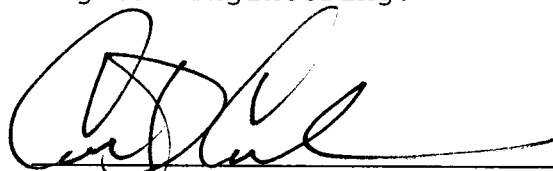


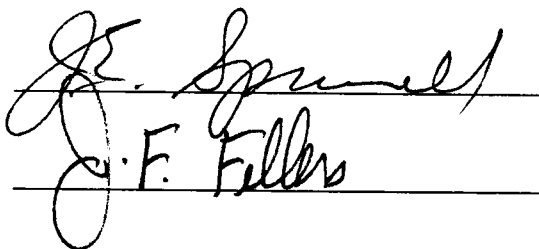
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Joining of Carbon Carbon Composite Materials

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Henry J. White

December 1992

DEDICATION

This document is dedicated to my mother; Dolores White, my sisters; Catherine and Cassandra White; and my niece; Tiffany Issacs who have supported my efforts over these years. I hope to return home soon to maintain the family tradition of returning the favor.

ACKNOWLEDGMENTS

I would like to thank: Boeing Tennessee and Mr. Scott Webb for initiating and supporting the Carbon Carbon Composites Joining Program, the faculty and staff at The University of Tennessee, Knoxville for their technical assistance, and The Materials Joining Group of The Metals and Ceramics Division at Oak Ridge National Laboratories for providing their financial and technical support.

ABSTRACT

An investigation of the fundamental considerations for joining of carbon carbon composite materials was performed. The joining method utilized in this study was the resistance brazing process. The workpiece configuration consisted of a metallic foil or powder interlayer sandwiched between carbon carbon composite materials. The geometry of the workpieces employed was selected to localize the flow of current during resistance brazing to channel the heat into the interlayer region and produce volumetric rather than areal type joints. The conditions (tap setting/duration of current flow) required to generate the heat necessary to melt the interlayer were determined by trial and error. A repetitive heating technique was used to provide melting of the interlayer.

Interlayer selection was based on wettability, adhesion, melting temperature and linear coefficient of thermal expansion (CTE). The carbon carbon composite material was qualitatively evaluated by Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) techniques to investigate the presence of antioxidants and the fiber bundle orientation which influences the wetting and adhesion of the molten interlayer on the carbon carbon composite material and affects brazement strength.

The wetting and adhesion behavior of the interlayer was evaluated prior to joining by simulating (by induction heating) the heating cycles experienced during resistance brazing to melt the interlayer on the surface of the composite material. Visual examination and planimetric surface area measurements of the solidified interlayer on the surface of the composite material were then performed to characterize the wetting behavior.

Alloying high melting temperature pure metallic interlayers with low melting temperature elements was employed to lower the melting temperature of the pure element and affect wettability.

Interlayers with CTE similar to carbon were chosen for joining of the carbon carbon composite materials. Thus, the inherent thermal expansion problem between the metallic interlayer and the carbon carbon composite material is reduced during the heating and cooling cycles which limits the formation of defects in the joint.

The joint strength was evaluated using a torsional shear type testing method. The strength was expressed as a ratio of the torsional shear strength of the brazement to the virgin carbon carbon composite material. An evaluation of the torsional shear tested fracture surfaces showed that the wetting behavior varied across the joint, and that fiber pull out occurs.

Evaluation of brazement cross sections showed different joint characteristics ranging from areal to volumetric. The joint characteristics were categorized for each of the interlayers. Titanium-Copper alloy interlayers showed the best potential for wetting and produced a volumetric type joint which had the highest torsional-shear strength ratio of all the metallic interlayers and approximately 50% of the strength of the virgin material.

The resistance brazing method can potentially produce brazements with higher strengths than those produced by furnace heating due to the steeper temperature gradient which localizes the flow; penetration; wetting and adhesion of the interlayer producing localized volumetric joints instead of areal type joints. Increased interaction (wetting/adhesion) between the interlayer and load bearing fiber bundles of the carbon carbon composite material is characteristic of volumetric type joints and aids in increasing strength.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
Material Properties	1
Applications	3
II. LITERATURE REVIEW	9
Material Characterization	9
Manufacturing Processes	13
A. Fibers	13
1. Discontinuous Fiber Composites	15
2. Continuous Fiber Composites	16
B. Matrix	17
1. Carbonization	17
2. Chemical Vapor Infiltration	18
(a) Isothermal	19
(b) Thermal Gradient	20
C. Matrix/Fiber Interaction	22
D. Three-Dimensional Carbon Carbon Composites	24
Oxidation Protection	26
Joining of Carbon Carbon Composites	27
A. High Temperature Brazing Technology	28
B. Wettability of Carbon	32
C. Graphite Joining Technology	38
1. Consumables	38

(a) Commercial	38
(b) Non-Commercial	40
2. Other Joining Techniques	42
D. Resistance Brazing	43
Summary	49
III. EXPERIMENTAL PROCEDURES	50
Introduction	50
Resistance Brazing: Operational Features.....	55
A. Original Welding Machine Design.....	56
B. Resistance Welder Modification.....	59
1. Modification to the Timer/ Controller....	59
2. Fast Follow-Up Electrode Holder.....	61
3. Current Monitor.....	63
4. Argon Chamber.....	63
C. Electrode Material and Design.....	65
D. Alignment of Electrodes.....	67
E. Formation of Volumetric Joint Configuration ..	69
Workpiece Preparation	70
A. Carbon Carbon Composite Specimen Preparation..	70
B. Monitoring of Surface Conditions.....	75
C. Preparation and Application of Interlayers and Stop-off.....	78
D. Joining Methodology.....	86
Testing and Evaluation.....	90
A. Destructive Testing.....	90
B. Brazement Polishing Technique	94
IV. RESULTS AND DISCUSSION.....	95

Carbon Carbon Composite Material.....	95
Interlayer Properties.....	100
Variables Effecting the Joining Process.....	102
A. Wetting Theory Applied to Resistance Brazing.....	102
B. Resistance Brazing Theory.....	111
C. Thermomechanical and Chemical Considerations.....	114
D. Composite Material Consideration.....	115
Evaluation of Brazement Strength.....	118
Macroscopic Examination of Fracture Surfaces.....	123
Microscopic Surface Examination.....	129
Evaluation of Brazement Cross Sections.....	141
V. CONCLUSIONS.....	150
VI. FUTURE WORK.....	155
LIST OF REFERENCES	156
VITA	164

LIST OF TABLES

TABLE		PAGE
I.	Comparative Applications for Oxidation-Protected Carbon Carbon Composite Materials..	5
II.	Typical Commercially Available Noble Metal Filler Metals for High Temperature Brazing..	29
III.	Other Selected High Temperature Filler Metals.....	31
IV.	Sessile Drop Test Results of the Wetting of Carbon by Copper Alloys with 1 at% Elemental Additions.....	34
V.	Flow Characteristics of Several Commercial Alloys on Graphite.....	39
VI.	Electrode Material Properties.....	66
VII.	Carbon Carbon Composite Material Brazing Component Dimensions.....	72
VIII.	Dimensions of the Interlayers Used For Joining.....	100
IX.	Interlayer Properties Important to Brazing.....	101
X.	Potential Wetting Characteristics.....	108
XI.	Wetting Test Results.....	109
XII.	Heat Generated at the Contact Surfaces and to Melt the Interlayer.....	113
XIII.	Torsional Strength Ratios.....	120
XIV.	Description of Fracture Surfaces for each Interlayer Tested.....	128
XV.	Cross Section Characteristics for each Interlayer.....	149

LIST OF FIGURES

FIGURE		PAGE
1.	The strength to density ratio for high temperature metallic, ceramic, and composite materials.....	2
2.	Carbon carbon thermal protection system for the space shuttle.....	4
3.	Estimated temperatures on the surface of the space plane.....	6
4.	The phase diagram for carbon.....	9
5.	Tightly bonded, hexagonally arranged carbon layers which are held together by weak Van der Waals forces.....	11
6.	Turbostratic (amorphous/glassy) structure of carbon.....	12
7.	Melt spinning apparatus used to produce non-circular carbon fibers.....	14
8.	Models of fiber arrangements for four short fiber fabrication techniques.....	16
9.	Isothermal chemical vapor deposition to infiltrate a fibrous carbon substrate.....	19
10.	Thermal gradient chemical vapor deposition..	20
11.	Schematic illustration of pore-filling and pore-blocking mechanisms during vapor deposition of pyrolytic carbon.....	21
12.	Two fiber arrangements for carbon carbon composites.....	25
13.	Defined reaction product morphologies on the wetted surface of carbon.....	35
14.	Reaction product profiles from sessile drop test on the surface of carbon.....	37
15.	Series Resistance of a typical Resistance Brazing Configuration.....	45
16.	Studer's illustration of surface contacts...	47

17.	Distribution of current flow in the workpieces based on geometry of the interlayer.....	51
18.	CTE in ppm/C versus melting temperature data.....	53
19.	Heat source employed for joining of carbon carbon composite materials.....	55
20.	Original operation chart for the timer/controller.....	56
21.	Force gauge used to monitor the consistency of the applied force in the no current mode.....	58
22.	Modified operation chart for the timer/controller.....	60
23.	Fast follow-up type electrode holder used to maintain the force on the workpieces throughout the brazing cycle.....	62
24.	Plexiglas chamber for shielding workpieces during brazing.....	64
25.	Schematic of the pointed nose electrode used for brazing.....	65
26.	Method employed to determine if the electrodes are properly aligned.....	68
27.	Schematic of the cross sectional joint configuration after brazing.....	71
28.	Surfaces of a carbon carbon composite material immediately following the cutting procedure.....	73
29.	Typical composite component prepared for surface contact resistance evaluation.....	74
30.	Contact resistance measured at the electrode/composite interface.....	76
31.	Contact resistance measurement at the composite/composite interface.....	77
32.	Masking technique used for application of foil type interlayers.....	79
33.	Composite component prepared for joining....	80

34.	Masking off the composite material surface in preparation for joining with a powder type interlayer.....	82
35.	Application of the powder/acetone slurried type interlayer.....	83
36.	Composite material component prepared for joining with a powder type interlayer.....	84
37.	Joining surfaces preconditioned with 0.01 mm (0.0004") of Titanium prior to application of a wettable interlayer.....	85
38.	Workpiece placement between electrodes.....	87
39.	Sandwich type (lap) workpieces aligned between the electrodes.....	88
40.	Localization of heat during current flow.....	89
41.	Brazement loaded in a vise prior to mechanical testing.....	91
42.	Torque wrench and an eight point 12.7 mm (0.5") socket used to grip the brazement for torsional shear testing.....	92
43.	Modification of the AWS Torsion Test Method #8.....	93
44.	Macrograph of the Coated Carbon Carbon Composite Material.....	96
45.	SEM micrograph revealing the coating on the surface of the composite material.....	97
46.	SEM micrograph of a cut surface illustrating fiber orientation within a bundle.....	98
47.	Schematic illustration of the dimensionality of the composite material....	99
48.	Illustration of the effect of capillary forces causing penetration of the molten interlayer into the pores of the composite material.....	103
49.	Schematic of the peak temperatures across the interlayer region.....	105

50.	Schematic of the peak temperatures versus time at different distances from the center of the workpieces.....	106
51.	Planimetric profile of a Cu ₂ Ti solidified interlayer on the surface of the carbon carbon composite material.....	110
52.	Brazing Schedule Diagram showing brazing conditions for joining of carbon carbon composite materials.....	112
53.	Schematic cross section of joining surface showing fiber bundle orientation...	116
54.	Schematic cross section of joining surface showing disruption of fiber bundles.....	117
55.	Dimensions of the virgin material for torsional shear testing.....	119
56.	Brazing Schedule illustrating range in which the best strength can be attained....	122
57.	Type A fracture surface. Partial melting of the interlayer.....	124
58.	Type B fracture surface. Slight fiber pullout.....	125
59.	Type C fracture surface. Complete fiber pullout.....	126
60.	Type D fracture surface. Partial fiber pullout and presence of metallic areas.....	127
61.	SEM micrograph showing the edge of the titanium coated carbon carbon composite material surface.....	131
62.	SEM micrograph showing a titanium coated carbon carbon composite material.....	132
63.	SEM fractograph of the surface of a torsional shear tested carbon carbon composite brazement joined with a titanium interlayer.....	133

64.	Same area as shown in Figure 63. Titanium wet the fibers (bright areas) causing them to adhere as shown within the outlined region.....	134
65.	Photomicrograph of a fracture surface from a torsional shear tested carbon carbon composite material brazement.....	135
66.	Same area as outlined in Figure 65. Palisading fiber bundles at the pulled out bundle/ original orientation transition interface.....	136
67.	Fractograph produced after torsional shear testing of a carbon carbon composite brazement joined with a zirconium interlayer.....	137
68.	Fractograph from a torsional shear tested carbon carbon composite material brazement joined with a Lucanex 721 interlayer.....	138
69.	Fracture surface from a torsional shear tested carbon carbon composite material brazement.....	139
70.	Same area as in Figure 69. Fibers from a bundle adhered to the surface of the interlayer.....	140
71.	Type I cross section. A uniform linear interface with no interaction.....	144
72.	Type II cross section. A linear interface contained within a reaction zone.....	145
73.	Type III cross section. A uniform linear interface with no reaction zone and local isolated zones of penetration.....	146
74.	Type IV cross section. An intermittent interface.....	147
75.	Type V cross section. Complete volumetric interaction.....	148

CHAPTER I

INTRODUCTION

In 1958, carbon carbon composites were developed as an anisotropic, light weight, high temperature/corrosion resistant material with tailorable mechanical properties whose only negative aspects are their ability to resist oxidizing conditions at temperatures in excess of 600°C (1112°F), and their ability to be joined for structural applications. Oxidation resistance has been improved by using impregnation methods and coating systems, however the joining methodologies have not been satisfactorily addressed.

Material Properties

The United States Air Force space plane program, Dyna-Soar, the National Aeronautics & Space Administration (NASA) Apollo project and space shuttle program initially evaluated carbon carbon composite materials for thermal protection systems. The properties of carbon carbon composites which make them suitable for evaluation as thermal protection systems are their low coefficient of thermal expansion to minimize induced thermal stresses; oxidation resistance after coating sufficient to limit strength reductions; tolerance to impact damage; sufficient stiffness to resist flight loads and thermal gradients; and their ability to maintain reproducible strength levels at 1650°C (3002°F). In Figure 1, the absolute tensile strength of structural carbon carbon composite materials is compared to other elevated temperature materials. Reusable Carbon Carbon (RCC) composites (space shuttle thermal protection system material) made from low modulus type fibers exhibit strength superior to both

superalloys and ceramics at temperatures greater than 1000°C (1832°F); Advanced Carbon Carbon (ACC) composites made from woven carbon cloth are twice as strong as RCC composites; and Hybrid ACC composites made from unidirectional carbon fiber tapes interplied in woven cloth have the highest strength of all the structural composites [1].

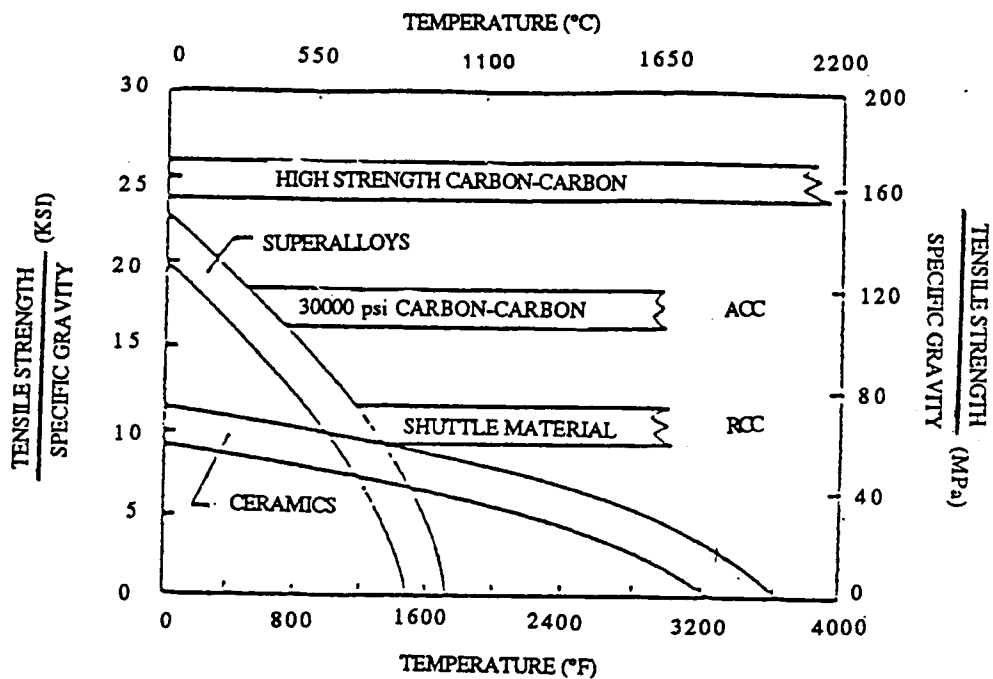


Figure 1. The strength to density ratio for high temperature metallic, ceramic, and composite materials. (Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368).

Applications

The initial success of the NASA space shuttle, a two stage-to-orbit space vehicle that uses monolithic carbon carbon composites for the wing leading edges, insulation panels, and nose cap thermal protection barriers, has stirred great interest in the development of "new" space travel ideas in the U.S. and in other parts of the world [2,3,4]. In Japan, the National Space Development Agency (NASDA) is developing "HOPE" (a two stage-to-orbit spacecraft that will be launched with the H-II rocket); the French version of the shuttle called "HERMES" will use the ARIAN-V to launch it into orbit; and the U.S. is currently embarking on "Shuttle II" which will use carbon carbon composite materials for both thermal protection and structural parts as shown in Figure 2. The wing leading edges and nose cap will experience temperatures up to 1600°C (2912°F), while the bottom surface, rudders, flaps, and ailerons will reach 1300°C (2372°F).

The 21st century probably will witness the development of completely reusable manned space vehicles, which will have single stage-to-orbit capabilities. Design criteria for the new hypersonic vehicles (NASA National Aerospace Plane (NASP), NASDA JASP, and the British "HOTOL") will call for more severe operating conditions which will be a challenge for the current carbon carbon composite materials technology. Operating conditions for the new hypersonic vehicles as well as other proposed applications for carbon carbon composites are shown in Table I. An estimated temperature distribution profile for the surfaces of the single stage-to-orbit space plane is shown in Figure 3. Another unique design for space travel proposed by the Germans is a two stage-to-orbit horizontal take-off/horizontal landing vehicle called "SANGER".

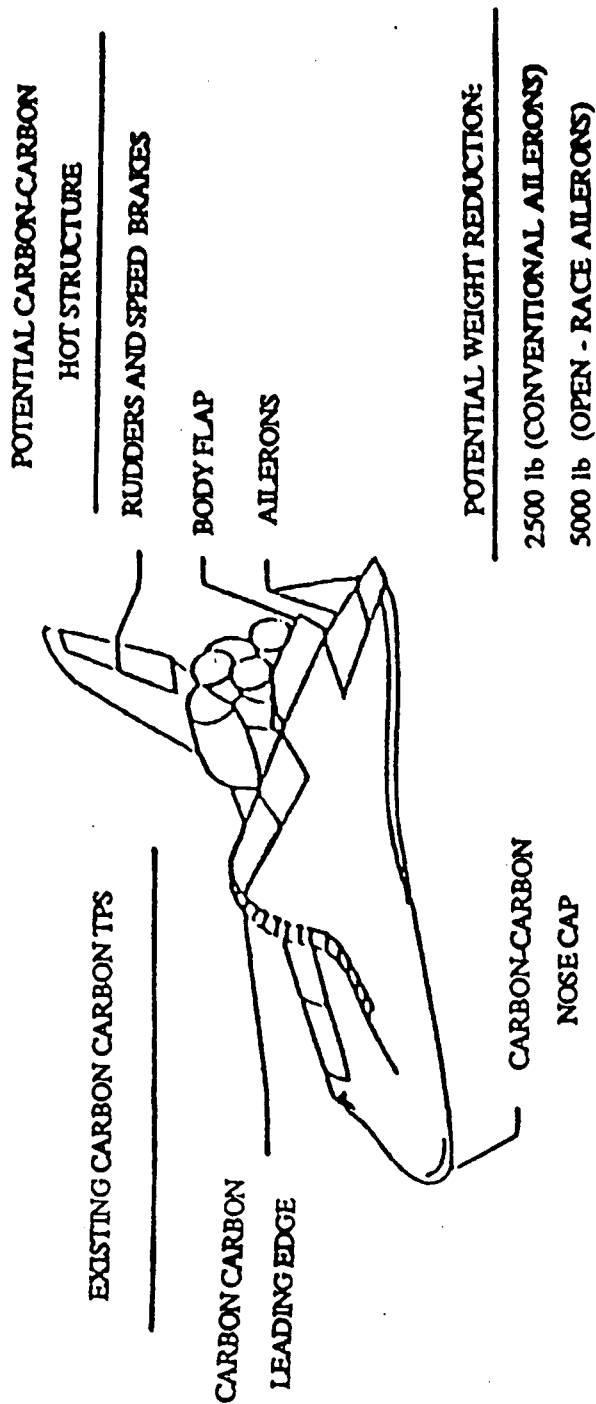


Figure 2. Carbon carbon thermal protection system for the space shuttle. (Source: B. A. Stein, et. al., "Airframe Materials for Hypersonic Vehicles," NASA CP-2482, Metal Matrix Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 22-23, 1987), pp. 1-23).

Table I. Comparative Applications for Oxidation-Protected Carbon Carbon Composite Materials

Conditions	Space Shuttle	Man-rated Turbine Engines	Cruise Missile Engines	Tactical Missile Combustors	NASP Control Surfaces
Number of Missions	100	Many	1	1	-
Hot Lifetime, (Hours)	100	>2000	5	0.2	Long
Design Temperature °C (°F)	1482 (2700) (a)	1371 (2500)	1927 (3500)	2760 (5000)	1482 (>2700)
Survivability Temperature °C (°F)	1650 (3000)	-	-	-	1650 (>3000)
Operating Environment	Air	Combustion Gases	Combustion Gases	Combustion Gases	Air
Operating Pressure (atm)	< 1	> 1	> 1	> 1	< 1
Mechanical Property Requirements	Low Stress and Modulus	High Stress	High Stress	High Stress	High Stress and Modulus

(a) Actual Flight Experience 1371 °C (2500 °F)

Adapted From: B. A. Stein, et. al., "Airframe Materials for Hypersonic Vehicles," NASA CP-2482, Metal Matrix Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DOD conference held at Cocoa Beach, Florida, January 22-23, 1987, pp. 1-23).

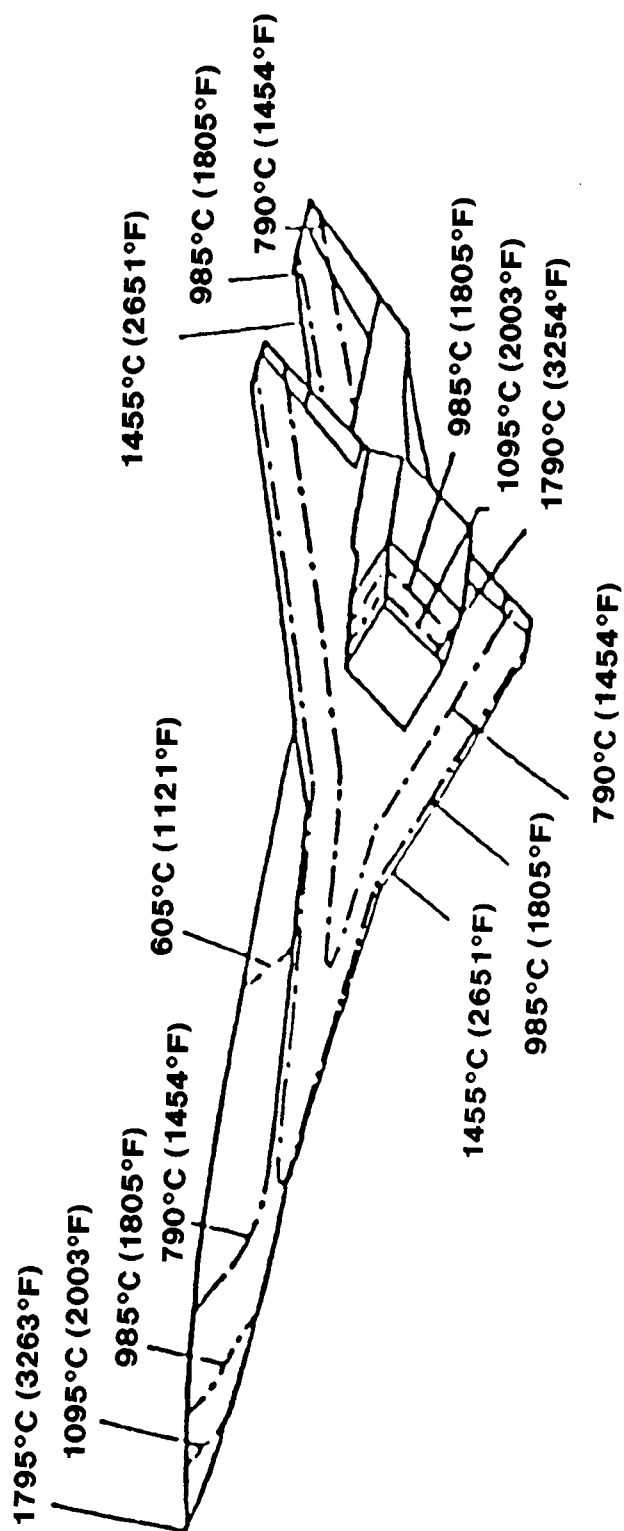


Figure 3. Estimated temperatures on the surface of the space plane. (Source: T. Kinjo, et. al., "Development of Advanced Carbon-Carbon Composites for Spaceplane Applications," Kawasaki Steel Technical Report, No. 23, October, 1990, pp. 54-60).

Based on the success of these vehicles, planes that can travel at speeds of 10,000 m.p.h. may be developed that would travel from New York to London in one hour; Washington, D.C. to Tokyo ("Orient Express") in two hours; and Paris to Sydney in three hours [5].

Carbon carbon composite materials technology will be one of the keys to the success of these projects. Previously, joining of carbon carbon composite materials used for the space shuttle was achieved by metallic fasteners at points exhibiting low temperatures internal to the structures. However after numerous exposure to high temperature, the coefficient of thermal expansion mismatch between the metallic fastener and the carbon carbon composite often caused detachment [6]. Holko [7] and Webb [8] have examined brazing carbon carbon composites for structural applications. Another idea is to mechanically design components so that carbon carbon composite bolts and nuts can join components [9,10].

Another popular application for carbon carbon composites is disc brake pads. Carbon carbon composites have been used for disc brake pads in racing cars, motorcycles, trains and tanks [11]. This application takes advantage of the composites' high friction coefficient; high heat capacity; thermal shock resistance; and thermal fatigue characteristics. Carbon carbon composites serve as a weight saving alternative for metallic brake linings and are also found to be less prone to warpage. Joining for this application has been successfully accomplished by Fisher and Fennell [12] using commercial brazing consumables such as Nicrobraz 30, Nicrobraz 160, Nicrobraz 180, and Colmony No. 5.

Future applications [11,13] for carbon carbon composites will be for machinery such as pistons and engine parts for automobiles; laboratory equipment such as crucibles for molten metals; and surgical implants because carbon carbon composites are bio-compatible, biodegradable, and as stiff and as strong yet more difficult to fracture than ordinary bones. Considerations for joining components in these areas may eventually have to be addressed.

CHAPTER II

LITERATURE REVIEW

Material Characterization

Carbon carbon composites are an unusual class of composite material with both the matrix and the fibers being similar. On a macro-scale, one would assume that the matrix and the fibers have the same properties. On a micro-scale however, the matrix and fiber properties are indeed quite different. Carbon can exist in several crystallographic forms [14,15] each exhibiting different mechanical and physical properties. Its basic forms, diamond and graphite, are shown on the P,T phase diagram in Figure 4.

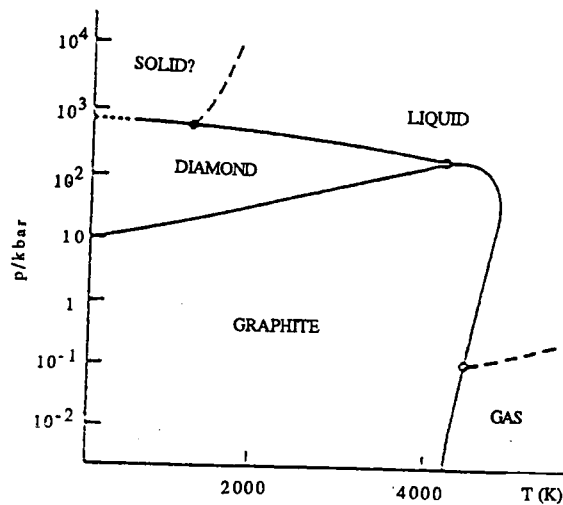


Figure 4. The phase diagram for carbon. (Source: P. W. Atkins, Physical Chemistry, 3rd ed., (New York: W.H. Freeman and Company, 1986), pp. 144-145).

At high temperatures and pressures carbon exists in its diamond form. Physically, diamond has a high specific gravity (relative to the other forms of carbon); is colorless; transparent; a poor conductor of electricity; and is cubic in crystallographic structure [16]. Mechanically, diamond has a high hardness; one of the highest absolute and specific moduli (second only to graphite amongst all known metallic and ceramic materials); and it has the ability to maintain its elasticity in all crystallographic directions. Thus, diamond would be an ideal material of construction for fibers in carbon carbon composite materials. Diamond has not yet been used in this application [17].

The other basic form of carbon shown on the phase diagram in Figure 4 is graphite. Graphite, has a lower specific gravity; is soft; opaque; slippery; a good conductor of heat; a good conductor of electricity; and is hexagonal in crystallographic structure [16]. The structure of graphite is shown in Figure 5. A characteristic of this structure is strong bonding in the basal (a-b) planes which generates the highest theoretical tensile strength of all known materials. Between the basal planes (c) weak bonding exists which produces low shear and cross-plane moduli. When graphite is used as fibers in carbon carbon and other composite materials, the weak bonds between basal planes significantly reduce the properties of the fibers [17].

The International Committee for the Characterization and Terminology of Carbon describes the layered hexagonal network present in graphite as graphene. Graphene layer planes are stacked in a three-dimensional fashion. Since the nature of the bonding between planes is weak, disorder frequently occurs between planes resulting in a two dimensional structure. If this occurs, the material is known as carbon or turbostratic (amorphous/glassy) graphite [1,17]. Figure 6 shows the crystallographic structure of turbostratic carbon.

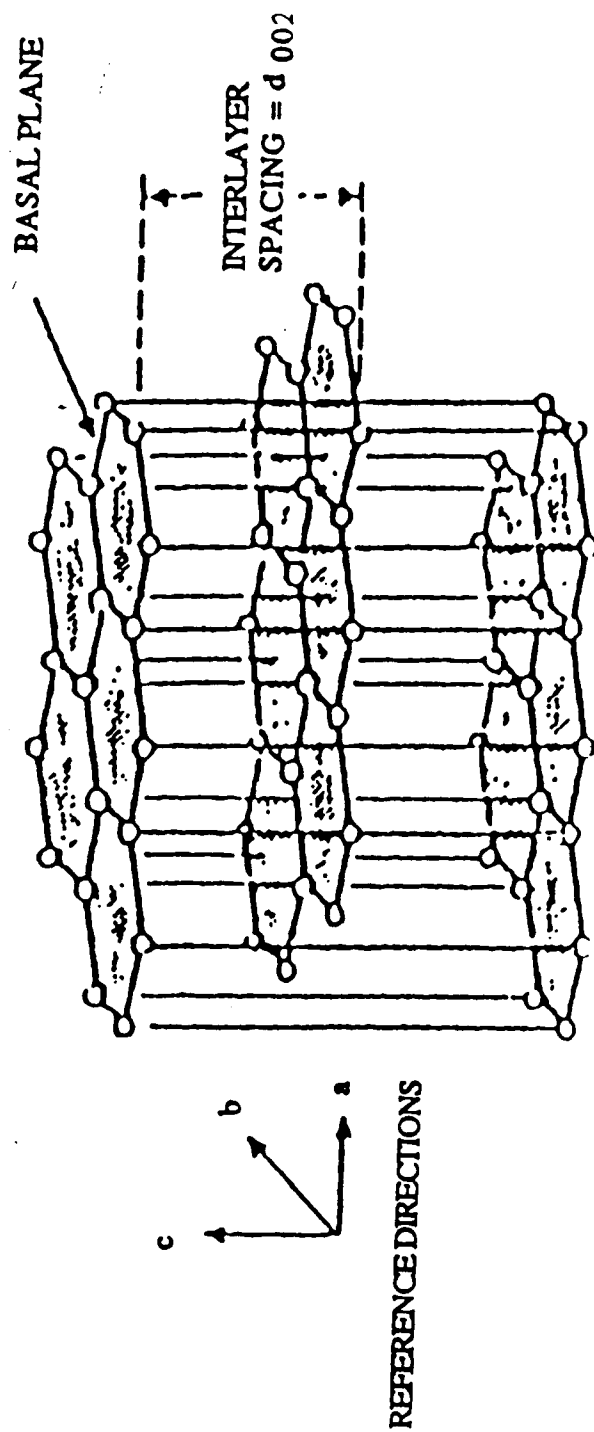


Figure 5. Tightly bonded, hexagonally arranged carbon layers which are held together by weak Van der Waals forces. (Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368).

