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PYROLYTIC GRAPHITE COATED THROAT
INSERTS

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August 1974

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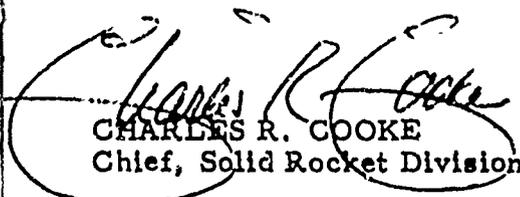
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FOREWORD

This paper was prepared by the Motor Components and Design Branch, Solid Rocket Division, Air Force Rocket Propulsion Laboratory under Project 3059. The paper was presented at the AIAA/SAE 9th Joint Propulsion Specialist Conference of November 1973 in Las Vegas, Nevada as AIAA Paper No. 73-1260.

This report has been reviewed and is approved.


CHARLES R. COOKE
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the flame temperature, is chemically non-reactive, resists mechanical erosion, and is structurally isotropic. In the real world, such a throat insert material does not exist. The AFRPL has investigated a system of materials which, as a system, could approach the characteristics of the ideal throat insert and still be less costly than the often used forged tungsten or pyrolytic graphite (PG) washer pack. This paper describes the AFRPL investigation of the material system starting with initial test efforts of PG coating on AGSR compressed graphite substrate. An evaluation of the problems encountered has led to an effort which theoretically will culminate with a PG coating placed on a graded silicon-carbide SiC/PG undercoating which has been placed, in turn, on a structural high grade graphite such as ATJ. Development work on the SiC/PG system has produced a structure in which the SiC is uniformly dispersed in the form of miniature needles oriented perpendicular to the PG deposition plane. This needle phase has the effect of decreasing the degree of anisotropy of the parent material, PG. Nozzle components have been fabricated using the SiC/PG coating and a variety of firings conducted at the AFRPL. The test results of the nozzle throat inserts are summarized in the paper.

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INTRODUCTION

Intermittent, unproductive efforts have been underway for at least thirteen years to develop reliable performance of pyrolytic graphite coated graphite throat inserts in liquid and solid motors. Pyrolytic graphite is an extremely anisotropic material, in both thermal and mechanical properties. The a-b plane is as conductive as copper, permitting use of the material as a heat sink nozzle in the form of washers. In the form of a coating, the a-b plane helps counteract the sharply peaked heat fluxes that occur in the throat regions of a submerged nozzle in a solid propellant rocket motor. Pyrolytic graphite is simultaneously an excellent insulator in the c direction, providing a heat barrier when used as a coating in high temperature propellant systems. The c direction strength is poor, and the thermal expansion in that direction is an order of magnitude higher than the a-b direction.

Development of pyrolytic graphite washers has been successfully accomplished virtually in the entire range of solid propellant motor environments. Many structural failures have been experienced with washers on new designs because of the susceptibility of delamination in bending and the need to accommodate significant axial thermal expansion. These problems were solved by straightforward design modifications.

The same problems produce different potential failure modes in a-b plane exposures of pyrolytic graphite structures, such as coated inserts. The large radial thermal gradients produce compressive thermal strains that complicate the situation. These problems are difficult to analyze and have not been inclined to disappear by simple redesign practices. In addition, the control of defects in manufactured components has been inadequate and undoubtedly has contributed to the long record of unsuccessful tests. It is the intent of this paper to briefly review recent attempts to overcome the structural problems inherent in a-b plane exposures of pyrolytic graphite throat inserts.

The potential erosion performance of a-b plane pyrolytic graphite has been well established, both by the successful subscale tests and by an

extensive laboratory and analytical effort to model erosion processes of significance in solid propellant environments¹. The erosion resistance exists, not merely because of a high density of carbon atoms in pyrolytic graphite, but also because the reaction is kinetically limited. Up to now, one can predict excellent performance potential, but no one has yet been able to design and produce structures that can reliably deliver the performance in hardware tests. Perhaps with better appreciation of the specific problems, adequate structural solutions to the design problem can be developed.

CONTINUOUSLY NUCLEATED PYROLYTIC GRAPHITE

The initial attempt to make and test large pyrolytic graphite coated throat inserts necessitated the scale-up of coatings made by the Atlantic Research Corporation (ARC) in Alexandria, Virginia². The process involved thermal decomposition of methane at atmospheric pressure, which produces a continuously nucleated (or "re-nucleated") structure. This process was chosen because of a long period of successful tests of small diameter inserts over a period of many years. A deposition development effort was conducted to learn how to make large coated inserts free from delaminations. The substrate employed was AGSR graphite from large billets, primarily because of its low thermal expansion coefficient and favorable prior experience. The deposition trials confirmed the well documented critical stress balance that exists in a coated graphite composite after cool-down from the high deposition temperatures. Frequent delaminations in early coatings were observed, and occasional substrate fractures were experienced, especially with thick coatings. The use of grooves in the substrate at the ends of the inserts was effective in prevention of edge delaminations. Ultimately, coated inserts of 7-inch and 12.5-inch internal diameter without defects were made on a routine basis. Special inspection techniques, involving holographic interferometry, were employed with great effectiveness to locate hard-to-find delaminations in the coating³.

When 7-inch diameter inserts were available, a series of five firings were conducted on the AFRPL 84-inch diameter heavyweight test motor. The test environment was a 5600°F flame temperature, 21 percent aluminum uncured solid propellant which produced approximately 1000 psi for 30 second durations. The insert configuration and nozzle design is shown in Figures 1 and 2. None of the tests were successful. Several different failure modes were observed, including partial coating failure and, on one occasion, a massive substrate failure. In the first two 7-inch inserts tested, the coating microstructure had large cone angles and exhibited cracking and spallation in the test firing. It was later shown, with flexure tests of coating specimen removed from the substrate, that the large cone angles have poor strengths and were very prone to delamination as part of the failure process. Specimen from coatings with cone angles typical of commercial plate material exhibited better strengths and freedom from delamination in the fracture surfaces (Figure 3). This can be considered a qualitative indication of c direction fracture strength. Direc. measurement of this property in coatings of 0.050-inch thickness is extremely difficult. Gebhardt and Berry⁴ reported some measurements on a-b plane torsional strengths of 0.2-inch plate with substrate nucleated and continuously nucleated microstructures (all produced at low pressures). The reported values were 1555 and 2880 psi, respectively, from room temperature to 5000°F. The a-b plane torsion and c direction fracture strength are both measurements of degree of bonding between the planes and indicative of delamination tendencies. No comparable measurements are available on the continuously nucleated pyrolytic graphite made at atmospheric pressure. If there is any superiority of continuously nucleated material, it is the higher resistance to delamination exhibited by the a-b planes, probably due to cone boundary effects.

One of the 7-inch insert tests had no loss of the coating thickness after a 36 second exposure at 663 psi maximum pressure, confirming the excellent erosion resistance of the pyrolytic graphite. An axial crack occurred during this test which also emphasizes the problem of structure

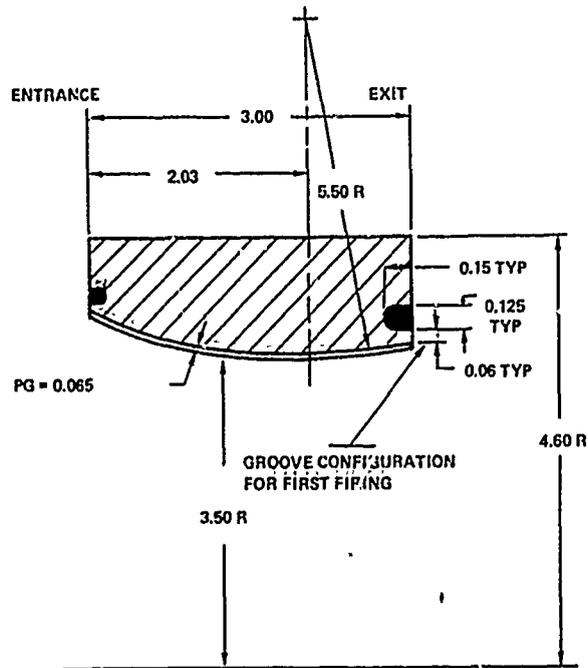


Figure 1. Pyrolytic Graphite Coated AGSR Graphite Throat Insert.

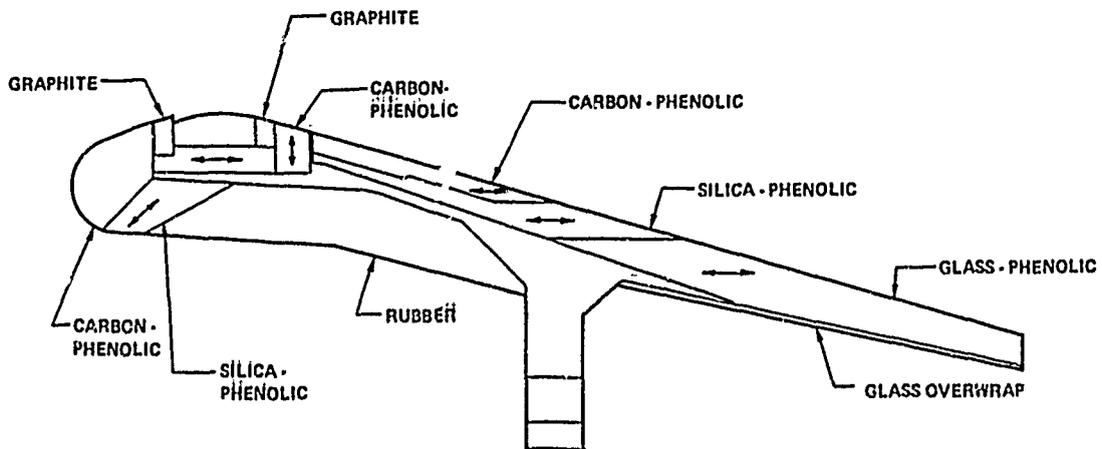


Figure 2. Nozzle Design - 7-inch Diameter Throat.

