)} = \frac{Mc}{I} = \frac{L}{2} \times \frac{4}{3} \times \frac{D}{2} \times \frac{D^4}{64}$$

where L = the maximum load in pounds

D = the diameter in inches

HIGH-TEMPERATURE TENSILE TESTING

The high temperature tensile testing was performed in a 10,000-pound Instron Tensile Machine. The sample was heated by a resistance furnace which fitted between the crossheads of the tensile machine. The furnace was manufactured by Astro Industries Incorporated of Santa Barbara, California, and has a temperature capability of 3000°C. Fig. 6A is a photograph of this testing machine with the furnace in place and a broken

Fig. 5. "Thirds Point" Flexure Testing Device.

sample in the grips. The tensile sample was placed in a cold furnace under no tensile load. The system was then evacuated and subsequently back-filled with flowing helium gas. The temperature of the sample was measured by a Leeds and Northrup disappearing-filament pyrometer which had been corrected for refraction errors through the optical train. When the sample reached the temperature desired for testing, the load was applied. The loading rate was set at 0.02 in/min. of crosshead travel.

One problem in the tensile testing of materials at high temperature is arranging for failure to occur within the desired region of the specimen. A threaded sample of the type shown in place in Fig. 6B was used; fracture always occurred in the reduced portion. In the case of bonded samples, the joint was always placed in the center of the gage length and fracture always occurred in this area of the sample.

METALLOGRAPHY AND ELECTRON MICROSCOPY

Metallographic evaluation was done on both untested and tested material. Generally, the samples exhibiting the highest flexure strength and the lowest strength were examined. The examination of the high- and low-strength samples was performed to determine whether the mode of failure was different within a series.

In general, metallographic samples were given standard mounting and polishing. However, it was necessary to use a vacuum-cathodic etching technique^{2, 15}, to develop the microstructure of the matrix and precipitated graphite. Conventional-light microscopy is adequate for revealing the significant structural features of the sample.

In the electron microscopy, the replication technique described by Gregory⁴ of the Los Alamos Scientific Laboratory was used. Once again, the graphite was cathodically etched to reveal the features of the

(A)

(B)

Fig. 6A. High-Temperature Tensile Test Furnace
in Place in an Instron Tensile Machine.

Fig. 6B. High-Temperature Tensile Sample in
Place in the Furnace.

precipitated graphite in the joint area.

X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction analysis on all of the sample series tested utilized a Picker Biplane Diffractometer and the technique is described by Cullity.⁷ The diffraction measurements were made using nickel-filtered CuK α radiation. The scanning rate was 1° per minute and the counts per second were varied to adjust to the intensities of specific diffraction lines. In general, the scan was performed in the range of 20° to 88°. This particular range was used because it yielded the greatest amount of information regarding the type of phases present. Only the low angle reflections were considered as these patterns have been well indexed for the systems of interest.²⁰

The technique employed for determining the phases present involved measuring the diffraction pattern from the fracture surface of the joined sample. In most cases, both sides of the fracture were examined and a difference in the diffraction patterns was observed. From the variations in intensity of specific diffraction peaks of the graphite, it was possible to make some general assumptions with regard to orientation of the graphite plates. From these patterns it is possible to deduce whether the graphite has been precipitated from a melt or from solid solutions, a further check on the temperature measurement and processing history for the samples.

CHAPTER IV

RESULTS AND DISCUSSIONS

GRAPHITE PROPERTIES

The material used for all of the joining experiments was produced from a single lot of extruded material. This starting material was evaluated using the same tests which were subsequently applied to the joined material. The room-temperature flexure strength of the extruded Los Alamos graphite is $7,000 \pm 500$ psi, a value significantly greater than the strength of joined material. It should be noted that this material is extruded and the flexure test is performed with the grain of the graphite, thereby yielding higher strength than would be expected if the tests were performed across the grain.

The graphite starting material has also been tested in tension at elevated temperatures. Fig. 7 consists of a plot of the ultimate tensile strength of Los Alamos graphite versus testing temperature. The peak strength of the Los Alamos material occurs at 2300°C , when the strength begins to decrease more rapidly. The strength at 2500°C is approximately 7500 psi. This strength value is significantly greater than that observed for ATJ graphite. (ATJ is a high-quality pitch-bonded nuclear graphite.) The elevated-temperature strength of ATJ graphite versus testing temperature is shown as Figure 8.

The X-ray diffraction pattern of Los Alamos graphite was prepared by examining the face perpendicular to the extrusion direction. The diffraction pattern is shown in the appendix as Figure 32. A comparison of the

Fig. 7. Tensile Strength vs. Temperature
for Extruded Los Alamos Graphite.

Fig. 8. Tensile Strength vs. Temperature for ATJ Graphite.

intensities of the various peaks yields important information regarding the orientation of the graphite. Wallace²³ has supplied a tabulation of the intensity ratios of various diffraction peaks in a randomly oriented graphite and compared them with Los Alamos extruded graphite. These results are shown in Table II.

TABLE II
RATIOS OF INTENSITIES OF DIFFRACTION PEAKS OF LOS ALAMOS
GRAPHITE AND RANDOMLY ORIENTED GRAPHITE

<u>Diffraction Peak</u> <u>hkl</u>	<u>(I_{hkl}/I₀₀₂) obs x 100</u>	<u>(I_{hkl}/I₀₀₂) Random x 100</u>
002	100	100
100	8	1
101	11	5
004	3	7
110	8	1

The analyses of this diffraction pattern comparison indicate that the graphite is oriented with the C axis of the crystallites parallel to the extrusion direction.