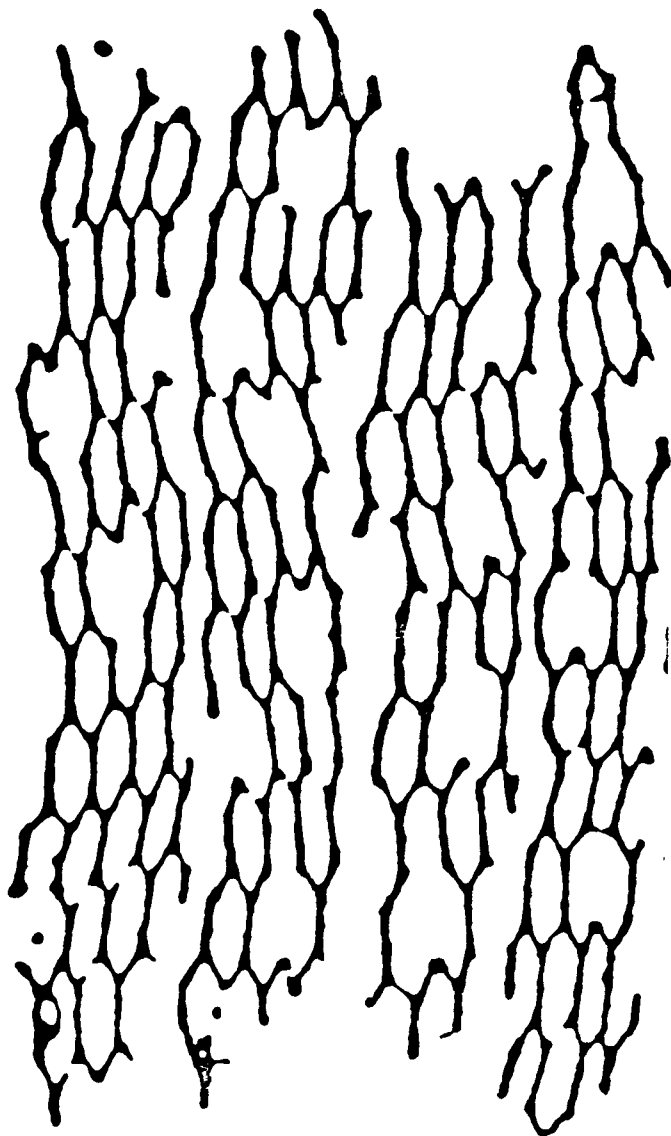


Figure 6. Turbostratic (amorphous/glassy) structure of carbon. (Source: E. Fitzer, "The Future of Carbon Carbon Composites," Carbon, Vol. 25, No. 2, 1987, pp. 163-190).

Manufacturing Processes

A. Fibers

Tows (filament bundles of fibers), tapes (flat narrow strand of fibers) and woven cloths are used to create continuous, discontinuous; unidirectional lay-up, or multi-dimensional weave type fiber bundle configurations whose tensile moduli range from 28 GPa (4,000 ksi) to 690 GPa (100,000 ksi). Carbon fibers, typically 0.0051 mm (0.0002") to 0.0102 mm (0.0004") in diameter, are produced from rayon [11,17,18,19,21], polyacrylonitrile (PAN) [17,18,19,20,21,22,23,24,26,27,28,29,30,32], petroleum pitch [17,18,19,20,21,27], polyvinyl alcohol (PVA), dehydrated PVA, phenolic, and aromatic polyamide type precursors [31]. Carbon fibers produced for commercial carbon carbon composite materials are most often made from rayon, PAN, and petroleum pitch [17].

Rayon type precursors are produced by pyrolyzation, carbonization, and graphitization [1,17,18]. Pyrolyzing the fibers at temperatures greater than 400°C (752°F) causes the cellulosic material to decompose to form carbon and graphite. Carbonizing at temperatures greater than 1000°C (1832°F) causes the pyrolyzed carbon structure to gain some orientation. Graphitization at temperatures between 2000°C (3632°F) to 3000°C (5432°F) produces a 100% graphite/carbon ordered fiber structure. Rayon type fibers produced in this fashion usually have low tensile moduli ~28 GPa (4,000 ksi) [1]. Higher modulus rayon type precursor carbon fibers can be produced, however, if the ordered carbon fibers are stretched during graphitization [1,17].

PAN type fibers have tensile moduli and strength of ~344 GPa (50,000 ksi) and ~2 GPa (300 ksi) respectively [1,11,17,20]. They are produced by initially stretching the

fibers 500-1300%, stabilizing or cross-linking in oxygen at 200°C (392°F) to 280°C (536°F) (in tension), carbonization between 1000°C (1832°F) to 1600°C (2912°F), and finally graphitization at temperatures greater than 2500°C (4532°F) [1].

Mesophase petroleum pitch type fibers are processed exactly the same as PAN fibers except they do not undergo the extensive stretching steps during heat treatment to maintain preferred alignment of the crystallites. Shaping of pitch type fibers is controlled by melt spinning as shown in the apparatus in Figure 7. Round, c-shaped, trilobal and hollow pitched type fibers produced by melt spinning were studied to determine which had the best mechanical properties. Round fibers had lower tensile strengths of ~2 GPa (300 ksi), while c-shaped and hollow fibers were superior with strengths of ~4 GPa (600 ksi) [11,20].

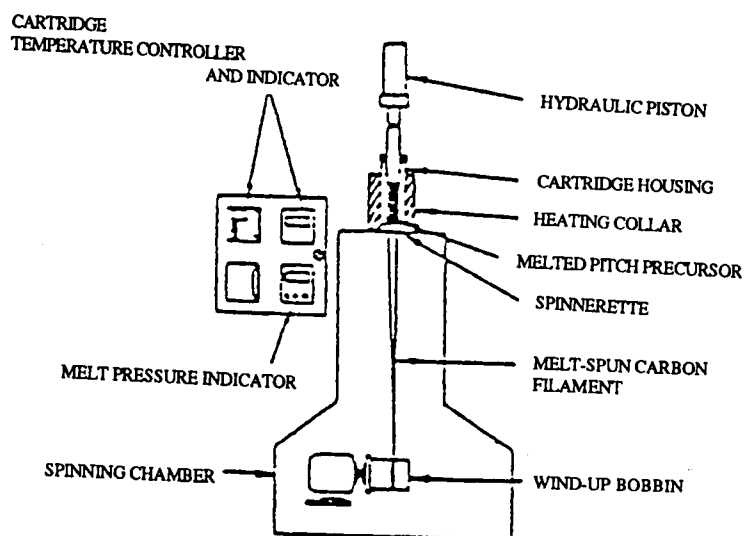


Figure 7. Melt spinning apparatus used to produce non-circular carbon fibers. (Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368).

In general, the type of fiber used, the orientation of the bundles, and the processing technique all have an effect on the strength of the resulting carbon carbon composite material.

1. Discontinuous Fiber Composites

Carbon carbon composite materials made from discontinuous carbon fibers (0.203 mm (0.008") to several cm in length) combined with a pyrolytic carbon [36] matrix (also termed Chemically Vapor Deposited (CVD) carbon, carbon deposited at $\sim 1100^{\circ}\text{C}$ (2012°F) by thermal pyrolysis of a carbon bearing gas) [19] or a pyrolyzed organic matrix are fabricated for applications where the need for fiber reinforcement properties are not the governing criteria. Short discontinuous carbon fibers in a carbon matrix increases fabrication capabilities of large scale monolithic structures; achieves a more isotropic material; increases the composites interlaminar tensile strength; and when used in conjunction with continuous filament substrates, a stronger composite material is formed by providing additional nucleation sites which reduces composite porosity. Most often, discontinuous fiber carbon carbon composites are fabricated either by carbonized rayon felt fibers in a pyrolytic carbon matrix or short chopped fibers in a pitch based matrix. The most widely used forms of discontinuous carbon fibers are flocking lay-ups, pulp molding, isotropic casting and spray lay-ups as shown in Figure 8.

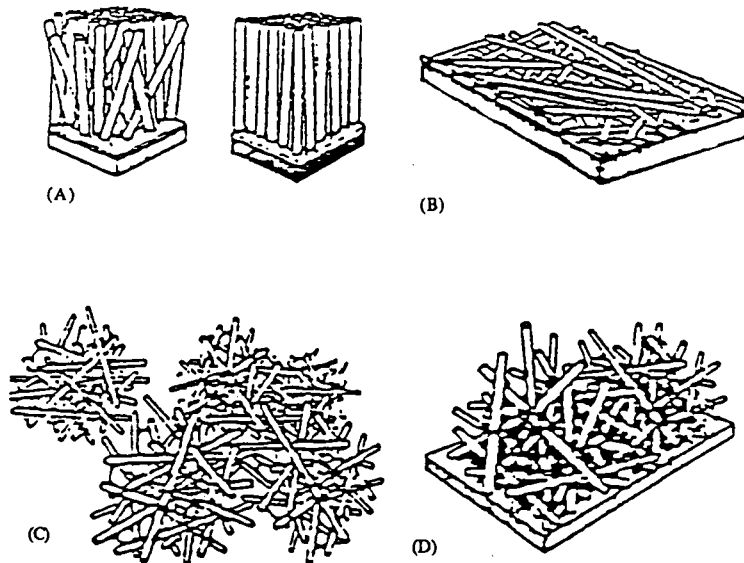


Figure 8. Models of fiber arrangements for four short fiber fabrication techniques: (A) flocking layup; (B) pulp molding; (C) isotropic casting; and (D) spray layups. (Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, 1988, pp. 364-368).

2. Continuous Fiber Composites

Continuous filament substrates are employed to take advantage of the high strength properties of the filaments or to achieve a high degree of preferred orientation on the macro-scale of the matrix [1,17]. The two variables which must be considered when fabricating continuous fiber composites are the directionality of the filament, and the amount of layer interlocking within the substrate [1]. Unidirectional tapes and plies when used for continuous filaments produce material with no interlocking between layers. Woven fabrics used in two-dimensional carbon carbon composite materials also do not interlock between layers.

Helical filament windings produce interlocking between adjacent layers, and complex weaving patterns or yarn placements result in multi-layer interlocking [1,18]. The directionality and interlockability of three-dimensional carbon carbon composite materials will be described later.

B. Matrix

The impregnation of carbon fibers with a carbon matrix is done either by carbonization of an organic solid or liquid (for thick parts) [40] or by chemical vapor deposition (CVD) of carbon from gaseous hydrocarbons [1,13,19,36].

1. Carbonization

Matrix formation by carbonization employs the use of prepregged fabrics or yarns. The precursor is processed as follows: (1) pre-treatment at $\sim 100^{\circ}\text{C}$ (212°F); (2) curing of laminates at 125°C (257°F) to 175°C (347°F) and ~ 3 MPa (400 psi); (3) post-curing at 200°C (392°F) to 275°C (527°F) (pyrolysis is initiated); (4) carbonization at higher temperatures; (5) re-impregnation and re-carbonization cycles; and (6) graphitization.

The initial pre-treatment of the prepreg creates flow in the resin or laminate formation. The laminates are then cured, pyrolyzed, and carbonized to create a char (carbon matrix and fibers). Curing produces compact impregnated fabrics which tend to shrink upon the initiation of pyrolysis. Simultaneously, the vapors released from pyrolysis tend to expand the composite structure. Thus, vapors resulting from pyrolysis must be released at a slow rate to prevent damage to the char. During carbonization,

the char thermally expands producing a composite of a particular density. Re-impregnation (in a vacuum environment at a high mechanical pressure) to fill in pores, and re-carbonization steps are repeated until the desired density is achieved [1,8,11,13,17,18,19,20,23,24,35,37,38,40]. Furfuryl alcohol is typically used during the pyrolysis and re-impregnation steps [1,26,38]. Graphitization may be employed after the carbonization step or at the end of a re-impregnation/re-carbonization cycle to improve the strength [1]. Other polymers that decompose to form carbon in inert atmospheres are polyvinylidene chloride, polyvinyl butyrate, polyvinyl pyrrolidone, polyacrylonitrile (PAN), polyphenol formaldehyde, polyfurfuryl alcohol, polyacrylamide, polyvinyl ethyl ether, cellulose, cellulose acetate, polyvinyl acetate, polyvinyl alcohol, chlorinated polyvinyl chloride, chlorinated rubber, and polyvinyl chloride. Dollimore and Heal determined the decomposition temperatures and properties of the resulting carbon formed from these polymers [25].

2. Chemical Vapor Infiltration

Matrix formation by CVD [11,18,19,33,36,37,40,42] of a hydrocarbon gas (methane, benzene, propane, or propylene) [13,17] can be accomplished by isothermal, thermal gradient, pressure gradient, and pressure pulsation techniques. The two most often used techniques as described by Buckley [1] are the isothermal and thermal gradient techniques.

(a) Isothermal

The isothermal technique involves heating the substrate with an inductively heated susceptor so that the hydrocarbon gas and substrate (fibers) are held at a uniform temperature. The substrate is infiltrated at $\sim 1100^{\circ}\text{C}$ (2012°F), ~ 6 KPa (50 Torr), and a flow rate determined by the fiber surface area. Using this technique, a crust forms that requires machining and multiple infiltration cycles. Figure 9 shows a schematic of the apparatus used for the isothermal technique.

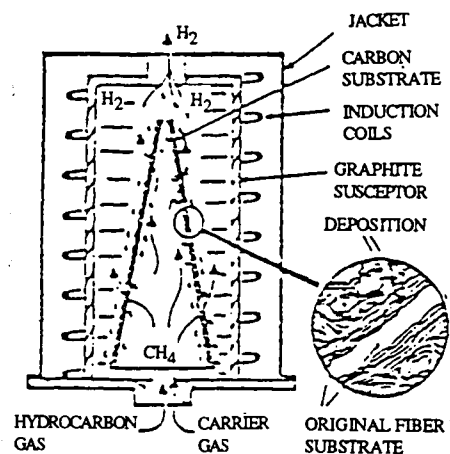


Figure 9. Isothermal chemical vapor deposition to infiltrate a fibrous carbon substrate. (Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368).

(b) Thermal Gradient

The thermal gradient technique uses an inductively heated mandrel to support the part to be infiltrated. The mandrel is used to create a temperature gradient from the inside heated surface of the infiltrated part to the cool exterior, thus very little deposition of carbon occurs on the exterior surface of the part, and crusting is eliminated. Figure 10 shows a schematic of the apparatus used for the thermal gradient CVI process.

Matrix developing processes, producing a wide range of carbon structures with various properties, are performed at temperatures between 800°C (1472°F) to 1500°C (2732°F). Once the substrate fibers are processed with the matrix to form the carbon carbon composite, a graphitization treatment at ~3000°C (5432°F) can further improve composite properties [1,19].

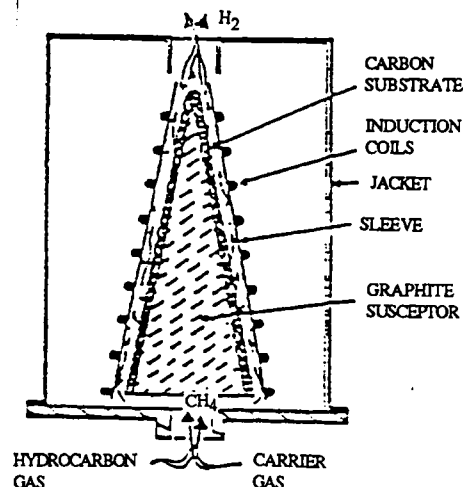


Figure 10. Thermal gradient chemical vapor deposition.
(Source: J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368).

Matrix formation by CVD is less effective than formation by carbonization because pores can close off instead of being filled which creates delaminated regions during processing see Figure 11 [13,17,37]. The bottlenecking of pores can be remedied by heat treatment at elevated temperatures to induce cracking followed by subsequent CVD to fill in pores [17]. Carbonization and CVD used together during processing is also a good practice [1,11,17,41].

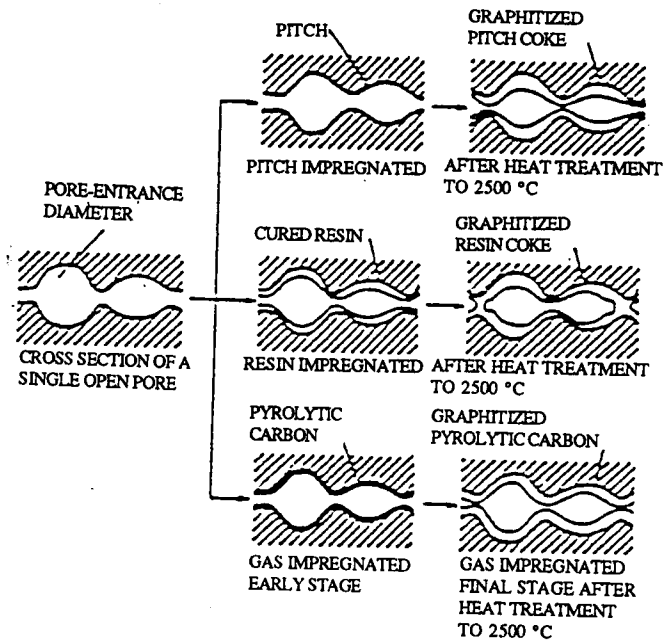


Figure 11. Schematic illustration of pore-filling and pore-blocking mechanisms during vapor deposition of pyrolytic carbon. (Source: R. J. Diefendorf, "Continuous Carbon Fiber Reinforced Carbon Matrix Composites," Engineered Materials Handbook, Vol. 1, Composites, Metals Park, OH: ASM International, 1987, pp. 911-914).

C. Matrix/Fiber Interaction

Reproducible tensile, compression, shear, bearing, transverse tensile, and flexural properties are the mark of quality processing procedures in the development of carbon carbon composite materials [29]. X-ray, scanning electron microscopy, conventional microscopy, Vicker's hardness, and ultrasonics have been used to maintain quality during the impregnation stages [40,43]. The wettability or interaction of the fibers with the matrix has a strong influence on the mechanical properties of the composite [28]. High tensile strength/high Young's modulus type fibers are usually used to fabricate high performance carbon carbon composite materials. Composites made from these fibers usually exhibit low shear strength; and when used in compression, separation of the fiber/matrix interface and buckling of the unsupported fibers results [11,28].

Kimura, Tanabe, and Yasuda [26], and Kowbel and Shan [29] found that strong binding at the matrix/fiber interface has a negative influence on the mechanical properties of carbon carbon composite materials. High modulus type fibers in the oxidized and non-treated conditions impregnated by carbonized and CVD matrix precursors were studied. Carbon carbon composite materials with oxidized fibers and carbonized matrix showed low strength after carbonization. The matrix/fiber interaction was strong and the tensile strength of the composite was dominated by the matrix. Thus, cracks initiating in the matrix during carbonization tended to cut through the fibers easily because of the strong interactions at the interface. Graphitization of carbon carbon composites with strong matrix/fiber interactions retarded the traverse of matrix cracks into the fibers resulting in an increase in strength.

Carbon carbon composites with non-treated fibers in a carbonized matrix had higher strength than carbonized composites with oxidized fibers. Bonding at the matrix/fiber interface was reported to be weak, therefore, cracks initiating in the matrix during carbonization branched at the matrix/fiber interface instead of traversing into the fibers. Thus, the fibers served as a source of reinforcement. Graphitization tended to lower the strength below levels achieved in the carbonized condition. Fracture of weakly bonded carbon carbon composites occurs in shear resulting in the loss of strength.

CVD matrix impregnated carbon carbon composites are heat treated at $\sim 1300^{\circ}\text{C}$ (2372°F) prior to carbon depositing thus the influence of surface treatment of fibers is removed. Bonding at the interface is weak so high strength exists. CVD carbon carbon composites tend to have higher strength than carbonized carbon carbon composites because of the presence of a greater amount of porosity. After graphitization, the mechanical properties of CVD impregnated carbon carbon composites did not change.

Kimura, Tanabe, and Yasuda believe that the matrix/fiber interaction of carbonized carbon carbon composites is enhanced due to shrinkage and coefficient of thermal expansion mismatch between the matrix and the fibers. This mismatch leaves high residual stresses at the interfaces when surface bonding is strong. Thus, material with low thermal shrinkage or high carbon yields are better for matrix precursors. CVD and pressure carbonization techniques are the best methods for applying matrix precursors [26].

Kowbel and Shan [29] believe that successful translation of the fiber properties into the composite is necessary for future structural applications of carbon carbon composites. It was stated that this can be achieved by optimizing the bonding between the fibers and the matrix as follows: no

bonding, but a greater mechanical compressive stress exerted on the matrix and fiber which improves tensile, flexure and interlaminar shear strength; or by a large coefficient of friction between the fiber and the matrix. Thomas [44] showed that a surface treatment process (heat treatment in argon) was beneficial to improve the strength of carbon carbon composites by reducing the fiber surface reactivity.

D. Three Dimensional Carbon Carbon Composites

Improved properties of carbon carbon composites can be achieved mechanically by starting with a three-dimensional preform which eliminates shrinkage problems [13]. Three dimensional carbon carbon composites were initially fabricated by aligning fibers in the orthogonal direction as shown in Figure 12. These configurations provide less cracks and delaminations and thus a more structurally stable finished product [19,21,35,38]. Further improvements in properties were achieved by replacing the x-y fibers by a woven fabric. Higher tensile strengths and lower coefficients of thermal expansions in excess of the properties of graphite were achieved. Pressure impregnation of the woven three-dimensional carbon carbon composite preforms with pitch, and CVD infiltration treatments improved the density, thermal conductivity, and the physical properties of the final composite [19].

Fiber bundle orientation; volume fraction of the fibers in the required direction; fiber bundle spacing; woven density; yarn packing efficiency; and fiber type all play a role in enhancing the physical properties [19]. Mechanical properties can be enhanced by multiple controlled re-impregnations/carbonization treatments prior to final graphitization [38].

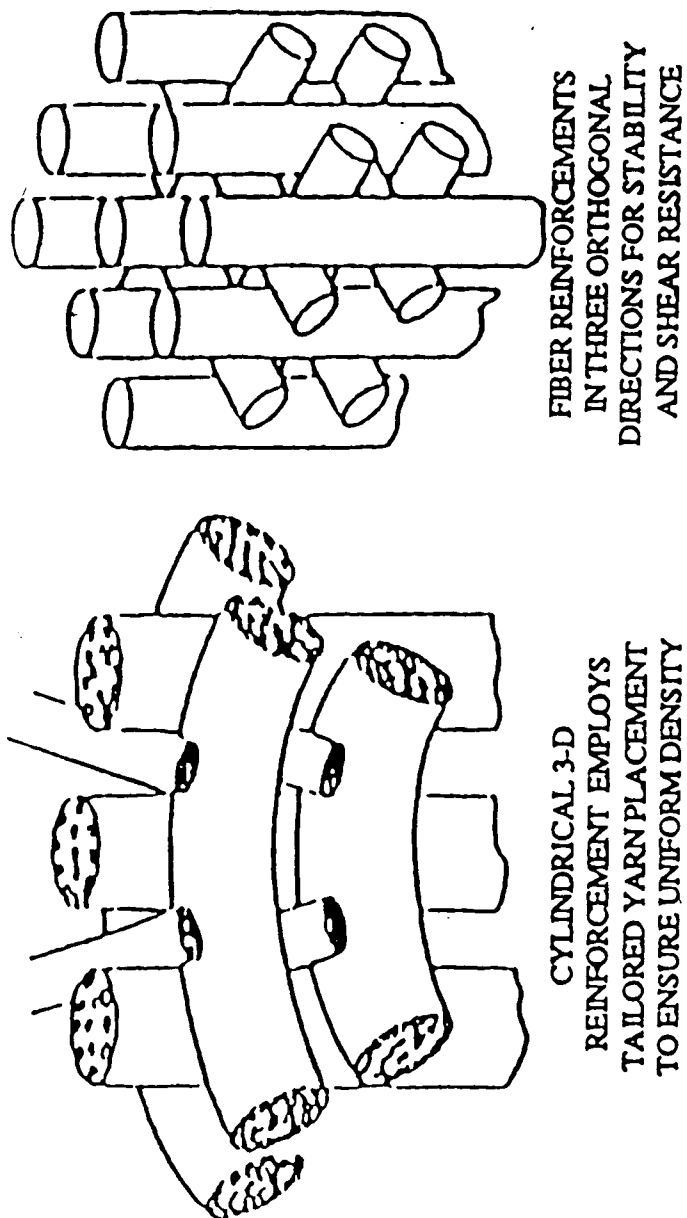


Figure 12.

Two fiber arrangements for carbon carbon composites. (Source: J. W. Wheeton, et. al., Engineers' Guide to Composites, Metals Park, OH.: ASM International, 1987, pp. 1.4, 2.5, 8.39-8.44).

Oxidation Protection

Carbon carbon composites can withstand temperatures greater than 3000°C (5432°F) in vacuum or inert atmospheres. In oxygen containing atmospheres however, they oxidize and sublime at 600°C (1112°F), and must be protected [1,39]. The most comprehensive study containing more than 50 years of coating practices on carbon is given by Strife and Sheehan [45].

Fitzer [13] describes an oxidation protection system whereby inorganic salts such as boron-oxides and phosphates are impregnated into the carbon carbon composite material. These systems are adequate for use in intermediate temperature (500°C (932°F) to 600°C (1112°F)) applications.

Becker [43] and Fitzer [13] describes an oxidation protection system which employs 10% alumina, 30% silicon, and 60% silicon carbide powder packed around structural carbon carbon composite materials and heated to ~1650°C (3000°F) in an argon atmosphere. A silicon carbide layer is deposited on the surface of the carbon carbon composite. Upon cooling from 1650°C (3000°F), micro-cracks form due to the mismatch of coefficient of thermal expansion between the silicon carbide coating and the carbon carbon composite structure. Sol gel techniques using tetraethylorthosilicate impregnated into the cracked areas leaves silica in the cracks which enhance the oxidation protection of the system [11]. This idea has led to the development of a new oxidation resistant composite material, carbon fiber reinforced-silicon carbide composites [13].

Glasso and Veltri [18] produced a more protective and uniform silicon carbide layer on carbon carbon composites by pre-treating the material with a 0.025 mm (0.001") to 0.127 mm (0.005") layer of graphite prior to coating. This was

performed in an argon atmosphere using methane at high temperatures under pressure.

Lewis [46] reported CVD of hafnium oxide on the surface of carbon carbon composites. This coating provided both oxidation protection, and the ability to facilitate the joining of carbon carbon composites.

Goldstein, Carter, and Klutz [47] studied the improvement of oxidation resistance of graphite using ZrB_2 , HfB_2 , TiB_2 , NbB_2 , TiC , ZrC , VC , and Cr_3C_2 . In the graphite-metal diboride systems, ZrB_2 showed excellent oxidation resistance while HfB_2 , TiB_2 , and NbB_2 showed poor results. In the graphite metal-carbide systems, ZrC showed excellent results; TiC showed fair results; and VC also showed good results.

Joining of Carbon Carbon Composites

The joining of carbon carbon composites has been previously studied by Holko [7], Fisher and Fennell [11], Webb [8], Davis [48], and Dadras and Nagai [71]. Holko's work involved furnace brazing and welding of two-dimensional carbon carbon composites with metallic foil and powder interlayers for elevated temperature applications. Fisher and Fennell's work involved joining of carbon carbon disc brake linings by furnace brazing using metallic and non-metallic interlayers for intermediate and high temperature applications. Webb used a resistance brazing technique to join carbon carbon composites with pure metallic foil interlayers for elevated temperature services. Davis joined carbon carbon composites by furnace brazing using commercially available bonding systems for the joining of graphite. Dadras and Nagai joined carbon carbon composites using boron and titanium disilicide interlayers.

A. High Temperature Brazing Technology

Pattee's [49] work on high temperature brazing gives a detailed description of commercially available brazing filler metals and the metallurgical interactions that occur at elevated temperatures. He states that,

...the properties of the base metals must be well defined to permit selection of compatible filler metals. When assemblies that will be subsequently heat treated are brazed, it is imperative to select filler metals and brazing cycles that are suited to the heat treatment. The brazing cycle (i.e., heating rate, brazing temperature, time at temperature and cooling rate) and the metallurgical reactions that occur during brazing must be carefully considered to avoid forming undesirable intermetallic compounds.

Low temperature brazing filler consumables (suitable for temperatures below 260°C (500°F)) are based on aluminum, silver, copper, and other low melting temperature metals. High temperature brazing filler material are based on nickel, cobalt, iron, noble metals, refractory metals, and some of the reactive metals. Tables II and III list commercially available high temperature and other high temperature brazing consumables. Section II (Part C) of the American Society of Mechanical Engineering Specifications and the American Welding Society Specifications also contain brazing consumables which are suitable for intermediate and high temperature joining [50].

Table II. Typical Commercially Available Noble Metal
Filler Metals for High Temperature Brazing

Filler Metal	Temperature,	Temperature,	AWS Designations
	°C (°F)	°C (°F)	
	Solidus	Liquidus	
Re	3180 (5756)	3180 (5756)	-
Ru	2500 (4532)	2500 (4532)	-
Ir	2450 (4442)	2450 (4442)	-
Rh	1968 (3574)	1968 (3574)	-
Pt	1769 (3216)	1769 (3216)	-
Pt-40Ir	1950 (3542)	1990 (3614)	-
Pt-40Rh	1935 (3515)	1950 (3542)	-
Pt-20Pd-5Au	1645 (2993)	1695 (3083)	-
Pt-60Cu	1200 (2192)	1250 (2282)	-
Pd	1552 (2826)	1552 (2826)	-
Pd-70Ni	1290 (2354)	1320 (2408)	-
Pd-36Ni-10Cr	1232 (2250)	1260 (2300)	-
Pd-40Ni	1238 (2260)	1238 (2260)	-
Pd-35Co	1230 (2246)	1235 (2255)	-
Pd-82Cu	1080 (1976)	1090 (1994)	-
Au	1063 (1945)	1063 (1945)	-
Au-35Pd	1427 (2601)	1440 (2624)	-
Au-25Pd	1380 (2516)	1410 (2570)	-
Au-25Pt	1210 (2210)	1410 (2570)	-
Au-13Pd	1260 (2300)	1305 (2381)	-
Au-8Pd	1190 (2174)	1240 (2264)	-
Au-35Ni	965 (1769)	1075 (1967)	-
Au-22Ni-6Cr	974 (1785)	1038 (1900)	-
Au-34Pd-36Ni	1135 (2075)	1169 (2136)	-
Au-25Pd-25Ni	1102 (2016)	1121 (2050)	-
Au-22Ni-8Pd	1005 (1841)	1037 (1899)	-
Au-70Cu	1015 (1859)	1035 (1895)	-
Au-62Cu-3Ni	975 (1787)	1030 (1886)	-

Table II. (Continued)

Filler Metal	Temperature,	Temperature,	AWS Designations
	°C (°F) Solidus	°C (°F) Liquidus	
Au-65Cu	990 (1814)	1010 (1850)	BAu-3
Au-65Cu-3Ni	990 (1814)	1025 (1877)	-
Au-62.5Cu	990 (1814)	1005 (1841)	BAu-1
Au-78Cu-2In	975 (1787)	1025 (1877)	-
Au-60Cu	980 (1796)	1000 (1832)	-
Au-6Cu	965 (1769)	990 (1814)	-
Au-50Cu	955 (1751)	970 (1778)	-
Au-20Cu-5Ag	885 (1625)	896 (1645)	-
Au-45.5Cu- 2.8Ag	924 (1695)	963 (1765)	-
Au-18Ni	950 (1742)	950 (1742)	BAu-4
Au-39.6Cu- 2.1Ag	904 (1660)	921 (1690)	-
Au-16.5Cu-2Ni	910 (1670)	925 (1697)	-
Au-37Cu-3In	860 (1580)	900 (1652)	-
Au-20Cu	908 (1666)	910 (1670)	BAu-3
Ag	961 (1761)	961 (1761)	-
Ag-33Pd-3Mn	1149 (2100)	1232 (2250)	-
Ag-20Pd	1070 (1958)	1160 (2120)	-
Ag-27Pt	995 (1823)	1160 (2120)	-
Ag-20Pd-5Mn	1071 (1960)	1121 (2050)	-
Ag-10Pd	1002 (1835)	1066 (1950)	-
Ag-4Mn	961 (1762)	961 (1762)	-
Ag-15Mn	960 (1760)	971 (1780)	-
Ag-25Pd-21Cu	900 (1652)	950 (1742)	-
Ag-22.5Pd- 18.9Cu-10Ni	980 (1796)	1010 (1850)	-
Ag-20Cu-15Pd	900 (1652)	900 (1652)	-

Table III. Other Selected High Temperature Filler Metals

Filler Metal	Temperature,	Temperature,
	°C (°F)	°C (°F)
	Solidus	Liquidus
Ta	3007 (5455)	3007 (5455)
Mo	2620 (4748)	2620 (4748)
Cb	2416 (4380)	2416 (4380)
No-10Si	2120 (3848)	2150 (3902)
Mo-Ru	1900 (3452)	1900 (3452)
Zr	1847 (3357)	1847 (3357)
Ti	1675 (3047)	1675 (3047)
Ni	1455 (2651)	1455 (2651)
Fe-36Ni	1445 (2633)	1455 (2651)
Co-37Mo	1330 (2426)	1330 (2426)
Ni-46.5Mo	1320 (2408)	1320 (2408)
Cu-45Ni	1230 (2246)	1300 (2372)
Cu-30Ni-0.6Fe	1170 (2138)	1240 (2264)
Mn-16Ni-16Co-1B	1004 (1840)	1021 (1870)
Co-21Cr-21Ni-8Si-	1177-1204	-
0.8B-4W-0.4C	(2150-2200) *	-
Cu-36Ni-5In	1204-1218	-
	(2200-2225) *	-
Cu-28Ni-10Mn-2Si	1116-1127	-
	(2040-2060) *	-
Mn-30Ni	1029 (1885)	1049 (1920)
Cu-25Ni	1150 (2102)	1205 (2201)
Cu	1083 (1981)	1083 (1981)
Fe	1537 (2798)	1537 (2798)
Ti-48Zr-4Be	900-954 (1650-1750) *	-
Ti-15Cu-15Ni	954-971 (1750-1780) *	-
Ti-28.5Ni	942 (1728)	942 (1728)

* Brazing temperature

B. Wettability of Carbon

Bartell and Smith [74] studied the activation of carbon by heat treatment and found that changes in surface energy and adhesion tension may result from differences in crystal structure or changes in the lattice energy of the carbon atoms on the surface; differences in the amount of absorbed impurities per unit area, such as, adsorption or desorption of hydrocarbons formed through decomposition; and the formation of a pitted or porous surface which might alter the surface tension or the interfacial tension of the carbon-liquid system.