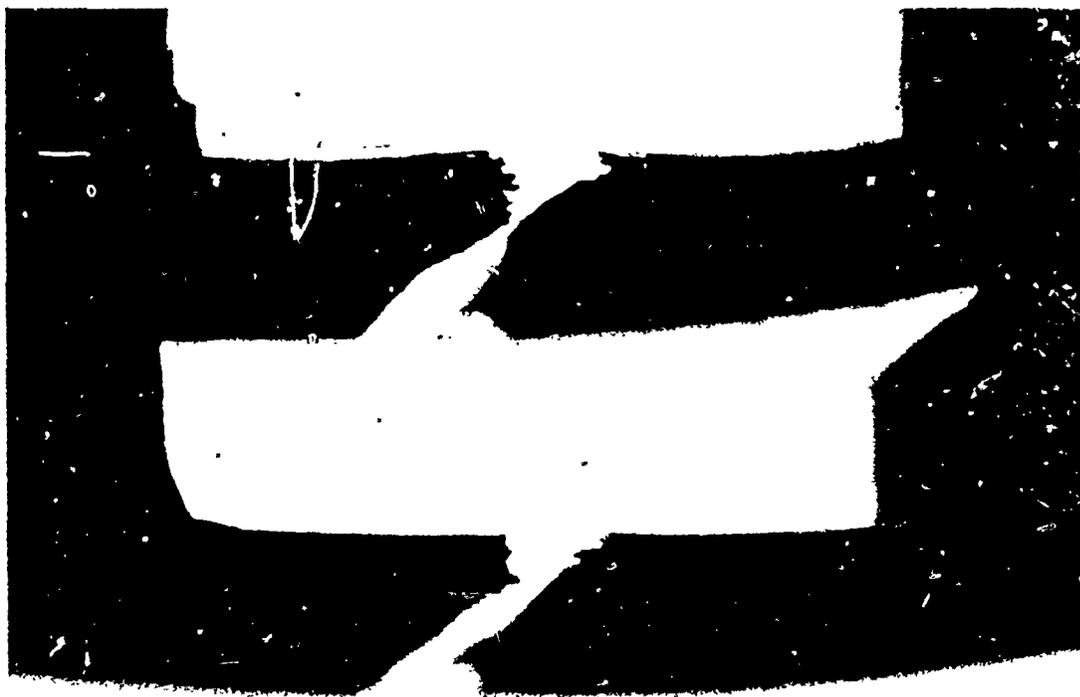


Figure 3. Flexure Test Specimen After Fracture With Large Cone Angles (top) Compared to Low Cone Angles (bottom).

integrity (Figure 4). After disassembly, the coating showed considerable additional damage (Figure 5). An adjacent secondary crack was discovered during microexamination showing the extensive delamination induced by high compressive strains during the firing (Figure 6).

Structural analysis effort was undertaken to attempt to optimize the insert design for these tests. A simple linear stress analysis method was used along with literature property values for pyrolytic graphite to arrive at the substrate groove configurations (Figure 1). A sensitivity study was also conducted to establish the effect of input property variations on substrate stress level. The coefficient of thermal expansion of the substrate was the only first order sensitivity on substrate stresses and outer diameter deflections after cool-down, with stresses increasing with increasing coefficient. Reductions in the thermal expansion coefficient of PG in the a-b plane and the c plane also increased substrate stresses and deformations. Changes in the substrate modulus caused proportional second order changes in the substrate stresses, but did not influence deformations. Experimentally, a 7-inch insert made by ARC, using an AGSR substrate, would exhibit an increase in outer diameter of 20 mils at the entrance end and approximately 10 mils at the throat and exit end. This represents a tensile hoop strain of 5 mils, where uniaxial tensile tests on AGSR graphite indicate a maximum tensile strain of 1.5 mils to failure. This observation underscores the lack of understanding of the mechanical behavior of AGSR graphite in complex stress fields. (AGSR is a commercial employed graphite with no previous Aerospace interest).

A nonlinear deformation theory stress analysis code was used to analyze the 7-inch insert using literature property values⁵. The plastic analysis predicted net displacements only one half as great as the measured displacements after cool-down. The analytical results suggest that substrate failure should occur as a consequence of cool-down, and compressive failure of the coating was likely if the insert was not permitted to expand during firing. For example, a 5 mil radial gap was considered insufficient, but a 16 mil gap would be structurally adequate. Since these

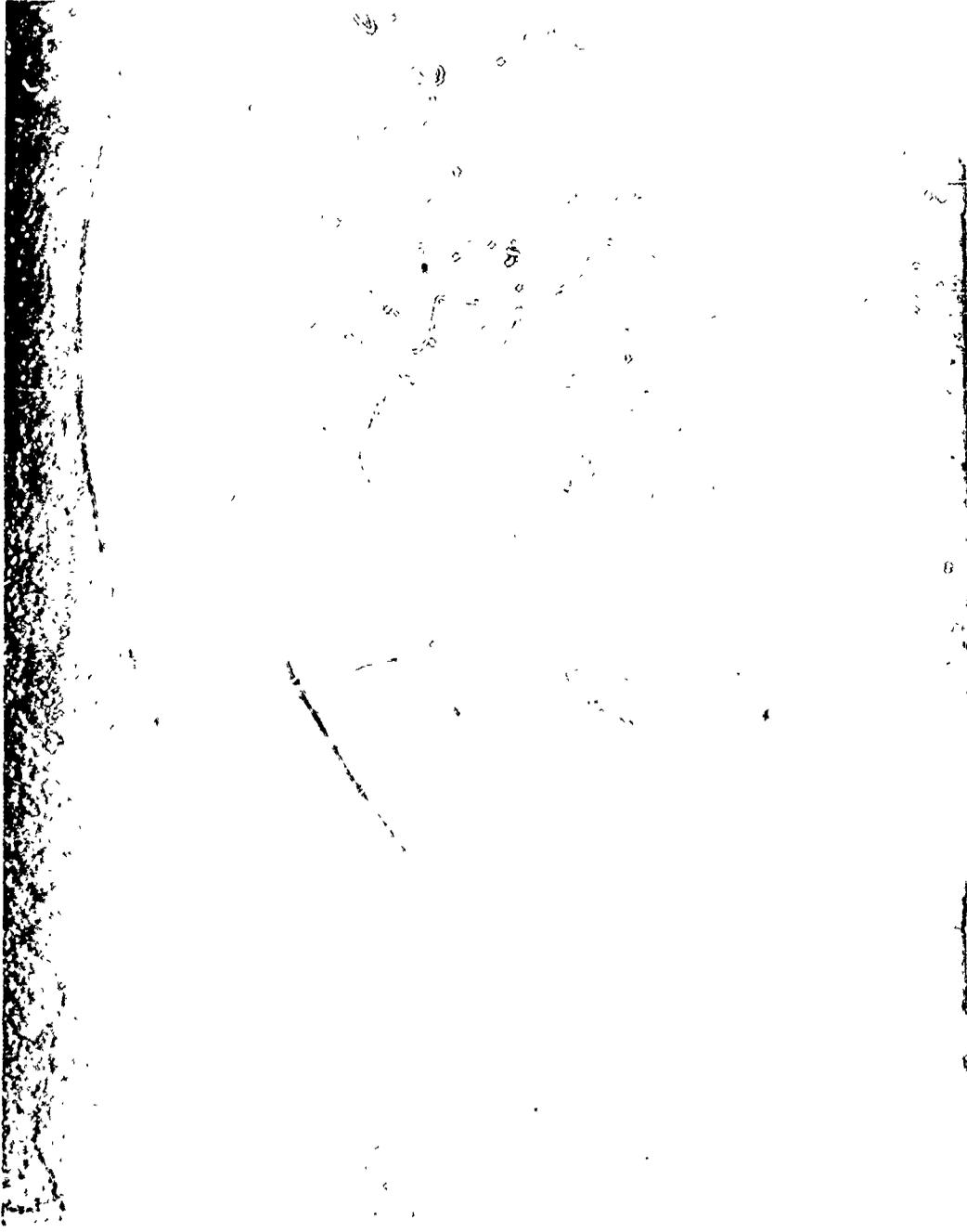


Figure 1. *Throat insert.* 15



Figure 5. Post Test View of Firing Damage, 7-inch Diameter Throat Insert.



Figure 6. Coating Section Showing Incipient Compressive Buckling Failure and Delaminations.

studies were completed, new property measurements on the ARC renucleated PG coatings and the AGSR substrate material have been published², and are shown in Tables 1, 2, and 3. The ARC continuously-nucleated material appears to have a significantly higher a-b plane expansion than the prior literature results on continuously nucleated plate material (produced at low pressures). The thermal expansion of AGSR graphite is approximately 15 percent higher than indicated in the literature. Use of the new properties in the stress analysis would result in lower cool-down stresses, but larger thermal gradient stresses in the coating, making the insert thermal growth problem during firing even more severe. The analysis and test results for large inserts suggest the possibility that the low strength levels of the AGSR substrate (and the wide property variation) may be unacceptable for reliable structural integrity.

SUBSTRATE NUCLEATED PYROLYTIC GRAPHITE

In 1969, a firing was conducted at AFRPL on a Boron Pyrolytic Graphite insert provided by the General Electric Space and Reentry Division⁷. This material was a substrate nucleated structure with 0.5 percent by weight boron addition. The insert had a 2.3 inch diameter throat with a 0.100 inch coating on ATJ graphite. The test conditions were \approx 750 psi chamber pressure and 22 second duration with a 6500°F flame temperature 27 percent aluminum propellant. An average erosion rate of 0.7 mil per second was measured. Several axial cracks and massive delamination and debonding at the insert edges were apparent after cool-down, some of which occurred during the firing. The substrate was nearly two inches thick and undoubtedly produced compressive failures in the coating.

