FINAL REPORT

on

EVALUATION OF NONMETALLIC THERMAL PROTECTION MATERIALS FOR THE MANNED SPACE SHUTTLE

VOLUME I (Task 1)

Assessment of Technical Risks Associated With Utilization of Nonmetallic Thermal Protection System

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

October 15, 1970

by

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FOREWORD

This volume is one part of the results of a program supported by NASA at the Columbus Laboratories of Battelle Memorial Institute. The work was performed under NASA Contract NAS 9-10853. Emily W. Stephens, Thermal Protection Branch, Materials and Structures Division, Manned Spacecraft Center, is the project manager. The overall program is concerned with the assessment of technical risks associated with the development and/or use of nonmetallic materials for the reusable manned space shuttle. To date, the program has been limited to the performance of three tasks. The results of the efforts involved in these three tasks have been published in three volumes as noted below.

VOLUME I. EVALUATION OF NONMETALLIC THERMAL PROTECTION MATERIALS FOR THE MANNED SPACE SHUTTLE

(Task 1) Assessment of Technical Risks Associated with Utilization of Nonmetallic Thermal Protection System

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October 15, 1970

VOLUME II. EVALUATION OF NONMETALLIC THERMAL PROTECTION MATERIALS FOR THE MANNED SPACE SHUTTLE

(Task 2) Experimental Verification of Planned Evaluation Procedures for Surface Insulator Material Candidates

by C. W. Kistler, W. H. Wilkinson, E. W. Ungar, and
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October 2, 1970

VOLUME III. EVALUATION OF NONMETALLIC THERMAL PROTECTION MATERIALS FOR THE MANNED SPACE SHUTTLE

(Task 3) Results of Evaluations to Provide Screening Data

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and E. L. Foster

March 1, 1971

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENT

The performance of this Task drew upon the experience and talents of many of Battelle's Columbus Laboratories staff members. In the main, these contributions were made to the program by participation in planning and review meetings and by the generation of written thoughtful reviews or discussions on subjects within their technical specialities. To varying extents these contributions have been incorporated in this written summary.

SUMMARY

Because the development of a low-cost, reusable manned space shuttle will require development and eventual qualification of new classes of thermal protection systems (TPS) materials, special evaluation and risk assessment methods will be required. This program reviewed the technical problems of design and flight qualification of the proposed classes of surface insulation materials and leading edge materials and defined a Screening Test Plan in detail and outlined a Preliminary Design Data Test Plan and a Design Data Test Plan.

This program defined the apparent critical differences between the surface insulators and the leading edge materials, structuring specialized Screening Test plans for each of these two classes of materials. Unique testing techniques were shown to be important in evaluating the structural interaction aspects of the surface insulators and a separate task (Task 2) was defined to validate the test plan.

As an additional part of Task 1, a compilation of available information on proposed material (including metallic TPS), previous shuttle programs, pertinent test procedures, and other national programs of merit. This material was collected and summarized in an informally structured Workbook.

INTRODUCTION

Development of a manned space shuttle with emphasis on low cost operation and reuse imposes new technical requirements on thermal protection system (TPS) materials. Consequently, flight qualification of a new class of TPS materials and materials combinations will be required. It is the intent of this program to perform continued assessment of technical risks associated with utilization of candidate materials for space shuttle TPS, generate recommendations for material qualification testing to reduce technical risks and to generate recommendations for a test program to develop statistically significant thermal and structural design data. This proposed program will provide direct support to NASA/MSC in its continued assessment of TPS materials.

Since the materials of concern are generally complex/composite structures, a considerable degree of the concern regarding feasibility of flight qualification is related to the internal characteristics of the material and the relationship among these characteristics, property measurement procedures, property utilization and the response of the material to thermostructural loads. Reuse represents a relatively uncharted ground and raises questions related to cyclic and integrated effects on composite ceramics.