Mortimer and Nicholas [72] explain how carbon fibers are wet by carbide and non-carbide forming liquid metals to produce metal matrix composites. Successful infiltration of carbon fibers with liquid metals requires that the liquid metal-carbon fiber contact angle be less than 90° and that the fibers not be degraded by extensive chemical reaction with the liquid metal. Unfortunately, no pure metals are known that satisfy both conditions: iron and nickel, which wet carbon, also seriously degrade it. Non-carbide forming metals such as copper and tin do not wet carbon. Aluminum is non-carbide forming and non-wetting at temperatures below $\sim 1200^\circ\text{C}$ (2192°F) and forms carbides and wets carbon above this temperature. An alloy composed of a carbide forming metal and a wetting metal may improve the wettability of the non-carbide forming/non-wetting metal on carbon and prevent degradation of the carbon fibers. Takomori and Akanuma [52] used copper alloys containing 25 to 68% chromium to braze pyrolytic graphite. Naidich and Kolesnichenko [75] studied the wettability of graphite and diamond substrates by copper alloys and found that chromium-copper, titanium-copper, manganese-copper, and vanadium-copper alloys promote wetting.

Mortimer and Nicholas [72] performed wettability test on two forms of carbon with significantly different crystallite sizes (HX30: 1000 Å and Vitreous Carbon: 15 to 25 Å). Copper alloys with 1 at% of 20 different elemental additions were developed for sessile drop tests. The results of these tests are shown in Table IV. Metallographically, four reaction product morphologies were described as shown in Figure 13. Many of the alloying additions to copper did not result in wetting ($\theta > 90^\circ$). This is clearly because graphitic carbon is a solid substrate with a low surface energy and therefore, as described by Wenzel [73], the metal/carbon interfacial energy would also have to be low for wetting to occur. This is inherently unlikely because of the different lattice bonding mechanisms operative in carbon and in some metals. Copper alloys with 1 at% elemental additions chosen from group IVa elements of the periodic table showed the best wetting potential. Usually, there is a link between the wetting behavior of an alloy and the chemical reactivity of the active constituents. However, this was not true for the wetting behavior on carbon because there was no correlation between the alloy-carbon substrate contact angle on either form of carbon used, and the free energy of formation of the most stable reaction product carbides. The work of Bartell and Smith [74] on wettability of carbon, as mentioned earlier, offers a feasible explanation for this phenomenological occurrence.

Table IV. Sessile Drop Test Results of the Wetting of Carbon by Copper Alloys with 1 at% Elemental Additions

ALLOYING ELEMENTS	VITREOUS CARBON		HX30 GRAPHITE	
	SUBSTRATE		SUBSTRATE	
	CONTACT	REACTION	CONTACT	REACTION
	ANGLE	PRODUCT	ANGLE	PRODUCT
	AFTER 1 hour (degrees)	TYPE	AFTER 1 hour (degrees)	TYPE
B	159	O	-	-
Al	-	-	127	O
Ca	111	B	-	-
Sc	147	B	-	-
Ti	135	B	128	A
V	68	A	117	C
Cr	50	A	45	A
Mn	139	B	-	-
Fe	149	O	-	-
Co	140	O	-	-
Ni	132	O	-	-
Zr	152	D	143	D
Nb	152	C	136	C
Mo	131	B	123	B
Hf	130	D	-	-
Ta	143	C	116	C
W	134	C	116	B
Re	138	B	-	-
Pt	135	O	-	-
U	118	A	128	A

O - No Reaction Product

Source: D. A. Mortimer and M. Nicholas, "The Wetting of Carbon by Copper and Copper Alloys", Journal of Materials Science, 5 (1970), pp. 149-155.

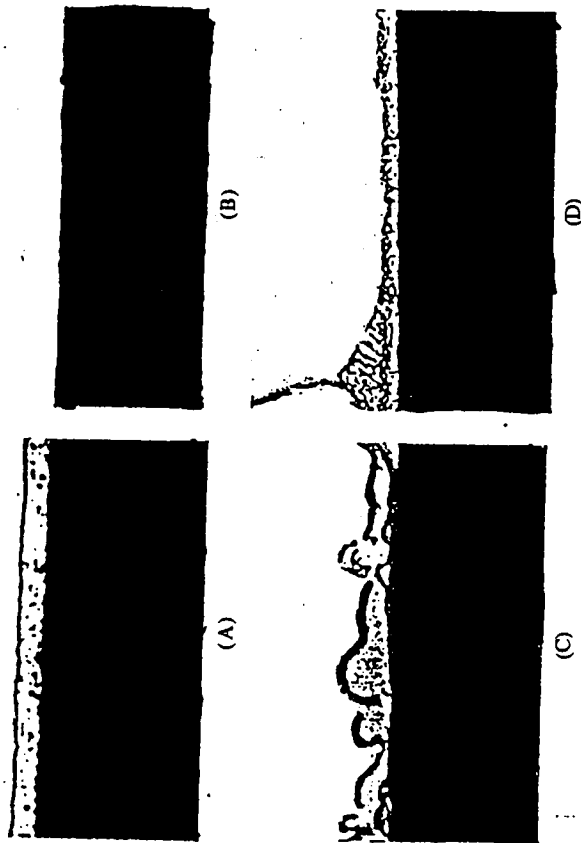


Figure 13.

Defined reaction product morphologies on the wetted surface of carbon.
 (Adapted From: D. A. Mortimer and M. Nicholas, "The Wetting of Carbon by
 Copper and Copper Alloys", Journal of Materials Science, 5 (1970), pp.
 149-155).

Bartell and Smith's [74] wettability analysis was based on an assumption that the metal/substrate interfacial energy γ_I is identical for alloy/carbon and alloy/carbide systems as shown in Figure 14. This implies that a layer of reaction product is present on the surface of the carbon substrate when in contact with any of the carbide-forming alloys. Thus, Young's equation for an alloy on the carbon substrate is as shown in Equation 1.

$$\gamma_{svC} = \gamma_{lv_{m+x}} \cos \theta_{m+x/C} + \gamma_I \quad (1)$$

In this equation, γ_{svC} is the surface energy of carbon; $\gamma_{lv_{m+x}}$ is the surface energy of the liquid alloy; $\theta_{m+x/C}$ is the contact angle of the alloy drop; and γ_I is the metal/carbon interfacial energy.

If the carbon substrate is replaced by xc, the reaction product carbide, Young's equation can be written as shown in Equation 2.

$$\gamma_{svxc} = \gamma_{lv_{m+x}} \cos \theta_{m+x/xc} + \gamma_I \quad (2)$$

Subtraction of Equation 1 from 2 yields Equation 3, an equation which describes wetting behavior of a liquid alloy on carbon and on the appropriate reaction product carbide in terms of surface energies of carbon and of the carbide was developed.

$$\gamma_{svxc} = \gamma_{lv_{m+x}} [\cos \theta_{m+x/xc} - \cos \theta_{m+x/C}] + \gamma_{svC} \quad (3)$$

If this analysis is correct, a plot of γ_{svxc} vs. $[\cos \theta_{m+x/xc} - \cos \theta_{m+x/C}]$ should be linear with a slope equal to $\gamma_{lv_{m+x}}$ and an intercept of γ_{svC} . The intercept is the surface energy of carbon which varies from 119 to 1750

ergs/cm². The two basic assumptions made are; (1) $\theta_{m+x/xc} = \theta_{m/xc}$ and (2) $\gamma_{lv_{m+x}} = \gamma_{lv}$. The first assumption was chosen arbitrarily due to the limited quantity of reported data. However, the second assumption is valid provided that the pure alloying elements have a higher surface tension than m (in this case Cu) and the oxides formed by the alloy in the experimental environment are easily reduced. The essential condition for any alloying addition (x) to promote wetting of carbon by an inert metal (m) is that the interfacial energy between inert metal (m) and reaction product carbide (xc) is less than the surface energy of carbon.

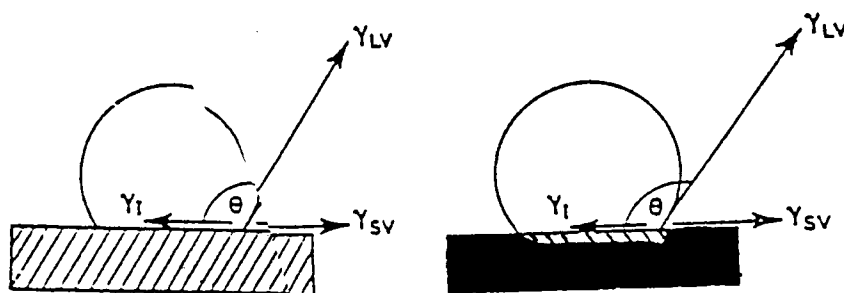


Figure 14.

Reaction product profiles from sessile drop test on the surface of carbon. (Source: F. E. Bartell and C. N. Smith, "Adhesion Tension Values of Different Types of Carbon Black against Water and against Benzene", Industrial and Engineering Chemistry, Vol. 21, No. 11, (November 1929), pp. 1102-1106).

C. Graphite Joining Technology

The ability to form carbides and promote wettability are two important aspects to consider when joining graphite [34,51,52,53,54,55,56,57,58]. Ikeuye and Grow [34] and Pattee, Evans and Monroe [54] stated that Ti, Zr, Si, Cr, and Nb readily wet and form carbides on pyrolytic graphite. Others [51,52,57] extended these ideas by stating that the CTE of graphite, which ranges from $2.0 \times 10^{-6}/^{\circ}\text{C}$ ($1.1 \times 10^{-6}/^{\circ}\text{F}$) to $8.0 \times 10^{-6}/^{\circ}\text{C}$ ($4.4 \times 10^{-6}/^{\circ}\text{F}$) between 25°C (77°F) and 1000°C (1832°F), also plays an important role in the joining process. Thus, brazing filler materials that have a CTE similar to graphite will better survive the brazing cycles and possible in-service thermal cycling conditions without failure.

Werner and Slaughter [59] suggested CVD coating of graphite with tungsten or molybdenum (CTE's similar to graphite) will result in a more wettable surface for joining with commercially available filler materials.

Hammond and Slaughter [60] used carbon and chromium oxide powders to produce a metallurgically bonded chromium carbide layer on the surface of graphite. This technique also allows for brazing with commercially available filler materials.

1. Consumables

(a) Commercial

Two commercially available filler metals 68.8 Ag-26.7 Cu-4.5 Ti (wt %) and 70 Ti-15 Cu-15 Ni (wt %) have been reported to effectively join graphite to graphite for low and intermediate temperature applications [51,55,57,58,61]. Results of other commercial filler metals that have been investigated are shown in Table V.

Table V. Flow Characteristics of Several Commercial Alloys on Graphite

Alloy	Brazing Temperature °C (°F)	Flowability
Ni-Cr-B-Si (AMS 4775)	1180 (2156)	none
Ni-Cr-P	1000 (1832)	none
Ni-Si-B (AMS 4778)	1040 (1904)	none
Ni-Cr-Si-B (AMS 4777)	1040 (1904)	none
Ni-Cr-Si	1180 (2156)	poor
Au-Ni	1000 (1832)	none
Ag-Cu (Ti cored)	950 (1742)	good

Adapted From: R. G. Donnelly, et. al., "The Development of Alloys and Techniques for Brazing Graphite," Proceedings of the 4th National SAMPE Symposium Materials Compatibility and Contamination Control Process, Hollywood, California, (November 13-15, 1962).

(b) Non-Commercial

Experimental brazing filler metals containing one or more of the carbide formers as alloying elements have been developed for furnace brazing under argon, helium or in vacuum [51]. An alloy containing 48 Ti-48 Zr-4 Be (wt %) was developed by Donnelly, Gilliland, Fox, and Slaughter [57]; and reported upon by others [55,58,61]. The original development of this brazing consumable started with 50 Ti-50 Zr (wt %) which was selected because both titanium and zirconium have coefficients of thermal expansion similar to graphite, and the alloy exhibits excellent flowability and wettability characteristics on graphite. Beryllium was added to the system to lower the melting point from ~1600°C (2912°F) to ~1000°C (1832°F), making the brazing operation more practical. Brazing temperature and time had to be monitored carefully so that the brazing filler metal did not flow out of the joint area.

The 49 Ti-49 Cu-2 Be (wt %) alloy system with a brazing temperature of 980 C (1796°F) also has been successfully used to braze graphite [57,58,62]. Brazing with this consumable requires careful control of the brazing parameters to avoid flow-out.

The 35 Au-35 Ni-30 Mo (wt %) and the 70 Au-20 Ni-10 Ta (wt %) systems were also studied by Donnelly, Gilliland, Fox, and Slaughter [57]. Others [53,55,58,61,63] have also reported on brazing of graphite using these alloy systems. While the Au-Ni-Ta system produced satisfactory joints, the Au-Ni-Mo system formed brittle joints which cracked during the brazing cycle.

Takamori and Akanuma [52] studied furnace brazing of pyrolytic graphite using more than 130 brazing filler metal combinations. The main objective was to find, by trial and error, brazing alloys that provided high strength and good

ductility as well as acceptable wetting and flow characteristics. Brazing was performed 50°C (122°F) higher than the melting point of the filler in an argon atmosphere. Graphite parts were joined and evaluated along the basal layer planes because strength in this direction was found to be ten times greater than in the direction perpendicular to these layered planes. The following alloys successfully joined graphite: 13-81% Cr in Ag-Cr, 20-60% Ti in Ag-Ti, 10-50% Zr in Ag-Zr, 19-60% Cr in Au-Cr and 25-68% Cr in Cu-Cr.

Pattee, Evans, and Monroe [54] stated that zirconium wets graphite well, but because of the mismatch in coefficient of thermal expansion between the zirconium carbide formed during brazing and the graphite structure, brittle failure occurred in the joint. Sandstrom [56] studied brazing of graphite with pure Zr, Ta, Mo, and W metallic foil interlayers. He found that strong carbide-interface joints (no evidence of the interlayer in the bulk of the material away from the joint interfaces) were produced by carbides that have negative heats of formation (exothermic). Zirconium produces the strongest carbide joint. In elevated temperature mechanical tests, fully diffused joints (evidence of the interlayer can be seen in the bulk material away from the joint interfaces) were superior to carbide type joints. Others [55,58,61] have also successfully joined graphite to graphite with pure zirconium interlayers.

Schwartz [61] and others [55,58] reported that pure titanium and molybdenum disilicide readily wet graphite. Au-Ni-Cr, Ni-Cr-Si, and Pd-Ni-Cr [52,58] ; Ti-Cr [55,58] ; Ni-Cr-B and Ag-Mn [58] ; and Ni-Ti, 54 Ti-21 V-25 Cr (wt %), 43 Ti-42 Zr-15 Ge (wt %), and 47 Ti-48 Zr-5 Nb (wt %) [55] are also useful metallic interlayers for joining graphite.

2. Other Joining Techniques

Anikin [64,65] and Bondarev [66] used "eutectic diffusion brazing" to join graphite with nickel, aluminum, molybdenum, and iron interlayers. In this process, a pure metallic interlayer is placed between the graphite components. The components are pressed together at a specific pressure and are heated to the temperature of formation of the carbon-metallic element eutectic. Subsequent heating of the components to higher temperatures results in dissociation of the carbon-metallic eutectic phase at the interface, and precipitation of fine crystalline deposits (secondary carbon), which, interact with basic graphite (primary graphite) to form a joint. Experimental procedures for determining the degree of secondary carbon formation were reported in the literature [13,35].

Taylor and Dykes [67] furnace brazed graphite for service temperatures $\sim 2800^{\circ}\text{C}$ (5072°F) by using a paste composed of hafnium carbide, uranium oxide and a thermosetting resin. After brazing, at 2600°C (4712°F) hafnium carbide and uranium dicarbide existed in the joint. Higher temperatures greater than 2800°C (5072°F) caused the uranium dicarbide to vaporize, producing a joint containing essentially only hafnium carbide. The hafnium carbide present in the joint has a coefficient of thermal expansion and an oxidation resistance similar to the parent graphite material.

Peterson [68] furnace brazed graphite with molybdenum powder. Heating to temperatures above the brazing temperature (following the brazing operation) caused transport of molybdenum from the interfaces into the bulk of the material resulting in an essentially molybdenum free joint.

Steinberg [69] furnace brazed graphite with metal foils and powders of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten. The carbides, which initially formed at the interfaces during the brazing operation, were heated to temperatures which cause volatilization of the carbides thus resulting in a joint essentially free of the carbides initially formed.

Schwartz, Ranstrom, and Bjareklint [70] joined graphite members using resistance heating and special interlayers. They described the operation as follows:

The method comprises interposing a thermally sensitive material between the graphite members to be joined, applying pressure forcing the graphite members together, applying sufficient heat to the graphite members to melt the thermally sensitive material, and providing a period of time for cooling before releasing the applied pressure.

The thermally sensitive material can be plastic, metallic or ceramic having a low melting point or glass transition temperature. Polyvinyl chloride, tetrafluorinated ethylene, polyvinylidene fluoride, polypropylene, and polyethylene were all listed as possibilities for thermally sensitive plastic materials.

D. Resistance Brazing

The Resistance Welder Manufacturers Association (RWMA) defines resistance brazing as follows: A brazing process in which the heat required is obtained from the resistance to current flow in a circuit of which the workpiece is a part

[76]. An essential variable in the resistance brazing process is understanding the concept of heat generation. The total heat produced in a resistance brazing circuit is given in Equation 4.

$$H = \int i^2 R \, dt \quad (4)$$

In the equation, (H) is the heat in watt-seconds or joules, (i) is the current in amperes, (R) is the resistance in ohms, and (t) is the time in seconds. The resistance welding machine transforms the high voltage and low current supplied by the power lines to low voltage and high current needed in the secondary circuit for welding. The variation of the actual secondary current with time depends on the waveform of the supplied voltage and the total impedance (resistance to the flow of current) of the secondary circuit. The impedance in the workpieces is often comparable to that of the secondary conductors at the start of current flow and usually decreases rapidly as the bond forms.

The current flow is the same in all parts of the circuit regardless of the resistance at any point, and thus the heat at a given position is directly proportional to the resistance at that position. Examining the part of the secondary circuit where the workpieces and the electrode are located, nine series resistance locations exist as illustrated in Figure 15. The most efficient circuit design attempts to optimize the heat generated at position #5, so that the interlayer will melt, and to minimize the heat generated at other locations.

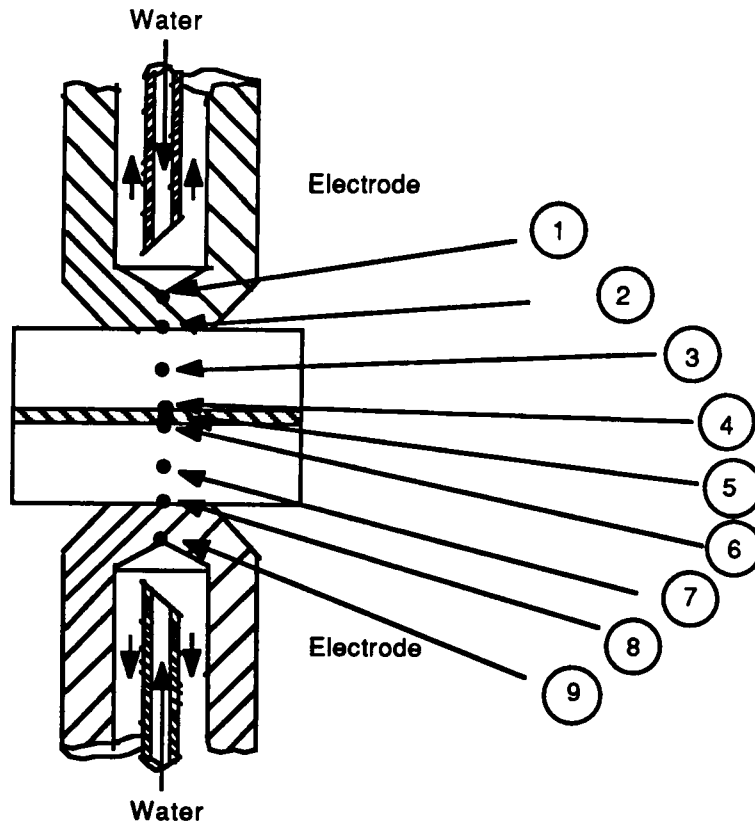


Figure 15. Series Resistance of a typical Resistance Brazing Configuration. (Adapted From: E. J. Del Vecchio, Resistance Welding Manual 3rd. ed., Volume 1, Resistance Welder Manufacturers' Association, Philadelphia, Pennsylvania, 1969).

The positions along the circuit are described as follows: position 1, upper electrode electrical resistance in the circuit; position 2, contact resistance between the upper electrode and the upper base material; position 3, electrical resistance of the upper base material; position 4, contact resistance between the interlayer and the upper base material; position 5, electrical resistance of the interlayer; position 6, contact resistance between the interlayer and the lower base material; position 7,

electrical resistance of the lower base material; position 8, contact resistance between the lower electrode and the lower base material; and position 9, the lower electrode electrical resistance in the circuit.

In resistance brazing, the maximum resistance occurs at the following locations: the electrode and the top surface of the base material and the resistance between the interlayer and the base material. Tylecote [78] describes the current flow at these locations by characterizing surface contact resistance using Studer's model. He states that the electrical resistance across the boundary between two conducting surfaces is based on the flow of current through minute areas of intimate type contacts at the boundary surface, and the resistance of thin films of a foreign substances (i.e. oxides, oil, grease, etc.) between the surfaces of the material. Further, he states that if two flat surfaces of ordinary finish are pressed together they touch at very few points. As the force increases, the initial contact points will yield; elastically and then plastically creating new and larger contacting areas. Figure 16 illustrates the contact resistance of various types of surfaces.

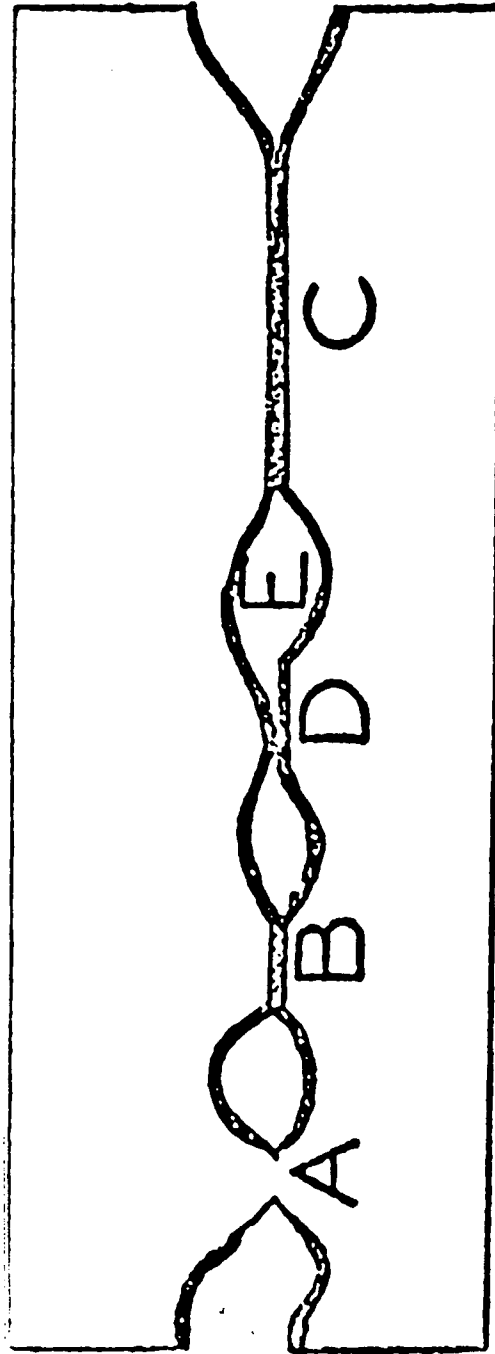


Figure 16.

Studer's illustration of surface contacts. (Adapted From: R. F. Tylecote, "SpotWelding: Part III Contact Resistance," Welding Research Supplement, Dec. 1941, pp. 591s-602s).

Region A represents a condition where the yield strength of a material has been exceeded, surface films have broken down, and intimate contact exists. In region B, the yield strength of the material has been exceeded and the surface film is contained within the boundaries of the two surfaces. The current flow through region B is less than A but greater than the current flow through uninterrupted films. In region C, the yield strength of the material has been exceeded and surface contaminants of the two surfaces exist encompassing a large number of molecules. Region D, the elastic limit of the material has not been reached, and the surface contaminants are either ruptured or left intact. The current flow in region D is similar to A, B, and C. Region E, a physical separation, represents the location of zero current flow. Studer's model is significant because carbon carbon composites are porous and conditions A-E may exist at the interfaces.

In resistance brazing, the pressure applied to the workpieces by the electrodes is needed for electrical contact only and serves no additional purpose in the brazing operation [77]. Since the filler material flows by capillary action in the joint area, only enough pressure to ensure intimate contact is employed in the process. Fast follow up/low inertia electrodes are employed to maintain the force on the workpiece during the melting of the interlayer. Separation of the electrode from the workpiece due to insufficient follow up causes arcing between the electrode and the workpieces, expulsion of the filler material from the joint area, and an increase in the contact resistance.

Summary

Joining of carbon carbon composites is a task with a considerable amount of complexity because an understanding of the forms of carbon (turbostratic, diamond, and graphite); the composite manufacturing procedure (fiber, matrix, dimensionality of the composite); and the materials limitations (oxidation resistance) amongst other considerations all must be understood to predict what interactions will occur during this elevated temperature operation.

A complete description of the types of carbon and their physical properties; the manufacturing procedures of the fibers and the matrix; matrix/fiber interactions; dimensionality; state of the art in oxidation protection systems; current joining philosophy for both graphite and carbon carbon composites; and the resistance brazing process were discussed.

CHAPTER III

EXPERIMENTAL PROCEDURES

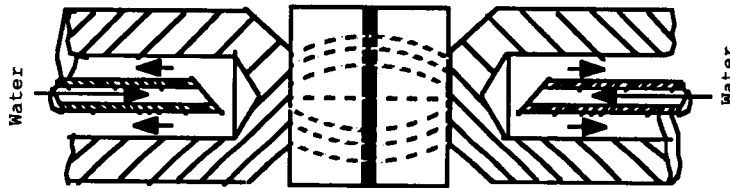
Introduction

The main objective of the Carbon Carbon Composite Materials Joining Program is to employ an interlayer which will; (1) produce a joint with strength equal to or better than the parent carbon carbon composite material and (2) produce a brazement that can survive its intended service application.

Previous joining programs, mentioned in the literature, have addressed joining for friction and wear applications with "Microbraz" type consumables [11], and repairing furnace heating elements using adhesives as consumable materials [48]. In both studies, furnace brazing is used to join the components.

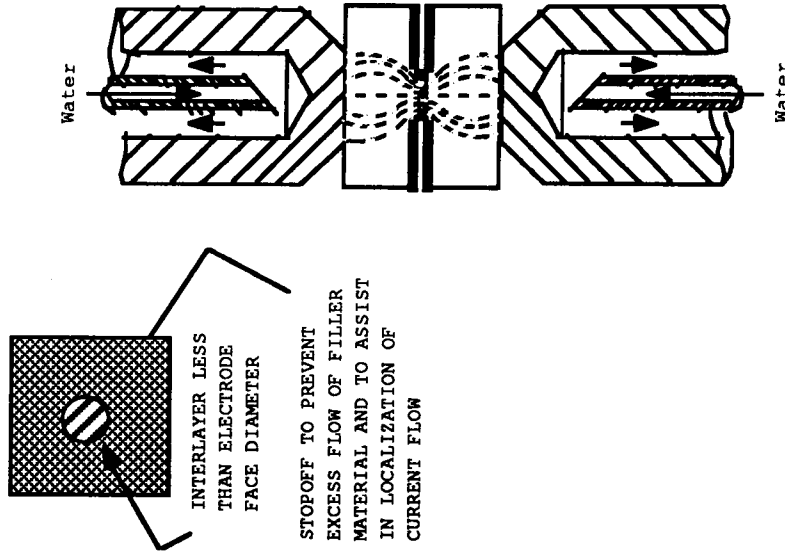
In this study, resistance heating will be employed to braze a three dimensional, chemically vapor deposited /carbonized, inhibited and coated carbon carbon composite material intended for space shuttle and National Aerospace Plane (NASP) applications. A method of localizing current flow in the circuit based on Tylecote's [78] ideas will be investigated. The methodology which will be examined is based on using an interlayer with a diameter less than or equivalent to the face of the electrode, an insulating type stop-off material to prevent flow of the interlayer in undesirable areas, and shims to aid in current flow and heat dissipation. It is expected that by using this methodology, the current will flow only in the region in which the interlayer resides causing the interlayer to melt/wet and infiltrate the composite material producing a volumetric rather than areal brazed joint (See Figure 17).

UNIFORM CURRENT FLOW



a)

LOCALIZED CURRENT FLOW



b)

Figure 17. Distribution of current flow in the workpieces based on geometry of the interlayer.
a) A 1/2" in diameter interlayer, current is uniformly distributed. b) Less than a 1/4" in diameter interlayer, current is localized.

Selection of the metallic interlayers used in this study is based on wettability and adhesion; linear coefficient of thermal expansion (CTE); and melting temperature. Wettability is an important variable in selecting a suitable interlayer. If the interlayer does not wet the composite material, a bond will not form. The wettability of carbon carbon composite materials by alloy interlayers whose wetting behavior are unknown will be evaluated using a simple mechanistic approach to the adhesion/tension theory and the results will be used to predict the potential bond strength. Interlayers which have been reported in literature to have wet graphite are utilized in this study.

Other variables which have importance to the joining process as well as the service environment are the melting temperature and the CTE of the interlayer. It is technically foolhardy to form a heterogeneous bond for the space shuttle or NASP applications in which the service temperature exceeds the melting temperature of the interlayer employed and in which the CTE is orders of magnitude higher than the parent composite material. The former case may cause the bond strength to reduce during service, while the latter could produce thermal stress cracking either during the steep thermal gradients experienced during the brazing cycle or during service. The shaded region of the CTE versus melting temperature plot shown in Figure 18 clearly indicates some of the interlayers which are employed in the resistance brazing study.

COEFFICIENT OF THERMAL EXPANSION VS. MELTING TEMPERATURE

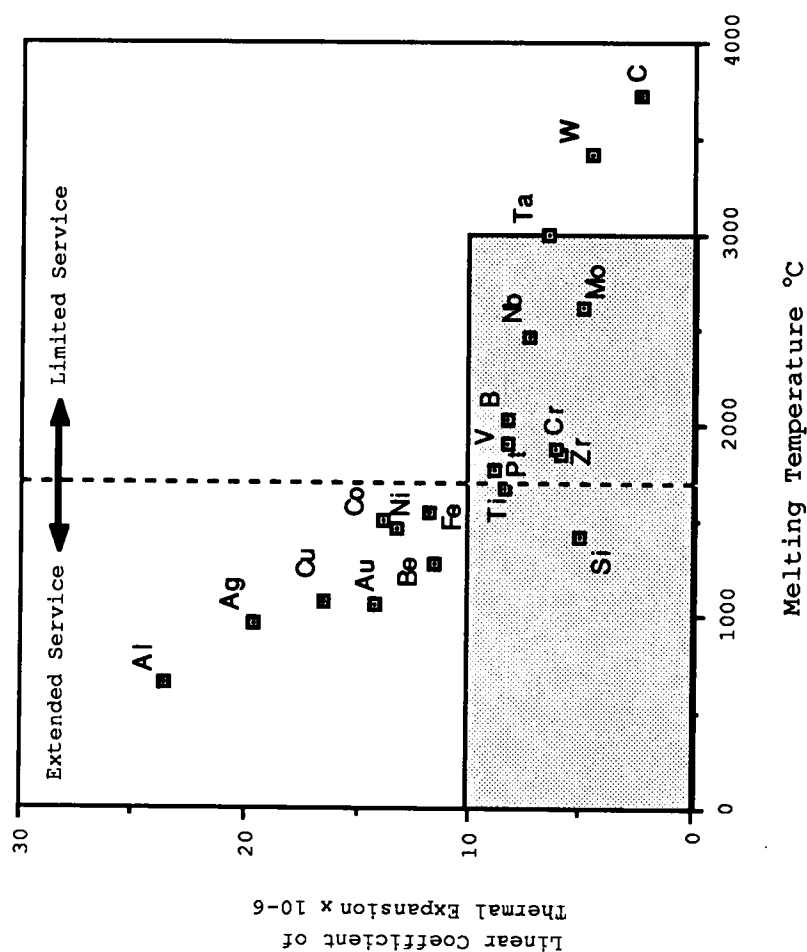


Figure 18.

CTE in ppm/C versus melting temperature data. Shaded region represents interlayers which will be employed in this study. (Data Source: Metals Handbook, Properties and Selection of Metals, Volume 1, 8th edition, American Society For Metals, Novelty, Ohio, 1961).

The concept of heat generation in the brazing circuit is addressed. The amount of heat needed to melt each interlayer employed is calculated and this value is compared to the amount of heat generated at the contact surface during the brazing schedule. A suitable operating range for heat generation based on tap setting and brazing time is established which will melt the interlayer and dissipate the heat rapidly enough to preserve the integrity of the electrodes.