Recently, a series of firings have been conducted on 2.3 inch diameter pyrolytic graphite throat inserts supplied by T. Parmee of the Rocket Propulsion Establishment (RPE) of the Ministry of Defense. The RPE coatings have been successfully tested in small sizes in a variety of environments and configurations⁸. This material is substrate nucleated

TABLE I THERMAL EXPANSION OF PYROLYTIC GRAPHITE, A-B PLANE

Ref.	Material	1000°F	2000°F	DL/L (x1000)		4500°F	5000°F	
				3000°F	4000°F			
	PG Plate SN	0-0.5	1.0-1.8	2.6	4.5	5.5	--	
5	PG Plate	0.212	(standard deviation 0.067 for 14 furnace runs)					
9	U.K. Coating SN	0.05	0.9	1.6	3.2	--	--	
19	ARC PG Coating CN	0.70	2.2	4.4	7.6	11	21	
16	Isotropic(Gulf/SiC/PG*)	1.3	3.3	5.8	9.7	11.9	13.4	
19	ARC SiC/PG CN							
13	Range	1-2	3-5	6-9	9-13	--	--	
	Typical 13%SiC	1.3	3.3	5.8	9.7	11.8	13.3	
	18w/o	1.4	3.6	6.4	10.4	12.6	14.2	
	27w/o	1.6	4.0	6.9	11.0	13.2	15.1	
	41w/o	1.7	4.3	7.5	11.5	13.7	15.4	

* Nominal 15w/c SiC
 SN Substrate nucleated microstructure
 CN Continuously nucleated microstructure

TABLE 2 THERMAL EXPANSION OF PYROLYTIC GRAPHITE, C DIRECTION

Ref.	Material	$\frac{10000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$	$\frac{2000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$	$\frac{30000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$	$\frac{40000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$	$\frac{45000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$	$\frac{50000^{\circ}\text{F}}{\Delta\text{L}/\text{L}}$
5	PG Plate SN	11-12	25-28	37-43	49-59		62-73
	PG Plate	13.5	(standard deviation 0.60 for 14 furnace runs)				
9	U.K. Coating SN	14	28	45	--	--	--
19	ARC PG Coating CN	9	22	36	50	55	37
16	Isotropic(Guif)SiC/PG*	1.3	3.3	5.8	9.7	11.9	13.4
19	ARC SiC/PG CN						
	Typical 13w/o SiC	1.8	5.0	9.5	15	16	15.5
	18w/o	1.3	4.3	8.5	13.5	15.5	16
	27w/o	1.3	4.4	8.3	12.3	14.5	15
	30w/o	1.5	4.6	8.4	12.5	14.5	14.5

* Nominal 15w/o SiC
 SN Substrate nucleated microstructure
 CN Continuously nucleated microstructure

TABLE 3 THERMAL EXPANSION OF GRAPHITES

Material	1000°F	2000°F	AL/L (x1000) 3000°F	4000°F	5000°F
AGSR (annealed)	WG 0.7	2.2	4.1	6.3	8.6
	AG 1.2	3.4	5.9	8.8	12
AGSR (fine grain U.K.)	WG 1.2	2.9	--	--	--
	AG 1.8	4.4	--	--	--
ATJ	WG 1.2	3.2	6.0	9.3	13.1
	AG 1.5	4.5	7.7	11.9	16.1
HLM	WG 1.4	3.5	--	--	--
	AG 2.0	4.7	--	--	--
SPEER882*	WG 1.2	3.6	--	11.6	--
	AG --	--	--	13.6	--
PO3 Isostatic	1.8	4.5	8	13	--

WG with grain
 AG across the grain
 * WG CTE for 35 billets - Average CTE 3.08×10^{-6} (0.17 standard deviation)

PG formed from acetylene at reduced pressures and conventional temperatures. The graphite substrate used by RPE for these inserts was small billet fine grain AGSR rather than the large billet coarse grain AGSR employed by Atlantic Research Corporation. The finer grain AGSR billets have a higher density and much better strength, but presumably a less compatible thermal expansion coefficient with the PG coating. The RPE inserts (Figure 7) are made with coating wrapped around the leading edge at least 1/4 inch and occasionally the entire front and rear face. Holographic interferometry inspection of these inserts always showed delamination (probably between the coating and substrate) of the front and rear faces⁹. The delaminations generally extended only 1/8 inch beyond the radius itself into the throat region and did not propagate during the firings.

The initial test involved a conventional insert configuration tested for 30 seconds in a 650 psi chamber pressure environment with 16 percent Al, 5700°F flame temperature PBAN propellant. The throat exhibited a total erosion of 0.0015 inches or an erosion rate of 0.025 mils/second. The post test appearance was excellent - many of the initial coating imperfections (small projections) were still clearly visible.

Two inserts with the full-front-face-wraparound-coating configuration were evaluated. The first insert was evaluated in the 16 percent Al, 5700°F flame temperature PBAN environment at 650 psi chamber pressure for 30 seconds. The measured erosion rate was 0.05 mils/second and the post test appearance of the insert was outstanding. A second exposure was conducted at 750 psi chamber pressure for 34 seconds using a 10 percent Al, 5250°F flame temperature PBAN environment. The measured erosion rate on this pulse was minus 0.15 mil per second for a net reduction in throat diameter with the two cycles. The coated insert was in excellent condition after both pulses.

The second wraparound insert was evaluated in a PVC gel propellant (Arcite 504) with 21 percent aluminum and 5600°F flame temperature. The test consisted of a 67 second exposure with 650 psi chamber pressure. The average throat erosion rate was 0.25 mils/second. The insert experienced

U. K. PG Insert



front face



Outer Surface Erosion

Figure 7. Post Test Appearance of the Substrate Nucleated UK PG Insert Exposed to Two Pulses of 5600oF PBAN Propellant

a hoop fracture during firing in one place through the coating and substrate, but did not break up. A number of secondary fractures occurred in the coating, apparently during the cool-down. The insert did not have the benefit of a backside expansion gap which is undoubtedly necessary for a full 60 second firing.

There are no stress analysis results available to support the RPE insert designs, primarily due to the lack of property measurements. Joint AFRPL/RPE efforts have been underway to correct this situation. Preliminary information is now available on the thermal expansion coefficients for the substrate nucleated plate from RPE and several potential graphite substrate candidates. The thermal expansion of the British pyrolytic graphite coincides with the lower bound of the prior measurements reported on U.S. substrate nucleated material for the a-b plane and the upper bound of prior measurements for the c plane (Table I and II). A series of unit cell height measurements (C_0 in angstroms) were made on the RPE material (10) indicating a range of values from 6.885 for the initially deposited material to 6.865 for the finally deposited layer in the coating. This is a slightly greater degree of order than found in the U.S. material.

Test firings will be continued on larger throat inserts supplied by RPE, with emphasis on 7-inch throat diameters. The test environment will be 16 percent aluminum, 5700°F flame temperature PBAN and 18 percent aluminum, 6300°F flame temperature HTPB propellants with 1000 psi chamber pressure. Holographic inspection will be employed on all inserts to eliminate (or at least document) any delaminations that might appear. If possible, design engineering work will be initiated when a property base is established.

A NASA-Lewis Research Center report published in 1968 describes a series of four firings of 7.8 inch diameter coated throat inserts in a liquid thrust chamber with 100 psi chamber pressure¹¹. Conventional substrate nucleated pyrolytic graphite coatings were employed. One insert was a 0.010 inch coating on a National Carbon grade PT0178 graphite substrate. The other three inserts used a graphitized graphite cloth phenolic resin

substrate developed by the Lewis Research Center with properties allegedly similar to grade PT0178. Coatings of 0.050 inch, 0.100 inch and 0.010 inch thickness were dequentially deposited and tested with the same substrate component. All four coated inserts exhibited delamination and cracking within 60 seconds.

LeCarbone has produced a variety of small pyrolytic graphite coated inserts, primarily deposited on thin molded graphite as substrates, using grades 3780 and 3730WEG¹². Good results were also indicated on grades 2239 and 5890 as well. The properties of these molded graphites are shown in Table 4 from reference 13, along with comparable data on ATJ, AGSR and PO3 graphite. LeCarbone has evaluated both substrate nucleated and "polynuclear" (continuously nucleated) pyrolytic graphite. No known applications for pyrolytic graphite have developed in France, limiting the process development to small components and plates.

There have been several attempts to make substrate nucleated pyrolytic graphite coatings with carbon-carbon composite materials. The manufacturers of these parts made them available for application of the holographic interferometry nondestructive evaluation techniques to look for delaminations and any other detectable discontinuities. A seven inch diameter throat was made with a Pycobond substrate, a CVD bonded graphite cloth. The coating thickness was 160 mils at the forward end and 140 mils at the aft end. Delaminations were visually evident at both ends of the inserts. The holographic examination indicated that the delaminations extended approximately 25 percent of the axial distance from each end through the insert. A second part with 12.5 inch inner diameter was made using the AGCARB carbon-carbon substrate. This inspection revealed several delaminations and voids in the substrate that were visible on the fringe patterns on the coating surface. Most of the forward end was delaminated. A few delaminations were noted in the aft end. The delaminations showed several degrees of "softness" that probably reflected delaminations at different thicknesses in the coating. The conclusion is that the coating-substrate compatibility must be satisfied before components

TABLE 4 PROPERTIES OF LeCARBONE GRAPHITE SUBSTRATES

Grade	Density (gm/cc)	Grain Size (10 ⁻³ inch)	Thermal Expansion Coefficient* (10 ⁻⁶ /°C)	Open Porosity (%)
3780	1.60	4-8	3	24
3780WEG	1.70	--	3.4	16
2239	1.80	--	4	10
5890	1.82	--	4.2	8
ATJ	1.73	6	2.2WG 3.4AG	--
AGSR (large cylinders)	1.54	250	1.2WG 1.9AG	--
PO3				

* Temperature range of 30-to-100°C

with structural integrity can be expected. It will be fortunate if any of the present commercial graphites or carbon or graphite composites satisfy the compatibility requirements.

TECHNOLOGY REASSESSMENT - PYROLYTIC GRAPHITE

The lack of success in the development of large pyrolytic graphite coated throat inserts naturally produces a reexamination of the technology elements required to solve the problem. The three most important weak elements are (1) availability of an adequate substrate; (2) critical property characterization and (3) engineering design criteria for use of the component in a rocket nozzle application.

The most important influence on coating-substrate compatibility is the thermal expansion behavior, since a coated part must cool down from the typical 4000 degree Fahrenheit furnace temperature without failure. Excessive residual stresses would reduce the strength available to withstand the loading from the motor environment. In the literature, one finds insufficient data and conflicts in the reported values that are available. Serious variation of thermal expansion behavior appear typical in many conventionally processed graphites. The overall measurement accuracy of thermal expansion at elemented temperatures is probably 5 percent and variability in a material like ATJ appears to be at least 10 percent. Table 3 shows some "typical" thermal expansion values for routine commercial graphites. AGSR is the only graphite listed with an expansion close to the ARC pyrolytic graphite and prior tests show that AGSR has insufficient mechanical properties to survive the environment. It is possible that the AGSR could be reinforced after manufacture with resin reimpregnation or carbon vapor decomposition to improve the substrate properties. Other substrates could perhaps be found with suitable thermal expansion properties.

The ideal solution to this problem may be to develop a carbon-carbon composite substrate tailored to the properties of the coating; the Air Force Materials Laboratory will be supporting development work in this area.

Even then, the low pressure pyrolytic graphites and the ARC atmospheric pressure pyrolytic graphite differ by as much as 2x in thermal expansion, and two separate substrates may be required.