OBJECTIVES

The objectives of the program were:

(a) To conduct continued assessment of technical risks associated with utilization of candidate materials for space shuttle thermal protection system (TPS) based on currently available data and on tests to be performed.

(b) To generate recommendations for a material qualification testing program that is intended to reduce technical risks to an acceptable level.

(c) To generate recommendations for a program to develop statistically significant thermal and structural design data.

APPROACH

In the performance of this program, a management approach was adopted in which a small core team of senior staff members well-grounded in both materials technology and reentry design problems were assigned the program management, principal investigator(s), and NASA liaison functions. The core team was supported by a larger group of technical specialists who drew upon the full extent of Battelle's capabilities.

The initial project effort centered on the collection of available and applicable information on space shuttle TPS requirements with special emphasis on the unique design aspects associated with the nonmetallic TPS materials. First order concerns were for the property and performance data that would be necessary for design and qualification for a single flight. This was known to be relatively straightforward for the inhibited carbon/carbon leading edge materials but not at all assured for the generally structurally weak surface insulators. Whereas the inhibited c/c composite leading edge materials could be expected to survive a single flight despite poor performance that could lead to significant ablation and material loss, the external insulators had no related performance base for even one flight.

As insight into the unique characteristics and design problems was increased, the viewpoint was shifted to the requirements for reuse--the crux of the space shuttle concept. A sample of each class of material (external insulator and c/c leading edge) was examined by laboratory materials specialists to bring practical focus to the material considerations and characterizations. These investigations also included consideration of nondestructive testing (NDT) techniques that might be appropriate for both production control and eventual recertification of a vehicle after each flight.

With particular emphasis on the designer's requirements for satisfactorily applying the materials, a Screening Test Plan was to provide means for ranking the candidates as to development potential so that the best risk candidates could be identified and the higher risk candidates eliminated from the development program. In addition, consideration of the (possible) future needs for property and performance data on the candidate was included to aid in keeping the screening program an integrated part of the entire data acquisition program.

RESULTS AND DISCUSSION

Task 1 is divided into three subtasks along the lines of the objectives stated above. Task 1A is the organization and evaluation of the existing information base. In the subsequent reporting, Task 1B is further subdivided into the separate supportive aspects with separate Screening Test Plans for the surface insulators and the leading edge materials and culminated in the presentation of Preliminary Design Data and Design Data Test Plans. Task 1C broadens the assessment perspective to the ultimate requirements of flight qualifications for reuse.

ACQUISITION AND COMPILATION OF INFORMATION--TASK 1A

The purpose of Task 1A was to provide information on properties and determination procedures, mission requirements and design requirements for the materials of concern in the space shuttle thermal protection system. In accomplishing this purpose, subtasks were performed as follows:

(1) Information on past shuttle literature

(2) Information from current shuttle programs

(3) Description of test procedures

(4) Identification of national programs pertinent to property data and measurement procedures.

In addition, an informal workbook of material properties was compiled and will be revised as additional data becomes available on pertinent materials. The Table of Contents of this Workbook is given in Appendix A.

On the initiation of Task 1A, a sample of each of the two types of material (LI-1525 insulation and Inhibited LTV c/c composite) were available for laboratory examination. These laboratory studies were performed and reports written. The reports are included in the workbook noted above.

INFORMATION ON PAST SHUTTLE LITERATURE

Studies(1,2)* have been conducted to determine the temperature likely to be encountered on the outside surfaces of space shuttle vehicles, both orbiter and booster stages. One assessment indicates that about 32 percent of the surface of a vehicle will require a temperature capability of 500-800 F, 13 percent will require 800-1500 F capability, 30 percent will require 1500-2000 F capability, 23 percent will require 2000-2200 F capability, and about 23 percent will require a temperature capability of greater than 2200 F.