MOLYBDENUM-BONDED GRAPHITE

The choice of molybdenum as a joining material is in part dictated by the chemical stability of the carbides of molybdenum in atmospheres to be found in some high-temperature gas-cooled reactors. The joining temperatures which have been selected were based upon a study of the molybdenum-carbon phase diagram which is included as Fig. 35 in the Appendix. The first temperature considered for joining was 2150°C and the time at temperature was varied from 3 min. to fifteen min. This variation in time was considered to determine whether diffusion of carbon into molybdenum would affect the properties of the joined graphite. At this

temperature the reaction must be purely a solid state reaction as the Mo-Mo₂C eutectic occurs at 2205°C ± 3°C. The other temperatures considered for joining were 2450°C, which is below the peritectic melting temperatures of Mo₂C and MoC_{1-x}, but above the Mo-Mo₂C eutectic temperature; 2650°C, which is in excess of the melting points of all the carbide phases in the molybdenum-carbon system; and 2850°C, which is considerably above the melting temperatures of the carbide phases.

The room-temperature flexure strength of samples joined at these temperatures is summarized in Fig. 9. The results show distinct trends. Increasing the joining temperature yields an improvement in room-temperature flexure strength up to 2650°C while increasing time at the joining temperature appears to degrade the room-temperature properties of the joint. Also, increasing the joining temperature to 2850°C appears to degrade the properties of a fully diffused joint. The reasons for degradation of properties for a fully diffused joint are not clearly understood, but could be due to the size of primary graphite flakes produced at the joining temperature. Increasing time or temperature could result in an increase in graphite flake size which would affect the micro-crack structure of the graphite. The figure also shows a vertical line which serves to define the temperature above which a fully diffused joint is produced as opposed to a solid-carbide interface. The effect of the fully diffused joint is shown more clearly in the high-temperature tensile properties.

Fig. 10 consists of a summary of the high-temperature tensile properties of graphite jointed with molybdenum foil at temperature which yield either continuous-carbide or fully diffused joints. The curves are the results of at least three tests at the temperature of interest. The samples which had fully diffused joint structures have average

Fig. 9. Room-Temperature Flexure Strength of Graphite Joined with 0.0006-in. Mo Foil vs. Joining Temperature.

Fig. 10. Tensile Strength vs. Temperature for Los Alamos Graphite Bonded to Itself with 0.0006-in. Mo Foil.

tensile strengths which are approximately 3 to 4 times greater than the strength of the solid-carbide material. In fact, the properties compare favorably with those obtained for ATJ graphite at elevated temperatures. This similarity to ATJ is probably due to the fact that the pitch-bonded ATJ is a fully graphitized structure which is more nearly like the primary graphite which is precipitated in the joint of a diffusion-bonded sample. The matrix graphite, a furfuryl alcohol resin-bonded material, is not fully graphitized but is actually composed of glassy carbon which may account for the higher strength values at high temperatures. The fact that the solid-carbide-interface properties have shown an increase is due to an anomaly in the tensile-test procedure. The samples were actually placed in a compressive load by thermal expansion during heating for testing. This resulted in the production of a diffused joint at the 2600°C test temperature. If the joint had been subjected to a tensile preload during the heating cycle, failure would probably have occurred at the melting point of the carbide.

The metallographic evaluation of graphite joined with molybdenum has revealed several features which are interesting and apparently unique to the molybdenum-carbon system. Samples from all series of joining conditions have been examined and representative photomicrographs have been prepared. Fig. 11 consists of three photomicrographs of a joint which was joined at 2150°C for fifteen minutes. The structure developed is more sensitive to temperature than time; thus it is representative of material joined at shorter times. Fig. 11A consists of a photomacrograph of the fracture trace showing that the fracture alternates on either side of the joint at the carbide-graphite interface. Fig. 11B shows that the fracture progressed along the interface between the precipitated primary

(A)

5X

(B)

500X

(C)

500X

1 cm

Fig. 11. Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0006-in. Mo at 2150°C. Total Heating Time 15'.

- A. Macrostructure showing fracture trace. This photo indicates that fracture progresses along the carbide-graphite interface.
- B. Photomicrograph exhibiting detail of fracture trace. Note the precipitated graphite on the carbide layer.
- C. Typical unfractured structure showing precipitated primary graphite.

graphite and the matrix graphite. Fig. 11C consists of a photomicrograph showing the matrix graphite and precipitated primary graphite which appears parallel to the solid carbide joint.

The precipitation is believed to take place upon cooling from the joining temperature. There are three sources of primary graphite precipitation from solid solution. These occur along the phase boundary between $\beta \text{ MoC}_{1-x}$ and $\beta \text{ MoC}_{1-x} + \text{C}$; the eutectoidal decomposition of $\beta \text{ MoC}_{1-x}$ to $\alpha \text{ MoC}_{1-x} + \text{C}$, additional precipitation due to the carbon solubility change occur in the $\alpha \text{ MoC}_{1-x} + \text{C}$ phase field, and finally the eutectoidal decomposition of $\alpha \text{ MoC}_{1-x}$ to $\beta \text{ Mo}_2\text{C} + \text{C}$ at 1655°C . The primary graphite precipitation is noted here because it is unique to the molybdenum-carbon system. In order to have the precipitation from solid solution, it is necessary to have phase boundaries which have changing solubility. In systems where the phase boundary is independent of temperature, the precipitation of primary graphite from solid solution will not be observed.

Fig. 12 consists of photomicrographs of the structure developed in graphite joined with molybdenum at 2450°C for a time of 3 minutes. The structure of Fig. 12A reveals a solid-carbide interface with precipitated primary graphite along the carbide interface. The significant feature of this structure is that there is evidence of carbide diffusion into the graphite matrix. The diffused carbide particles may be due to the development of a small amount of liquid phase formed by the eutectic reaction between molybdenum and $\beta \text{ Mo}_2\text{C}$. Fig. 12B shows the etched carbide phase which possesses the characteristic Widmanstätten structure¹⁷ and is composed of $\beta \text{ Mo}_2\text{C}$ and carbon with some retained $\alpha \text{ MoC}_{1-x}$. This structure has been produced by a eutectoidal decomposition of the high temperature

(A)

500X

(B)

500X

Fig. 12. Microstructure Developed in Graphite Joined to Graphite with 0.0006-in. Mo Foil at 2450°C. Total Heating Time 3'.