The torsional strength ratios of the brazed joint relative to the virgin material are calculated to rank the interlayers studied. The conditions used to create satisfactory joints are determined by evaluating the brazing schedules employed. The fracture surfaces and joint cross sections are also evaluated by Optical Light Microscopic (OLM) and scanning electron microscopic methods to determine the joint characteristics which provide the best strength.

Resistance Brazing: Operational Features

The Kimura Denyoki Ltd. SW-605; which is a 440V, 60 Hertz, alternating current, single phase resistance spot welding machine, is used as a heat source for joining the carbon carbon composite material. The resistance welding machine is shown in Figure 19.

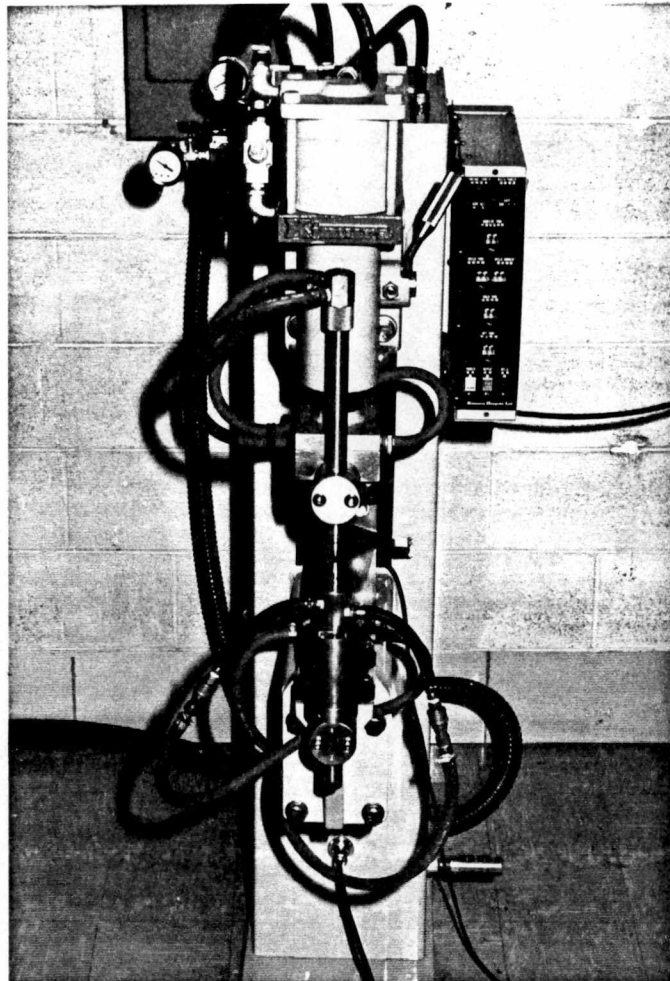


Figure 19. Heat source employed for joining of carbon carbon composite materials.

A. Original Welding Machine Design

The SW-605 is an pneumatically operated resistance spot welding machine in which the welding cycle is initiated by the depression of a foot switch and controlled by a synchronized timer. Figure 20 shows a schematic of the weld cycle sequence. The alternating current from the high voltage-low current power supply is transformed to low voltage-high current when the welding cycle initiated. The transformer is rated at 60 kva for a 50% duty cycle, thus it is capable of delivering 60 kva for 30 seconds of weld time without damaging the transformer components.

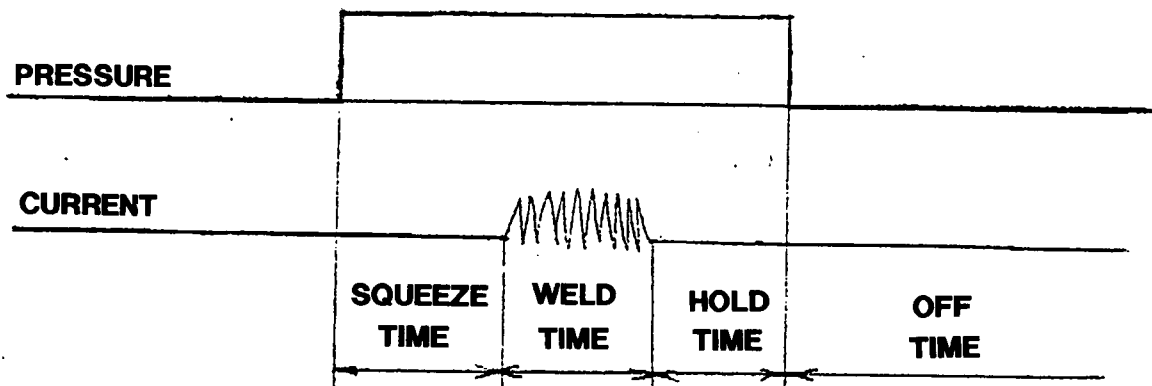


Figure 20. Original operation chart for the timer/controller. (Source: Kimura Denyoki, Ltd.)

A two position lever (initiated during pressurization) and vertically adjustable electrode holders (RW5 socket tips) allow for adjustment of the electrode stroke so that the most efficient spacing to accommodate the workpieces and to perform the joining operation can be achieved. The throat depth can also be horizontally adjusted to establish the best conditions for joining.

Selection of process variables for joining were developed by trial and error. The best conditions were determined to be a tap setting of 80, 40 Hertz and a 84 kg (185 lbs.) force. The brazing cycle timer/controller has five functions: squeeze time, braze time, hold time, off time, and braze current. The range of tap settings is 0 to 99, while brazing times range from 0 to 99 Hertz (1.65 seconds). The magnitude of the applied force is determined by the value set on the air pressure gauge. Air pressures between 0 and 100 psig can be selected. Using the simple mathematical relationship in Equation 5, based on the air pressure and the diameter of the air cylinder, the electrode force can be approximated.

$$\text{Electrode Force (lbs.)} = (\text{Air Pressure}) \times 18.5 \quad (5)$$

A force gauge (0 to 90 kg (200 lbs.) with 1 kg (2 lb) graduation) was employed to measure the applied load. Figures 21 shows the force gauge and the manner in which the force is measured.

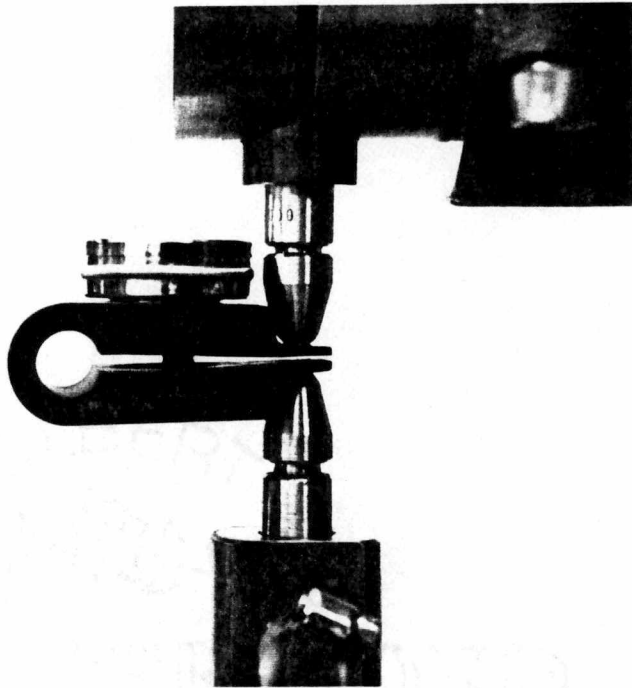


Figure 21. Force gauge used to monitor the consistency of the applied force in the no current mode.
(Supplied By: Unitek Equipment Inc.)

Resistance Welder Modification

1. Modification to the Timer/Controller

The original braze cycle timer/control sequence is initiated by depressing the foot switch. The squeeze time (electrodes force the workpieces together); braze time (current is initiated to perform the joining operation); hold time (after squeezing and brazing, the current is terminated and the brazement is still loaded under the original electrode force until the melt zone solidifies); and the off time (intermediate time between braze cycle sequences) are sequenced until the brazement is complete. During the brazing process flow of the interlayer between the faying surfaces is controlled by capillary action. Control of the brazing cycles is required so that the filler metal has time to flow and complete the joint. Figure 22 shows the modified time/control sequence which was instituted to aid in the brazing procedure. Comparing the original braze/time control sequence (Figure 20) to the modified version (Figure 22) it can be clearly seen that the modified time/control allows the operator independent control of the force. Independently controlling the force allows for proper alignment of the workpieces between the electrodes without extra fixtures; and the ability to measure static contact resistance.

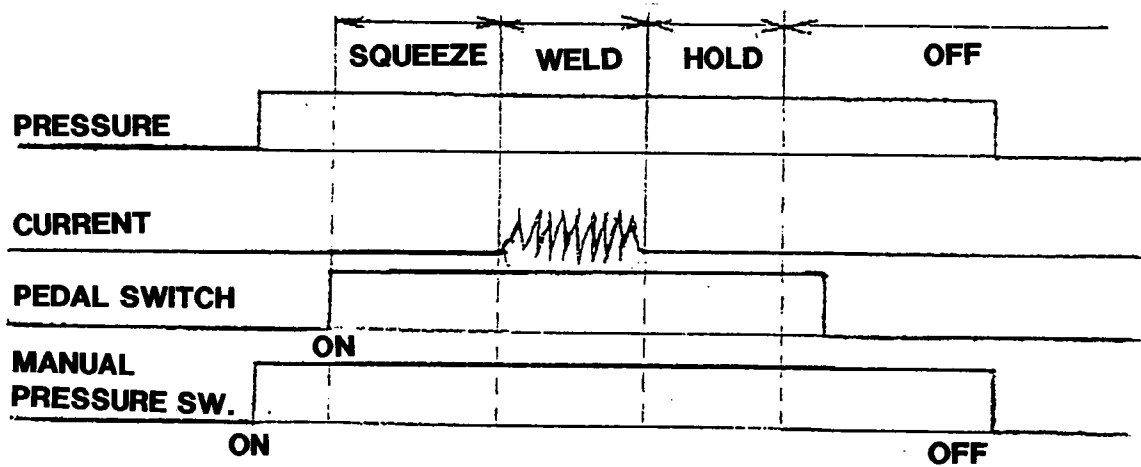


Figure 22. Modified operation chart for the timer/controller.

2. Fast Follow-Up Electrode Holder

The lower standard ejector type electrode holder was replaced with a fast follow-up/low inertia electrode holder to maintain the force on the workpieces during the brazing process. The fast follow-up type electrode holder is shown in Figure 23. A constant force aids in the joining process by keeping the workpieces in contact with each other throughout the melting and flow sequence so that proper capillary action and maximum filling of the joint area can be achieved; and prevents arcing between the electrode and the base material, flow out of the filler material, and a change in the contact resistance at the contact surfaces.

It was experimentally determined that an electrode force in excess of 90 kg (200 lbs.) deformed the carbon carbon composite material workpieces prior to the application of the brazing current. Thus, a 136 kg (300 lbs.) maximum force fast follow-up electrode holder was employed. The base of the electrode holder in Figure 23 shows calibration hash marks. The hash marks signify the following: Mark 2 (3.175 mm (0.125")), 63 kg (140 lbs.); Mark 3 (6.4 mm (0.5")), 90 kg (200 lbs.); Mark 4 (9.525 mm (0.375")), 113 kg (250 lbs.), and beyond Mark 4 (12.7 mm (0.5")), 136 kg (300 lbs.). Accurate measurement of air pressure at forces below 90 kg (200 lbs.) was achieved by modifying the original air pressure gauge system (0 to 150 psi with 10 psi graduations) by utilizing a low pressure range gauge (0 to 30 psi with 1 psi graduations). The new air pressure gauge system was designed so that the low pressure gauge can be isolated from the system to allow for high pressure operation. The standard type lower electrode holder must be used at air pressures exceeding 16 psig because higher pressures exceed the design loading capabilities of the fast follow-up/low inertia holder.

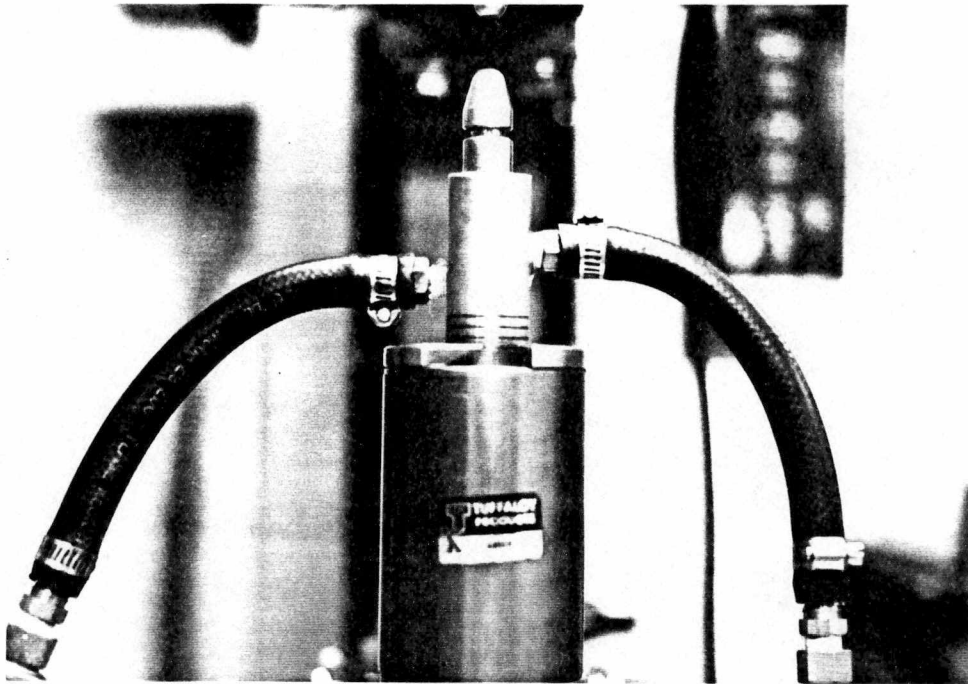


Figure 23. Fast follow-up type electrode holder used to maintain the force on the workpieces throughout the brazing cycle.

3. Current Monitor

A Duffer's Scientific 8140 Weld Program Monitor, which is capable of accurately measuring root mean square and peak current values up to 200,000 amperes for continuous currents or pulses (as short as a fraction of 0.5 Hertz) was utilized to measure the current and time during brazing. A toroidal pick-up coil is placed in the secondary circuit, creating a magnetic field which is directly proportional to the amount of current in the circuit. The root mean squared current was measured in the secondary circuit. The current (in kiloamperes) and time (in Hertz) were recorded for each brazing operation.

4. Argon Chamber

A method of protecting the workpieces from the environment using argon shielding gas was devised to prevent oxidation of the interlayer and the carbon carbon composite material during brazing. A 9.0 cm (3.5") x 13 cm (5") x 1.91 cm (0.75") envelope was created by attaching a Plexiglas chamber to the lower horn of the resistance welder. The chamber is illustrated in Figure 24. The workpieces are centered within the shielding envelope and argon enters the bottom of the chamber and leaves the chamber through the openings required for electrode access. During brazing of carbon carbon composites using an aluminum interlayer in air, a white oxide film appeared in the joint area. Under the same conditions in the argon shielded envelop, the joint area was silvery which indicated that the envelop provided efficient shielding of the workpieces.

Side View

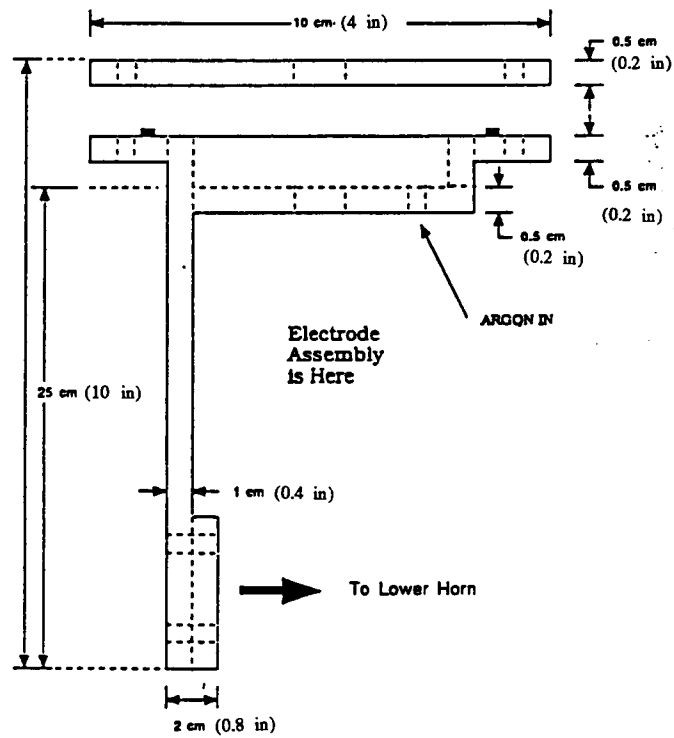


Figure 24. Plexiglas chamber for shielding workpieces during brazing.

C. Electrode Material and Design

RWMA Class 2 shank and pointed nose male cap electrode construction was used in this study to localize the current into the interlayer area. The male cap geometry and electrode material properties are shown in Figure 25 and Table VI respectively.

POINTED NOSE MALE CAP ELECTRODE
(RWMA CLASS 2)

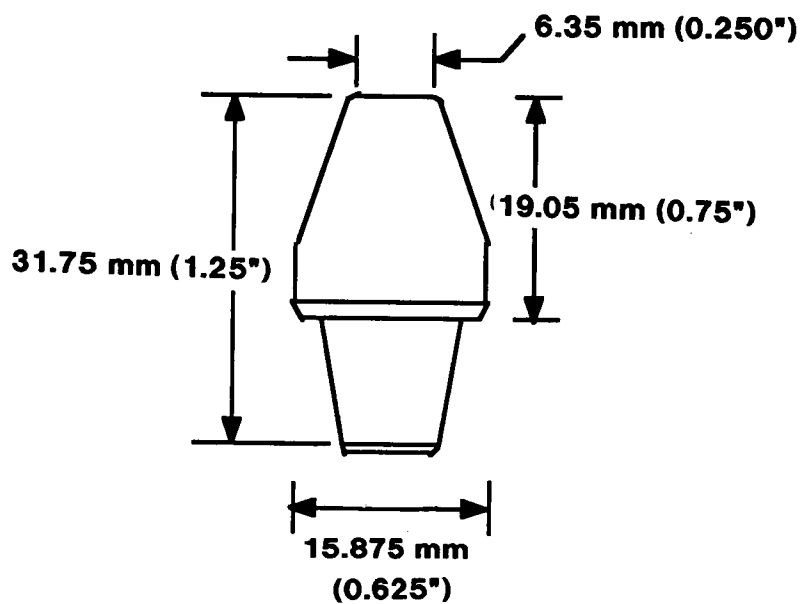


Figure 25. Schematic of the pointed nose electrode used for brazing. (Dimensions From: Tuffaloy Resistance Welding Products Catalog 880).

Table VI. Electrode Material Properties

Classification	Chemistry	Rockwell B Hardness	Electrical Conductivity %IACS
RWMA Class 2	0.8% min. Cr, Cu rem.	65-75	75

6 Data Adapted From: Tuffaloy Resistance Welding Products Catalog 880

D. Alignment of Electrodes

Improper alignment of electrodes during resistance brazing leads to reduction of current flow into the circuit; non-uniform heating of the brazement; and incomplete melting of the interlayer. Thus, proper alignment of the electrodes is necessary to maximize the flow of current into the brazement.

Proper alignment of the electrodes was achieved by positioning the upper and lower electrode horns and by adjusting the upper and lower electrode holders. Prior to the brazing operation; the alignment of the electrodes was determined by (1) sandwiching a piece of white paper between two pieces of carbon paper, (2) placing the three sheets between the electrodes, (3) applying a force in the no current mode which leaves an impression on the white paper, (4) releasing the force, and (5) punching out the impression formed with a 6.35 mm (0.25") in diameter punch to examine the impression for circularity and proper alignment. Figure 26 shows the procedure for aligning the electrodes. A circular impression from a previous test is indicated by the arrow.

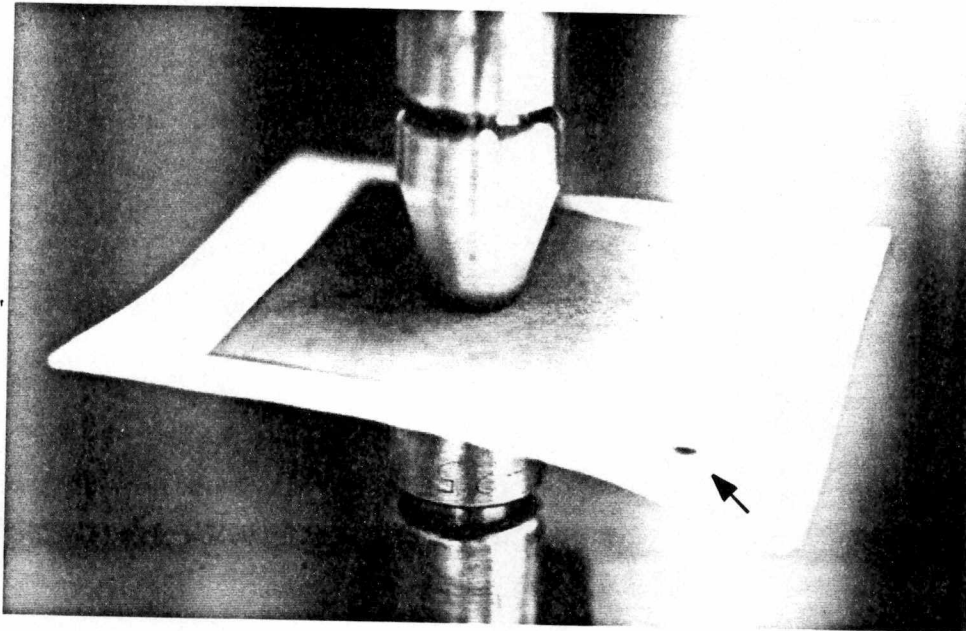


Figure 26. Method employed to determine if the electrodes are properly aligned.

E. Formation of a Volumetric Joint Configuration

The volumetric heating generated by the composite materials body resistance and/or the heat generated at the interlayer/composite contact surfaces can be utilized to melt a wettable interlayer and join the carbon carbon composite materials. By concentrating the current into the interlayer region, the amount of time required for the brazing operations is decreased. Thus, it is unnecessary to heat up the entire volume of the composite material to melt the interlayer. Figure 17 shown earlier illustrates a schematic of the workpieces prior to joining.

The workpieces were arranged (discussed in detail in the next section) by carefully aligning the composite material so that the interlayer was located at the center of the face of the electrode as shown later in Figures 38; shielding the brazement to reduce the potential for oxidation during joining and applying the required force as shown later in Figure 39; and selecting the proper tap setting and cycles so that the heat will be localized and dissipated before the electrodes can melt. Figure 40, also shown later, illustrates the localization of heat. A schematic illustration of the joint configuration is shown in Figure 27. A volumetric rather than an surface areal joint configuration when joining carbon carbon composite materials is desirable so that the individual fibers within a bundle have the potential for being wet thus increasing the brazement strength.

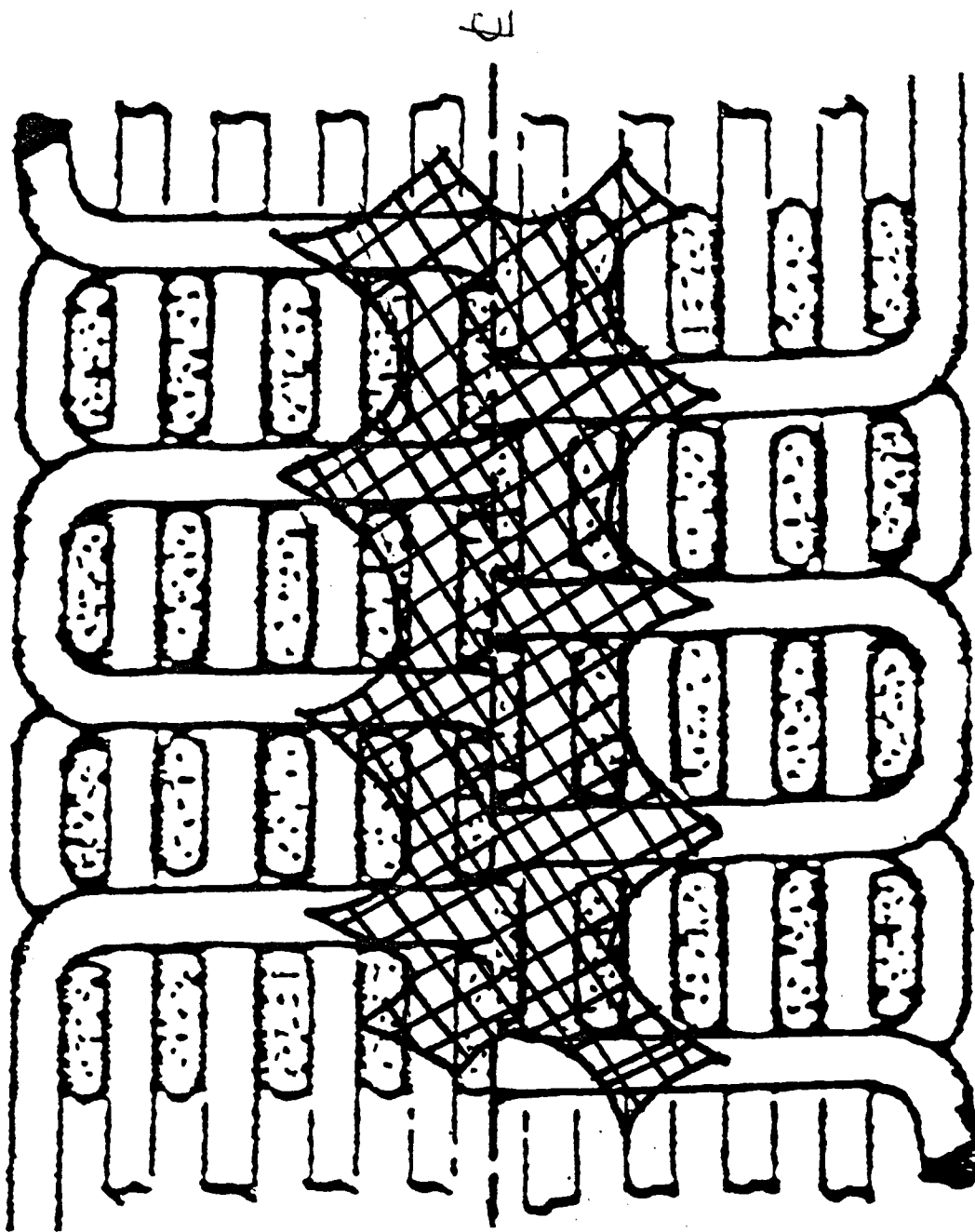


Figure 27. Schematic of the cross sectional joint configuration after brazing.

Workpiece Preparation

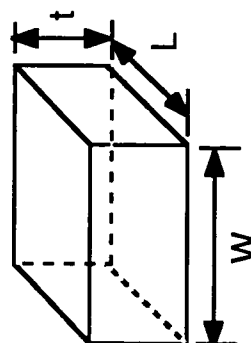
A. Carbon Carbon Composite Specimen Preparation

The brazing procedure specimens were fabricated to the dimensions shown in Table VII by sectioning the carbon carbon composite material using a thin sectioning machine equipped with a 0.152 mm (0.006") silicon carbide cut-off wheel. During the cutting procedure, acetone was employed to cool the cut-off wheel.

The surface condition of the composite material after the cutting operation is shown in Figure 28. After cutting, each specimen was ground flat to the required thickness using 600 grit silicon carbide paper and ultrasonically cleaned in acetone for 15 minutes. Ultrasonic cleaning, aided in removal of free carbon particles (dust) formed during the cutting operation. A typical carbon carbon composite specimen ground and ultrasonically cleaned for surface evaluation is shown in Figure 29. The dimensional orientation of the fiber bundles can be clearly seen on a surface which is ground flat.

Table VII. Carbon Carbon Composite Material Brazing Component Dimensions

Composite Dimensions	
Length (L)	$12.7 \pm 1.27 \text{ mm } (0.5 \pm 0.05")$
Width (W)	$12.7 \pm 1.27 \text{ mm } (0.5 \pm 0.05")$
Thickness (t)	$3.175 \pm 0.51 \text{ mm } (0.125 \pm 0.02")$



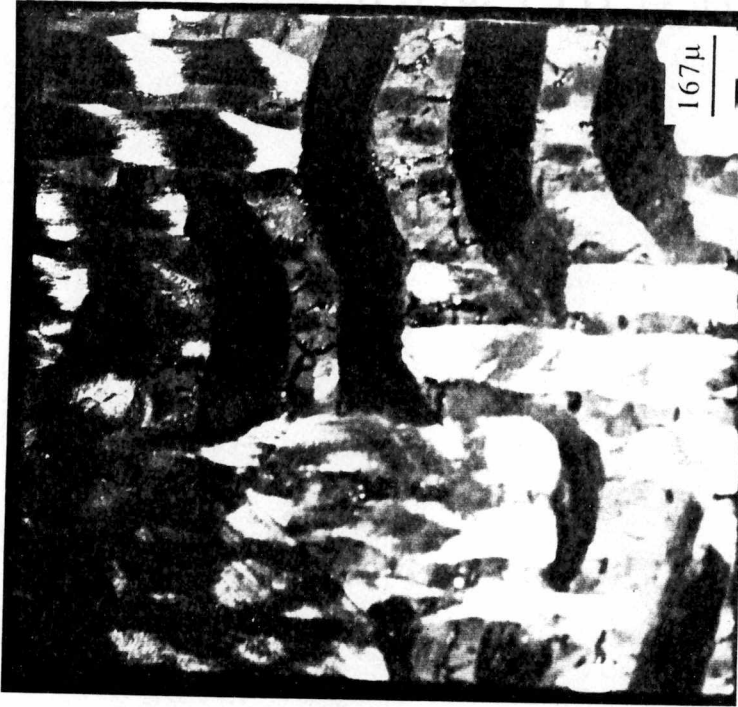


Figure 28. Surface of a carbon carbon composite material immediately following the cutting procedure.

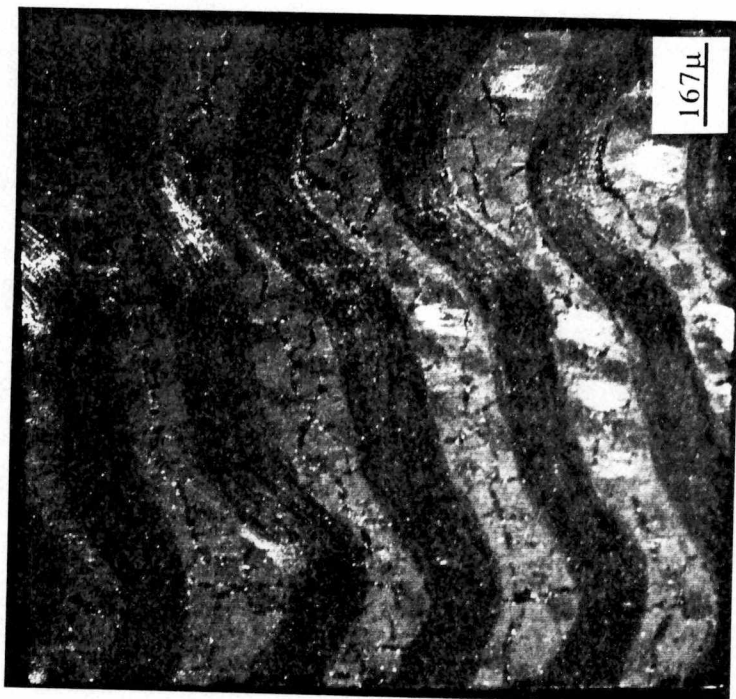
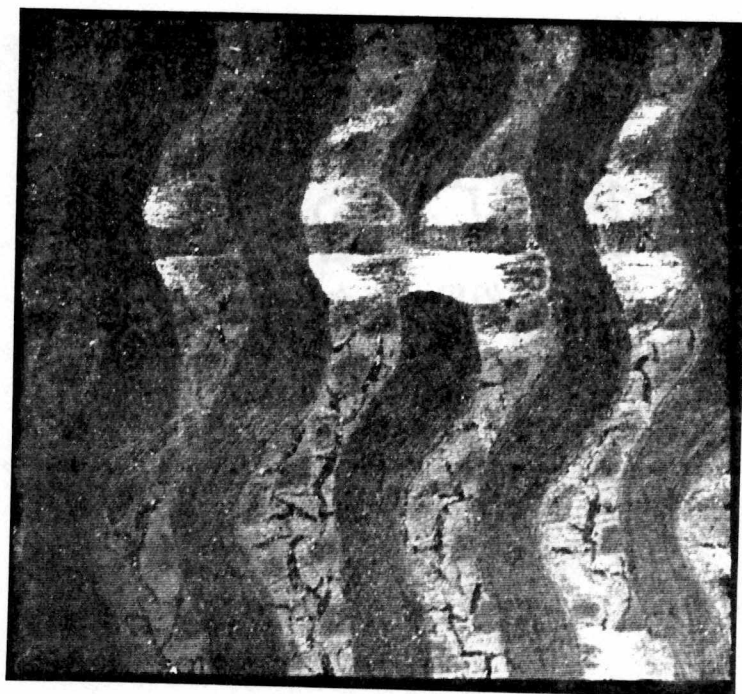


Figure 29.

Typical composite component prepared for surface contact resistance evaluation. Notice the dimensional alignment of the fiber bundles on the flat surface.