A variety of configurations and schemes for fabrication of these surfaces to provide the proper temperature capability and insulating characteristics have been proposed. They include: composites, foams, metals in multilayer or shingle configuration, multilayer ceramics, fibers and superinsulations. Because of the temperature variations over the shuttle vehicle (orbiter or booster), it is likely that at least two different materials will be used in the critical areas of the vehicle. This program has two candidates for shuttle thermal protection: (1) c/c composite for leading edges where temperature capability in excess of 2500 F is required and (2) ceramic composite insulators for other vehicle areas where a temperature capability of less than 2500 F is required.

Information in past shuttle literuatre is limited. Only one insulation material LI-1500, has been studied extensively.

A wealth of information is available on general c/c composites(3).

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*Refers to sources of information listed in Reference Section, page 101.

These general materials are not suitable for space shuttle leading edges without the addition of some oxidation preventative. This preventative is referred to as an "oxidation inhibitor". Physical, mechanical, and thermophysical properties of many c/c composite materials are shown in the materials workbook prepared in this program and referred to earlier.

A compilation of available literature which has direct application to the space shuttle vehicle has been prepared and filed at Battelle-Columbus. A listing of this information is included in this report in Appendix B - Sources of Information. The papers are available for study and reference at all times.

INFORMATION ON CURRENT SHUTTLE PROGRAMS

The discussion in this section will be divided into two parts. The first part will pertain to c/c composites (leading edge material) and the second will pertain to external insulations.

Carbon/Carbon Composites

General Characteristics

Carbon/carbon (c/c) composites are a relatively new class of materials which are composed of carbon fibers in a carbon matrix. These materials are characterized by:

(1) Lightweight

(2) High strength and modulus along the carbon filament direction

(3) Low strength and modulus in any direction other than with the fiber

(4) High thermal stability

(5) Good chemical stability except with oxygen.

They are of interest in leading edge areas on the space shuttle vehicle because of their temperature stability in spite of their oxidation characteristics. However, protection against oxidation must be provided to accomplish the necessary reusability in the materials.

Morphological[*] Details. Morphology is defined as a study of structure or form. In the study, the features comprised in the structure or form of the organism or any of its parts constitute the basis of the study. Carbon/carbon composite materials contain a minimum of two phases of carbon; carbon filaments and a carbon matrix. The filaments may be any of several different types, depending on the precursor; polyacrylonitrile, cellulose, pitch, etc. The matrix will likely be derived from a resin, pitch or pyrolytic carbon, or it may be a combination. The characteristic properties of a material will not only depend upon the combination of filament and binder selected but it will also depend upon the filament orientation and the processing characteristics. The morphological study provides means of assessing the integrity of the material.

Carbon/carbon composites per se are not of interest in the space shuttle. It is necessary to add a third phase material for oxidation inhibition. It may also be necessary to coat the surface with still another material. Morphological examinations using optical and scanning electron micrographic

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[*] Morphology - A study of structure or form - the features comprised in the form and structure of an organism or any of its parts.

Organism - A complex structure of interdependent and subordinate elements whose relations and properties are largely determined by their function in the whole.

methods will assess the features of these parts as they relate to the substrate or basic c/c composite. This microstructural examination is useful in both pre- and posttest examinations to reveal likely areas of weakness and causes of failure. It is used predominantly in guiding development efforts.

Carbon filaments may be placed in a carbon matrix in a variety of configurations. Probably the most common for plates and simple noncylindrical shapes is parallel cloth layup. In this configuration, layers of woven carbon cloth are simply stacked on top of each other. Fill and warp fibers may be oriented within the plane of the flat material as desired. This material is clearly two-dimensional if no reinforcing filaments are oriented in the third (thickness) dimension.

Cylinders are often formed by winding tape around a form. This material is referred to as tape wound. Yarn may be substituted for the tape in which case the material is filament wound. Tape-wound cylinders are two-dimensional, since the tape is overlapped causing a simulated continuous filament in the axial direction. Filament-wound structures are one-dimensional, since there are no reinforcement filaments in either the thickness or the axial directions.