- A. Structure of the graphite showing precipitated graphite along the joint interface. Also, note diffused carbide in matrix suggesting some liquid formation.
- B. Structure of the etched carbide layer. This structure is composed of MoC_{1-x} and $\beta\text{Mo}_2\text{C}$. Also, note diffused carbide in the matrix.

a MoC_{1-x} phase. The joint, nevertheless, is essentially a solid-carbide interface and for this reason it is considered to be temperature-limited. The temperature limitation is twofold in that the melting point of the carbide phase imposes an upper limit to the temperature under which this joint may still bear a load and, secondly, the carbide strength will diminish with increasing temperature.

Fig. 13 consists of four photomicrographs which are typical of material joined with molybdenum at 2660°C . The photomicrograph in Fig. 13A is typical of the gross characteristics of the joint showing intrusion of molten metal carbide into low-density areas in the graphite. Fig. 13B is typical of the type of intrusion of carbide into the low-density areas of the graphite. The magnitude of the intrusion indicates that there must have been liquid-phase formation as the distance traversed by the carbide from the joint is too large for a solid-state reaction. Fig. 13C consists of the typical structure developed at this joining temperature. This structure is composed of isolated metal-carbide particles in a matrix of precipitated primary graphite. The primary graphite was precipitated out of a carbon-super-saturated solution. The significant feature of this type of "fully diffused" joint is that it is not temperature-limited. This structure possesses the properties of graphite at temperatures in excess of the joining temperature. Fig. 13D is typical of the fracture trace of a sample tested in flexure. This structure indicates that the fracture occurs between the layers of the precipitated primary graphite. The layered structure in the joint area is, in general, deposited with the layers perpendicular to the axis of the sample. This layered direction is the weaker direction for either tensile or compressive loadings and is also perpendicular to the

(A)

5X

(B)

100X

1 cm

(C)

500X

(D)

500X

Fig. 13. Microstructure Developed in Graphite Jointed to Graphite with 0.0006-in. Mo Foil at 2660°C. Total Heating Time 3'.
A. Macrostructure of the gross joint showing the absence of a solid-carbide interface. B. Example of intrusion of molten carbide into the voids in graphite. C. Joint area exhibiting precipitated primary graphite and randomly distributed carbide particles. D. Trace of fracture surface demonstrating cleavage between platelets in precipitated primary graphite.

preferred orientation imparted by extrusion.

Fig. 14 consists of composite mosaics of electron micrographs which were prepared at a magnification of 6000X. The two different types of joints, i.e., fully diffused and solid-carbide, are represented in these prints. The joint that was made at 2700°C exhibits the isolated carbide particles in a primary graphite matrix whereas the joints prepared at 2400°C exhibit the solid-carbide bonded to the matrix graphite. The details of these micrographs reveal a complete lack of "binder" carbon in the fully diffused joint. The binder carbon is seen as the mottled un-layered material in the graphite matrix. The absence of this binder carbon in the diffused joint is an additional feature in favor of the argument that the primary graphite in the joint area has been precipitated from a supersaturated solution.

The X-ray diffraction patterns developed in the joints made at the various times and temperatures with molybdenum foil are shown as Figures 15 and 16. The diffraction patterns were determined on both sides of the fracture pattern and, in the case of the low-temperature solid-carbide joints, some significant features of the fractures are shown. One side of the samples joined at 2150°C for 3 minutes reveals very strong lines of the (006) α MoC_{1-x} and (002) β Mo₂C at two values of 36.9° and 37.9° respectively. The other half of this sample reveals lower-intensity reflections of these particular lines. In addition, this particular sample does not reveal any evidence of certain other carbide reflections; e.g., (110) β Mo₂C, (103) β Mo₂C, (200) β Mo₂C, which strongly suggests that the fracture is progressing along the carbide-graphite boundary as opposed to propagation through the carbide or graphite entirely. A second very significant feature of this structure is the absence of any

Fig. 14. Composite Electron Micrographs of "Fully Diffused" and Solid-Carbide-Interface Graphite Joined with Molybdenum.

Fig. 15. X-Ray Diffraction Patterns of Solid-Carbide-Interface Low-Temperature Graphite Joints Produced with Molybdenum.

Fig. 16. X-Ray Diffraction Patterns of Partially Diffused and Fully Diffused Carbide-Interface Graphite Joints Produced with Molybdenum.

reflections attributable to molybdenum metal. This suggests that in the time required for joining, the metal was completely transformed to the carbide phase. The diffraction pattern reveals that increasing the time at 2150°C to 15 minutes increases the relative amount of MoC_{1-x} as would be expected.

Fig. 16 consists of the X-ray diffraction patterns of graphite joined with molybdenum at 2450°C, 2650°C, and 2850°C for three minutes. The pattern produced in material joined at 2450°C indicates that some liquid phase was formed. In the joints produced at 2650°C and 2850°C the diffraction pattern is essentially identical. These patterns reveal random orientation of the carbide particles and additional reflections of graphite. The diffraction patterns are essentially identical on both sides of the fracture. This feature substantiates the observation that the fracture propagates through the precipitated graphite in a fully diffused joint.

TUNGSTEN BONDED GRAPHITE

The choice of tungsten as a material for bonding graphite to itself is once again dictated by the chemical stability of tungsten carbide to the atmospheres expected in certain high-temperature gas-cooled reactors. In principle, one would expect the chemical properties of tungsten carbide to be somewhat similar to the properties observed in the other Group VIA carbides. The phase diagram of tungsten and carbon, however, is not at all like the molybdenum-carbon system and, in fact, there is only a slight similarity in the carbides of the two systems.¹⁹ The tungsten-carbon phase diagram is included in the Appendix as Fig. 36. The significant feature of this diagram, insofar as joining experiments are concerned, is noted at the phase boundary separating WC and WC+C. This

phase boundary occurs at a C/W atom ratio of 1 and the solubility of carbon in tungsten is not a function of temperature.