A second weak element is the state of property characterization for both pyrolytic graphite and substrate materials. Thermal expansion data must be quite accurate to provide reasonable stress analysis results and there is significant variation in published data and in the commercially available materials. Values of thermal conductivity for PG in the a-b direction found in the literature are shown in Figure 8. The data published by Southern Research Institute (SRI) on the ARC continuously-nucleated PG falls in the band of previous SRI results on PG plate. Two additional curves, marked company A and B, represent the data input used by two solid propellant companies in their computer thermal analysis programs. The differences, while not shocking, do represent the difficulty of establishing valid input properties and could influence the usefulness of design analysis on a critical problem like a pyrolytic graphite shell in a severe thermal environment. The a-b plane variations are of greatest concern for analysis of PG washer configurations.

Similar problems exist with c direction thermal conductivity, but for different reasons. The c direction results are influenced by microflaw structure that varies widely with processing, pressure, and test atmosphere. The data published by Southern Research Institute on the ARC continuously-nucleated PG falls very close to the c direction data published in the LMSC Polaris Materials Manual (Figure 9). The curves shown for company A and B again imply some significant variations in critical thermal analysis results. The c plane variations affect the thermal gradients and, therefore, the compressive strain levels in the coating, believed to be the primary failure mode of concern. This range of property variations could produce significant variations in calculated strains and failure mode conditions. Stress-strain curves are required for the nonlinear structural codes, at both elevated and room temperatures, and in compression as well as tension. This type of information is hard to find. The review published by Bradshaw and

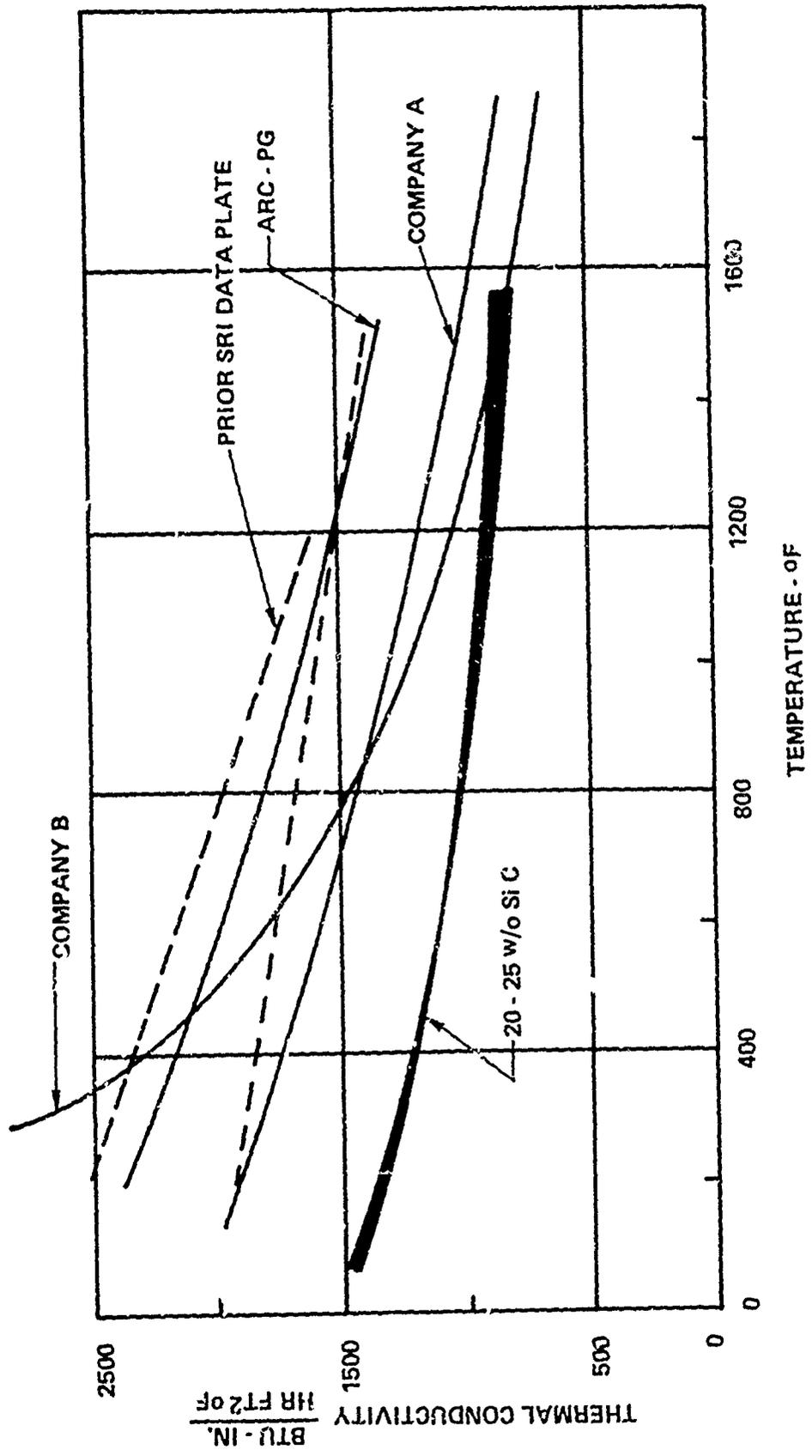


Figure 8. Thermal Conductivity in the 'A-B' Direction

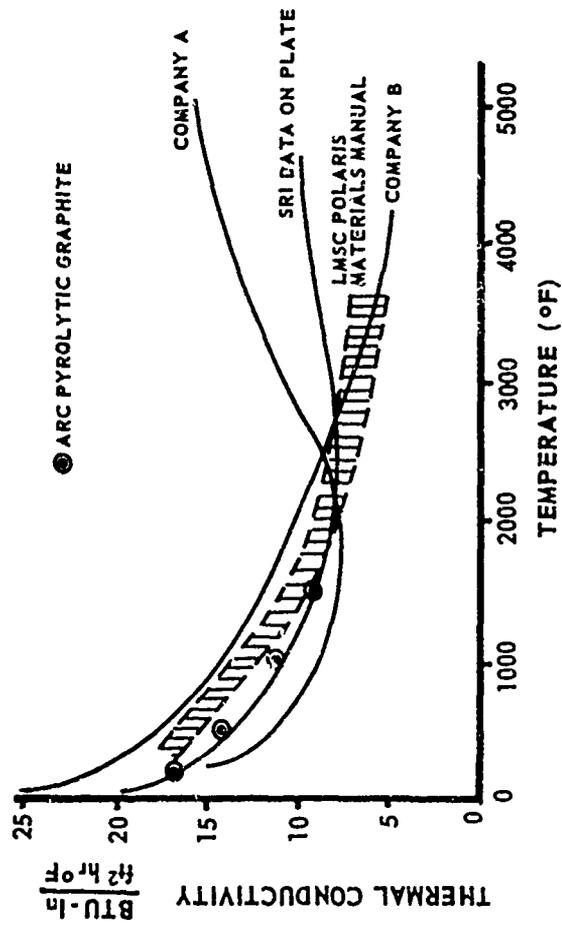


Figure 9. C Direction Thermal Conductivity Pyrolytic Graphite.

Armstrong¹⁴ remains the best available review on the variation of properties in pyrolytic graphite and the sources of such variations.

One caution needs to be exercised on measurement of properties for thin coatings. Testing specialists for elevated temperature properties prefer long specimens of reasonable thickness with no curvature. Specimens cut from large plate are very reasonable to the test artist. However, deposition conditions for plate may differ in significant flow parameters compared to short inserts with double curvature. The task of extracting reasonable samples of representative material to accurately measure high temperature properties may be unsolvable for many properties of interest. A reasonable alternate to the complete solution of the testing problem is the use of subscale inserts made under conditions similar to real inserts and tested in a manner that simulates as closely as possible real nozzle environments. The thermal stress specimen developed by TRW (Figure 10) provides a reasonable heat flux simulation delivered to the inner surface of a 1-2 inch cylinder using an electron flux in a vacuum¹⁵. The clean environment permits very accurate instrumentation for temperature and deformation measurements. Reasonable surface temperatures, thermal gradients and heating times of 60 seconds can be simulated. The pressure of a firing is not simulated, and the change in stress state that accompanies erosion processes is absent. The residual fabrication stresses are those typical of small, rather than large, inserts, but can be varied by coating/substrate geometry variation and special test techniques¹⁶. These limitations do not prevent the effective use of the thermal stress results to "calibrate" the structural models intended for ultimate design engineering. Thermal gradients can be measured directly to confirm (or adjust) thermal conductivity properties. Diametrical dimension measurements permit confirmation of thermal expansion properties. Strain gages permit confirmation of stress analysis models. Axial dimension measurements permit similar calibrations in the axial direction. Variations in specimen dimensions and heat flux can be used to examine the failure modes associated with thermal gradients, especially compressive strain failures in the coating