Each of the above methods utilize carbonized cloth, tape, or yarn in relatively mild forming methods. Recently, techniques have been initiated for weaving carbonized yarn into more complex orientations. There is little reason to perform weaving except to acquire a third-dimensional reinforcement in the material. This is a very adequate reason for some applications because of the very marked anisotropy in any one- or two-dimensional carbon composite material.

Two methods are currently used for three-dimensional weaving. Either may be applied to flat plates, or curved configurations. In one method the filaments are woven in three orthogonal directions. This is the most straightforward method and gives a true third-dimensional character to the material. It can easily be shown that the maximum volume filament displacement in this type of material occurs when the yarns in each direction are equal in size, the maximum fill (assuming circular yarns) being $\pi/4$ x 75 percent or

~59 percent. One major attribute to this material is the true three-dimensional characteristic; whereas one major deficiency is in difficulty with densification to obtain the maximum filament-to-matrix ratio.

The other three-dimensional weaving process (G.E.'s omniweave) never produces a true third-dimension filament configuration. Instead, yarn is woven through the two-dimensional weave at some angles less than 90°, and, on occasion, in several different directions. The omniwoven yarns may not extend completely through the thickness direction of the woven material. However, the yarns do join two or more two-dimensional laminates together whereas the two-dimensional layup depends entirely on the matrix for interlaminar properties. One important attribute of this three-dimensional material is its ability to deform under pressure to obtain a high filament-to-matrix ratio without damage to the filaments. A deficiency is the anisotropy of the third-dimension which means that the third-dimension properties are always lower than the properties in the other two directions because the yarns are not orthogonally placed.

Other processes may yield c/c composites which are somewhat three-dimensional in character. These include needled felt, macerated cloth (UCC's PT series) and short filament materials. None have the very high mechanical property characteristics of other c/c composites but they are more isotropic and may have higher strength than bulk carbons.

Fabrication Procedures. Carbon/carbon composites may contain a matrix which is derived from either pyrolyzed plastic (resin) materials or from a gas-phase reaction using a suitable gaseous hydrocarbon to form pyrolytic carbon. The latter is referred to as a chemical vapor deposited (CVD) matrix.

In some cases CVD processes are used to densify materials which are primarily bonded with pyrolyzed resins.

When resins are used as the matrix in filament wound or two-dimensional layups, the yarn, tape, or cloth is usually preimpregnated with the liquid resin before being wound or layed up. After the initial processing step, the part is densified by uniaxial or isostatic pressing and cured at slightly elevated temperatures. Curing is performed under mechanical pressure. The remainder of the processing cycle is a pyrolysis heat treatment and graphitization if desired. A prepyrolysis soak at elevated temperature may be used to catalyze crosslinking in the polymer and promote formation of carbon during pyrolysis.

Regardless of the system of bonding employed, the matrix carbon formed is dissimilar from that of the filaments. This dissimilarity is manifest principally in the thermal expansion coefficient of the two carbons. High modulus fibers have a very low-expansion coefficient along their axis, whereas bond carbons, by virtue of their highly crosslinked nature, have a high coefficient. Additionally, matrices which are formed by pyrolysis of resins shrink considerably during pyrolysis and can cause both microcracking and macrocracking.

The resin system is more easily processed, in particular, where formed surfaces (such as leading edges) are desired. This suggests that both systems might be desirable--the resin system first to obtain the desired shape followed by CVD to increase the density and enhance the bond.

Some of the proposals for c/c composite materials advocate the two-bond approach.

Mechanical and Thermophysical Properties. Table 1 lists common strength and modulus values for various grades of c/c composite materials. The one-dimensional filament wound materials usually exhibit the highest strength and modulus in the filament direction simply because there are more fibers present than in other c/c materials. However, the strength in the other two directions is that of the matrix, usually less than 10 percent of the fiber direction.

In two-dimensional c/c materials the strength and modulus tends to be equivalent in two directions especially if the warp and fill filaments in the cloth or tape are identical. These properties are not as great in either direction as filament wound for the reason cited. Again, as with filament wound structures, the interlaminar properties are degraded compared to those along the laminations.