In the tungsten-carbon system only three joining temperatures were considered. Two temperatures were selected below the eutectic melting points which occur in the system and one temperature above the published eutectic temperatures. Fig. 17 consists of a plot of the room-temperature flexure strength of graphite joined to itself with 0.0005 in. tungsten foil at 2450°C, 2650°C, and 2850°C for either 3 minutes or 10 minutes. The data reveal a slight increase in average room-temperature flexure strength with an increase in joining temperature. Once again, a vertical line is drawn on the graph which represents the WC_{1-x} -WC eutectic temperature, which occurs at 2720°C ±10°C. It was believed that joining temperatures in excess of this eutectic temperature would produce a fully diffused joint. Metallography performed on these samples substantiates this postulate. Fig. 18 consists of a plot of the elevated-temperature tensile strength of graphite joined with tungsten versus the testing temperature for material having either a diffused or solid-carbide interface. The diffused joint exhibits values of properties which are greater than those obtained for ATJ graphite, but not as great as Los Alamos graphite. The strength properties compare favorably with those obtained by a diffused joint with molybdenum. The reason for the minimum at 2800°C is not known. In the case of the material having an undiffused joint, the decrease in strength from a testing temperature of 2400°C to 2600°C can be explained on the basis of the characteristic decrease in strength which would be expected in the carbide due to increasing temperature. The increase in strength at test temperatures of 2600°C to 2800°C is believed to be caused by the formation of a

Fig. 17. Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. W Foil vs. Joining Temperature.

Fig. 18. Elevated-Temperature Tensile Strength of Graphite Joined with 0.0005-in. W Foil vs. Testing Temperature.

diffused interface during the heating prior to tensile testing.

Photomicrographs of the solid-carbide joint produced at 2450°C are shown in Fig. 19. Fig. 19A consists of an unfractured structure with the graphite etched. It is significant that little or no primary graphite has precipitated out of the carbide-interface layer. Also, since the strength of the tungsten-bonded material is higher than that of molybdenum-bonded material, it appears that the precipitation of primary graphite from solid solution in a very ordered structure results in a decrease in flexure strength. Fig. 19B shows the fracture trace with the carbide interface etched to reveal structure. The carbide appears to consist of a single phase and the fracture has occurred through the matrix graphite. Fig. 20 consists of photomicrographs of the fully diffused joint structure resulting from joining at 2850°C for three minutes. The structure in Fig. 20A appears to be similar to that observed for a fully diffused joint in which molybdenum was used. The precipitated primary graphite is randomly oriented in the joint area. Fig. 20B indicates that the fracture has progressed through the precipitated primary graphite.

X-Ray diffraction patterns were determined on both sides of the fracture surfaces and the significant ones are reproduced as Fig. 21. The series joined at 2450°C for 3 minutes has some unique features. The comparison of diffraction patterns reveals that failure has occurred along the interface between the carbide and the parent graphite. The $WC_{1.0}$ diffraction peaks are extremely strong on the pattern shown and the graphite reflections are weak. The graphite reflections are strong on the mating half of this sample indicating orientation from extrusion rather than from precipitation. The diffraction trace for samples joined at 2650°C reveals that the sample failed in graphite. The diffraction

500X

(A)

500X

(B)

Fig. 19. Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. W Foil at 2450°C.

- A. Structure shows solid-carbide interface with no evidence of precipitated primary graphite from the carbide joint.
- B. Fracture trace of a sample with a solid-carbide interface. The structure of the carbide suggests a single phase α WC.

500X

(A)

1 cm

500X

(B)

Fig. 20. Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. W Foil at 2850°C.

- A. Structure shows isolated pools of carbide in a matrix of precipitated primary graphite.
- B. Fracture trace indicating fracture progresses through the precipitated primary graphite.

Fig. 21. X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. W Foil at Various Temperatures.

pattern for the half not shown revealed only graphite reflections while the sample pattern of the side shown reveals a mixed-carbide phase. This mixed-carbide phase should be expected from the eutectoidal decomposition which would occur on cooling. The eutectoid temperatures are 2530°C and 2450°C, respectively. The diffraction traces for a sample joined at 2850°C were identical indicating that fracture had occurred through the precipitated primary graphite. It is significant to note that there is no preferred orientation of the precipitated graphite. There is no evidence of the (004) graphite reflection in this series.

TANTALUM-BONDED GRAPHITE

Tantalum has been chosen for consideration in graphite joining experiments as a material representative of the Group VA carbide-forming metals.¹⁹ The Group VA metals in general form two carbides, one of the Me_2C and the other of the form MeC . The temperatures and times considered for joining using tantalum were dictated by the phase diagram which is shown in the Appendix as Fig. 34. The joining temperatures used have resulted in only one carbide phase independent of the joining temperature within that range.

The room-temperature flexure strength of material joined with tantalum is summarized in Fig. 22. The trend in properties suggests that increasing the joining temperature results in an increase in room-temperature flexure strength. In all cases the failure occurred at the graphite-carbide interface. Typical microstructures developed in material joined with tantalum are shown in Fig. 23. The samples which were chosen for reproduction were joined at 2450°C and 3000°C and are shown as Fig. 23A and Fig. 23B, respectively. The unique feature of these samples is their similarity in appearance even though the joining temperatures were over

Fig. 22. Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Ta Foil vs. Joining Temperature.

500X

(A)

1 cm

500X

(B)

Fig. 23. Microstructural Characteristics of Graphite Bonded to Graphite with 0.0005-in. Ta Foil at 2450°C and 3000°C.

- A. Sample bonded at 2450°C. Note the similarity to sample bonded at 3000°C. The structure is representative of a single carbide phase.
- B. Sample bonded at 3000°C.

500°C apart. The structure consists of a single-carbide phase and there is no evidence of precipitated graphite at the carbide-graphite interface.