B. Monitoring of Surface Conditions

A digital precision multimeter was employed to measure the contact resistance in μ ohms at the electrode/composite and composite/composite interfaces prior to joining. This procedure is helpful in determining if the cleaning procedure employed prior to joining produces consistent surface conditions. Improper alignment of electrodes and variations in the applied force will have an effect on the contact resistance measured.

A pictorial description of the contact resistance measurement procedure is shown in Figures 30 and 31. The laminated bus bar is detached so that the resistance in other parts of the secondary circuit (i.e the transformer) does not effect the contact resistance measured. After alignment of the electrodes and measurement of the desired applied force (these procedures will be described in a later section), the contact resistance between the electrode/ composite interface was measured as shown in Figure 30. Figure 31 shows the procedure for measuring the contact resistance at the composite/composite interface.

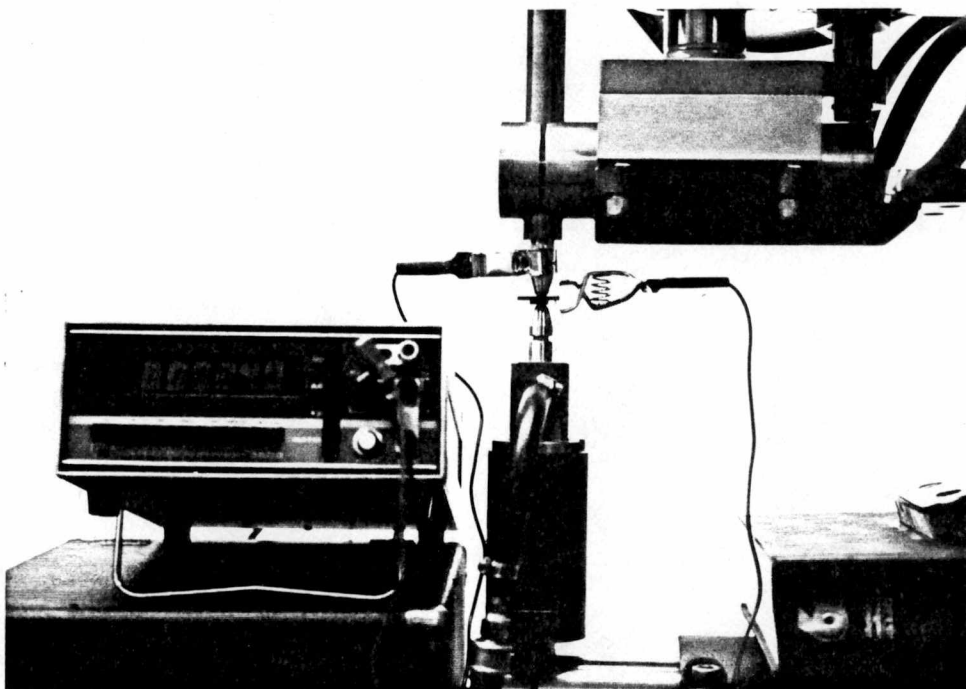


Figure 30. Contact resistance measured at the electrode/composite interface.

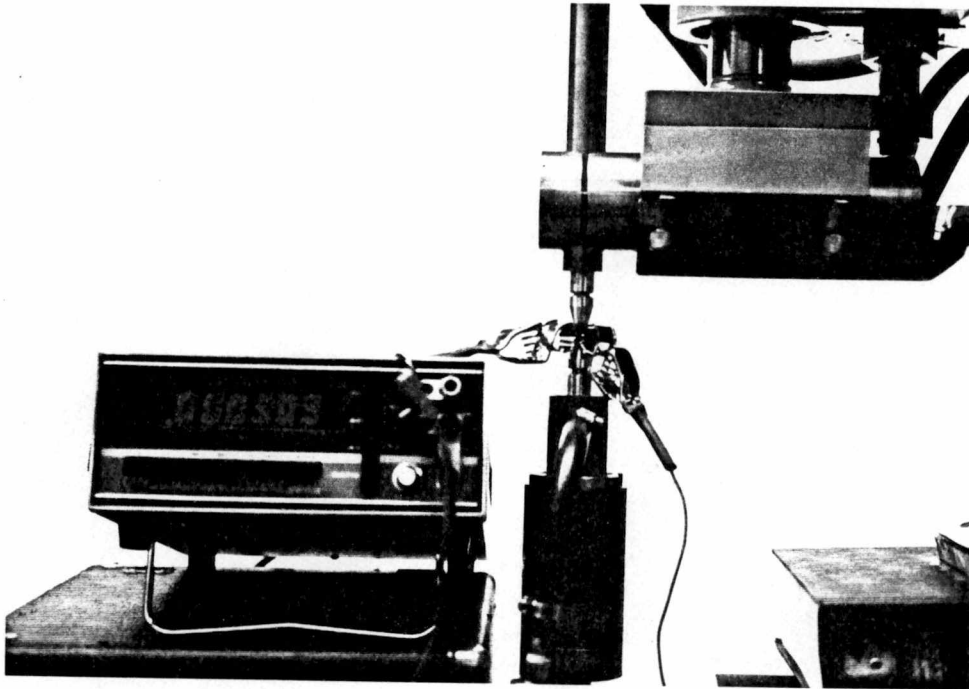


Figure 31. Contact resistance measurement at the composite/composite interface.

C. Preparation and Application of Interlayers and Stop-Off

Foil interlayers disks 6.35 mm (0.25") in diameter were extracted with a circular punch. Face centered cubic structured interlayers (i.e. platinum) tended to be too soft to punch, and thus a circular template and x-acto knife were used to extract the interlayer. The thickness of the interlayers employed varied from 0.0127 mm (0.0005") to 0.127 mm (0.005").

After extraction, the interlayer was mechanical cleaned with Scotchbrite prior to application to the surface of the composite material component. This step is crucial to the brazing process because unclean surfaces will reduce joint strength and affect the flow of current into the joint area. If the current flow is restricted, the interlayer may not melt, and therefore a joint will not form. Also, metallic oxides because of their high interfacial energy will not wet the surface of carbon.

The preparation of the carbon carbon composite material component for joining involved masking the center of the components using black electrical tape slightly larger than the interlayer employed for joining as shown in Figure 32. Microbraz Green liquid stop-off was then brushed on the surface of the composite material and afterwards, the mask was removed as shown in Figure 33, and the interlayer was carefully set in place.

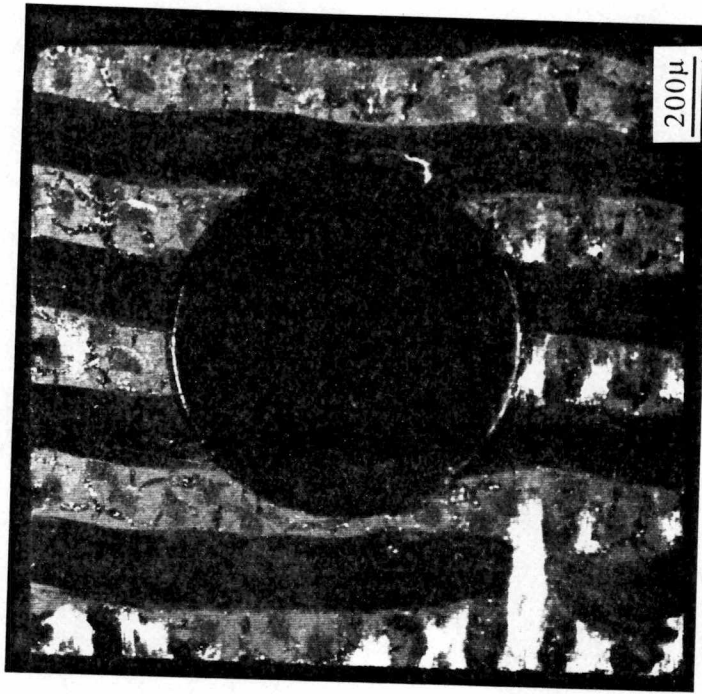


Figure 32. Masking technique used for application of foil type interlayers.

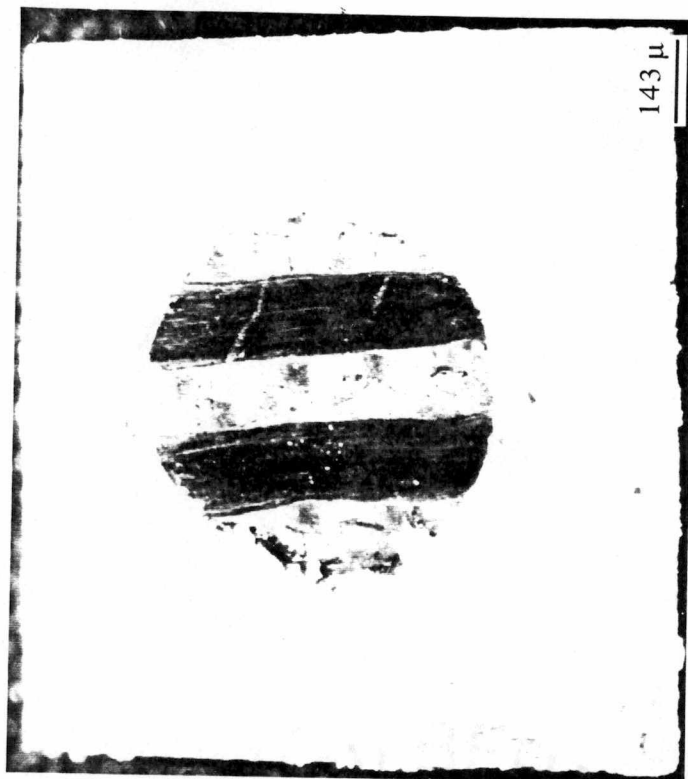


Figure 33.

Composite component prepared for joining. White area is Microbraz Green stop-off, dark area is the interlayer region.

Powder interlayers were mixed with acetone to form a slurry prior to application on the surface of the composite material. The interlayer was applied to the surface by masking the area around the center of the composite material with black electrical tape as shown in Figure 34, carefully brushing the slurry over the desired area as shown in Figure 35, and finally removing the tape so that the interlayer remained in the center of the composite as shown in Figure 36. After the interlayer was applied, Microbraz Green was brushed on the surface around the interlayer. The stop-off was applied to prevent adhesion of the interlayer in unwanted areas and to assist in directing the current flow in the circuit.

An electron beam evaporator was used to locally (approximately 6.35 mm (0.25") diameter) evaporate 0.0102 mm (0.0004") of titanium at the center of the composite material as shown in Figure 37. After coating, the remaining surface of the composite components were stopped off and a copper interlayer was placed on one of the preconditioned surface areas in preparation for joining. This technique was employed to enhance wettability, and to attempt to increase current flow in the circuit. Additional titanium-copper alloy interlayers were evaluated for comparative purposes.

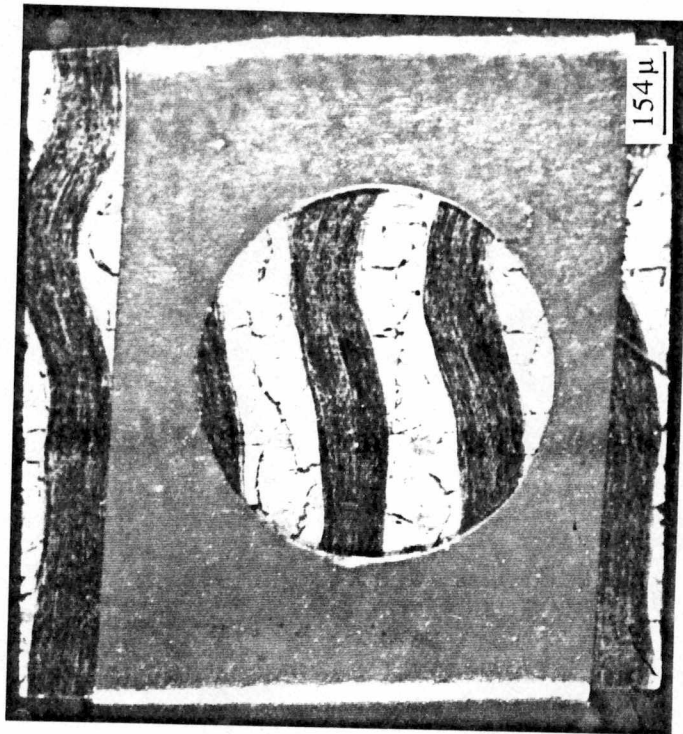


Figure 34. Masking off the composite material surface in preparation for joining with a powder type interlayer.



Figure 35. Application of the powder/acetone slurred type interlayer.



Figure 36. Composite material component prepared for joining with a powder type interlayer.

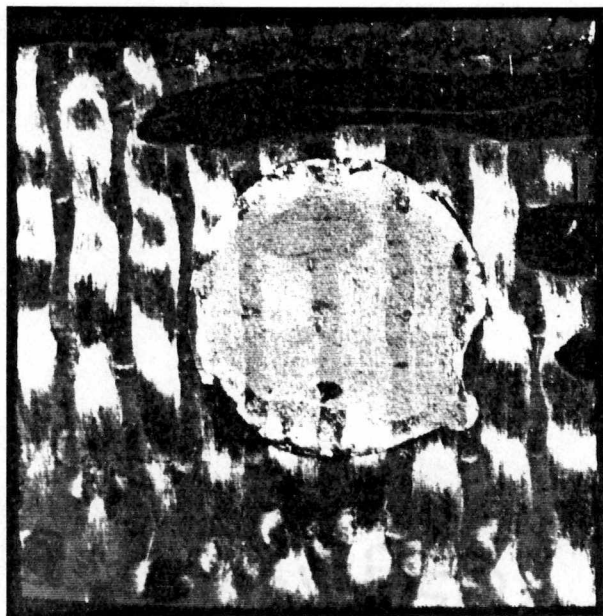


Figure 37.

Joining surfaces preconditioned with 0.01 mm (0.0004") of Titanium prior to application of a wettable interlayer.

D. Joining Methodology

After preparing the carbon carbon composite material (i.e. cutting, grinding, cleaning, applying the interlayer, and applying stop-off) for joining; the workpieces must be carefully positioned between the aligned electrodes to maximize the current flow in the secondary circuit. The composite material with the interlayer properly positioned (directly above and within the face of the copper electrode) was placed on the lower electrode as shown in Figure 38. Another stopped off composite workpiece was then placed on top of the composite containing the interlayer in a sandwich type (lap) construction. Figure 39 shows the workpieces between the electrodes within the argon envelope. In practice, if the workpieces are not properly positioned, non-uniform heating occurs during brazing resulting in only a portion of interlayer melting and a reduction in the joint strength.

Finally, a continuous flow of argon is established in the envelope and current is applied causing localized heating of the workpieces. Figure 40 shows how the heat spreads out after the current is terminated.

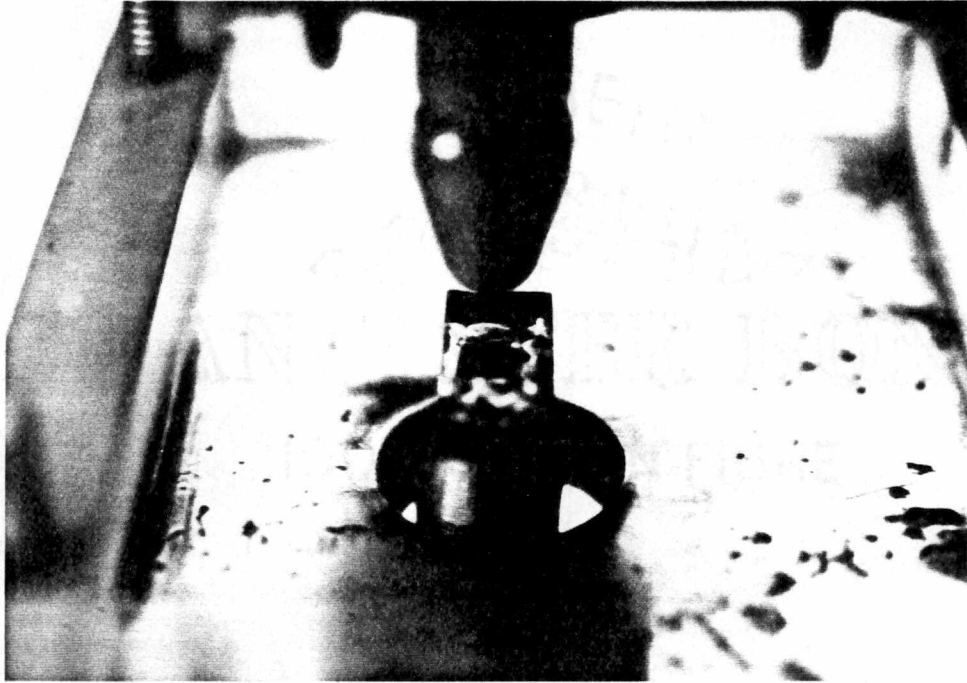


Figure 38. Workpiece placement between electrodes.

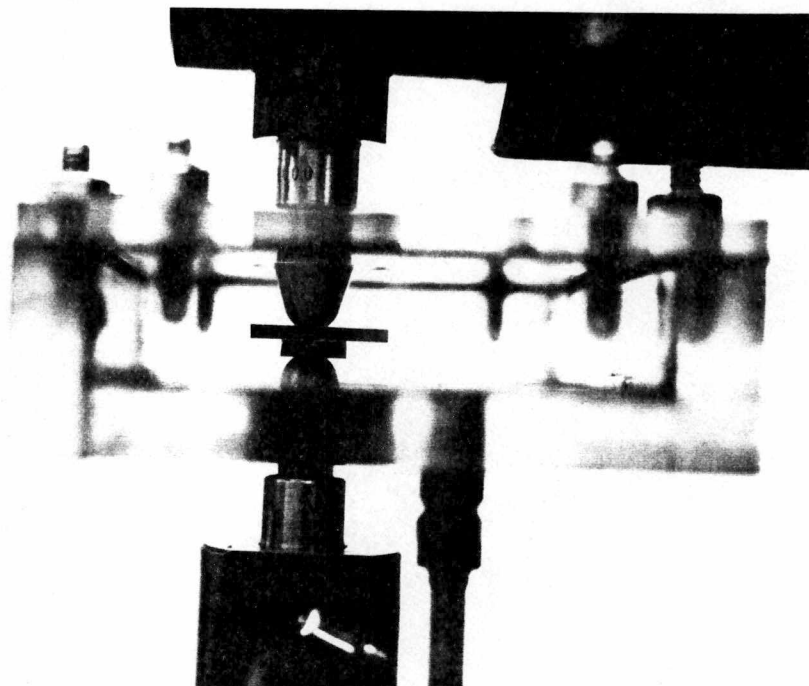


Figure 39. Sandwich type (lap) workpieces aligned between the electrodes.

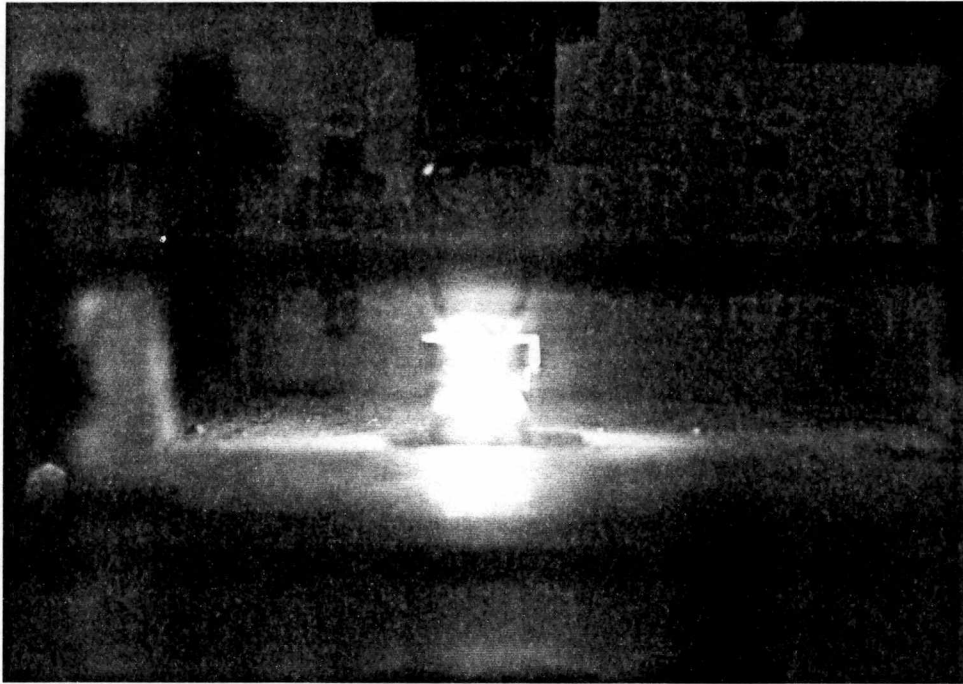


Figure 40. Localization of heat during current flow.

Testing and Evaluation

A. Destructive Testing

Following the joining operation, the brazement was placed in a vise as shown in Figure 41 and a modification of the American Welding Society (AWS) Torsion Test Method No. 8 (Twist Test) was employed to measure the bond strength. A torque wrench with a memory dial was used to measure the torsional strength required to break the bond. The torque wrench and the eight point socket used to grip the brazement during testing are shown in Figure 42. Figure 43 shows the test methodology. After testing, the bond area was measured on the fracture surface. The fracture surfaces were further evaluated by examining the surfaces for presence of the interlayer and fiber pullout; to determine the extent of composite adherence and if the interlayer wet the fibers. Additional workpieces were joined and sectioned so that the cross section of the locally heated region could be revealed. The morphology of each interlayer was categorized.

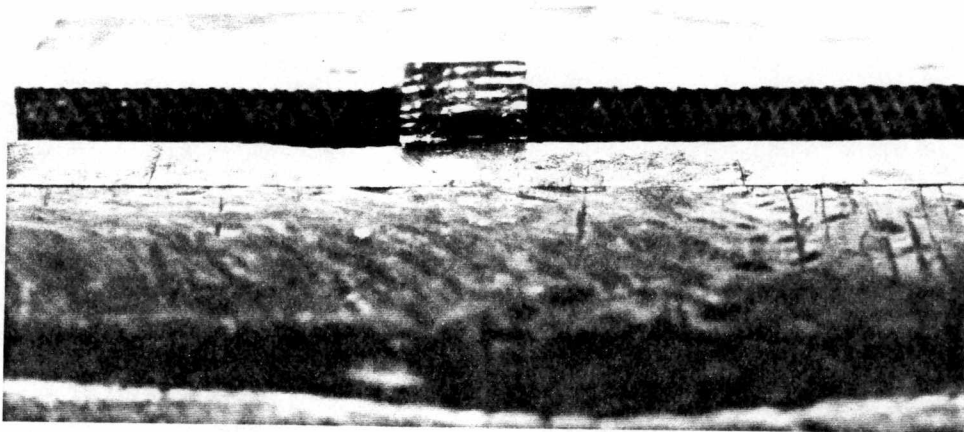


Figure 41. Brazement loaded in a vise prior to mechanical testing.

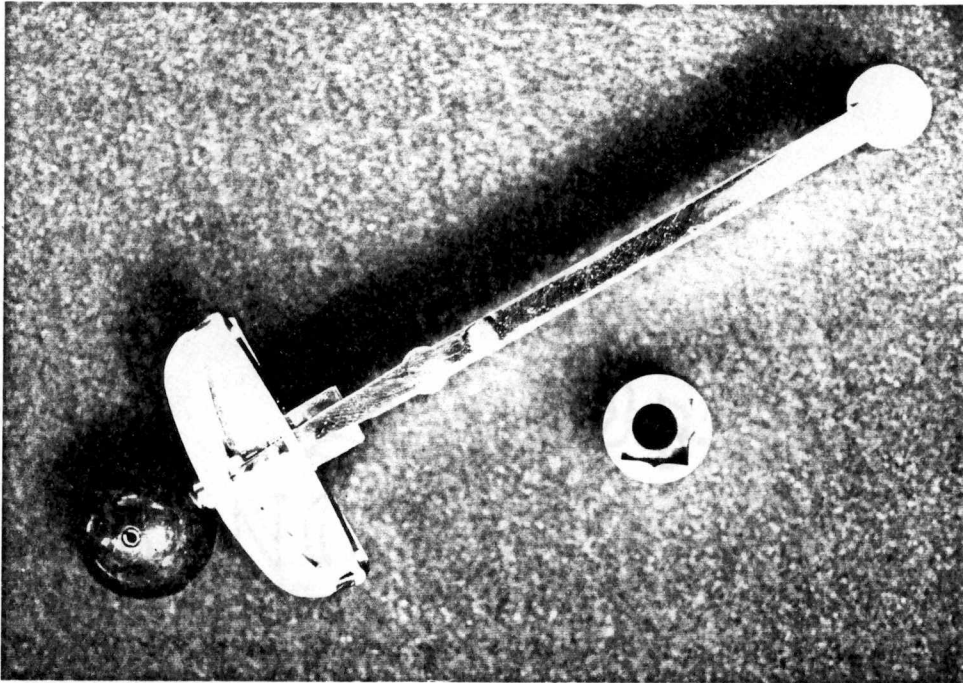


Figure 42. Torque wrench and an eight point 12.7 mm (0.5") socket used to grip the brazement for torsional shear testing.

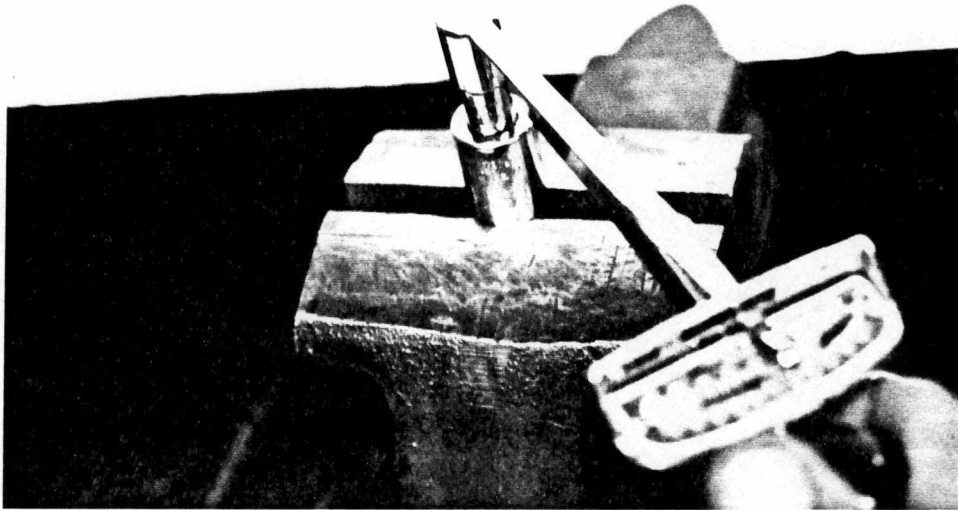


Figure 43. Modification of the AWS Torsion Test
Method #8.

B. Brazement Polishing Technique

Brazement sections were evaluated by SEM and OLM techniques. Specimens were mounted in epoxy and the cured mount was ground dry on 600 grit silicon carbide paper. Rough polishing of the cured mount was performed automatically on Texmet cloth using a #6 diamond paste/distilled water solution. Fine polishing, also automatic, was performed using Sylvet cloth and a 0.06 μ aluminum oxide powder/distilled water solution. Due to the surface features of the brazement (i.e. epoxy filled pores, hard metallic structure, and soft brittle composite structure); repolishing was often necessary until the desired microstructure could be revealed.

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the resistance brazing process was employed to join a three dimensional, angle interlock, oxidation inhibited and coated carbon carbon composite material supplied by Woven Structures Inc. a Hitco subsidiary. The following interlayers were employed to aid in the joining process: platinum, zirconium, and titanium pure metallic foil interlayers; Lucanex 721 (72% Ag- 28% Cu-coated with 5 to 10% Ti), Cu_2Ti (72.63% Cu- 27.37% Ti), and CuTi (57.02% Cu- 42.98% Ti) alloy metallic foil interlayers; a pure copper foil sandwiched between two pure titanium foils; a pure copper foil placed between titanium coated carbon carbon composite materials; and a Molybdenum Disilicide metallic powder interlayer.

Carbon Carbon Composite Material

The material selected for evaluation in this study was a coated three dimensional composite material inhibited for oxidation protection. The composition of the inhibitor employed was proprietary, however, qualitative SEM/EDS studies revealed that the surface as well as the bulk of the composite material contained aluminum, silicon, titanium, copper, iron, and chromium. A macrograph of the coated carbon carbon composite material is shown in Figure 44 and SEM micrographs of the surface coating and fiber bundle orientation are shown in Figures 45 and 46 respectively. A schematic illustration of the angle interlock fiber bundle orientation within the composite material is shown in Figure 47.

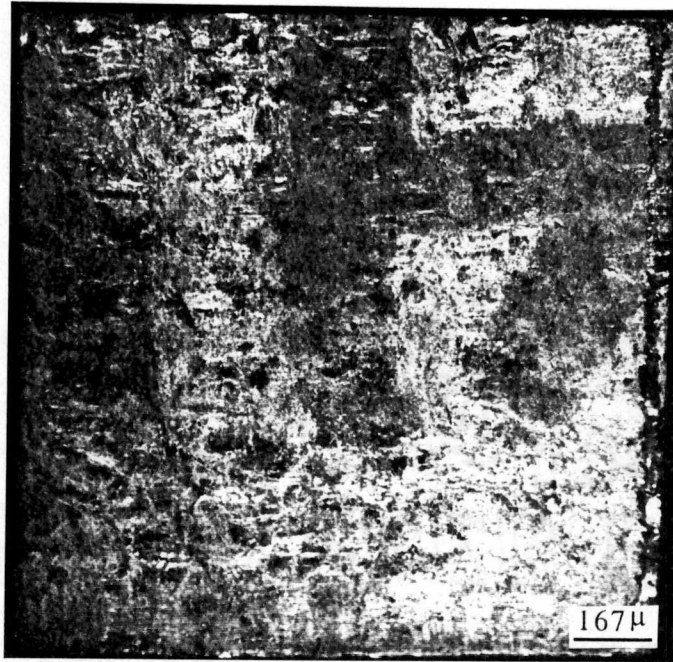


Figure 44. Macrograph of the Coated Carbon Carbon Composite Material.

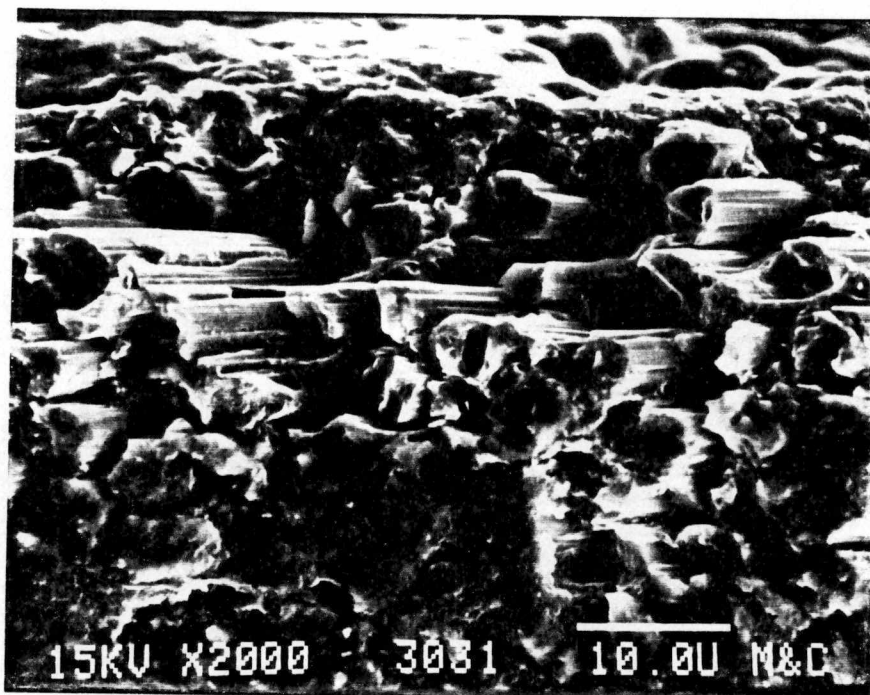


Figure 45. SEM micrograph revealing the coating on the surface of the composite material. Top of micrograph shows coating profile on the surface.

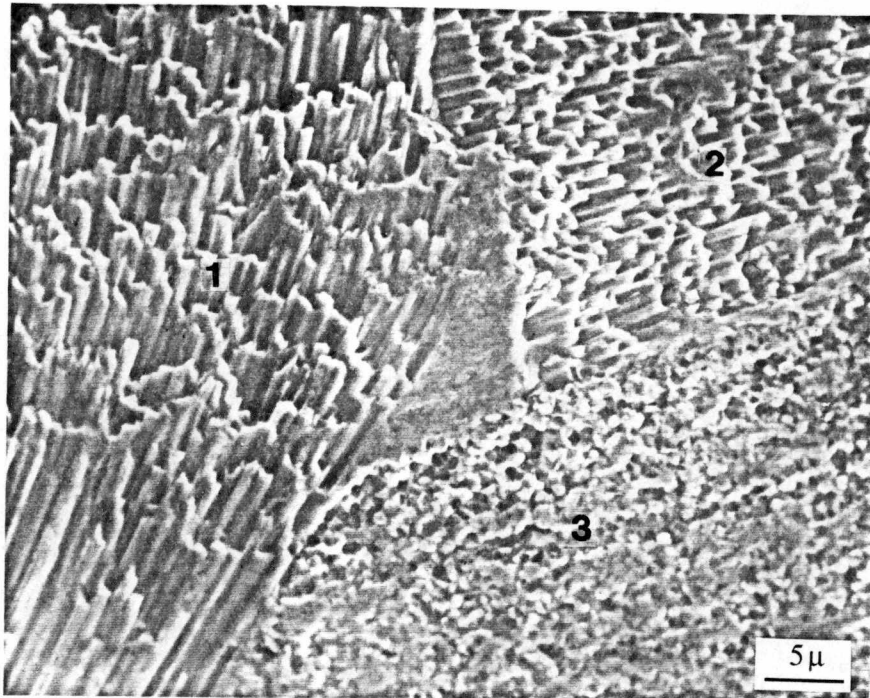


Figure 46. SEM micrograph of a cut surface illustrating fiber orientation within a bundle. Three different fiber bundle arrangements are shown in the figure.