Three-dimensional woven materials usually have less volume of fibers in either direction than one- or two-dimensional materials. Therefore, the strength and modulus in two directions are decreased, whereas these properties in the third direction are increased. The orthogonally woven materials can be perfectly isotropic in the three orthogonal directions, whereas the omniweave materials should exhibit some anisotropy. The anisotropy of omniweave materials results from the cross-woven filaments not being perpendicular to the other two filaments. In any composite, the strength and modulus drops toward that of the matrix as the angle between the stress vector and the filament direction increases.

The addition of ceramic or any other particulate material to a composite can only decrease the strength and modulus if it replaces part of either the matrix or filament phases without entering into the bond function. The influence will depend on the amount, size, and placement of the material in the matrix.

TABLE 1. TYPICAL PROPERTIES OF CARBON/CARBON COMPOSITES

Material	Density gm/cc	Strength, 10^3 psi			Modulus, 10^6 psi		Thermal Conductivity Btu ft/hr ft^2 °F	Coefficient of Expansion 10^6/°F
		Tensile	Flexural	Compressive	Tensile	Flexural		
				One Dimensional				
Fiber-Graph G-G	—	35	—	27	4.9	—	4-6	1.5
Carbitex 115	1.38	—	49.6	28$^{(a)}$	9.4	—	—	—
Carbitex 113	1.38	14.7	—	—	—	—	—	—
Carbitex 515	1.40	—	54.7	35.7$^{(a)}$	4.7	—	—	0.4
Carbitex 513	1.40	19.8	—	—	—	—	—	—
Carbitex 715	1.44	40	42	21.5$^{(a)}$	4.9	—	10.6	0.4
VYB Graph-Graph (UCC)	1.5	28	27	32.6	—	—	—	—
				Two Dimensional				
Fiber-Graph G-G	—	10	—	11.5	2.5	—	2-3	2.3
Hitco PC-500	1.40	11.4	14	9.5	2.2	1.9	—	—
Carbitex 100	1.38	8.1	14	10	2.4	—	12-3$^{(a)}$	0.9
Carbitex 500	1.40	8.8	16.5	12.3	2.1	—	10-10$^{(a)}$	0.4
Carbitex 700	1.44	6.2	12	7	2.1	—	31-13$^{(a)}$	0.4
AG Carbon 101	1.4	11	—	—	1.3	—	16-14$^{(a)}$	0.47
UCC PT 0111	1.10	2.3	3.2	—	—	—	—	—
UCC PT 0183	1.44	—	9.4	8.4	—	—	—	—
UCC PT 0228	1.43	10.2	11.5	5.6	—	—	—	—
Hitco PC-400	1.45	15.0	—	8.0	3.0	—	2.1	—

TABLE 1. (CONTINUED)

Material	Density gm/cc	Strength, 10^3 psi			Modulus, 10^6 psi		Thermal Conductivity Btu ft/hr ft^2 • F	Coefficient of Expansion 10^6/° F
		Tensile	Flexural	Compressive	Tensile	Flexural		
Three Dimensional								
Woven								
AVCO Spec. 237 Thornel 40	1.65	11.9$^{(b)}$	9.8$^{(b)}$	4.5(6.9)$^{(b)}$	4.6$^{(b)}$	3.7$^{(b)}$	42.4$^{(b)}$	0.8$^{(b)}$
AVCO 3-D Thornel 50	1.5	13.3	7.2	11.3	3.4	—	—	—
GE Omniweave 4-Direction	1.6	3.6	7.4	2.1	3.6	2.3	1.5	—
Random Fiber								
UCC-PTA	1.14	1.2	1.71	2.9	1.2	—	16.3	0.6
UCC-PTB	1.45	2.8	4.0	12.5	1.7	—	—	1.1
UCC-PTC	1.30	1.4	2.6	4.0	1.3	—	24	0.7
Felt-Pyrolytic								
Supertemp RPB	1.7	8	10	20	—	—	—	—

(a) In "Z" direction.