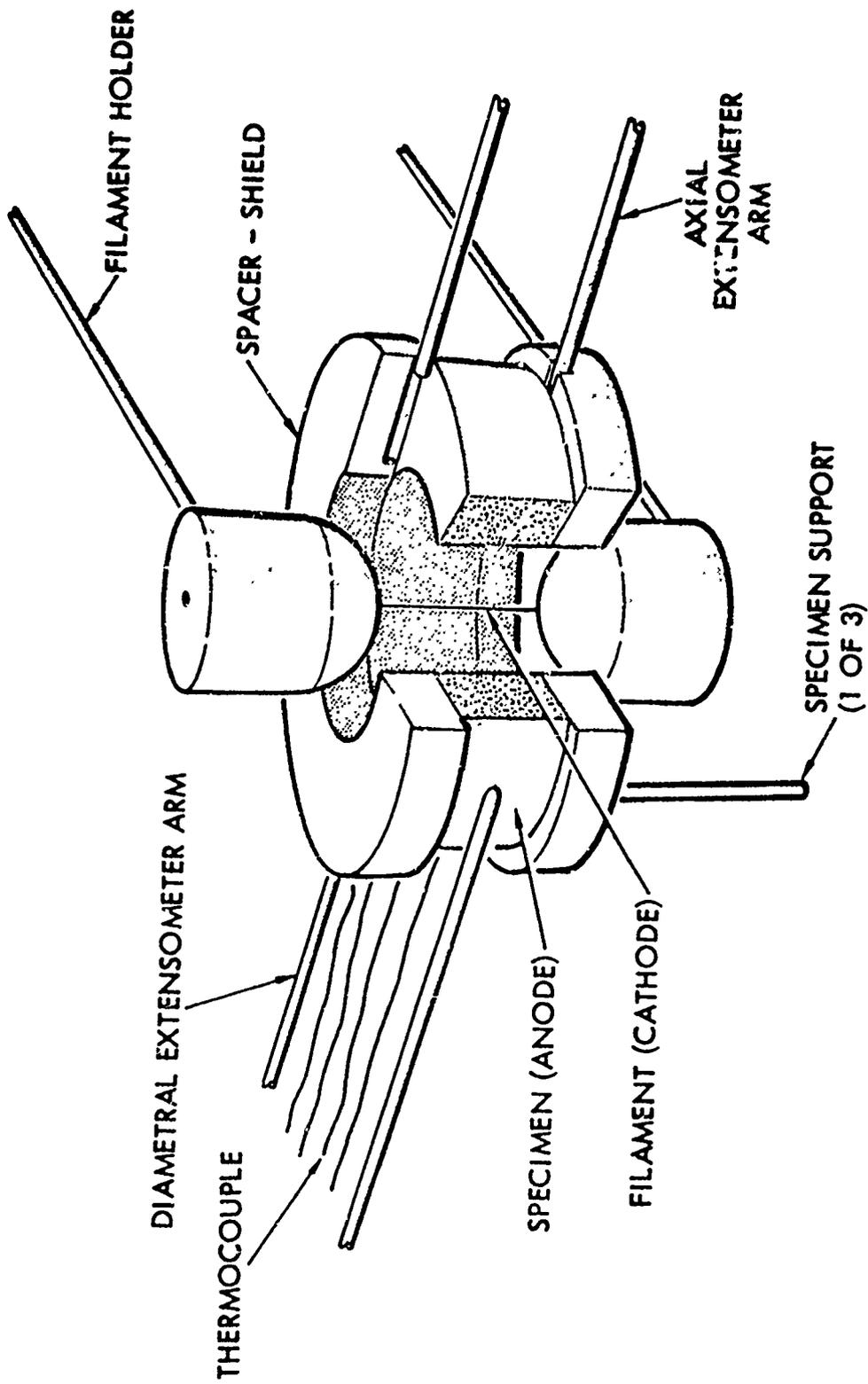


Figure 10. Electron Gun, Thermal Stress Test Specimen, and Extensometer.

and outer diameter tensile failure of the substrate. Coupled with instrumented burst tests of full size inserts and other routine evaluations, a reasonable picture of the engineering properties of inserts in the motor environment could be obtained.

The third weakness is the lack of overall design criteria for structural integrity in the nozzle assembly. Normally, a .002 to .005 inch gap is provided between parts to facilitate assembly. The gaps are then filled with an adhesive during fabrication. These gaps seem to work satisfactorily for small diameter inserts, but large inserts will require gaps of 0.010 to 0.050 to facilitate thermal expansion without introducing additional compressive strains into the coating. The gap material must provide support for the cold insert to prevent tensile failure of the substrate upon pressurization. If the gap material decomposes too soon, gas paths will be created that would allow pressurization behind the insert and produce compressive spallation of the coating. The gap material really becomes a critical structural member in the overall design, along with the gap size and insulation-material-support characteristics. The structural analysis needs to incorporate realistic models of these gaps and gap materials. Present models simply assume the adhesives disappear at some temperature and examine the limiting conditions. No critical laboratory work has been accomplished to investigate the structural response of the available gap materials. In fact, an experimental technique to conduct the work has not been developed. The TRW thermal stress specimen could be used to evaluate non-ablative fillers, such as grafoil or variable density carbon foams, using a complicated double cylinder sandwich technique. However, the need for a clean vacuum environment precludes investigation of the thermally decomposing adhesives commonly used in nozzles. The engineering control of the insert gap is vital to successful use of low strain capability graphite materials. The gap problem may not be as important with carbon-carbon substrate materials.

SILICON CARBIDE MODIFIED PYROLYTIC GRAPHITE

The pyrolytic graphite literature contains many attempts to chemically modify pyrolytic graphite with boron and hafnium and zirconium. The

strengths are improved, but the property changes are often detrimental for coatings bonded to available graphites. Some outstanding work on isotropic coatings with silicon carbide additions has been reported by Bokros and co-workers¹⁷. In 1971, effort was initiated at Atlantic Research Corporation to pursue silicon additions in an atmospheric pressure codeposition process with continuously-nucleated-anisotropic coatings (abbreviated SiC/PG). Under certain process conditions, the silicon carbide phase deposits as needles perpendicular to the deposition surface, providing reinforcement in the c direction and vastly improved shear strength between the a-b layers of the pyrolytic graphite matrix. The SiC/PG coating could be deposited on ATJ graphite, an aerospace grade with reasonable definition of properties and superior mechanical properties compared to AGSR. The bond between the coating and substrate was outstanding - coating separations from the substrate, even in mechanical tests to failure, were not observed. The thermal stability of SiC is expected to be poor, since it begins to sublime at 4300°F and dissociates below 5000°F at atmospheric pressure. Firings indicate the decomposition zone is shallow and the reinforcement effect remains operative in the bulk of the coating.

The early development involved small throat inserts and exploratory firings to establish target compositions and morphology, and to provide preliminary performance data^{18,19}. A preliminary set of design properties were generated in several research programs, along with small insert firing data²⁰. Deposition efforts were sponsored to learn how to make large inserts for possible ICBM applications requiring throat sizes as large as 13 inches in diameter. Holographic inspection was applied to verify freedom from delaminations, although the type of cracks typical for thin pyrolytic graphite coatings have not been experienced in the ARC prototype components. A substantial amount of design engineering analysis was accomplished initially with linear stress analysis methods and finally with more sophisticated nonlinear codes such as DOASIS (Aerotherm) and SAASIII (Atlantic Research Corporation and TRW). Particular emphasis was placed on the "calibration" of engineering design models using the TRW

thermal stress specimen. Thermal stress testing provides a verification of thermal conductivity and of thermal expansion parameters and permits an exploratory investigation of failure modes and conditions.

From a property standpoint, the SiC modification has been very successful. The introduction of 15 to 20 weight percent SiC produces a nearly isotropic material with the thermal coefficient of expansion in the range of reasonable-quality-graphite substrates such as ATJ as shown in Figure 11. The addition of SiC to PG increased the strength, stiffness, and strains-to-failure in both tension and compression over the temperature range 70°F to 3000°F. The c direction thermal conductivity is increased by the SiC, ranging from a factor of 3 at high temperatures to 10 times at low temperature (Figure 12), while the a-b plane thermal conductivity is reduced perhaps 40 percent (Figure 8). This compromise in insulation ability is not a serious drawback.

The deposition development has progressed from the small one inch diameter inserts to successful manufacture of 3.5-inch, 7-inch and 12.5-inch diameter inserts with coatings from 0.150 to 0.300 inches thick. A 12.5-inch diameter prototype insert is shown in Figure 13. Some process optimization effort is still required for the 7-inch and 12.5-inch diameter inserts. Coated entrance and exit rings are being developed, as well as the throat insert. An in-process 4000°F annealing treatment has been adopted for the 7- and 12.5-inch inserts after deposition of the coating in order to provide slight thermal coefficient adjustment of the coating to minimize the cooldown residual stresses. The magnitude of cooldown residual stresses in 12.5-inch inserts is now being measured by J. Baetz of Aerospace Corporation. Metallography and unit cell height measurements have been used to characterize the coatings on inserts of various size. Some variations between different sizes occurs because of the different furnaces, injectors, internal configurations, and flow rates employed. The exact source of the variations is not understood because of the inadequate process research for pyrolytic deposition reactions. With experience, conditions are modified to allow production of very similar coatings in the various

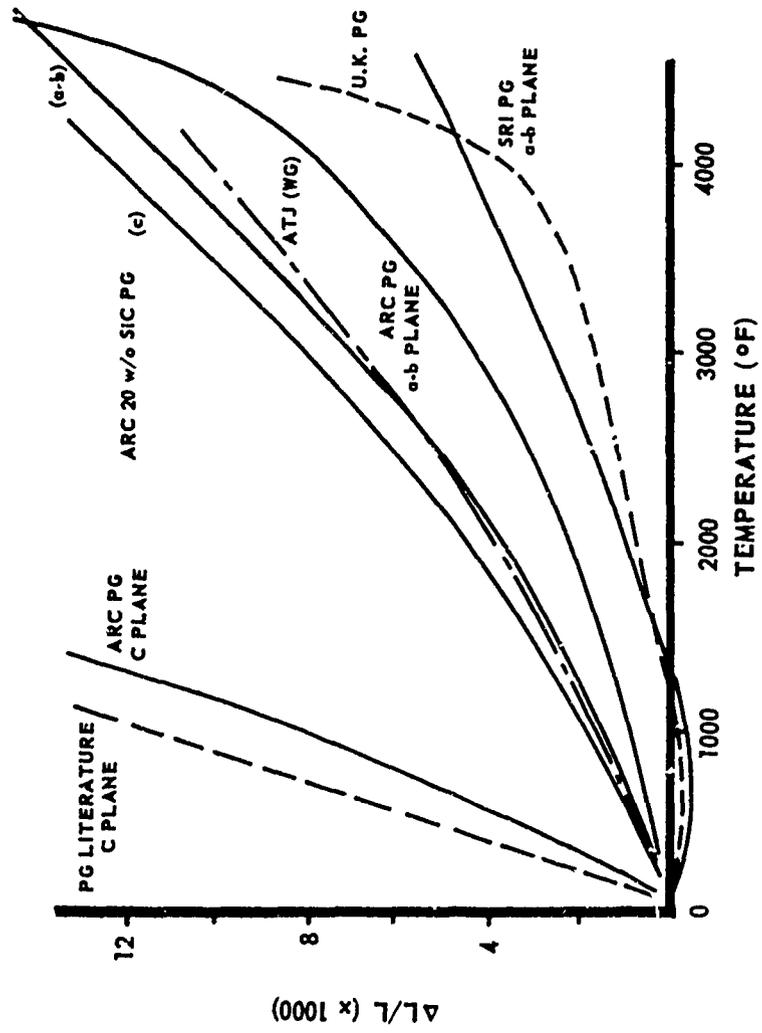


Figure 11. Thermal Expansion Results.