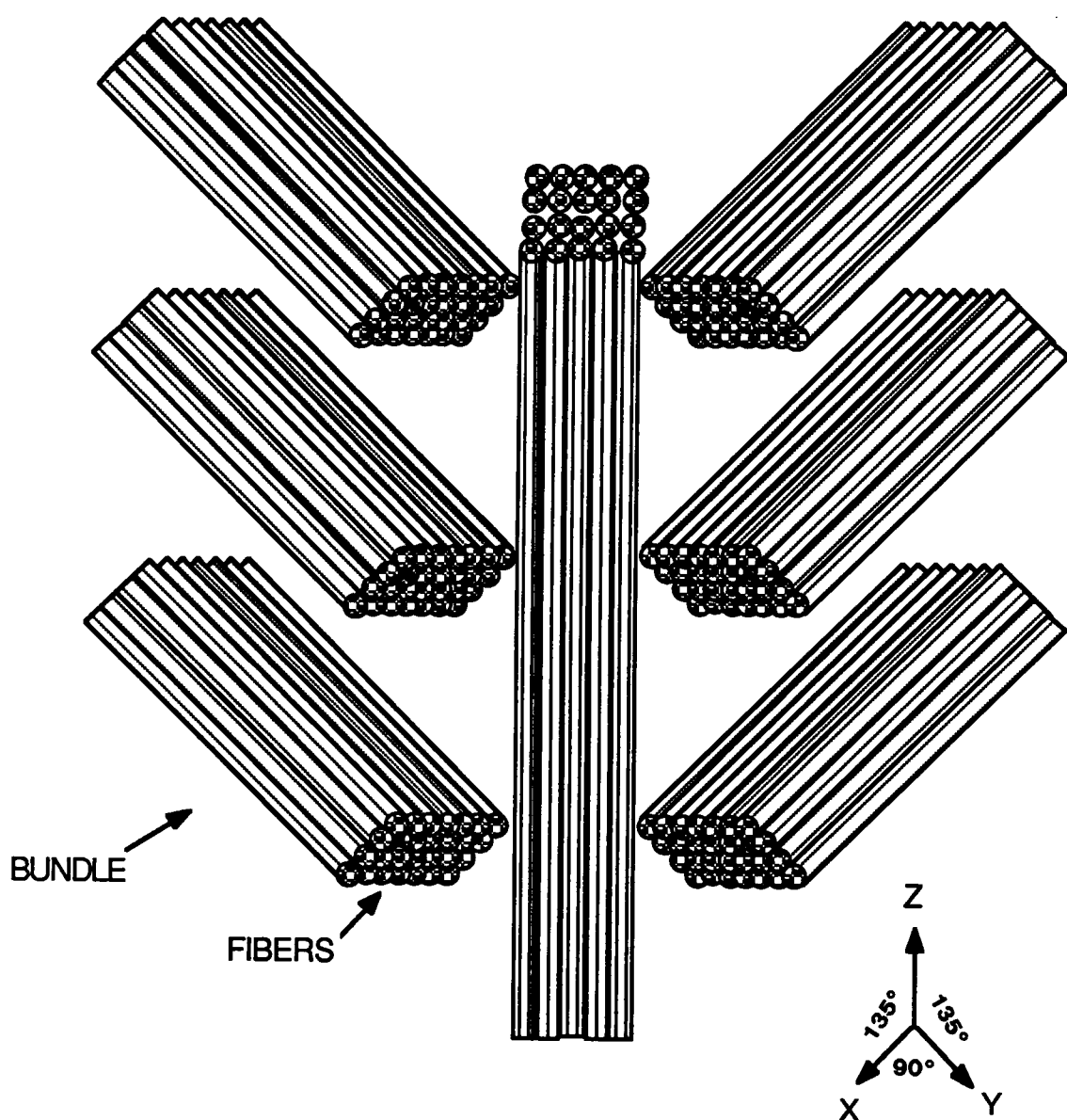


Figure 47. Schematic illustration of the dimensionality of the composite material.

Interlayer Properties

Zirconium; titanium; platinum; Molybdenum Disilicide; Lucanex 721; Cu_2Ti ; CuTi ; and copper were employed as interlayers in this study. The dimensions of the interlayers employed and the properties of the interlayer material important to the brazing operation are shown in Tables VIII and IX.

Table VIII. Dimensions of the Interlayers Used For Joining

	Thickness mm (inches)	Diameter mm (inches)
Zirconium	0.127 (0.005)	6.35 (0.25)
Titanium	0.0127 (0.0005)	6.35 (0.25)
Platinum	0.025 (0.001)	6.35 (0.25)
Copper	0.025 (0.001)	6.35 (0.25)
Cu_2Ti	0.025 (0.001)	6.35 (0.25)
CuTi	0.025 (0.001)	6.35 (0.25)
Molybdenum	-	6.35 (0.25)
Disilicide		
Lucanex 721	0.127 (0.005)	6.35 (0.25)

Table IX. Interlayer Properties Important to Brazing

Interlayers	Melting Temperature °C (°F)	Crystal Structure	α ppm/ °C (ppm/ °F)	Youngs Modulus 20 C x 10 ⁶ psi	Resistivity μ ohm-cm 20 C
Zirconium	1852 (3366)	HCP	5.85 (3.25)	13.7	40
Titanium	1678 (3052)	HCP/BCC*	8.41 (4.67)	16.8	42
Platinum	1769 (3216)	FCC	8.9 (4.94)	21.3	10.6
Copper	1083 (1981)	FCC	16.5 (9.17)	16	1.67
Cu ₂ Ti	892 (1638)	Orthorhombic	-	-	-
CuTi	982 (1800)	Tetragonal	-	-	-
Molybdenum	2032 (3690)	Tetragonal	8.1 (4.5)	58	37.24
Disilicide					
Lucanex 721	780 (1436)	-	-	-	-
* above 880 C					

(Source: Metals Handbook, Properties and Selection of Metals, Volume 1, 8th edition, American Society For Metals, Novelty, Ohio, 1961).

Variables Effecting the Joining Process

A. Wetting Theories Applied to Resistance Brazing

Brazing is a complex "science" in which many variables must be addressed to theoretically predict if a strong bond can be produced by employing a particular interlayer. Equations 6-8 (i.e. Young's equation, Work of Adhesion equation, and Dupree's equation respectively) have been used to theoretically predict if a strong bond can form.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (6)$$

$$W_{AD} = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \quad (7)$$

$$W_{AD} = \gamma_{lv} (1 + \cos \theta) \quad (8)$$

The theory implies that the higher the value of the work of adhesion, the stronger will be the bond strength.

Applying this theory to resistance brazing of carbon carbon composite materials presents several problems. The surface tension (γ_{lv}) and the spreading tension (γ_{sv}), mentioned in the equations above, are values measured from unconstrained surfaces at equilibrium. Pores within the composite material; forces to bring the faying surfaces in mutual contact; temperature variations during the heating cycle; and the duration of the heating cycle effect both the surface and spreading tensions and subjects question to the validity of the present theory to the resistance brazing process.

The presence of pores causes penetration of the molten interlayer into the composite material as shown in Figure 48. Thus, capillary forces created within the pores of the composite material, which are not considered in the present theory, become a significant factor.

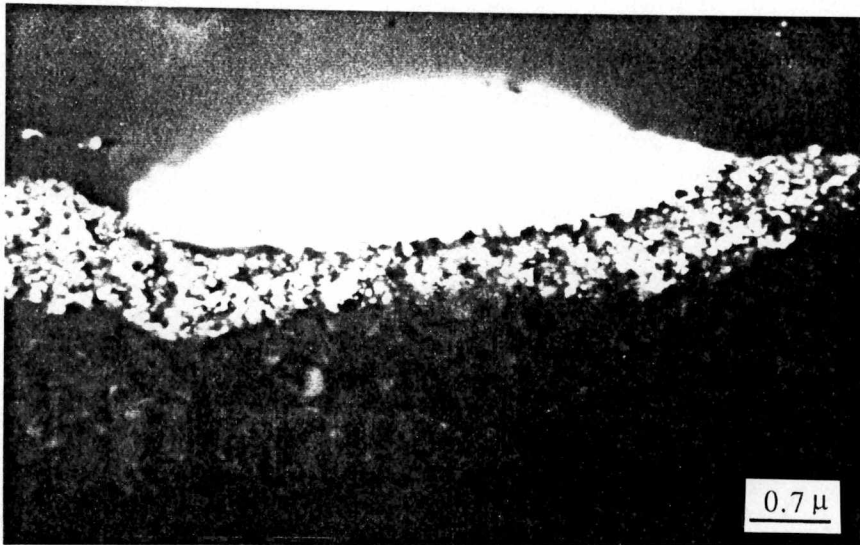


Figure 48. Illustration of the effect of capillary forces causing penetration of the molten interlayer into the pores of the composite material.

Parallel and at some angle to the faying surfaces, the spreading and surface tensions exist respectively. The application of a force on the workpieces creates an additional force parallel to the faying surfaces. This force is more significant than the surface tension forces presented for unconstrained surfaces, and causes the molten interlayer to flow out from between the faying surfaces.

The variations in the peak temperature distribution from the center of the interlayer region towards the outer edge is shown in Figure 49. The distribution of peak temperatures is highest near the center of the interlayer region, where the current is localized, and decreases as the distance from the center increases. Thus, since the surface and spreading tensions are temperature dependant, the variation in their quantities across the joint zone will result in a variation in the wetting behavior.

The contact angle (the angle at which the surface tension of the molten interlayer is relative to the faying surfaces) decreases as the duration of time at or above the melting temperature increases [72,75]. The schematic thermal cycle as plotted in Figure 50 can predict the duration of time above the melting temperature at each position along the joint zone.

$$T_0 > T_1 > T_2$$

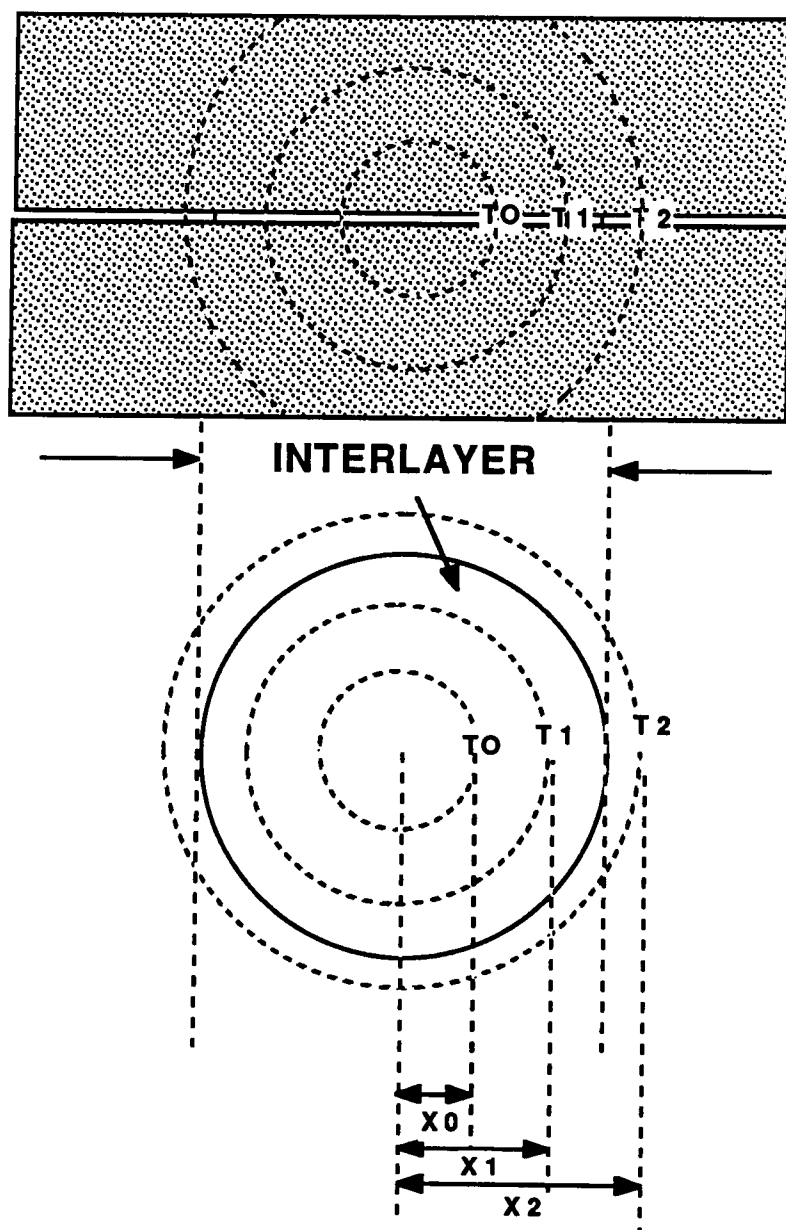


Figure 49. Schematic of the peak temperatures (T_0 , T_1 , T_2 , etc.) across the interlayer region (x_0 , x_1 , x_2 , etc.).

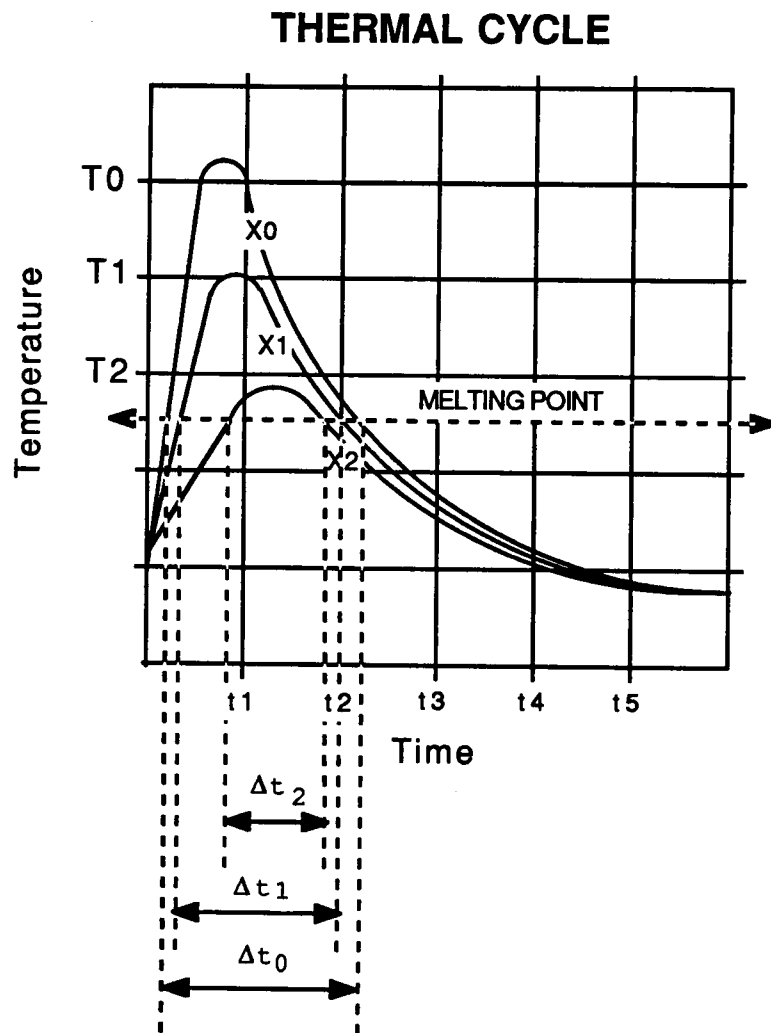


Figure 50.

Schematic of the peak temperatures versus time at different distances from the center of the workpieces.

The time (Δt) above the melting temperature is greater at the center of the brazement (near x_0) than at the edges. Thus, the center of the brazement should show the best wetting behavior and the greatest depth of interlayer penetration.

Surface tension, spreading tension, and contact angle data can be used to calculate the work of adhesion at various times and temperatures in a partially shielded argon environment. A simpler method, however, based on evaluation of the wetted surface area and the profile of the solidified molten interlayer resting on the surface of the carbon carbon composite material was performed to determine the suitability of the interlayer for joining. The thermal cycles experienced during brazing were simulated by inductively heating the components in an argon environment. The wetting behavior of Lucanex 721, Cu_2Ti , and CuTi was examined by comparing the wetted surface area to the area of the interlayer prior to heating; evaluating the concavity and/or convexity of the solidified molten interlayer on the surface of the carbon carbon composite material; and visually examining the solidified molten interlayer to determine if oxidation had occurred. A tabulation of the potential wetting characteristics and results from test performed on Lucanex 721, CuTi , and Cu_2Ti is shown in Tables X and XI respectively.

Table X. Potential Wetting Characteristics

Area Ratio (Af/Ao)	Profile	Flow	Appearance	Potential
≥ 1	Concave	W,P	O	-
≥ 1	Concave	W,P	C	+
≥ 1	Planar	S,P	O	-
≥ 1	Planar	S,P	C	+
≥ 1	Convex	W,P	O	-
≥ 1	Convex	W,P	C	+
≥ 1	Omega *	W,P	O	-
≥ 1	Omega *	W,P	C	+
< 1	Concave	P	O	-
< 1	Concave	P	C	+
< 1	Planar	NW	O	-
< 1	Planar	P	C	+
< 1	Convex	NW	O	-
< 1	Convex	NW	C	-
< 1	Omega *	P	O	-
< 1	Omega *	P	C	+

Af/Ao= Solidified area/Original area
 W= Wets the surface
 NW= Non-wetting
 S= Spreads on the Surface
 + excellent joining potential
 P= Penetrates the Surface
 O= oxidation
 C= Clean
 Omega *= Concave-Convex-Concave
 - poor joining potential

Table XI. Wetting Test Results

Interlayer	Area Ratio	Profile	Appearance	Potential
Lucanex 721	0.8	Omega	O	-
Cu ₂ Ti	1.6	Omega	C	+
CuTi	0.6	Omega	O	-

Limited trials were performed for the interlayers in Table XI and Cu₂Ti exhibited the best potential as a candidate interlayer for joining because it exhibited the best wetting potential. Wetting of Cu₂Ti on the surface of the composite material is shown in the macrograph in Figure 51. Examination of the appearance of Lucanex 721 and CuTi near the solid/solidified liquid interface showed that discoloration had occurred (evidence of oxidation). The reduced surface area ($A_f/A_o < 1$) of the interlayer after testing indicates "balling-up" (non-wetting). Further evaluation of interlayers using this technique needs to be performed to obtain a statistical average of the results.



Figure 51. Planimetric profile of a Cu_2Ti solidified interlayer on the surface of the carbon carbon composite material.

B. Resistance Brazing Theory

The heat necessary for melting the interlayer during the resistance brazing process is generated by the resistance to the flow of current in a circuit which contains the workpieces. The maximum quantity of heat is generated at the interfaces between the interlayer and the composite material; and the interfaces between the electrodes and the composite material. In the case of carbon which has a very high resistivity, the body resistance of the material may have more of an effect on the heating potential than the contact surfaces depending on the tap setting and the duration of current flow. Therefore, care was exercised in arranging the workpieces to produce the required heating to form a bond without damaging the electrodes. The secondary circuit consists of two RWMA Class II pointed nose electrodes with 6.35 mm (0.25") faces; two carbon carbon composite materials 12.7 mm (0.5") x 12.7 mm (0.5") x 3.175 mm (0.125"); and a 6.35 mm (0.25") metallic interlayer sandwiched between the two composite workpieces and centered between the electrode faces. The Brazing Schedule Diagram plotted in Figure 52 illustrates the conditions which were used to attain suitable heating. This diagram was developed by heating two carbon carbon composite material components 12.7 mm (0.5") x 12.7 mm (0.5") x 3.175 mm (0.125") at different tap settings and durations of current flow until the maximum and minimum limits of heating could be established. The minimum amount of heat was created by the resistance to the flow of current at the contact surfaces and was localized within the cylindrical volume centered between the electrode faces. The maximum amount of heat was dictated by the melting point of the electrode material and was developed by the body resistance of the carbon carbon composite materials.

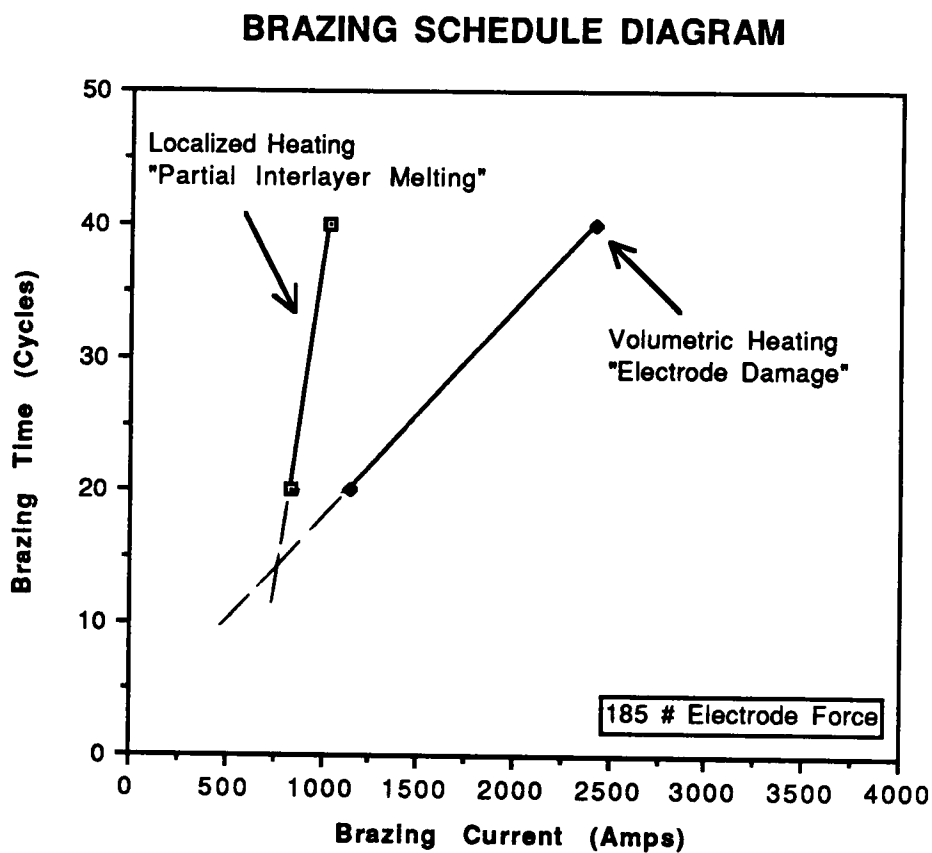


Figure 52. Brazing Schedule Diagram showing brazing conditions for joining of carbon carbon composite materials.

The amount of heat needed to melt the interlayer can be calculated by using Equation 9.

$$\text{Heat} = (\text{specific heat}) \times (\text{temperature change}) \quad (9)$$

The required heat for melting was determined for platinum, zirconium, copper, and titanium as shown in Table XII. Equation 10 was used to calculate the heat generated at the composite/composite interface at an average effective resistance of 240 μ ohms, a time of 40 Hertz, and currents at the high end and low end of the Brazing Schedule Diagram (750 amps and 3050 amps) in Figure 52. These values are also shown in Table XII.

$$\text{Heat} = (\text{current})^2 \times (\text{resistance}) \times (\text{time}) \quad (10)$$

The heat generated at the composite/composite interface is sufficient to melt each interlayer employed if heat loss and variation in resistance with temperature are negligible.

Table XII. Heat Generated at the Contact Surfaces and to Melt the Interlayer

Material	Peak Temperature °C (°F)	Current (amps)	Heat (joules)
Titanium	1678 (3052)	-	2*
Copper	1083 (1981)	-	4*
Zirconium	1852 (3366)	-	17*
Platinum	1769 (3216)	-	4*
Composite	-	750	90**
Composite	-	3050	1500**

* Calculated using equation 9.

** Calculated using equation 10.

C. Thermomechanical and Chemical Considerations

An understanding of the thermomechanical and chemical properties of the interlayer and the carbon carbon composite material during brazing is necessary so that the integrity of the brazement does not degrade during joining or while in service. In this study, one of the criteria for selection of the interlayer material was that its linear CTE was similar to that of carbon. Thus, during the brazing cycle or during servicing the potential for defect formation is diminished. Further, evaluation of thermomechanical effects can be developed from Equation 11.

$$\sigma = E \times \alpha \times \Delta T \quad (11)$$

In this equation, σ is the yield stress at a particular temperature; E is Young's Modulus at a particular temperature, α is the linear CTE at a particular temperature; and ΔT is the variation in temperature. If the yield strength (calculated from equation 11) of the interlayer is exceeded cracks will form at the interfaces.

The interaction of the interlayer with the composite material can cause chemical reactions to occur at the interfaces which can effect the joint strength. The original wetting theory assumes no chemical reactions, however, the theory proposed by Mortimer and Nicholas [72] considers the effect of chemical interactions. Chemical reactions occurred to some extent in all the brazement cross sections studied with the exception of platinum, which wets carbon but does not form carbides. Pure metals which do not form carbides and do not wet carbon, such as silver and copper were combined with carbide forming elements which wet carbon (such as titanium) to reduce the extent of chemical interaction and enhance wettability of the non-carbide forming/non-wetting metal.

D. Composite Material Consideration

Outgasing of the composite material, friability, and the surface conditioning all effect the strength of the brazement. Long times at high temperatures in argon atmospheres lower the interfacial energy of the composite material and enhance wettability. This was described by Thomas [44] who improved matrix/fiber interaction by heat treatment of carbon carbon composites in argon during processing. A disadvantage of the resistance brazing process in comparison to furnace brazing is that time for outgasing is limited unless the brazing schedule is repeated many times.

Friability of the composite material is another problem which effects joint strength. In a carbon carbon composite material, the fibers are the main strength bearing component, and the matrix precursor densifies the composites and supports the fibers. Both the matrix and fibers are quite brittle, so during cutting and grinding, the structural integrity of the material is weakened and the fibers of the bundles can be easily pulled out. The wetting behavior on the composite material may be sufficient during the joining operation, but because of the nature of the material, a weak bond will still be produced.

Surface preparation, by roughening the surface will tend to increase the contact resistance (decrease current flow) which is undesirable for the resistance brazing process. Roughening the surface destroys the structural orientation of the fibers which also is an undesirable factor (See Figures 53 and 54).

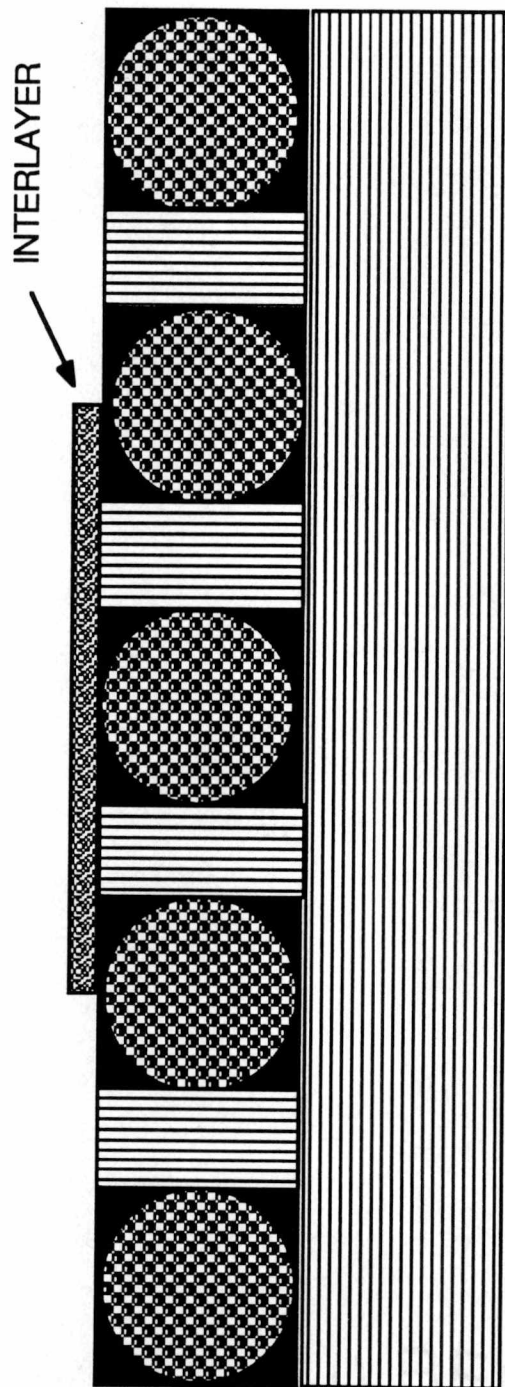


Figure 53. Schematic cross section of joining surface showing fiber bundle orientation.

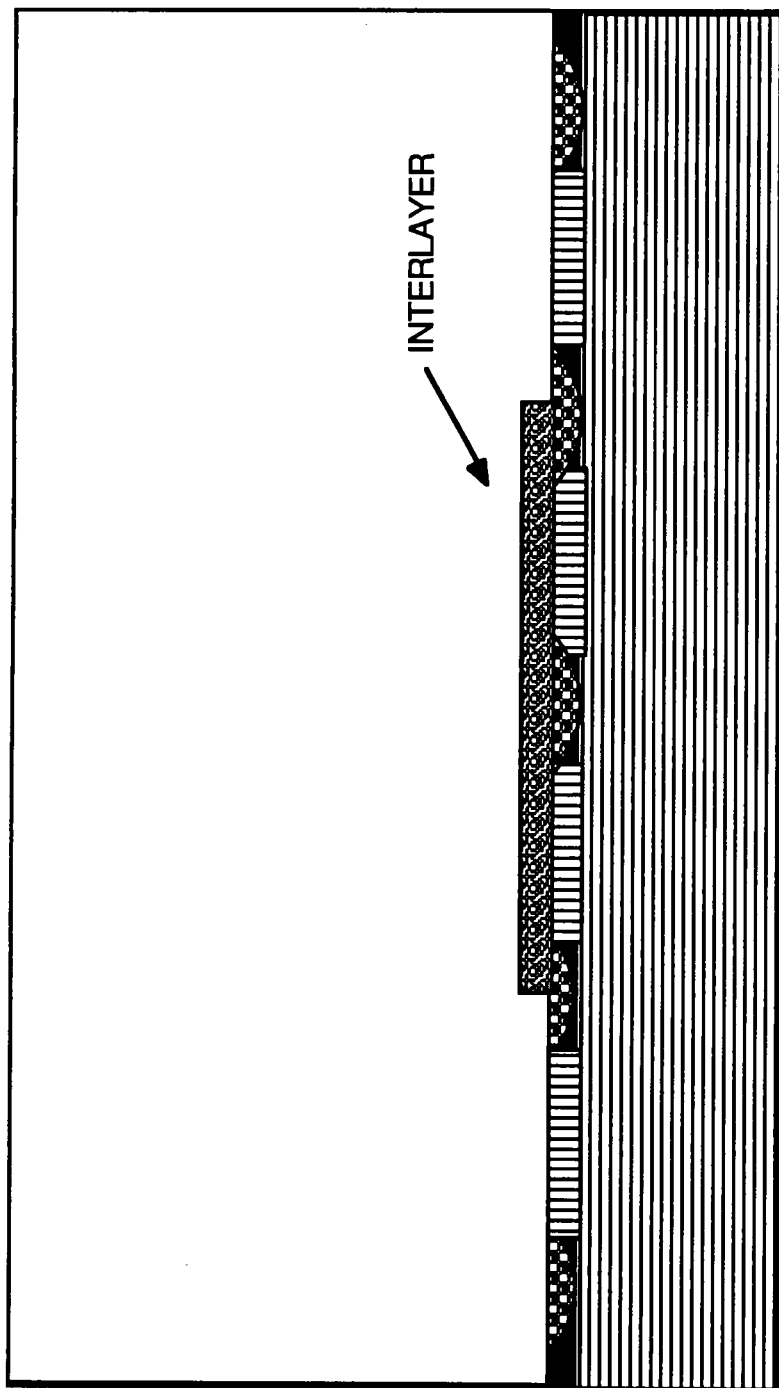


Figure 54. Schematic cross section of joining surface showing disruption of fiber bundles.

Evaluation of Brazement Strength

A variation of the AWS torsional shear test, as described in the experimental procedures, was employed to determine the strength of the brazements. Three brazements were produced using each interlayer at one, five, and ten repeated heating cycles. Each brazement was torsional shear tested and the torsional strength was recorded. Three carbon carbon composite materials 12.7 mm (0.5") x 12.7 mm (0.5") x 6.35 mm (0.25") were machined to the dimensions shown in Figure 55. The machined composites were prepared to determine the torsional strength of the virgin material over a similar area. The average torsional strength was obtained and used as a baseline for the evaluation of the brazement. All brazement strengths were expressed as a ratio of the torsional shear strength of the brazement to the torsional strength of the virgin material.