The X-ray diffraction patterns on the series of tantalum joined material are shown in Fig. 24. The results of the diffraction analysis give very good correlation with the metallographic results, i.e., only one carbide phase, TaC, is noted. Series 16, which was joined at 2850°C, is significant in that the (100), (101), and (004) graphite reflections are not observed. An examination of this sample revealed that the fracture had progressed in such a fashion as to leave carbide entirely on one side of the fracture. The fact that only one carbide phase is present is partially substantiated by the color of the joint which is in all cases the characteristic gold of tantalum monocarbide.

A hypothesis which can be made concerning the increase in flexure strength with increased joining temperature for the tantalum-bonded series is as follows: As the joining temperature increases, the strength of the graphite increases up to ~ 2700°C and then diminishes only slightly. The carbide, on the other hand, behaves more like a metal and actually decreases in strength with increased temperature. The result on cooling, then, is for the carbide to crack through the carbide phase rather than at the carbide-graphite interface. The crack structure of the carbide tends to relieve the stress along the joint interface resulting in a lower state of residual stress along this interface at room temperature. The reason that this trend is most noticeable in the tantalum-graphite system is due to the development of a single phase and the wide temperature range of its existence. This postulate should be applicable to all systems in which a single phase, stoichiometric carbide is formed.

Fig. 24. X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. Ta Foil at Various Temperatures.

ZIRCONIUM BONDED GRAPHITE

Zirconium has been selected for cursory joining investigations and is representative of the Group IVA metals. The metals in Group IVA only form one carbide phase which is of the type MeC .¹⁹ The temperatures selected for joining were dictated by the phase diagram which is shown in the Appendix as Fig. 33.

The first temperature considered for joining was 1750°C , which is well below the Zr-ZrC eutectic temperature of 1810°C . A temperature above the Zr-ZrC eutectic was then considered followed by samples at 2350°C , 2750°C , and finally 2850°C which is near the published value for the ZrC-C eutectic temperature. The results of room temperature flexure tests on this series of samples are summarized in Fig. 25. The shape of the flexure strength curve for graphite joined with zirconium is generally similar to that observed for graphite joined with other metals, i.e., the strength increases with increased joining temperature. However, the strength of zirconium joined material is the highest of any strength reported in this thesis. The exact reason for this comparatively higher strength of zirconium joined materials is not known, but is probably due to the strength of the metal-carbon bond²⁰ and to the fact that the Zr existed as a liquid for some time during joining which allowed the subsequent carbide to conform to the graphite surfaces.

The microstructural and fracture characteristics of the zirconium joined graphite have been examined. In material which was joined at 1850°C , there is good evidence of liquid phase formation. Fig. 26A shows the fracture trace. There is good evidence of intrusion of the metal carbide phase into the porous graphite structure indicating the presence of a liquid phase. Also, Fig. 26B shows evidence of expulsion of braze metal

Fig. 25. Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Zr Metal Foil vs. Joining Temperature.

5X

(A)

1 cm

250X

(B)

Fig. 26. Microstructure and Fracture Characteristics of Graphite Bonded to Graphite with 0.0005-in. Zr Foil at 2350°C. Total Heating Time 3'.

- A. Macrostructure showing trace of fracture.
- B. Microstructure showing protrusion of metal carbide into the graphite matrix. Note the absence of precipitated primary graphite.

at the surface with the accompanying wetting on the surface on either side of the joint. The carbide phase appears to be single phase in nature, a feature which is later borne out by X-ray diffraction. A second interesting feature of this system lies in the fact that this is the first time strong evidence for the presence of a liquid phase has been noted with no evidence of the accompanying precipitation of primary graphite. Fig. 27A is a photomicrograph of a sample joined at 2750°C. The lack of a sharply defined joint interface in this sample gives evidence that the foil was a liquid during some time of the bonding operation. Fig. 27B is a photomicrograph of a sample joined at 2850°C. This temperature should be in the range of the ZrC-C eutectic and there appears to be evidence in favor of the formation of a fully diffused joint. This particular series of samples had low strengths in comparison to the samples joined with zirconium at lower temperatures.

The X-ray diffraction patterns which were prepared on the zirconium-joined samples indicated that samples joined at temperatures less than 2750°C showed a marked orientation which was due to extrusion and that samples joined above 2750°C showed random orientation. This conclusion was drawn from a comparison of the intensities of the (100) peak to the (004) peak in graphite. For ideal randomness the ratio of these peaks should be about 1: $\sqrt{3}$ whereas they are by measurement 1.25:1 in the material joined at less than 2750°C. Fig. 28 consists of diffraction patterns of samples joined at 1750°C and 2750°C, respectively. In general, the diffraction peaks shown in both patterns are identical and differ only in intensity of different reflections.

(A)

500X

1 cm

(B)

500X

Fig. 27. Microstructure Developed in Graphite Joined to Graphite with 0.0005-in. Zr Foil at 2750°C and 2850°C. Total Heating Time 3'.

- A. 2750°C for 3'. Note greater amount of carbide phase still present.
- B. 2850°C for 3'. Diffused structure is beginning to appear.

Fig. 28. X-Ray Diffraction Patterns of Selected Joints of Graphite Joined with 0.0005-in. Zr Foil at Various Temperatures.

IRON BONDED GRAPHITE

Iron has been chosen as a diffusion promoter to illustrate the point that fully diffused joints are not temperature limited. The iron-carbon phase diagram was consulted in choosing the joining temperatures used in this investigation.¹² Unfortunately, the literature does not describe any phase diagrams in the iron-carbon system on the carbon rich side so temperatures for joining must be inferred from the reactions shown on the metal rich side of the diagram. The temperatures selected for joining were 1100°C, which is just below the $\gamma\text{Fe} + \text{Fe}_3\text{C}$ eutectic temperature, 1500°C which is just above the peritectic reaction of $\delta\text{Fe} + \text{L} \rightarrow \gamma\text{Fe}$, 2000°C, and 2500°C which are above any of the temperatures at which published reactions take place. These temperatures would most certainly put the joint in a phase field where a liquid rich in iron carbide would co-exist with solid graphite. The room temperature flexural strength developed in graphite joined with iron is summarized in Fig. 29. In this particular curve, the trend observed in all the previous experiments, i.e., increasing strength accompanies increasing temperature of joining, is observed again. The strengths are, in general, much lower and exhibit a wider spread than the strengths observed for the other series of samples, but the fully diffused joints do possess respectable flexural strength.