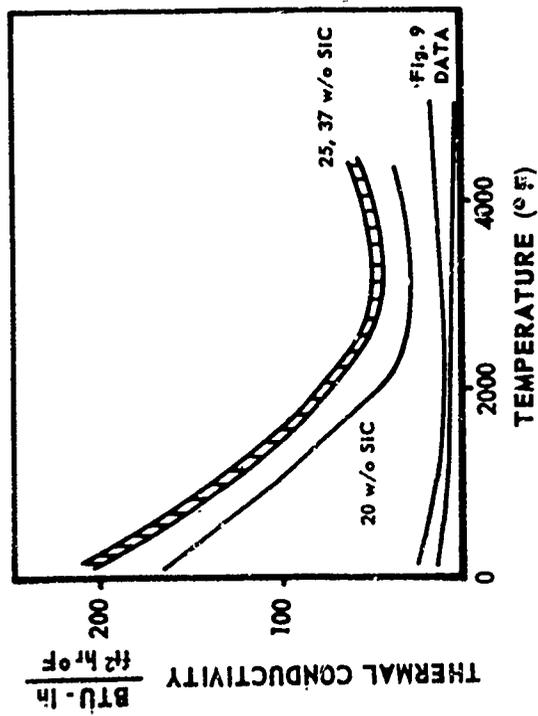
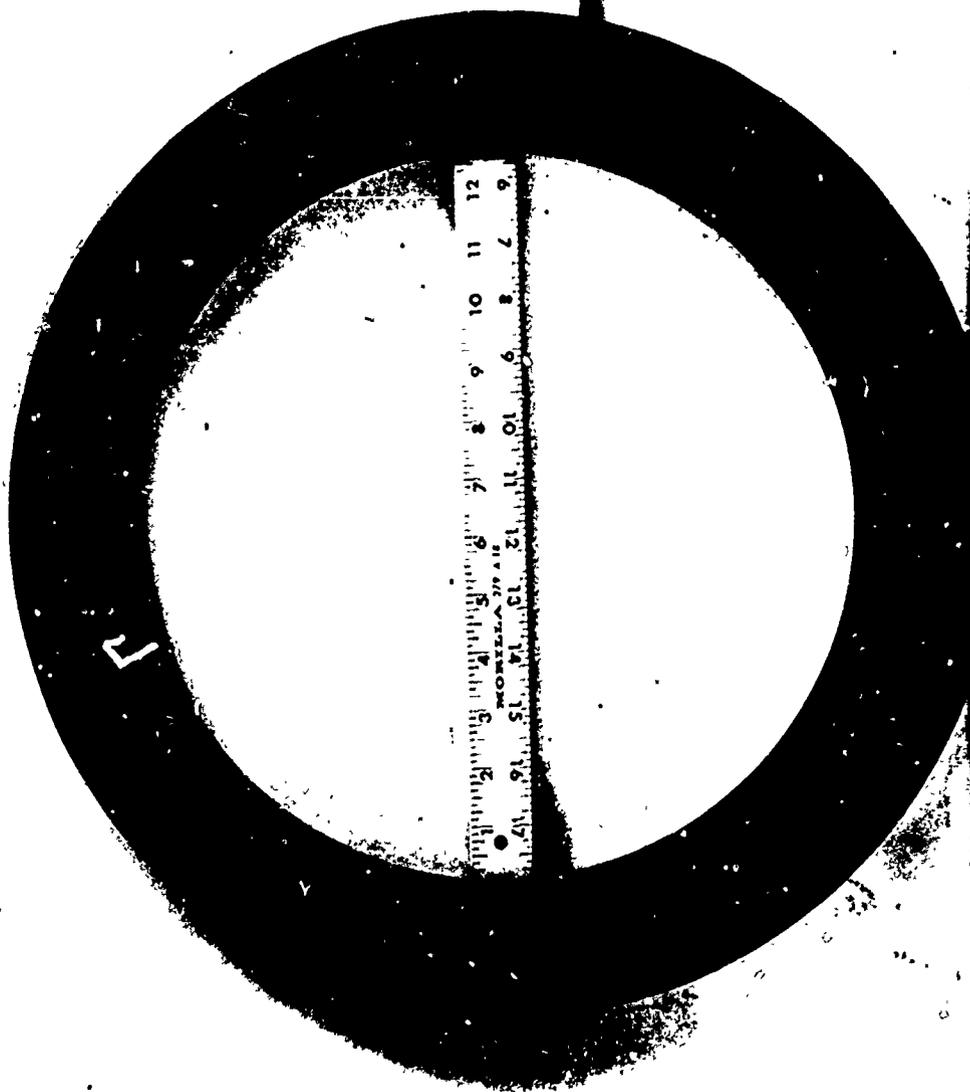


Figure 12. C Direction Thermal Conductivity.



sizes. Typical unit cell heights for the pyrolytic graphite (density of 2.14 gm/cc) produced in the 3300°F reaction with methane and methyltrichlorosilane have been 6.82 to 6.90 angstroms on the finally deposited material and 6.78 to 6.84 angstroms on the substrate side. Machining of the coating is possible with diamond tools required because of the hardness of the coating. Nearly all the deposition effort has been with ATJ substrates, although some experience has been developed on HLM graphite and a few trials conducted on SPEER 8882 and experimental carbon-carbon substrates. An example of a SiC/PG coating on a carbon-carbon substrate is shown in Figure 14. The substrate is a 45 degree cloth-layup material processed by Sandia Corporation with a laminate thermal expansion close to that of ATJ graphite in the grain direction. The coating is nearly 180 mils thick with a composition of 18 percent SiC.

Significant experience has been gained on SiC/PG coatings using the TRW thermal stress specimen. The variables of composition and geometry (coating and substrate thickness) have been examined. Compressive failures of the type expected during firing conditions have not been experienced using the test conditions employed to simulate the real motor environment. Special test techniques, specifically backside constraint, are required to produce inner bore compressive strains comparable to actual designs. The techniques have been employed for graphites¹⁶ and are now being employed in the final SiC/PG tests at TRW. A failure mode frequently encountered is a tensile strain failure during cooldown associated with the "stress reversal" effects. During cooldown, peak tensile strains are developed comparable to compressive strains developed during the heating cycle. Apparently, the SiC/PG has a much lower strain-to-failure in tension than in compression. The tensile failure strain after stress reversal in the thermal test was 0.3 percent compared to a failure strain of 0.5 percent in a uniaxial tensile test.

The "stress reversal" cracking tendency means that inserts and coated components might fracture after completion of the firings and such cracks will show up during post test evaluation. These cracks are cosmetically

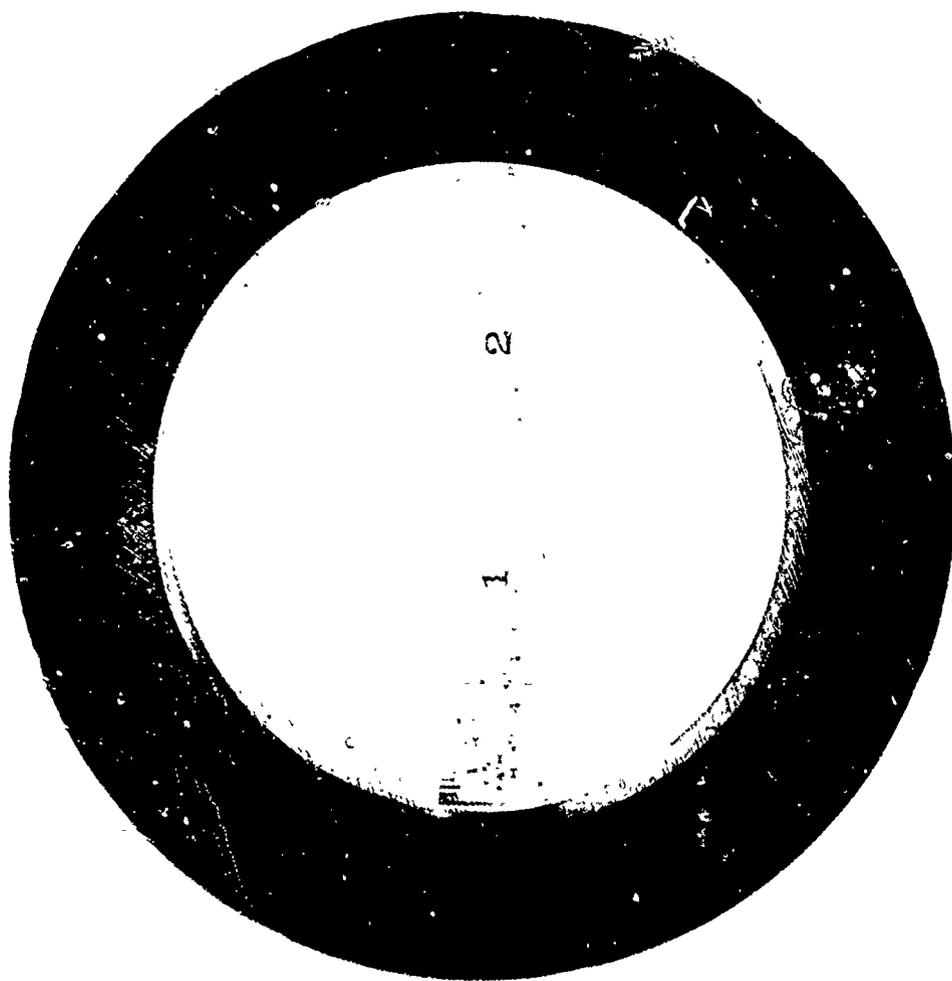


Figure 14. Thick SiC/PG Coating on a Sandia Carbon-Carbon Substrate.

undesirable, but would not preclude single cycle application of SiC/PG. The testing of thicker annealed specimens is now underway and preliminary indications are that the "stress reversal" cracking tendency may have been reduced or eliminated by the heat treatment.

Test results so far show confirmation and contradiction of this behavior. Considerable cracking has been observed in the high pressure 1.7 inch throat diameter nozzle components, probably of the stress reversal type during cooldown. Interestingly, no such cracking has been observed in four 1000 psi pressure firings of 3.5 inch throat diameter hardware. A very successful low pressure liquid engine test was conducted at AFRPL on a SiC/PG insert that included four restarts with no cracking evident²¹

In addition to failure criteria, the thermal stress results have been used to assess the adequacy of input properties to the structural models. Measurement of thermal gradients in the coating during the electron beam heating tests suggest that the effective thermal conductivity in the c direction is perhaps 80 percent higher than reported in the laboratory test program. The thermal expansion data was essentially confirmed by the thermal gradient tests.