(b) All in third direction.

Some of the thermophysical properties are influenced more than others by the anisotropic placement of filaments in c/c composites. For example, the coefficient of expansion is much more sensitive to filament direction than is the thermal conductivity. A bulk property such as specific heat is not sensitive to the filament direction. Generally, the mechanical properties are much more highly influenced by filaments than are thermophysical properties.

It should be noted in Table 1 that the thermal conductivity ranges from about 2 to about 30 Btu-ft/hr-ft^2-°F. This places these materials between the metals and insulators with respect to their thermal insulation qualities.

Oxidation Inhibitors. Various metals or metal compounds have been considered as oxidation inhibitors for graphite. Only phosphorous truly inhibits the reaction of oxygen with carbon and this only at relatively low temperatures (less than 800 C). No other solid material is known to inhibit this reaction. This leaves only one alternative for the prevention of graphite oxidation at high temperature, that of physically excluding oxygen from the graphite. To achieve this end, various techniques have been tried. The simplest in theory is an impervious non-oxidizing coating. This type of coating can be applied by flame spraying, chemical vapor deposition or a number of other ways. However, one serious defect in this system is incompatibility of the coating with the graphite. The coating tends to spall off, principally because of a mismatch of expansion coefficients, and is lost for all cycles after the first.

Another method that is employed with a commercially available material (JTA) incorporates ceramic powder into the bulk graphite such that upon oxidation of graphite particles, enough of the ceramic is exposed to form a continuous protective film on the remaining graphite. The three ingredients normally used with this protective system are boron, silicon, and zirconium. Boron compounds are for low-temperature protection; silicon compounds for higher temperatures.

The major difficulties with the latter protective method are:

(1) Processing problems in applying the necessary amount of material to the fibrous material in a homogeneous manner

(2) Loss of strength at high temperature

(3) Cyclic operation causing loss of the protective coating due to expansion mismatch between carbon and the material

(4) Boron may boil off of the material at high temperatures such that cycling can allow low-temperature oxidation in all cycles except the first

(5) Boron, if present as the oxide, can easily disrupt a graphite structure if water is present and the acid forms.

The above (regenerative) protective system, however, appears to offer a better solution than the present outside protective coatings.

Candidate Materials

The information discussed in this section is taken directly from proposals submitted by five of the six contractors supplying c/c composites.

General Electric. General Electric will use an omniweave (braided) pattern of filament orientation with a combination of resin coke and CVD (pyrolytic) carbon matrix. The fiber portion will consist of mixed carbon and silica filaments. The precursor for carbon filaments is not designated but the basic properties will feature a high strength and a low modulus.

Part of the oxidation inhibition will be impregnated into the material as a part of the matrix forming resin (similar to TTA). Another part will presumably be the silica filaments which are woven through the fiber part of the material.

General Electric has performed considerable work with omniweave c/c composites in connection with other aerospace programs. Patterns have been woven into materials that contain filaments which run in three to seven different directions. The material is quasi three-dimensional and generally has good "Z" direction properties but the "Z" direction filaments are not orthogonal to the other filaments. The following list of properties are anticipated:

Flexual strength - 8000-16000 psi
Modulus - 1-2 x 10^6 psi
Density - 1.8 - 2.3 gm/cm^3
Shear strength - 2000-3000 psi
Compressive strength - 40,000-50,000 psi

The inclusion of oxidation inhibitors in the G.E. material will undoubtedly affect the characteristic properties of the material. It is likely that the properties will be further affected by cycling the material through heat treatments, particularly since part of the fiber fraction will be silica which is subject to a reaction with carbon.