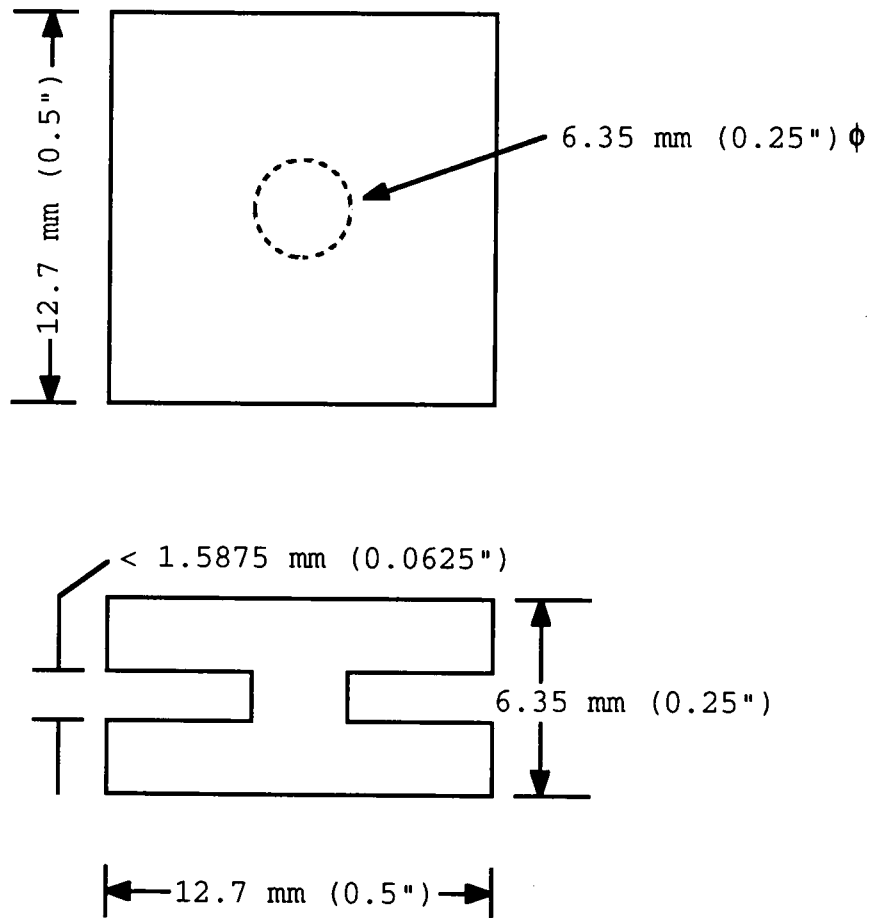


Figure 55. Dimensions of the virgin material for torsional shear testing.

Adhesive bonds were also developed by locally applying an adhesive in a 6.35 mm (0.25") diameter area on the surface of a 12.7 mm (0.5") x 12.7 mm (0.5") x 3.175 mm (0.125") carbon carbon composite material. The mechanical system of the resistance spot welder was used to apply a 84 kg (185 lbs.) force on the workpieces to assist in curing the bond. The maximum, minimum, and average torsional strength ratios obtained from both adhesive bonded materials and brazed components produced at a tap setting of 80 and 40 Hertz are shown in Table XIII.

Table XIII. Torsional Strength Ratios

Interlayer	Maximum Strength Ratio	Minimum Strength Ratio	Average Strength Ratio
Platinum	0.45	0	0.20
Zirconium	0.90	0.01	0.28
MoSi ₂ *	0.81	0.04	0.31
Titanium	0.57	0	0.21
Lucanex 721	0.65	0	0.32
CuTi	0.87	0.05	0.41
Ti-Cu-Ti **	0.70	0.12	0.48
CCCTi-Cu ***	0.91	0.10	0.42
Cu ₂ Ti	0.87	0.04	0.46
Cyanoacrylate	0.91	0.07	0.39
Epoxy	0.62	0.24	0.79

* Molybdenum Disilicide

** Copper foil sandwiched between two titanium foil

*** Copper foil sandwiched between two titanium coated carbon carbon composite materials

Resistance brazed components joined with alloy interlayers possessed better average torsional strength ratios than components joined with pure metallic interlayers. Epoxy produced joints with the highest average torsional strength ratio, while the average torsional strength ratio for cyanoacrylate was less than brazements produced with copper-titanium type alloy interlayers.

The current at a tap setting of 80 and 40 Hertz which produced the maximum and minimum torsional strength ratios for each of the interlayer was plotted on the Brazing Schedule Diagram shown earlier in Figure 52. It was determined that the best strength could be produced if a current in the middle of the range could be attained as shown in Figure 56. The contact resistance at the interlayer/composite interface has an effect on the ability of the brazing schedule employed to reach the required current range. By repeating the heating cycle, the resistance at the interlayer/composite contact surfaces decreases which allows more current and heat into the interlayer region on additional heating cycles. The decrease in the resistance of carbon at increasing temperatures also provides the opportunity for increasing current flow. Repeating the heating cycle can therefore increase the current flow in the circuit and create more uniform heating.

The higher the current attained at the end of the heating cycles tended to produce the higher torsional strength ratio in components joined with alloy metallic interlayers. Brazements joined with pure metallic components showed a reduction in strength with increasing current flow into the components after several heating cycles which may be due to either erosion of the composite material or flow out of the interlayer due to its excellent wettability.

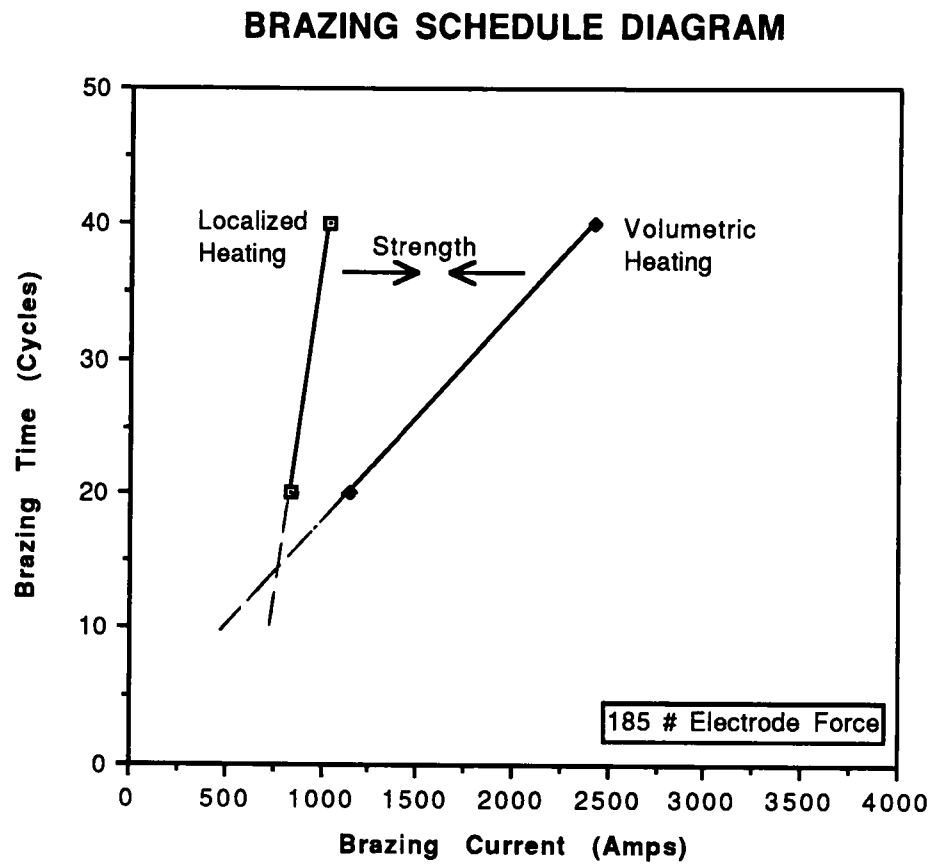


Figure 56. Brazing Schedule illustrating range in which the best strength can be attained.

Macroscopic Examination of Fracture Surfaces

The degree of melting of the interlayer, and fiber pullout were determined by examining the fracture surfaces of torsionally tested brazements. Typical fracture surfaces showing partial melting of the interlayer (Type A behavior); slight fiber pullout (Type B); complete fiber pullout (Type C); and fiber pullout and metallic areas (Type D) are shown in Figure 57-60 respectively. Table XIV describes the fracture surfaces of the torsionally tested brazements of the interlayer evaluated. Type A fracture surfaces indicate that insufficient heating occurred during brazing. Reduced current flow into the material due to improper alignment of the workpieces beneath the electrode faces can lead to this characteristic. Type B fracture surfaces indicate that the interlayer penetrated the composite leaving a small volume of the interlayer at the interface for joining. Excellent wetting behavior of the interlayer on the composite lead to Type B fracture surfaces. Type C fracture surfaces indicate that uniform melting of the interlayer occurred. Proper alignment of the interlayer between the electrode faces and repeated heating leads to Type C fracture surfaces. The only evidence of a Type C fracture surface appearance was when a powder interlayer was employed. Further evaluation of powder interlayers needs to be performed to determine if the form of interlayer is significant. Type D fracture surfaces indicate that the interlayer fully melted, wetting and adherence takes place on the surface; and penetration occurred. Variable wetting behavior is characteristic of Type D fracture surfaces which was found in all titanium and non-carbide forming/ non-wetting metal-titanium system interlayers. The non-carbide/ non-wetting element tended to restrict the wetting behavior and chemical reactivity of the carbide forming element which wets the composite.

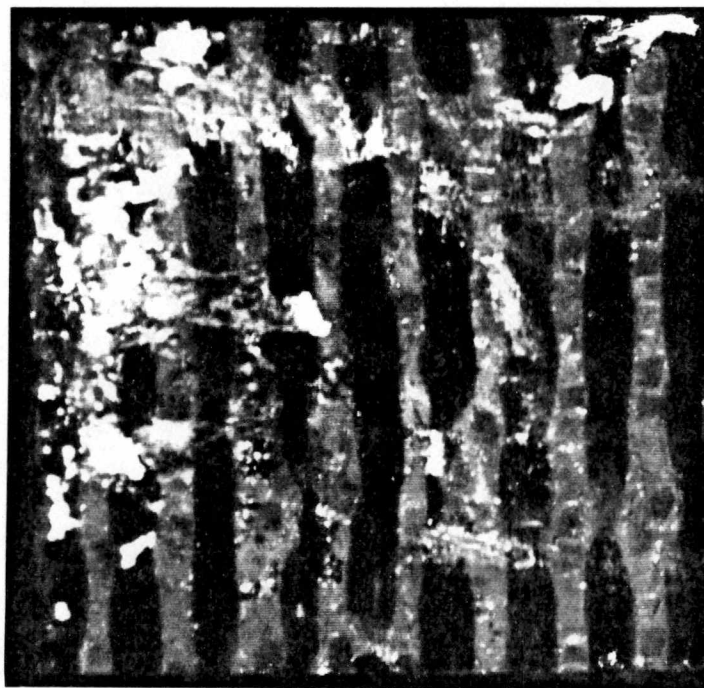


Figure 57. Type A fracture surface. Partial melting of the interlayer. Arrows on micrograph on the right indicate the periphery of the unmelted interlayer.



Figure 58. Type B fracture surface. Slight fiber pullout. Arrows on micrograph on the left illustrates this characteristic.



Figure 59. Type C fracture surface. Complete fiber pullout. Arrows on micrograph on the left illustrates this characteristic.

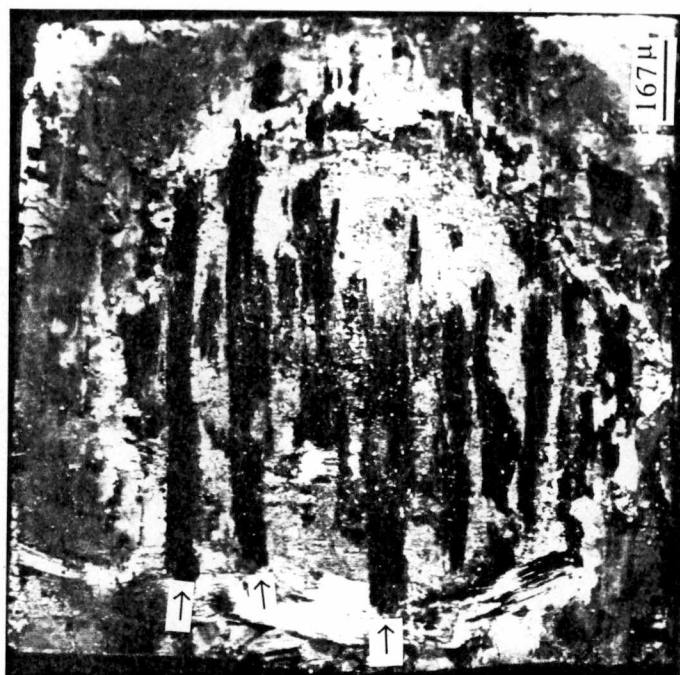


Figure 60. Type D fracture surface. Partial fiber pullout and presence of metallic areas. Arrow on micrograph on the left and right show metallic areas and fiber bundle pullout respectively.

Table XIV. Description of Fracture Surfaces for each Interlayer Tested

Interlayer	Type
Platinum	B
Zirconium	A
Titanium	D
CCCTi-Cu *	D
Ti-Cu-Ti **	D
Cu ₂ Ti	D
CuTi	D
MoSi ₂ ***	C
Lucanex 721	D

* Copper foil placed between titanium coated carbon carbon composite materials
 ** Copper foil placed between two titanium foils
 *** Molybdenum Disilicide

Microscopic Surface Examination

Microscopic evaluation of the fracture surfaces by SEM and Optical Light Microscopy (OLM) was performed to determine if the interlayer employed wetted the fibers and to investigate wetting and non-wetting behavior. The fibers in carbon carbon composite materials are oriented in such a manner to produce a composite material with directional strength and properties. Wetting of the fibers by the interlayer is crucial to the strength of the brazement. Figures 61 and 62 show the titanium coated composite material. Adherence of the evaporated titanium on the fibers is clearly evident. By depositing titanium on the surface prior to joining, a more wettable surface layer which adheres to the composite material is created, and also the nature of the contact resistance at the faying surfaces is altered to provide better current flow. A copper interlayer which wets titanium was employed to improve the strength of the brazement.

Evaluation of fracture surfaces after mechanical testing showed wetting of the fibers as illustrated in the SEM micrographs in Figures 63 and 64; strong adherence of the interlayer to the fibers as shown by the pullout of fibers in Figures 65 and 66 and the SEM micrograph in Figure 67; and variable wetting behavior as shown in the SEM micrographs in Figures 68-70. The wetting and adherence of the interlayer to the fibers as shown in Figures 62-67 is characteristic of all the interlayers investigated in this study except for Lucanex 721 whose wetting behavior is shown in Figures 68-70. An SEM micrograph taken near the outer edge of the joint area of a fracture surface from a mechanically tested brazement joined with Lucanex 721 is shown in Figure 68. Non-wetting behavior is shown. Near the center of the fracture surface, as shown in Figure 69, variable wetting and adherence exist.

Figure 70 shows adherence and non-wetting. The best interlayer for joining carbon carbon composite materials would contain the proper amount (wt%) of a non-carbide forming/non-wetting element and a carbide forming wetting element. Thus, the former element would prevent the carbide forming wetting element from extensive interface interaction with the composite while the later will enhance the wettability and interaction of the non-carbide forming/non-wetting element with the composite material.

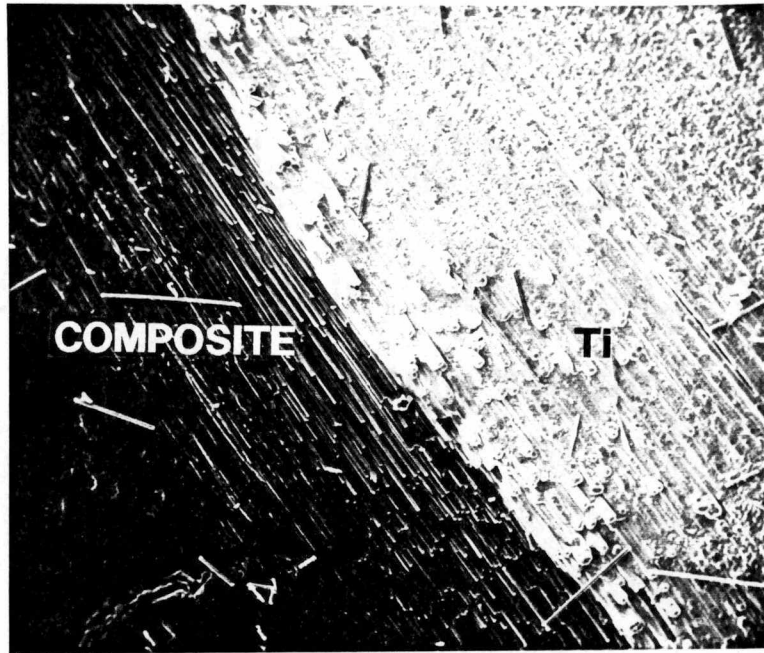


Figure 61. SEM micrograph showing the edge of the titanium coated carbon carbon composite material surface.

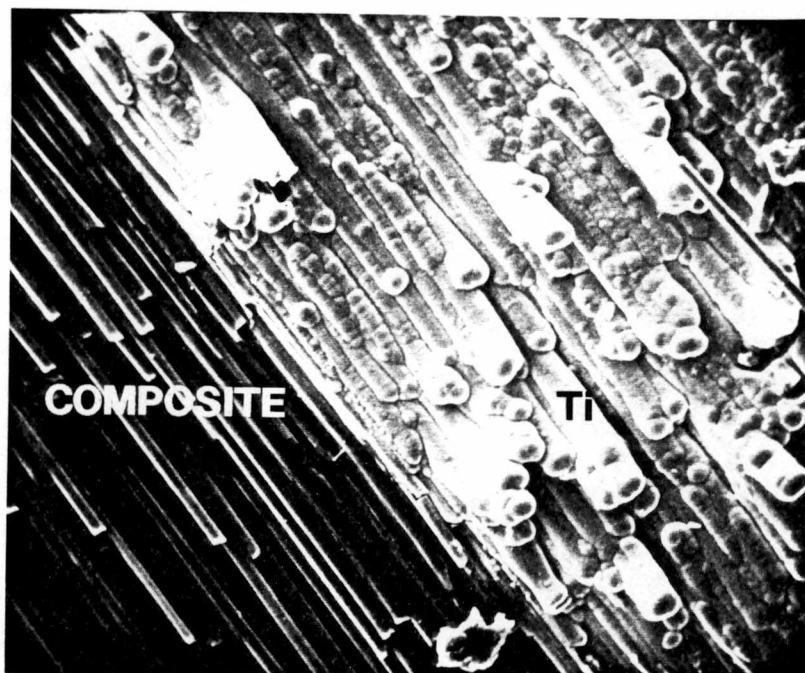


Figure 62. SEM micrograph showing a titanium coated carbon carbon composite material. Titanium adhered to the fibers.

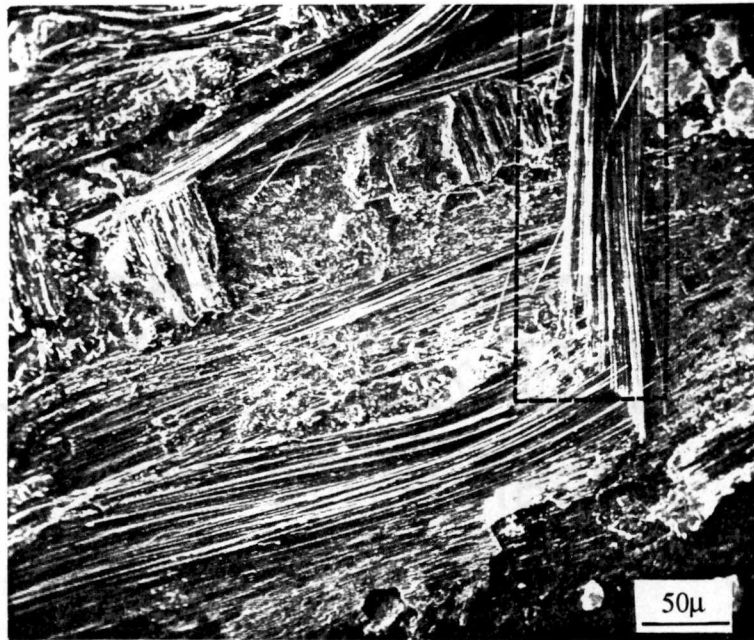


Figure 63.

SEM fractograph of the surface of a torsional shear tested carbon carbon composite brazement joined with a titanium interlayer. Fibers pulled out from the adjacent fracture surface are indicated within the outlined region.

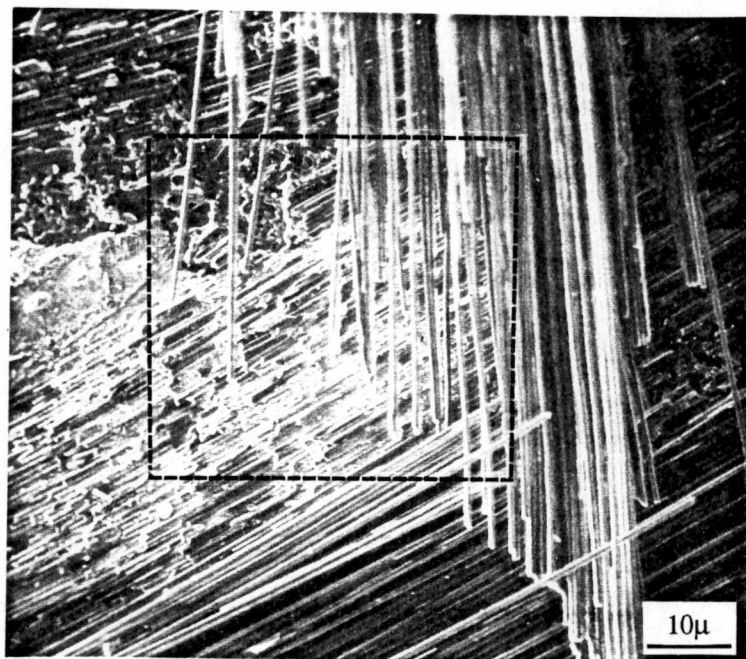


Figure 64. Same area as shown in Figure 63. Titanium wet the fibers (bright areas) causing them to adhere as shown within the outlined region.

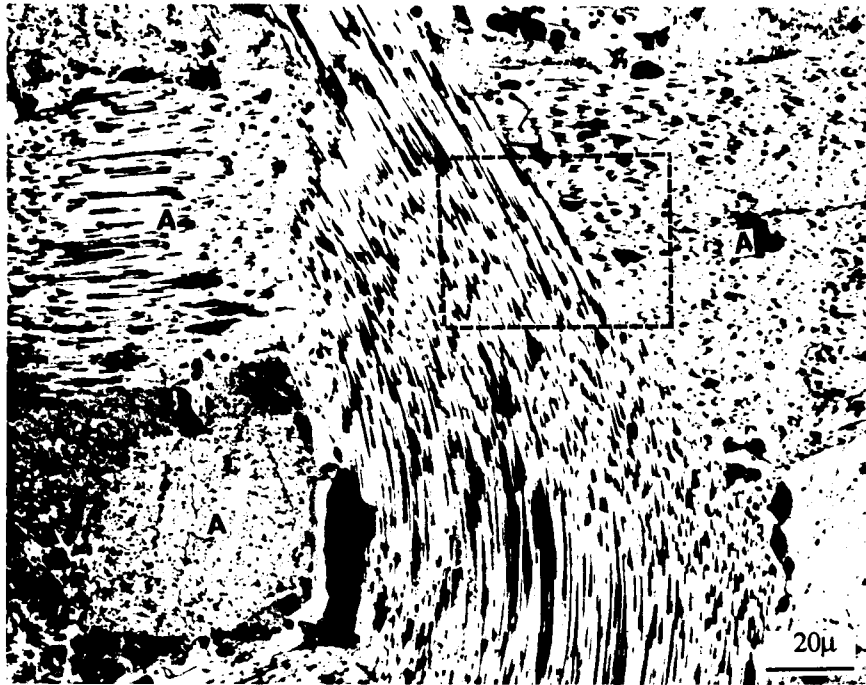


Figure 65. Photomicrograph of a fracture surface from a torsional shear tested carbon carbon composite material brazement. Evidence of portions of a bundle pulled out from the adjacent surface are indicated by (A).

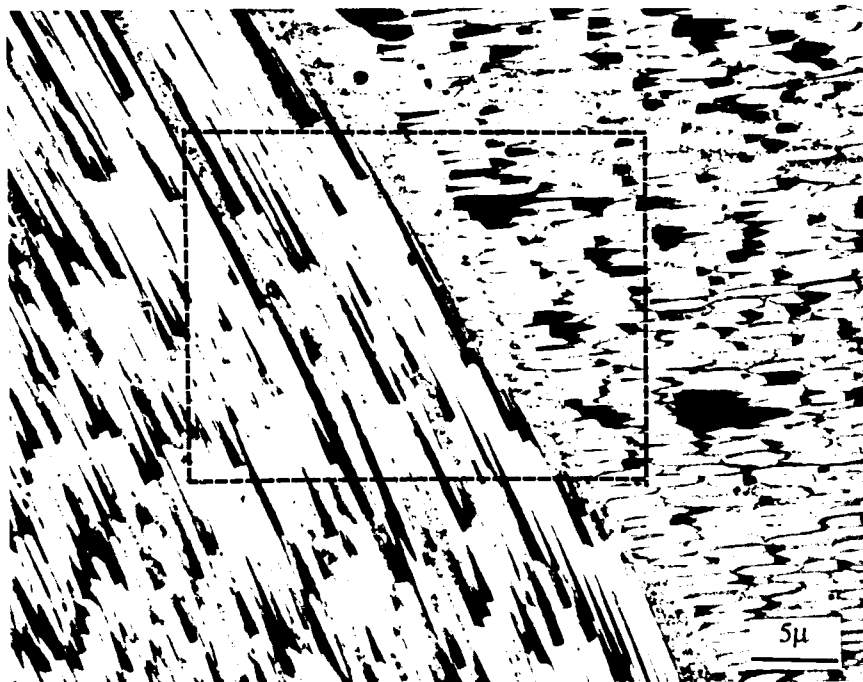


Figure 66. Same area as outlined in Figure 65. Palisading fiber bundles at the pulled out bundle/ original orientation transition interface is shown.

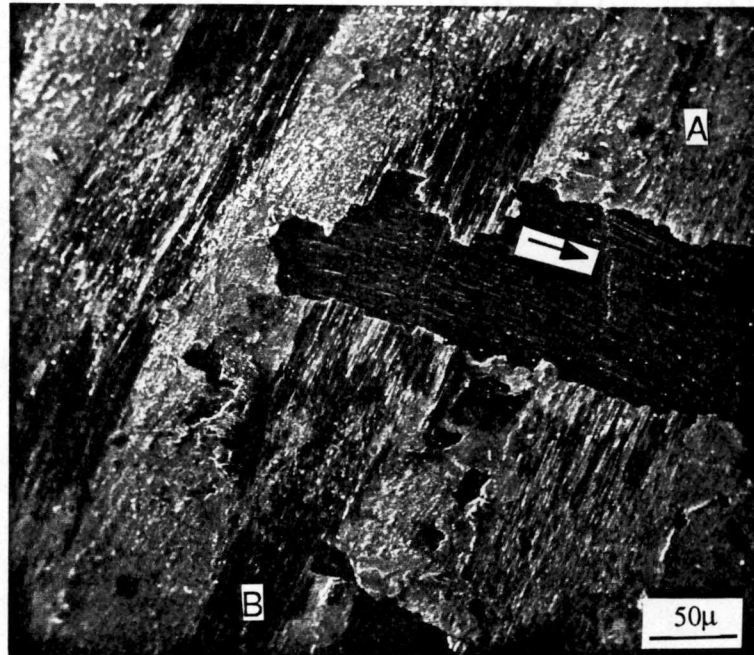


Figure 67.

Fractograph produced after torsional shear testing of a carbon carbon composite brazement joined with a zirconium interlayer. Evidence of the interlayer (A); pullout from the surface (see arrow); and pullout from the adjacent surface (B) are shown.

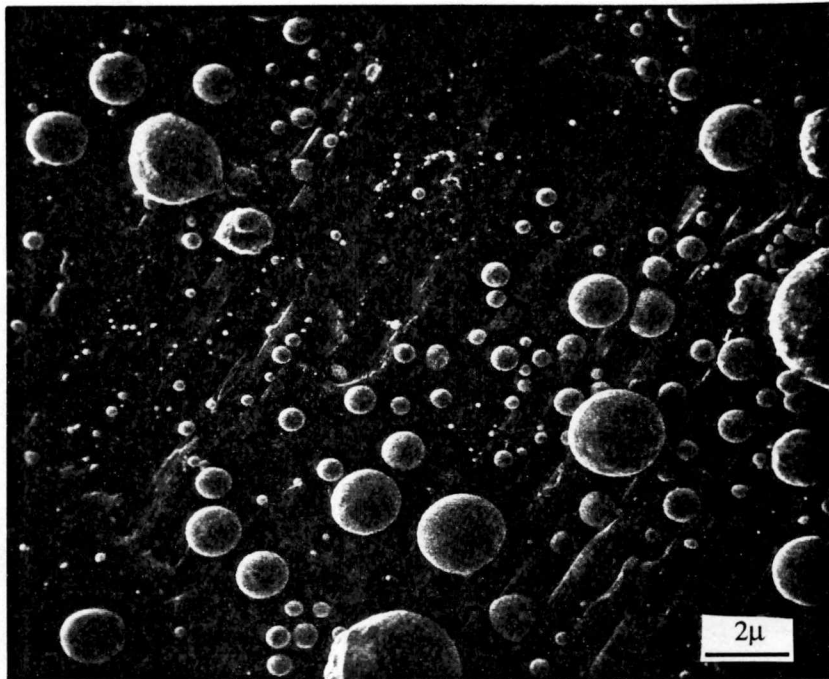


Figure 68. Fractograph from a torsional shear tested carbon carbon composite material brazement joined with a Lucanex 721 interlayer. Interlayer did not have sufficient time to wet and spread.

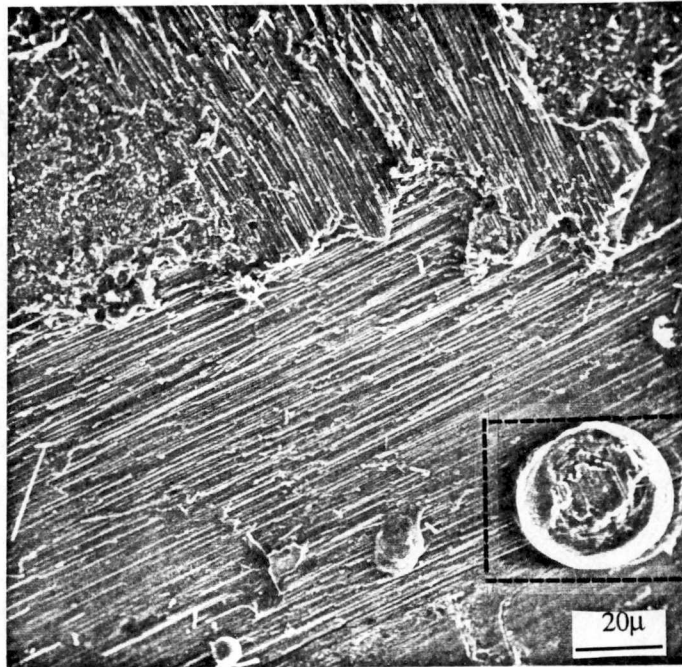


Figure 69.

Fracture surface from a torsional shear tested carbon carbon composite material brazement. Fibers from a bundle pulled out from the adjacent surface are seen at the top of the micrograph, and both non-wetting and adherence is depicted by the outlined region.

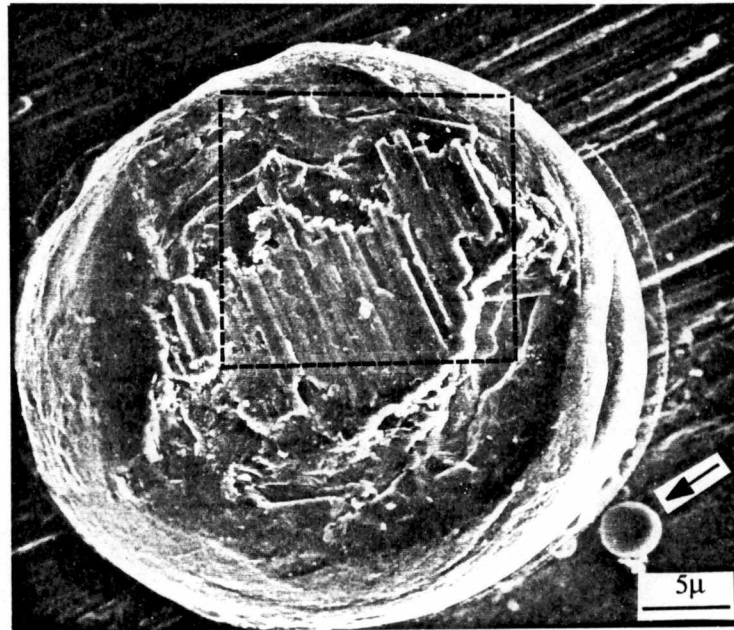


Figure 70. Same area as in Figure 69. Fibers from a bundle adhered to the surface of the interlayer. Arrow indicates more evidence of poor wetting beneath the periphery of the larger balled up region.

Evaluation of Brazement Cross Sections

An evaluation of the cross section of the brazement produced using platinum; molybdenum disilicide; titanium; Lucanex 721; copper sandwiched between two titanium foils; copper sandwiched between two titanium pre-conditioned carbon carbon composite material surfaces; CuTi; and Cu₂Ti indicates that five joint characteristics types existed as shown in Figures 71-75 respectively. A description of these characteristics are as follows:

- Type I: A uniform linear interface with no interaction
- Type II: A linear interface contained within a reaction zone.
- Type III: A uniform linear interface with no reaction zone and local isolated zones of penetration (0.381 mm (0.015") maximum)
- Type IV: An intermittent interface
- Type V: Complete volumetric interaction (0.635 mm (0.025") maximum).

Table XV shows the characteristics produced by each interlayer.