A variety of firings have been conducted to establish the erosion rate potential of the SiC/PG. The entire approach is based on the idea that a modest erosion rate penalty could be accepted if sufficient benefit in insert properties could be achieved. Table 5 provides a summary of erosion rates measured in sizes up to 3.5 inch throat diameter. The test inserts represent a range of compositions, microstructures and arbitrary design conditions. Probably the best interpretation to apply to these results is that the better results represent the potential of the SiC/PG coating when a reproducible production process is established. The combination of high pressure and CTPB propellant produces undesirably high erosion rates. This high erosion rate would preclude high performance air launch motor application except for short duration burn times. Performance in high temperature propellants at moderate pressures is very reasonable. Apparently, chamber pressure has more influence on erosion

TABLE 5 SUMMARY OF EROSION PERFORMANCE OF SiC/PG COATED GRAPHITE

Reference	Throat Material	Throat Diameter (inches)	Propellant Type	% Aluminum	Flame Temperature (°F)	Maximum Pressure (psi)	Duration (sec)	Erosion Rate (mils/sec)	Number of Firings
(19)	PG coating	1	PVC gel (Arcogel 112D)	28	6500	1100	27	1.2	1
19	PG washers	1	"	28	6500	1100	54	2.3	1
19	SiC/PG	1	"	28	6500	1000-1200	26-60	3-3.6	5
19	ATJ graphite	1	"	28	6500	1100	39	4	1
19	SiC/PG	1	PVC gel (Arcogel III)		6000	1000	66	2.8	1
22	SiC/PG	2.3	PBAN (UTP3001)	16	5700	700	30	0.8	1
(20)	SiC/PG	1	PVC gel (Arcite 373)	21	5600	2400	21	3.6	1
20	SiC/PG	1	"	21	5600	2900	11	7	1
20	SiC/PG	1	PVC gel (Arcite 493)	5	5100	1960	22	1.7	1
20	SiC/PG	2	PVC gel (APD 112D)	27	6500	1100	12	3-4	2
	SiC/PG	1.7	PBAN (UTP3001)	16	5700	2000-2600	20	5-8	4
	SiC/PG	1.7	CPTB (UTP11475)	18	6010	2600	12	16	2
	SiC/PG	1.7	CTPB (UTP13615)	5	5360	2800	12	9	1
24	SiC/PG	3.5	PBAN (UTP3001)	16	5700	1000	5-15	4-6	4

rate than flame temperature. The addition of SiC also appears to provide reasonably good erosion resistance in oxidizing (low aluminum content propellant) environments. The presently unanswered question is the performance of large inserts in advanced propellant systems. Tests will be conducted in 1974 on 7-inch inserts with advanced propellants. Kinetic reaction coefficients will also be measured in 1974 so that motor designers will be able to predict the likely performance in propellant environments of present and future interest.

Several stress analyses were conducted²⁵ with SAAS III finite element nonlinear stress analysis program developed by Crose and Jones of the Aerospace Corporation. The cooldown stress condition for the codeposited coating is mild tensile stresses in the coating and mild compressive stresses in the ATJ substrate. Compressive strains in the coating reach values of 1 to 2 percent early in the firings, with a significant decreasing strain gradient through the coating. Uniaxial compression testing could not be successfully conducted at these high temperatures and strains, but did indicate strains over 1 percent without failure. Based on experimental thermal stress tests, cooldown cracking would be expected providing any coating remains after the firing. Tensile strains build up at the substrate outer diameter at longer times (like 20 seconds) into the firing approaching the uniaxial capability of the ATJ graphite. All of the long duration calculated stresses and strains are very sensitive to the backside restraint and erosion rate assumed. Unfortunately, erosion rates are not yet predictable, and structural modeling for gaps filled with thermally decomposing adhesives and restraint from phenolic insulation sleeves is at best a crude estimate. Accurate long exposure stress analysis can only be expected after at least initial testing is conducted. The analysis results quoted above were generally conducted with an estimated erosion rate less than experienced in the tests. The numerical values are very much in doubt, except for the cooldown stresses. However, the general failure modes predicted seem to correspond to the post test analysis. When completion of the analytical erosion model is completed, realistic erosion rate predictions will be available to permit more realistic stress analysis.

The microstructure of the SiC/PG coatings is a fine distribution of particles and c-direction needles, quite difficult to describe quantitatively. SiC particle size has tended to become finer with development work in a given furnace size, and the particle size in one inch diameter parts is now difficult to resolve with optical techniques. The initial experiments with larger furnaces for the seven and 12 inch diameter parts produced fairly large SiC needles. Subsequent development work has produced needle distributions tending toward the normal size range. Examples of the range of microstructures encountered are shown in Figure 15.

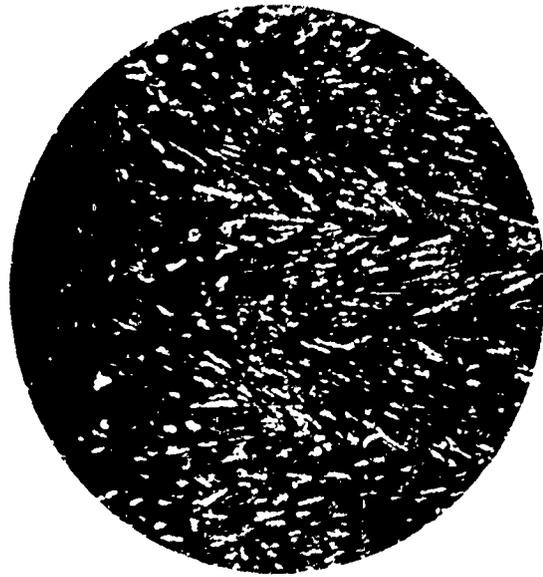
Limited scanning electron microscope examinations have been made on the codeposited silicon carbide pyrolytic graphite. Figure 16 shows several different surface appearances from deposited parts. The modular appearance is evident at the low magnification. The SiC and PG matrix are deposited independently and the SiC particles appear to lead the PG matrix in 16 (c) while equal rates are implied in 16 (b). The coating was annealed in hydrogen at 4000°F in Figure 16 (d) and the surface SiC has apparently decomposed. During firing, the SiC particles are decomposed by the gases, typical for a depth 0.003 to 0.005 inches as shown in Figure 17. The appearance of a fracture face from a thermal stress specimen is shown in Figure 18. The cone structure of the coating and contrasting features of the ATJ graphite substrate are clearly visible.

ADVANCED MATERIALS

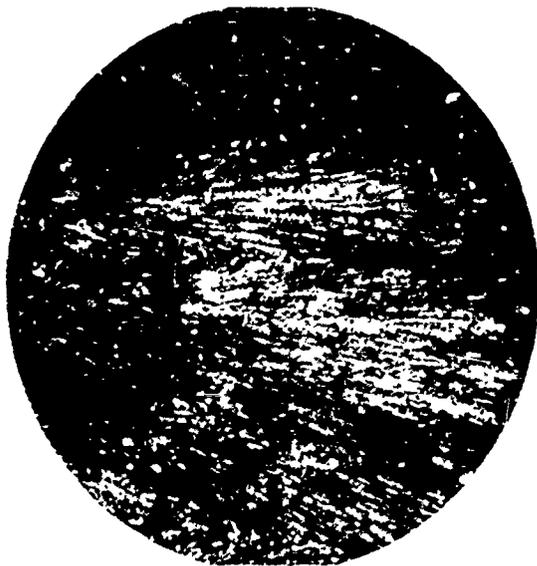
It seems likely that new composites will emerge eventually to provide improved structural integrity in severe environments. Goetzel²⁶ identified many of the possible material systems that could be developed. Most of these systems will require an organized engineering development, rather than an arbitrary development pattern. Their development for nozzle inserts is likely to be slow, because of indirect payoff rather than direct performance improvement. Research efforts should be continued to develop a knowledge of processing variables and resultant behavior of a range of these refractory composites.



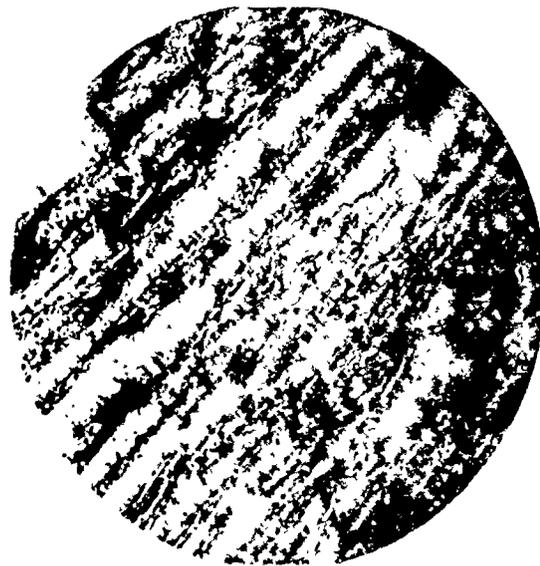
a. 21 w/o SiC-Fine Distribution



b. 25 w/o SiC-Normal Distribution

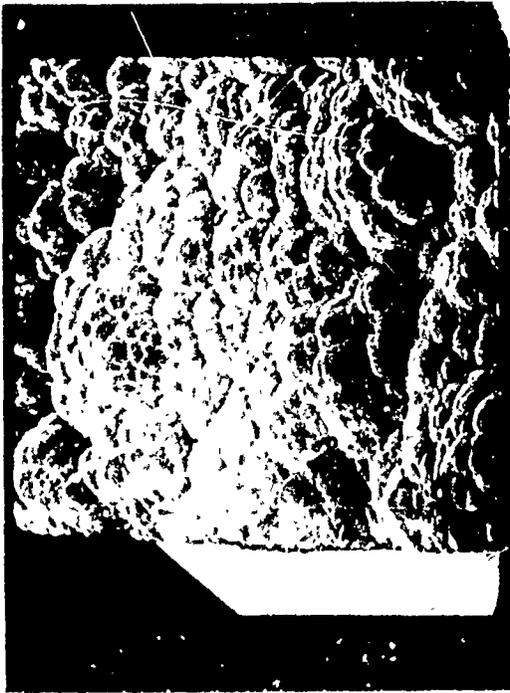


c. 25 w/o SiC-Long Needles



d. 30 w/o SiC-Coarse
Needle Structure

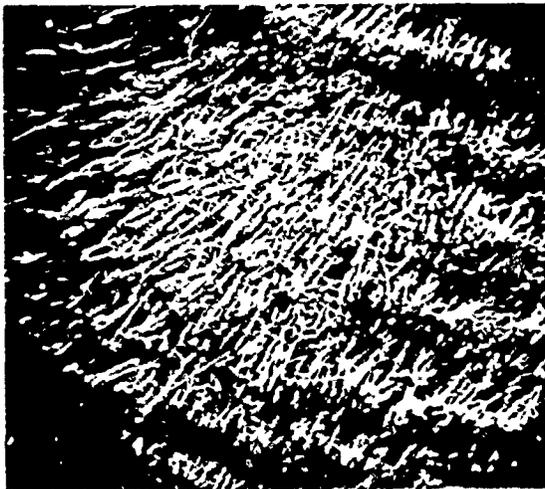
Figure 15. Range of Microstructures Observed with SiC/PG Coatings(x225)



a. Cone Structure (x40)



b. Cone Surface (x4000)



c. SiC Network (PG
Removed) (x1000)



d. SiC Network (PG
Removed) (x5000)

Figure 16. Scanning Electron Microscope Views
of Deposited SiC/PG Surfaces.