A very limited number of high temperature tensile tests were performed on the material joined with iron foil. The results of these tests are shown in Fig. 30. The joining temperature was 2500°C and the testing temperatures were 2200°C and 2400°C. Though the test temperature is less than the temperature used for joining, the point in favor of a diffused joint is still made since no carbide of iron exists in a solid state at the test temperatures.

Fig. 29. Room-Temperature Flexure Strength of Graphite Joined with 0.0005-in. Fe Foil vs. Joining Temperature.

Fig. 30. Tensile Strength vs. Temperature for Los Alamos Graphite Bonded to Itself with 0.0005-in. Fe Foil.

500X

(A)

500X

(B)

500X

(C)

1 cm

Fig. 31. Microstructures Developed in Graphite Joined to Graphite with 0.0005-in. Fe Foil at Various Temperatures.
 A. Structure of solid metal carbide showing evidence of poor bonding and no liquid phase formation. Bonding temperature = 1100°C. B. Structure of fractured sample bonded at 2000°C. Note massive metal carbide and precipitated graphite. C. Structure of fractured sample bonded at 2500°C. Note the reduction in size in the carbide phase and greater degree of dispersion.

The metallographic results obtained on samples joined with iron are shown in Fig. 31. Fig. 31A shows the structure obtained at 1100°C. There is essentially no bond between the carbided foil and the matrix graphite. The lack of bond formation is probably attributable to the instability of iron carbide. The literature indicates that the heat of formation of Fe_3C is +5 K cal/mole and would therefore not be very stable.¹⁶ Fig. 31B consists of the fracture trace of a sample which was joined at 2000°C. The fracture has occurred through the precipitated primary graphite. The metal-carbide phase is quite massive and the precipitated graphite zone is comparatively wide. Fig. 31C is representative of a fractured sample which was joined at 2500°C. The notable feature of this structure is that the carbide phase is more randomly dispersed and much smaller.

X-Ray diffraction patterns of iron-joined graphite have been prepared, but are not included as figures in this thesis. The interesting feature of the diffraction patterns of iron-joined material are that; (1) an ordered graphite phase has been produced in the joint area (implying precipitation from a melt), and, (2) there is still iron present in the joint even after heating to 2500°C illustrating the instability of iron carbide.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The conclusions drawn from the joining experiments described in this thesis are summarized as follows:

1. The Group IVA, VA, and VIA transition metals, in the form of foil, can be used to join graphite to itself.
2. Two types of joints; i.e., a diffused joint or solid-carbide-interface joint, can be developed in graphite depending upon the joining temperature.
3. It does not appear to be practical to produce fully diffused joints in graphite joined with metal foils from Group IVA or VA due to the high temperature of the eutectic reaction between the metal carbides and carbon.
4. The development of precipitated primary graphite from solid solutions appears to be present only in systems where the phase boundary between the metal carbide and the metal carbide + carbon exhibits decreasing carbon solubility with decreasing temperature. For this reason, the condition is only observed to any extent in the molybdenum-carbon system.
5. A fully diffused joint can only be developed when the joining temperature is in a range where the metal carbide coexists with carbon in a liquid form.
6. The elevated temperature tensile strength of joints which have

fully diffused graphite structures are superior to the strength of joints with solid interface structures.

7. The strongest joints in thirds-point flexure at room temperature are obtained from material with a solid-carbide-interface joined with a Group IVA metal, in this case, zirconium.

8. The strength of joints produced with iron foil are quite low. This feature adds credibility to the arguments regarding the relationship of joint strength to the thermodynamic heat of formation. In the iron-carbon system, the carbide of iron is extremely unstable and is correspondingly weak. The strength of the fully diffused joint does illustrate the point that the precipitation of primary graphite from a supersaturated solution can and does yield a joint which possesses significant strength at elevated temperature.

RECOMMENDATIONS

The areas which should be investigated in more detail are the effects of pressure on the strength of graphite joints. No systematic attempt to investigate this variable has been made since it was assumed that a pressure adequate for intimate contact would be sufficient for yielding consistent results. This assumption cannot be completely justified since this variable could certainly affect reaction rates and reaction temperature.

The effects of joining using the materials described by Steinberg¹⁸ in his patent should be more fully evaluated. The effect of temperature and crystallite size of the precipitated graphite should be more systematically evaluated. It is possible that with the use of thermal gradients the precipitation of graphite may be oriented in a manner analogous to directional solidification in metal castings.

APPENDIX

Fig. 32. X-Ray Diffraction Pattern of Los Alamos Extruded Graphite.

Fig. 33. Zirconium-Carbide Phase Diagram.

Fig. 34. Tantalum-Carbon Phase Diagram.

Fig. 35. Molybdenum-Carbon Phase Diagram.

Fig. 36. Tungsten-Carbon Phase Diagram.

TABLE III

ELEVATED-TEMPERATURE STRENGTH OF LOS ALAMOS GRAPHITE

<u>Sample No.</u>	<u>Testing Temperature (°C)</u>	<u>Breaking Load (lbs)</u>	<u>Stress (psi)</u>
1	2300	1150	7650
2	2300	1180	7850
3	2500	1040	6920
4	2500	1100	7320
5	2500	1130	7520
6	2700	930	6190
7	2700	960	6390
8	2700	1030	6860
9	2700	1100	7320
10	2900	800	5320

TABLE IV

ELEVATED-TEMPERATURE TENSILE STRENGTH OF ATJ GRAPHITE

<u>Sample No.</u>	<u>Test Temperature (°C)</u>	<u>Load (lbs)</u>	<u>Stress (psi)</u>
1	1500	730	4860
2	1500	760	5030
3	1500	695	4625
4	2000	700	4660
5	2000	800	5320
6	2300	770	5120
7	2300	760	5060
8	2300	730	4850
9	2300	710	4725
10	2500	765	5090
11	2500	930	6190
12	2500	1010	6720
14	2700	600	3995
15	2700	630	4195
13	2500*	1180	7850
16	2700	810	5390

*Heater element failed at the temperature indicated.