During resistance brazing of the carbon carbon composite materials with a platinum interlayer; the interlayer melted, wet, penetrated, and was expelled from the joint area producing Type III and Type IV characteristics. A uniform linear interface with localized regions of penetration existed near the center of the brazement cross section, while at the edges the joint zone was intermittent. The intermittent behavior at the edges of the joint zone are caused by expulsion of the interlayer during joining. An

interlayer which does not form carbides, but wets the carbon carbon composite material, such as platinum, will most likely produce resistance brazements whose cross section will exhibit Type III and Type IV behavior.

Joints produced using zirconium and molybdenum disilicide as interlayers exhibit the most varying characteristics of all the interlayers investigated. From the center to the edges of the joint area: complete interaction; a reaction zone surrounding a linear joint region; a uniform interface showing no appreciable interaction; and an intermittent interface exist cumulatively. Evidence of all characteristics except Type III was evident. Type III behavior did not appear because both zirconium and molybdenum disilicide are carbide formers and Type II behavior (chemical reaction) is favored over Type III. The ability of these interlayers to spread on the surface of the carbon carbon composite material produced the varying interfacial joint characteristics.

Brazements developed employing titanium and Lucanex 721 as interlayers showed Type I and Type IV behavior. Titanium wets and forms carbides with the carbon carbon composite material. However, the presence of oxides (titanium oxides form rather than titanium carbides) at the interlayer/composite interface limits the wetting behavior and the formation of carbides. Thus, a uniform linear joint showing no appreciable interaction was produced near the center of the brazement cross section, while at the edges flow out occurred and the joint zone is intermittent (Type IV). Lucanex 721, on the other hand, is only slightly chemically reactive and has restricted wetting characteristics (due to the presence of two non-wetting elements copper and silver). Thus, a linear interface existed at the center of the brazement cross section and Type IV behavior occurred near the edges.

All titanium-copper containing interlayers used for joining produced Type III, IV, and V behavior with the exception of Cu_2Ti which only exhibited Types IV and V behavior. From the center to the edges of the titanium-copper containing brazement cross sections the joint profile was as follows: complete interaction; uniform and linear with local areas of penetration; and intermittent. At the center of the brazement, a volumetric reaction zone was produced. Approaching the edges, copper reduces the chemical reactivity of titanium and the interlayer essentially behaves like a chemically inert wetting interlayer. At the edges of the joint cross section, the interlayer is intermittent due to expulsion. The Cu_2Ti interlayer may have contained the proper ratio of Cu to Ti, such that, an interlayer was developed which possessed good wettability and chemical reactivity. Thus, the brazement cross section was a volumetric reaction zone with expulsion occurring at the edges.

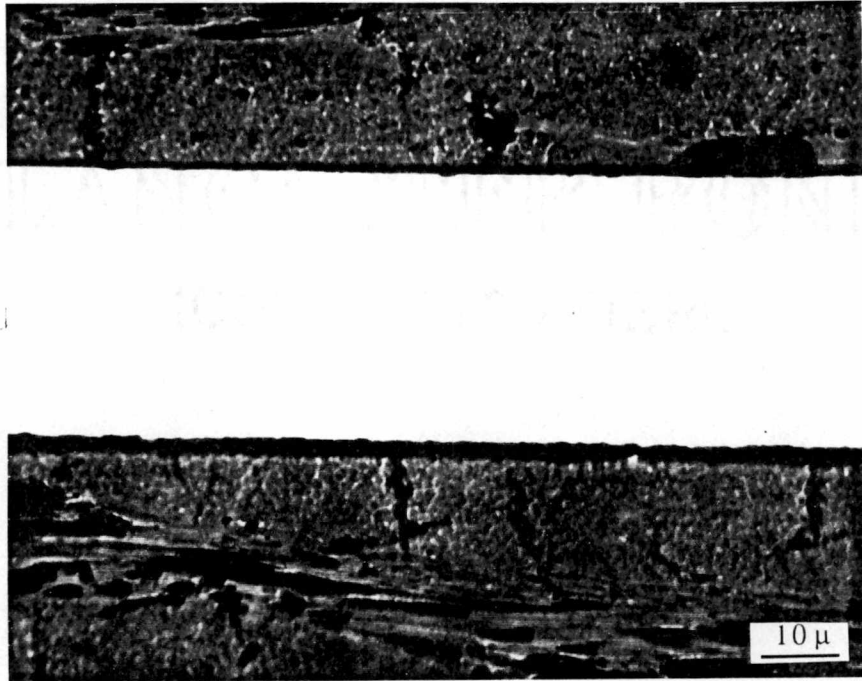


Figure 71. Type I cross section. A uniform linear interface with no interaction.

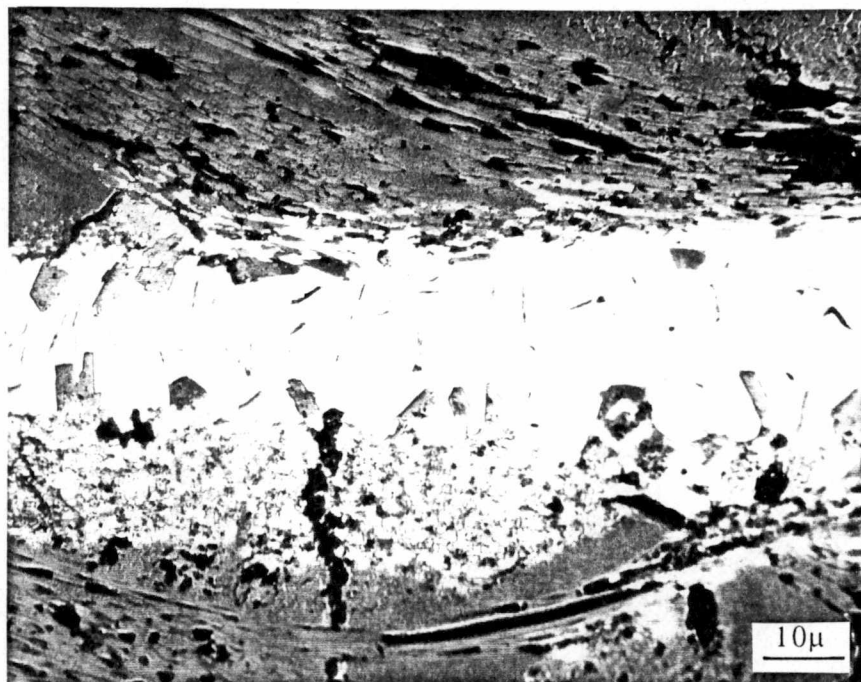


Figure 72. Type II cross section. A linear interface contained within a reaction zone.

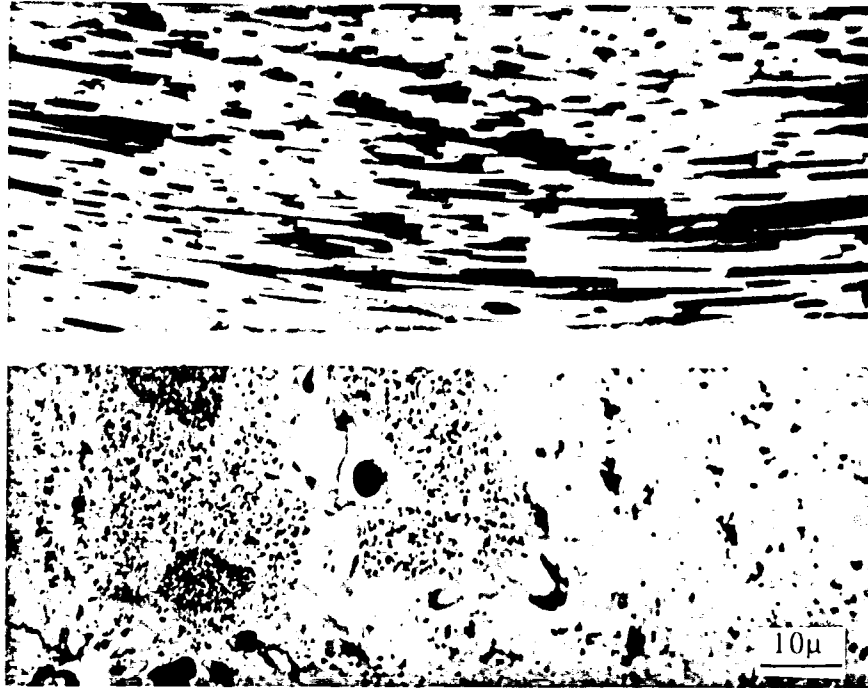


Figure 73. Type III cross section. A uniform linear interface with no reaction zone and local isolated zones of penetration.

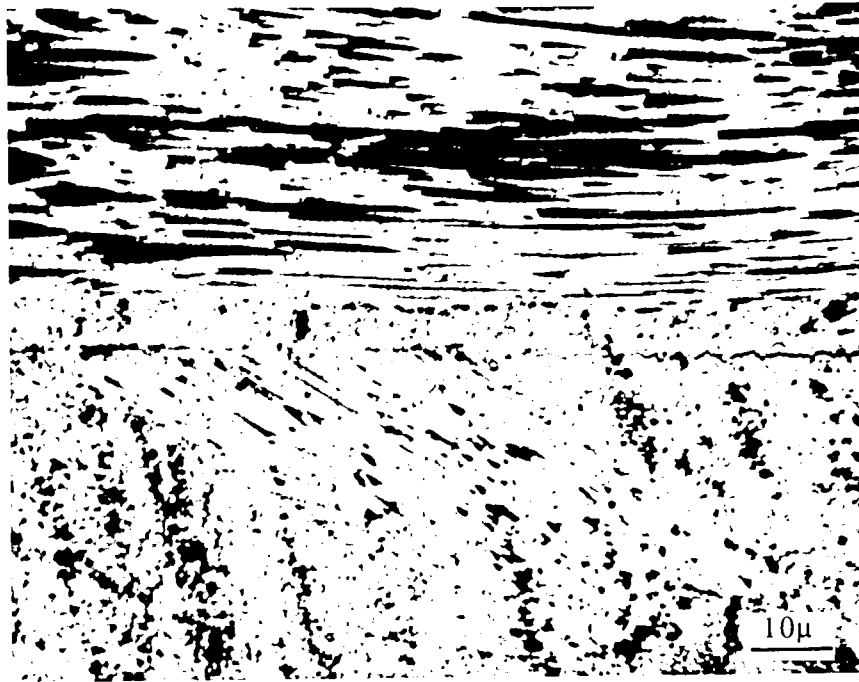


Figure 74. Type IV cross section. An intermittent interface.

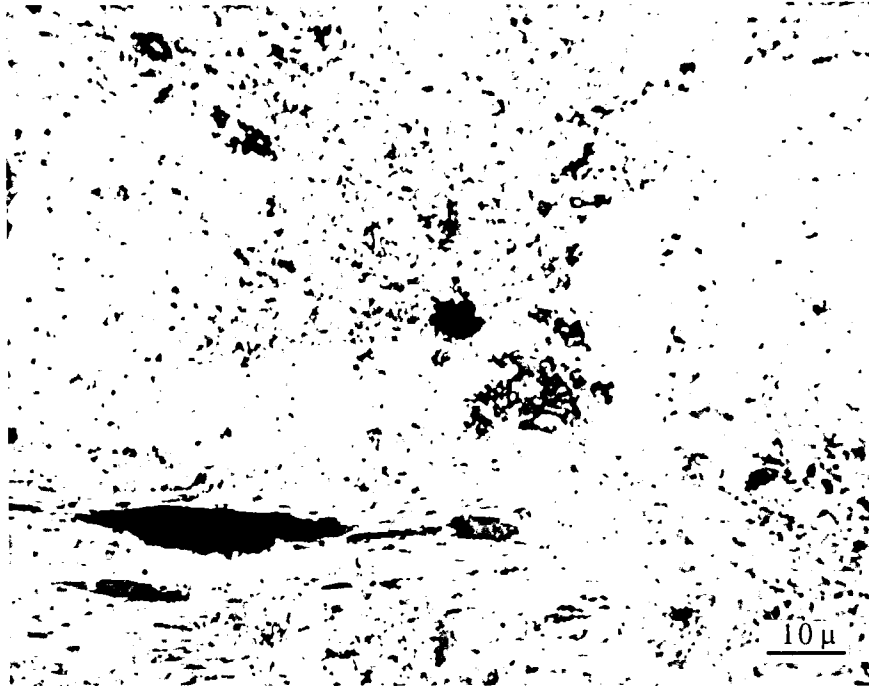


Figure 75. Type V cross section. Complete volumetric interaction.

Table XV. Cross Section Characteristics for each Interlayer

Interlayer	Reaction Zone Type
Platinum	III, IV
Zirconium	I, II, IV, V
MoSi ₂	I, II, IV, V
Titanium	I, IV
Lucanex 721	I, IV
Ti-Cu-Ti	III, IV, V
CCCTi-Cu	III, IV, V
CuTi	III, IV, V
Cu ₂ Ti	IV, V

Chapter V

CONCLUSIONS

Current research performed on carbon carbon composite materials has been directed towards improving matrix/fiber interaction and evaluating oxidation protection coating systems in service conditions. Limited joining studies have been performed using both metallic and adhesive type interlayers. In both cases, vacuum furnace heating was used to melt the metallic interlayer and also to cure the adhesive bond.

In this work an attractive alternative, resistance brazing, was studied. The resistance brazing technique is advantageous because; (1) it utilizes both local and rapid heating which reduces the oxide forming potential of the workpieces such that only an argon shielding environment is necessary for joining, (2) it increases fabrication capabilities by accommodating large scale components which can not fit within the heating zone of conventional vacuum furnaces, and (3) several other resistance heating techniques exist, which can accommodate several joint configurations, also increasing fabrication capabilities. This study was directed towards an understanding of the resistance brazing process as it applies to the joining of carbon carbon composite material rather than towards joining components to survive a particular service application.

The methodology employed to resistance braze carbon carbon composite materials included; (1) an evaluation of the carbon carbon composite material, (2) development of procedures for selection of interlayers, (3) determination of the most efficient process variables for joining, and (4) interpretation of the joint strength attained for the interlayers employed.

A. Carbon Carbon Composite Material

- (1) The load bearing components of the carbon carbon composite material are the fiber bundles. Preparation (cutting and grinding) of the carbon carbon composite material for joining disrupts the orientation and interlocking of the fiber bundles which effects the joint strength.
- (2) The composite material contains fabrication defects (cracks and pores) which provide penetration sites for interlayers which wet the carbon carbon composite material.
- (3) Evaporation of a thin layer (0.0004") of titanium on the surface of the carbon carbon composite material created a more wettable surface for joining.
- (4) The resistivity of carbon is approximately 100 times higher than the interlayers employed. Therefore, the bulk resistance of the carbon carbon composite material dominated the total resistance in the workpieces.

B. Interlayer

- (1) Coefficient of Thermal Expansion

Good judgement dictates that an interlayer with a linear coefficient of thermal expansion similar to the carbon carbon composite material should be employed to reduce the inherent thermal expansion problems which occur during the heating and cooling cycles.

- (2) Wettability

- a) Interlayers (MoSi_2 , Titanium, Zirconium, and Platinum) which have been shown previously to wet the surface of carbon type materials were used to produce brazements.

- b) The heat cycles experienced during resistance brazing were simulated by induction heating to evaluate the wettability of alloy interlayers. Lucanex 721, CuTi, and Cu₂Ti were investigated. Cu₂Ti showed the best wetting potential.
 - c) Examination of torsional shear tested fracture surfaces showed that the wetting behavior varied from the center to the outer periphery of the interlayer region due to the distribution of heat in the workpieces which is a function of the geometry of the electrodes. The maximum heating takes place at the center of the workpieces (between the the electrode faces) resulting in the greatest depth of molten interlayer penetration. Near the interlayer periphery (at the periphery of the electrode faces) less heat is generated which lowers the temperature and reduces the wettability of the interlayer.
 - d) Penetration of the molten interlayer into the bulk of the composite material (i.e. at defects (pores and cracks) or between fibers) occurred due to capillary forces.
- (3) Bonding
- a) The bond strength of the brazement was characterized by the degree of fiber pull out during torsional shear testing.
 - b) Interlayers which contain elements which form carbides (Titanium, Zirconium, MoSi₂, Lucanex 721 and the Copper based-Titanium alloys) produced brazements with torsional shear tested fracture surfaces exhibiting extensive fiber pull out.
 - c) Interlayers which have limited interaction with carbon (i.e. platinum) tended to produce brazements with torsional shear tested fracture surfaces showing limited fiber pull out.

C. Process Conditions

- (1) Proper placement of the workpieces between the electrode faces is critical because if the interlayer is not centered between the electrode faces, only a portion of the interlayer will melt. The resistance at the contact surface of improperly aligned workpieces is increased and the current flow into the workpieces is reduced.
- (2) A force was necessary to bring the faying surfaces in close contact which reduces the total resistance and permits higher current flow. A force of 84 kg (186 lbs.) was used. This force is below that required for indentation of the composite material surface.
- (3) Repetitive heating for a particular tap setting and at a specific time of current flow caused an increase in the measured current due to a decrease in the total resistance caused by flow and wetting of the interlayer resulting in the formation of a bond.
- (4) The thermal gradient created during the heating cycles caused local penetration of the molten interlayer into the composite material resulting in volumetric type joints whose penetration depth (0.635 mm (0.025")) is believed to exceed similar type joints produced by furnace brazing. The brazement strength can be enhanced by increased depth of penetration of the molten interlayer because a greater percentage of the load bearing fibers are wet within the joint region.
- (5) Argon shielding during resistance brazing limited the formation of oxides and improved bonding capabilities.

D. Joint Strength

- (1) Torsional shearing strength tests were used to rank (highest to lowest 1 to 6) the strength of the brazements produced using each of the interlayers (1- Copper based-Titanium alloys; 2- Lucanex 721; 3- MoSi₂; 4- Zirconium; 5- Titanium; 6- Platinum).

The values obtained during these tests can not be used for design purposes until; (1) a consistent method for measuring the bond area is developed, (2) the process variables are optimized, and (3) more specimens are tested to obtain a statistical average of the strength data.

- (2) Interlayers which wet the carbon carbon composite material, but do not form carbides (i.e. Platinum) had unsuitable strength levels due to limited fiber/interlayer interaction (bonding). The fracture surfaces produced by torsional shear testing showed limited fiber pull out.
- (3) Carbide forming interlayers (MoSi_2 , Titanium, and Zirconium), which wet the carbon carbon composite material, produced moderate joint strength levels. Fracture surfaces of torsional tested brazements produced using these interlayers showed fiber pull out indicating good bonding.
- (4) Titanium wets and forms carbides with the carbon carbon composite material, while Copper is non-wetting and non-carbide forming. Torsional shear testing of brazements produced employing Copper-Titanium alloy interlayers resulted in the best strength (approximately 50% of the strength of the carbon carbon composite material). Fracture surfaces of torsional shear tested brazements formed using these interlayers produce both metallic areas (rich in copper) and extensive fiber pull out.

Chapter VI

FUTURE WORK

It is recommended that future work be directed towards conditioning the surface of the composite material to increase current flow and wettability. Based on tests performed on the coated carbon carbon composite material, if pre-conditioning is used a new Brazing Schedule Diagram may have to be developed for efficient heating.

A method for brazing should be addressed to join the composite (i.e. fiber bundles) in a direction which can maximize the strength. The current study did not properly account for x-y fiber bundle orientation on the surface of the composite material prior to joining. Resistance butt brazing and resistance brazing would be suitable processes for joining unidirectionally orientated composites along the fiber bundle lengths to take advantage of tensile properties.

LIST OF REFERENCES

1. J. D. Buckley, "Carbon-Carbon, An Overview," American Ceramic Society Bulletin, Vol. 67, No. 2, (1988), pp. 364-368.
2. T. Kinjo, S. Takano, K. Hasegawa, O. Ebato, and T. Uruno, "Development of Advanced Carbon-Carbon Composites for Spaceplane Applications," Kawasaki Steel Technical Report, No. 23, (October 1990), pp. 54-60.
3. G. Bylinsky, "The 10,000-MPH Airliner," Fortune, (December, 1986), pp. 50-57.
4. T. J. Gregory, "Credibility of NASP," Aerospace America, (September, 1989), pp. 42-46.
5. J. I. Mueller, "Observation after Initial Flight," Ceramic Bulletin, Vol. 60, No. 1, (1981), pp. 1215-1217.
6. B. A. Stein, H. G. Maahs, and W. D. Brewer, "Airframe Materials for Hypersonic Vehicles," NASA CP-2482, Metal Matrix Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 22-23, 1987), pp. 1-23.
7. K. H. Holko, "Joining Methods for Carbon-Carbon Composites Structures," Advanced Materials & Manufacturing Processes, Vol. 3, No. 2, (1988), pp. 247-260.
8. S. Webb, Joining of Carbon-Carbon Composites for Structural Applications, private communications, 1989.
9. Introduction to Carbon/Carbon Manufacturing and Processing, Fiber Materials Inc., Biddeford, Maine.
10. Engineered Carbon-Carbon Composites for Commercial Applications, Kaiser Aerotech, San Leandro, California.
11. A. J. Klein, "Carbon/Carbon Composites," Advanced Materials & Processes, Vol. 130, No. 5, (November, 1986), pp. 291-293.
12. R. Fisher and T. G. Fennell, Bonding of Carbon- Based Components, U.K. Patent Number 4,742,948, (1988).
13. E. Fitzer, "The Future of Carbon-Carbon Composites," Carbon, Vol. 25, No. 2, (1987), pp. 163-190.

14. P. W. Atkins, Physical Chemistry, 3rd ed., (New York: W.H. Freeman and Company, 1986), pp. 144-145.
15. P. Gustafson, "An Evaluation of the Thermodynamic 24, No. 2, (1986), pp. 169-176.
16. The Encyclopaedia Britannica, Micropaedia, Ready Reference and Index, Vol. II, (Chicago: Encyclopaedia Britannica, Inc., 1977), p. 549.
17. R. J. Diefendorf, "Continuous Carbon Fiber Reinforced Carbon Matrix Composites," Engineered Materials Handbook, Vol. 1, Composites, (Metals Park, OH: ASM International, 1987), pp. 911-914.
18. F. S. Galasso and R. D. Veltri, Pyrolytic Graphite Pretreatment for Carbon-Carbon Composites, U.S. Patent Number 4,487,799, (December, 1984).
19. J. Delmonte, Technology of Carbon and Graphite Fiber Composites, (New York: Van Nostrand Reinhold Company, 1981), pp. 388-421.
20. Y. R. Yamaki and H. G. Maahs, "Influence of Fiber Surface Treatment on the Mechanical Properties of Carbon-Carbon Composites," NASA CP-3054 Part 1, Metal Matrix, Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 18-21, 1989), pp. 367-386.
21. R. J. Diefendorf, "Carbon/Graphite Fibers," Engineered Materials Handbook, Vol. 1, Composites, (Metals Park, OH: ASM International, 1987), pp. 49-53.
22. S. Sato, A. Kurumada, H. Iwaki, and Y. Komatsu, "Tensile Properties and Fracture Toughness of Carbon-Fiber Felt Reinforced Carbon Composites at High Temperatures," Carbon, Vol. 27, No. 6, (1989), pp. 791-801.
23. N. Murdie, E. J. Hippo, and A. Hyjazie, "Inhibition of Gas Carbon Reactions," NASA CP-3054 Part 1, Metal Matrix, Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 18-21, 1989), pp. 333-348.

24. E. J. Hippo, N. Murdie, and W. Kowbel, "The Effect of Acid Treatments on Subsequent Reactivity of Carbon-Carbon Composites," Carbon, Vol. 27, No. 3, (1989), pp. 331-336.
25. D. Dollimore and G. R. Heal, "The Degradation of Selected Polymers to Carbons in an Inert Atmospheres," Carbon, Vol. 5, (1967), pp. 65-72.
26. S. Kimura, Y. Tanabe, and E. Yasuda, "Discussions for Development of Carbon/Carbon Composites," Proceedings of the Fourth Japan-U.S. Conference on Composite Materials, Loews L'Enfant Plaza Hotel, Washington, D.C., (June 27-29, 1988), pp. 867-874.
27. H. Marsh, M. Forrest, and L. A. Pacheco, "Structure in Metallurgical Cokes and Carbons as studied by Etching with Atomic Oxygen and Chromic Acid," Fuel, Vol. 60, (May, 1981), pp. 423-428.
28. R. K. Aggarwal, "Evaluation of Relative Wettability of Carbon Fibres," Carbon, Vol. 15, (1977), pp. 291-293.
29. K. Kowbel and C. H. Shan, "The Mechanism of Fiber-Matrix Interactions in Carbon-Carbon Composites," Carbon, Vol. 28, No. 2/3, (1990), pp. 287-299.
30. G. Sines, Z. Yang, and B. D. Vickers, "Creep of Carbon Yarn and a Carbon-Carbon Composite at High Temperatures and High Stresses," Carbon, Vol. 27, No. 3, (1989), pp. 403-415.
31. A. Shindo and Y. Sawada, "Orientation Structure in Transverse Sections of Carbon Fibers from Dehydrated Polyvinyl Alcohol," Carbon, Vol. 18, (1980), pp. 419-425.
32. L. Aggour, E. Fitzer, E. Ignatowicz, and M. Sahebkar, "Chemical Vapour Deposition of Pyro-Carbon SiC, TiC, TiN, Si, Ta on Different Types of Carbon Fibers," Carbon, Vol. 12, (1974), pp. 358-362.
33. N. Murdie, J. Don, C. Kocher, R. Liew, and C. P. Ju, "Microstructural Analysis of C-C Composites used in Aircraft Braking Applications," NASA CP-3054 Part 1, Metal Matrix, Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 18-21, 1989), pp. 349-365.

34. K. K. Ikeuye and G. R. Grow, "Brazing Beryllium Oxide to Pyrolytic Graphite," Source Book on Brazing & Brazing Technology, (Metals Park, OH. ASM International, 1980), pp. 295-298.
35. H. Weissshaus, S. Kenig, E. Kastner, and A. Siegmann, "Morphology Development During Processing of Carbon-Carbon Composites," Carbon, Vol. 28, No. 1, (1990), pp. 125-135.
36. P. Ehrburger, J. Lahaye, and C. Bourgeois, "Characterization of Carbon-Carbon Composites-I: Textural and Microstructural Properties," Carbon, Vol. 19, No. 1-A, (1981), pp. 1-5.
37. J. W. Wheeton, D. M. Peters, and K. L. Thomas, Engineers' Guide to Composites, (Metals Park, OH.: ASM International, 1987), pp. 1.4, 2.5, 8.39-8.44.
38. J. L. Perry and D. F. Adams, "Mechanical Tests of a Three-Dimensionally- Reinforced Carbon-Carbon Composite Material," Carbon, Vol. 14, No. 1-E, (1976), pp. 61-70.
39. H. Chang and R. M. Rusnak, "Oxidation Behavior of Carbon-Carbon Composites," Carbon, Vol. 17, No. 5-C, (1979), pp. 407-410.
40. A. Pacault and A. Marchand, "A Summary of the Recent Work of French Laboratories Presented as a Tribute to Prof. Mrozowski," Carbon, Vol. 21, No. 4, (1983), pp. 385-386.
41. K. Leong, J. Dodson, C. Kiskiras, and J. Zimmer, "Single- Densification- Cycle Carbon-Carbon Composites with High Interlaminar Shear Strength," NASA CP-3054 Part 1, Metal Matrix, Carbon, and Ceramic Matrix Composites, Proceedings of a joint NASA/DoD conference held at Cocoa Beach, Florida, (January 18-21, 1989), pp. 327-332.
42. J. Lahaye, F. Louys, and P. Ehrburger, "The Reactivity of Carbon-Carbon Composites," Carbon, Vol. 28, No. 1, (1990), pp. 137-141.
43. P. R. Becker, "Leading-Edge Structural Material System of the Space Shuttle," Ceramic Bulletin, Vol. 60, No. 11, (1981), pp. 1210-1214.

44. C. R. Thomas, Proceedings of the 5th Conference on Carbon and Graphite, 1, (1978), p. 520.
45. J. R. Strife, and J. E. Sheehan, "Ceramic Coatings for Carbon-Carbon Composites," Ceramic Bulletin, Vol. 67, No. 2, (1988), pp. 369-374.
46. C. F. Lewis, "Complex Coatings with CVD," Materials Engineering, Vol. 106, No. 6, (June, 1989), pp. 35-38.
47. E. M. Goldstein, E. W. Carter, and S. Kluz, "The Improvement of the Oxidation Resistance of Graphite by Composite Techniques," Carbon, Vol. 4, (1966), pp. 273-279.
48. H. O. Davis, "Secondary Bonding of Carbon-Carbon Composites," Journal of Spacecraft & Rockets, Vol. 16, No. 6, (1979), pp. 432-435.
49. H. E. Pattee, "High Temperature Brazing," Source Book on Brazing & Brazing Technology, (Metals Park, OH: ASM International, 1980), pp. 17-63.
50. ASME Boiler and Pressure Vessel Code, Material Specification: Part II C, (United Engineering Center, New York: The American Society of Mechanical Engineers, 1986), pp. 127-145.
51. A. J. Moorhead and C. R. Kennedy, "Brazing of Carbon and Graphite," Metals Handbook, 9th. ed., Vol. 6, Welding, Brazing, and Soldering, (Metals Park, OH: ASM International, 1983), pp. 1061-1063.
52. T. Takamori and M. Akanuma, "Possible Braze Compositions for Pyrolytic Graphite," Ceramic Bulletin, Vol. 48, No. 7, (1969), pp. 734-736.
53. R. G. Donnelly and G. M. Slaughter, "The Brazing of Graphite," Welding Journal, Vol. 41, No. 5, (May, 1962), pp. 591-597.
54. H. E. Pattee, R. M. Evans, and R. E. Monroe, "Joining Ceramics and Graphite to Other Materials," NASA SP-5052, (1968), pp. 67-71.
55. Brazing Manual, (Miami, Florida: American Welding Society, Inc., 1963), pp. 232-242.

56. D. J. Sandstrom, Joining Graphite to Graphite with Transition Metal Foils, LA-3960, U.S. Atomic Energy Commission, Contract No. W-7405-ENG. 36, (July, 1968).
57. R. G. Donnelly, R. G. Gilliland, C. W. Fox, and G. M. Slaughter, "The Development of Alloys and Techniques for Brazing Graphite," Proceedings of the 4th National SAMPE Symposium Materials Compatibility and Contamination Control Process, Hollywood, California, (November 13-15, 1962).
58. Brazing Manual, 3rd. ed., (Miami, Florida: American Welding Society, Inc., 1976), pp. 235-246.
59. W. J. Werner and G. M. Slaughter, "Brazing Graphite to Hastelloy N for Nuclear reactors," Welding Engineer, Vol. 53, No. 3, (March, 1968), p. 65.
60. J. P. Hammond and G. M. Slaughter, "Bonding Graphite to Metals with Transition Pieces," Welding Journal, Vol. 50, No. 1, (1971), pp. 33-40.
61. M. M. Schwartz, "Brazing in a Vacuum," Source Book on Brazing & Brazing Technology, (Metals Park, OH.: ASM International, 1980), pp. 17-63.
62. C. W. Fox and G. M. Slaughter, "Brazing of Ceramics," Welding Journal, Vol. 43, No. 7, (July, 1964), pp. 591-597.
63. M. M. Schwartz, "The Fabrication of Dissimilar Metal Joints Containing Reactive and Refractory Metals," WRC Bulletin 210, (October, 1975), pp. 33-36.
64. L. T. Anikin, et al., "The High Temperature Brazing of Graphite," Welding Production, Vol. 24, No. 1, (1977), pp. 39-41.
65. L. T. Anikin, et al., "The High Temperature Brazing of Graphite Using an Aluminum Brazing Alloy," Welding Production, Vol. 24, No. 7, (1977), pp. 23-25.
66. V. V. Bondarev, "On the Problem of Brazing Graphite & Some Other Materials," Welding Production, Vol. 14, No. 6, (June, 1967), pp. 17-19.
67. A. J. Taylor and N. L. Dykes, Composition and Method for Brazing Graphite to Graphite, U.S. Patent Number 4,432,821, (February, 1984).

68. G. R. Peterson, U.S. Patent Number 3,946,932, (March, 1976).
69. M. A. Steinberg, U.S. Patent Number 2,979,813, (April, 1961).
70. S. Schwartz, O. Ramstrom, and A. Bjareklint, Methods for Joining Graphite to Graphite, U.S. Patent Number 4,382,113, (May, 1983).
71. P. Dadras and T. Nagai, "Joining of C-C Composites by Boron and Titanium Disilicide", Ceramic Bulletin, Vol. 69, No. 12 (1990), p. 1987.
72. D. A. Mortimer and M. Nicholas, "The Wetting of Carbon by Copper and Copper Alloys", Journal of Materials Science, 5 (1970), pp. 149-155.
73. R. N. Wenzel, "Resistance of Solid Surfaces to Wetting by Water", Industrial and Engineering Chemistry, Vol. 28, No. 8, (August, 1936), pp. 988-994.
74. F. E. Bartell and C. N. Smith, "Adhesion Tension Values of Different Types of Carbon Black against Water and against Benzene", Industrial and Engineering Chemistry, Vol. 21, No. 11, (November 1929), pp. 1102-1106.
75. G. A. Kolesnichenko, Y. V. Naidich, Soviet Powder Metallurgy and Metal Ceramics 2, 1963, p. 35.
76. Welding Handbook, Welding Technology, Volume 1, 8th ed., American Welding Society, Miami, Florida, 1987, p. 568.
77. E. J. Del Vecchio, Resistance Welding Manual 3rd. ed., Volume 1, Resistance Welder Manufacturers' Association, Philadelphia, Pennsylvania, 1969.
78. R. F. Tylecote, "SpotWelding: Part III Contact Resistance," Welding Research Supplement, Dec. 1941, pp. 591s-602s.
79. Metals Handbook, Properties and Selection of Metals, Volume 1, 8th edition, American Society For Metals, Novelty, Ohio, 1961.

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