Figure 17. SiC/PG Microstructure After Firing (Reference 18).



Figure 13. Fracture Surface of Thermal Stress Specimen Showing the Coating Cone Structure (bottom) and ATJ Graphite (100x).

Limited feasibility studies have been conducted on the use of the SiC/PG coated ATJ system as a "substrate" for deposition of the erosion resistant high temperature PG coating. ARC²³ reported two firings of one inch throat diameter nozzle inserts with "graded" coatings, as shown in Figure 19. These two firings indicated a higher erosion rate than previous PG/AGSR firings, possibly due to spallation. Additional development work is necessary with this complex system.

Some interesting work has been reported on fiber reinforced pyrolytic graphite (Pyrostrand) from the Atlantic Research Corporation^{27,28}. Pyrostrand is a graphite fiber composite with continuously nucleated pyrolytic graphite matrix. A broad range of properties is theoretically possible by variation of specific fiber (or yarn), fiber loading and geometry. The firing results so far have been small diameter inserts with considerable variation in reinforcement materials. The erosion rates have been significantly higher than for pyrolytic graphite coatings. More significantly, some firings have experienced spallation and massive failure in a few instances. Achievement of structural reliability with Pyrostrand will apparently require a significant development effort to identify the right ingredients and control the manufacturing process. Design properties will also have to be developed, and design models will have to be calibrated with thermal stress tests.

The Marquardt Corporation, under NASA sponsorship, has, since 1961, investigated the use of pyrolytic refractory materials in liquid rocket thrust chambers. The capabilities, limitations, and properties of more than thirteen different pyrolytic refractory materials have been evaluated theoretically, experimentally, and in rocket thrust chamber firings with earth storable and fluorinated propellant combinations^{29,30,31,32,33}. During these programs, the strength and reproducibility of free standing pyrolytic refractory components were materially improved through the cooperative efforts of the several pyrolytic materials producers.

The development of improved, free standing pyrolytic graphite components for fluorinated propellant thrust chamber application was



Figure 19. "Graded" Coating - Pyrolytic Graphite on a SiC/PG Coating and ATJ Substrate.

achieved and demonstrated during an Air Force funded program³⁰. More than 40 free standing PG thrust chambers were fired with four different propellant combinations for a total firing time of more than 65 minutes. This included one 16 minute firing with LF_2/MMH propellants at a 1000 pound thrust level using a PG thrust chamber weighing only 19 ounces. While this program demonstrated the high temperature operating capability of pyrolytic materials, the program also defined the need for greater fabrication flexibility and structural design criteria for operation at higher chamber pressures. The size of thrust chambers varied from 1.5 inches in diameter (100 lb thrust) and 6-9 inches long to four inches in diameter and 12 to 14 inches long. Chamber pressures ranged from 100 to 3000 psi.

Considerable effort has been expended on PG coatings on a Carb-I-Tex 713 shell and a PG shell overwrapped with thermal 50 graphite filament and infiltrated with PG. Other concepts evaluated include PG infiltrated carbon felt (Pyrobond), pyrocarbide (zirconium or hafnium alloyed PG) infiltrated carbon felt and multilamina pyrocarbide alloys with varying composition in the individual lamina. Some evaluations were conducted with pyrocarbide washers, although the processing of plate, even small plate, is presently very difficult²¹. Attempts to deposit ternary PG alloys, such as Hf-Ta-PG and Hf-Si-PG were unsuccessful.

The pyrocarbide alloys, containing zirconium or hafnium additions, are apparently composites with very small, ordered carbide particles distributed in the pyrolytic graphite (much like a precipitation hardened metal). Significant improvements in strength and modulus occur. In strongly oxidizing environments, improved oxidation resistance is achieved. The effect of alloying on thermal expansion is shown in Figure 20 and 21 for several compositions. The thermal expansion of PG produced at 1850°C in the same facility is included for comparison. The 20w/oZrC PG is still very anisotropic but the 70w/oZrC is nearly an isotropic material in thermal expansion. Oddly, the expansion of the 70w/oZrC is nearly identical to the expansion of the "Isotropic PG" (15w/oSiC) produced by Bokros in the fluidized bed. The effects of alloying on thermal conductivity at low

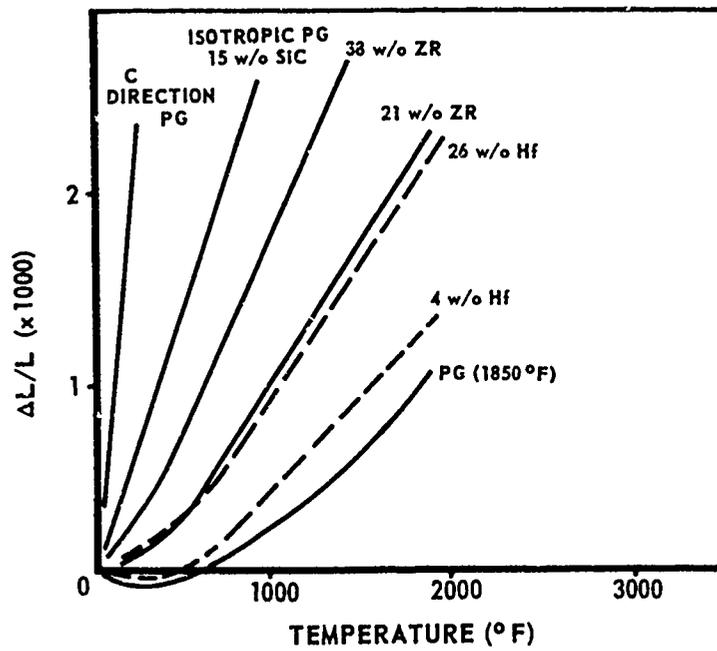


Figure 20. A-B Direction Thermal Expansion - Alloyed Pyrolytic Graphite.

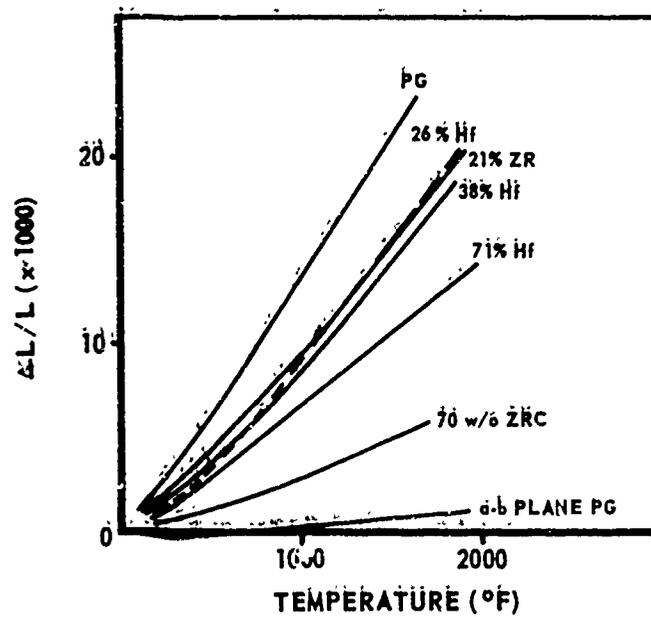


Figure 21. C Direction Thermal Expansion - Alloyed Pyrolytic Graphite.

temperatures are redirection of a-b plane conductivity and slight increases to c direction conductivity; high temperature measurements have not been reported.

The ability to modify the properties of PG with zirconium and hafnium additions could be useful to develop coated composites with integrity. The pyrocarbides have not received much attention from the solid propulsion nozzle community. The erosion resistance in solid propellant environments may be degraded by these additions and this should be investigated.

A limited effort to codeposit Zr or Hf with PG in an atmospheric pressure process was reported¹⁹. Small inserts were made and exposed to a 6500°F uncured solid propellant 1000 psi environment. Two tests with one inch throat inserts were reported. The first coating was 64 mils thick on AGSR graphite and contained 50 percent by weight of ZrC. The erosion rate was around 8 mils per second, much too high for interest in advanced propellant environments. The second insert was 33 mils thick on an ATJ graphite substrate and contained 18 percent HfC. The erosion rate was between 1-3 mils per second, which is considered good. The coating did exhibit spallation of one large piece in the entrance section during cooldown.

No property information was developed with this version of Zr and Hf alloyed PG as that comparison with the Raytheon pyrocarbides is not yet possible. The process development was never completed even for the one inch throat size.

CONCLUSIONS

The problems with a-b plane pyrolytic graphite are only partially understood. The tools are now available, specifically nonlinear stress analysis and effective laboratory thermal stress specimens, to support serious development efforts to achieve a high performance throat insert. The concepts with the best potential include:

- (a) Thick unbonded pyrolytic graphite shells
- (b) Coated carbon-carbon substrates

(c) The "graded" coating (SiC modified pyrolytic graphite substrate)

(d) Composite pyrolytic graphite with filament reinforcements such as Pyrostrand or second phase reinforcements such as SrC or HfC.

The SiC modifications of pyrolytic graphite have been very successful in producing the desired effects on the mechanical properties of pyrolytic graphite. The erosion behavior in oxidizing and low pressure high temperature environments has been excellent. Erosion rates appear to be excessive in the high pressure high temperature advanced propellant environments.

There is a serious lack of fundamental and applied research on the recent modifications to pyrolytic graphite. The development of composites like Pyrostrand and chemical "alloys" containing Zr and Hf has been retarded by immature knowledge of proper processing conditions and lack of basic property information on the composite material. A long range materials development effort should be established on both processing (including vacuum and atmospheric pressure) and relationships between structure and properties.

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