TABLE V

JOINING PARAMETERS AND ROOM-TEMPERATURE FLEXURE STRENGTH
OF GRAPHITE JOINED WITH 0.0006 INCH MOLYBDENUM FOIL

Sample No. and Series	Joining Temperature, °C*	Pressure Maximum (psi)	Heating Cycle (min)	Breaking Load (lbs)	Flexure Strength (psi)
1-01	2150	2465	3	199	3210
2-01	2150	2465	3	185	2980
3-01	2150	2465	3	226	3640
4-01**	2150	2465	3	--	--
1-02	2150	2465	15	162	2620
2-02	2150	2465	15	207	3360
3-02	2150	2465	15	159	2570
4-02**	2150	2465	15	--	--
1-04	2450	2465	3	265	4265
2-04	2450	2465	3	237	3805
3-04	2450	2465	3	158	2540
4-04**	2450	2465	3	--	--
1-05	2660	2465	3	280	4470
2-05	2660	2465	3	275	4390
3-05	2660	2465	3	278	4430
4-05**	2660	2465	3	--	--
1-06	2660	2465	10	211	3370
2-06	2660	2465	10	194	3090
3-06	2660	2465	10	200	3190
4-06**	2660	2465	10	--	--
1-07	2850	2465	3	265	4260
2-07	2850	2465	3	237	3800
3-07	2850	2465	3	158	2540
4-07**	2850	2465	3	--	--

*Temperature is always corrected to the center temperature as determined on a simulated black body specimen.

**Used for metallography.

TABLE VI

JOINING PARAMETERS AND ELEVATED-TEMPERATURE TENSILE STRENGTH
OF GRAPHITE JOINED WITH 0.0006 INCH MOLYBDENUM FOIL

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (lbs)</u>	<u>Tensile Stress (psi)</u>
97-1-2	2150°C for 3 min	2430	2400	78	519
97-3-4	2150°C for 3 min	2460	2400	55	366
97-5-6	2150°C for 3 min	2400	2390	77	512
97-7-8	2150°C for 3 min	2400	2605	107	712
97-9-10	2150°C for 3 min	2430	2600	127	845
97-11-12	2150°C for 3 min	2460	2600	143	950
97-13-14	2450°C for 3 min	2500	2400	126	840
97-15-16	2450°C for 3 min	2570	2400	170	1130
97-17-18	2450°C for 3 min	2570	2400	166	1105
97-19-20	2450°C for 3 min	2525	2600	224	1490
97-21-22	2450°C for 3 min	2570	2600	237	1575
101-15-20	2450°C for 3 min	2500	2600	242	1610

TABLE VI - Continued

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (lbs)</u>	<u>Tensile Stress (psi)</u>
101-5-23	2660°C for 3 min	2750	2400	186	1237
101-19 & 97-23	2660°C for 3 min	2750	2400	490	3260
101-12-13	2660°C for 3 min	2680	2400	660	4390
101-9-10	2660°C for 3 min	2610	2400	705	4690
101-17-18	2660°C for 3 min	2570	2600	280	1865
101-7-8	2660°C for 3 min	2720	2600	630	4190
93-2-10	2660°C for 3 min	2460	2600	520	3460
93-11-16	2660°C for 3 min	2500	2600	480	3195
93-21-8	2660°C for 3 min	2500	2800	585	3895
93-12-7	2660°C for 3 min	2430	2800	545	3625
93-20-23	2660°C for 3 min	2400	2800	540	3590
93-1-6	2660°C for 3 min	2650	2800	560	3730
93-4-9	2660°C for 3 min	2720	3000	575	3820
93-18-19	2660°C for 3 min	2460	3000	420	2795

TABLE VII

JOINING PARAMETERS AND ROOM-TEMPERATURE FLEXURE STRENGTH
OF GRAPHITE JOINED WITH 0.0005 INCH TUNGSTEN FOIL

Sample No. and Series	Joining Temperature (°C)	Maximum Joining Pressure (psi)	Heating Cycle (min)	Breaking Load (lbs)	Flexure Strength (psi)
1-08	2450	2430	3	291	4680
2-08	2450	2430	3	200	3220
3-08	2450	2430	3	246	3950
4-08*	2450	2430	3	--	--
1-09	2650	2430	3	182	2920
2-09	2650	2430	3	260	4160
3-09	2650	2430	3	262	4190
4-09*	2650	2430	3	--	--
1-10	2650	2430	10	273	4360
2-10	2650	2430	10	249	3990
3-10	2650	2430	10	278	4440
4-10*	2650	2430	10	--	--
1-12	2850	2430	3	305	4860
2-12	2850	2430	3	304	4870
3-12	2850	2430	3	222	3530
4-12*	2850	2430	3	--	--

*Used for metallography.

TABLE VIII

JOINING PARAMETERS AND ELEVATED-TEMPERATURE TENSILE STRENGTH OF GRAPHITE
JOINED WITH 0.0005 INCH TUNGSTEN FOIL

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (psi)</u>	<u>Tensile Stress (psi)</u>
85-1-2	2650°C for 3 min	2530	2420	424	2820
85-3-4	2650°C for 3 min	2500	2410	420	2795
85-5-6	2650°C for 3 min	2500	2400	361	2400
85-7-8	2650°C for 3 min	2500	2580	291	1935
85-9-10	2650°C for 3 min	2660	2605	210	1400
85-11-12	2650°C for 3 min	2540	2600	222	1475
85-13-14	2650°C for 3 min	2630	2805	332	2210
85-15-16	2650°C for 3 min	2570	2815	306	2035
85-17-18	2650°C for 3 min	2500	2825	241	1603
85-21-22	2850°C for 3 min	2550	2635	718	4776
85-23 to 92-23	2850°C for 3 min	2500	2620	755	5022
92-1-2	2850°C for 3 min	2500	2595	685	4560

TABLE VIII - Continued

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (psi)</u>	<u>Tensile Stress (psi)</u>
85-19-20	2850°C for 3 min	2500	2800	461	3070
92-5-6	2850°C for 3 min	2640	2820	390	2594
92-7-8	2850°C for 3 min	2500	3020	218	1450
92-11-12	2850°C for 3 min	2400	3000	472	3140
92-15-16	2850°C for 3 min	2500	3015	494	3286

TABLE IX

JOINING PARAMETERS AND ROOM-TEMPERATURE FLEXURE STRENGTH
OF GRAPHITE JOINED WITH 0.0005 INCH TANTALUM FOIL

<u>Sample No. and Series</u>	<u>Joining Temperature (°C)</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Heating Cycle (min)</u>	<u>Breaking Load (lbs)</u>	<u>Flexure Strength (psi)</u>
1-13	2400	2390	3	120	1930
2-13	2400	2390	3	117	1890
3-13	2400	2390	3	121	1950
4-13*	2400	2400	3	--	--
1-14	2775	2430	3	157	2500
2-14	2775	2430	3	147	2350
3-14	2775	2560	3	125	2000
4-14*	2775	2500	3	--	--
1-16	2850	2600	3	211	3340
2-16	2850	2500	3	138	2190
3-16	2850	2500	3	243	3860
4-16*	2850	2500	3	--	--
1-18	3000	2570	3	230	3650
2-18	3000	2600	3	232	3680
3-18	3000	2570	3	298	3130
4-18*	3000	2600	3	--	--

*Used for metallography.

TABLE X

JOINING PARAMETERS AND ROOM-TEMPERATURE FLEXURE STRENGTH
OF GRAPHITE JOINED WITH 0.0005 INCH ZIRCONIUM FOIL

Sample No. and Series	Joining Temperature (°C)	Maximum Joining Pressure (psi)	Heating Cycle (min)	Breaking Load (lbs)	Flexure Strength (psi)
1-23	1750	2140	3	227	3680
2-23	1750	2100	3	224	3620
3-23	1750	2100	3	212	3430
4-23*	1750	2100	3	--	--
1-28	2350	2320	3	332	5350
2-28	2350	2320	3	257	4150
3-28	2350	2360	3	253	4080
4-28*	2350	2360	3	--	--
1-29	2750	2390	3	389	6250
2-29	2750	2425	3	339	5430
3-29	2750	2390	3	422	6750
4-29*	2750	2500	3	--	--
1-30	2850	~ 2400	3	416	6610
2-30	2850	~ 2400	3	392	6240
3-30	2850	~ 2400	3	390	6190
4-30*	2850	~ 2400	3	--	--

*Used for metallography.

TABLE XI

JOINING PARAMETERS AND ROOM-TEMPERATURE FLEXURE STRENGTH
OF GRAPHITE JOINED WITH 0.0005 INCH IRON FOIL

<u>Sample No. and Series</u>	<u>Joining Temperature (°C)</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Heating Cycle (min)</u>	<u>Breaking Load (lbs)</u>	<u>Flexure Strength (psi)</u>
1-19	1100	1860	3	91	1470
2-19	1100	1860	3	80	1290
3-19	1100	1860	3	85	1380
4-19*	1100	1860	3	--	--
1-20	1500	2145	3	44	710
2-20	1500	2150	3	179	2850
3-20	1500	2100	3	69	1120
4-20*	1500	2070	3	--	--
1-21	2000	2325	3	220	3560
2-21	2000	2360	3	146	2360
3-21	2000	2290	3	187	3030
4-21*	2000	2360	3	--	--
1-22	2500	2395	3	212	3400
2-22	2500	2465	3	234	3750
3-22	2500	2500	3	176	2820
4-22*	2500	2540	3	--	--

*Used for metallography.

TABLE XII

JOINING PARAMETERS AND ELEVATED-TEMPERATURE TENSILE STRENGTH
OF GRAPHITE JOINED WITH 0.0005 INCH IRON FOIL

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (lbs)</u>	<u>Tensile Stress (psi)</u>
83-1-2	1500°C for 3 min	2100	1200	0	0
83-3-4	1500°C for 3 min	2100	--	--*	--
83-5-6	1500°C for 3 min	2100	1200	6	39.7
83-7-8	1500°C for 3 min	2100	--	--*	--
83-9-10	1500°C for 3 min	2100	2400	257**	1710
83-11-12	1500°C for 3 min	2100	2400	164	1092
83-13-14	1500°C for 3 min	2100	--	--*	--
83-15-16	1500°C for 3 min	2100	--	--*	--
83-17-18	1500°C for 3 min	2100	--	--*	--
83-21-22	2500°C for 3 min	2360	2200	140	930
83-23 to 88-24	2500°C for 3 min	2360	2200	140	930

TABLE XII - Continued

<u>Sample No.</u>	<u>Joining Temperature and Time</u>	<u>Maximum Joining Pressure (psi)</u>	<u>Tensile Testing Temperature (°C)</u>	<u>Maximum Tensile Load (lbs)</u>	<u>Tensile Stress (psi)</u>
88-1-2	2500°C for 3 min	2360	2400	226	1500
88-3-4	2500°C for 3 min	2360	2400	232	1540
88-5-6	2500°C for 3 min	2360	2400	357	2375
88-7-8	2500°C for 3 min	2360	---***	--	--
88-9-10	2500°C for 3 min	2360	2400	257	1710
88-11-12	2500°C for 3 min	2360	---***	--	--

*The lack of strength in this series is attributed to the formation of an unstable interface during joining.

**This series has strength since a fully diffused joint has been produced during the tensile test.

***Failed during specimen machining.

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