AVCO. AVCO has the potential of supplying orthogonally-woven three-dimensional c/c composites. They have performed considerable development activities with these materials on government-supported programs. However, the proposal indicates that three-dimensional c/c composites will not be supplied for this program. The biggest advantage of three-dimensional material is pointed out in the proposal; the properties in the "Z" direction are significantly improved over similar properties of two-dimensional composites. Table 2 gives the properties of three-dimensional and two-dimensional AVCO materials. It is pointed out that the properties in each direction is essentially equivalent. The interlaminar ("Z") direction tensile strength as reported in the table seems high. Often this strength is lower than 1000 psi, depending on the density and type of matrix. In two-dimensional material, the interlaminar strength is a function of the matrix and has little contribution from the filaments.

AVCO proposes using only a SiC coating as the oxidation protection. They point out that this coating is more effective and holds on the surface better if it is diffused to some depth under the surface of the composite. They have completed oxidation testing on coated control specimens (presumably two-dimensional material). The coated specimens actually show a weight gain after four hours (two cycles) at 2500 F in air. This indicates that SiC coating is being oxidized similarly to the results shown with LTV material tested earlier. Even though the coatings did not spall in two cycles, they may not survive additional cycles.

McDonnell-Douglas. MDC proposes a two-dimensional c/c composite with an oxidation inhibitor system similar to that used in JTA grade bulk graphite; silicon carbide and zirconium carbide. The particulate inhibitor materials will be added presumably to the binder just before it is added to the graphite cloth in a pre-impregnation operation. If this is the case, then the powders should be relatively well dispersed within the matrix carbon. MDC

TABLE 2. PROPERTIES OF AVCO C/C MATERIALS TAKEN FROM AVCO SPACE SHUTTLE PROPOSAL.

	Resin/Pitch Matrix Precursor				CVD Infiltrated Matrix	
	3D Block	Mod-3	3D Cylinder	1D Block	3D Block	2D Laminated Fabric
Density, gms/cm^3	1.65	1.65	1.60	1.75	1.5	1.51
Tensile Strength, psi	12,000	15,900	24,000		17,500	6,750 (Fabric Direction) 2,300 (interlaminar)
Modulus, psi x 10^{-6}	4.6	6.02	11.5			
Total Strain, %	0.18	0.3	0.18			
Compressive Strength, psi	7,000	8,800				
Modulus, psi x 10^{-6}	4.9	3.3				
Total Strain, %	0.15					
Flexural Strength, psi	10,000	10,000		60,000	20,700	10,600
Modulus, psi x 10^{-6}	4	2.5		32		
Shear Strength, psi	4,000			2,000	7,500	3,700
Thermal Expansion 1°F x 10^{-6} to 2000°F	0.3	0.3				
Specific Heat at 500°F	0.3	0.3				
Thermal Conductivity Btu/hr.-f.-°F	42 at 500°F 27 at 1500°F	20 at 250°F 20 at 750°F				

gives a list of characteristic properties for their material. They include: ρ = 1.48 gm/cc, ultimate tensile strength = 5400 psi (interlaminar strength is not given), modulus = 1.8 x 10^6 psi. It is anticipated that the material will have a flexural strength of 8000 psi and an emittance of 0.8. The surface recession in an oxyacetylene torch has been determined at 130 Btu/ft^2-sec and surface temperature of 3700 F (measured optically). The recession was much better than that for straight c/c composite. Comparison with other materials in this program is not possible from available data.

LTV Material. LTV proposes use of a two-dimensional c/c composite material protected from oxidation by a diffused tantalum-silicon carbide system. Preliminary examination of their diffused SiC system shows inhomogeneities across the piece and through the thickness of the piece.

No mechanical or thermophysical property data is available for material proposed for this program. Typical two-dimensional c/c composite mechanical property data is shown in the table included in this section. It is expected that the diffusion coating process with its conversion of carbon to SiC or TaC will weaken the composite somewhat. Thermophysical properties will also be altered depending on the amount of metal diffused into the material. Quality control will be very important with this material because the addition of metal is only indirectly controlled.

Hitco. Hitco proposes use of their Pyro-carb 703 material for this application. According to available information, this grade is a two-dimensional cloth layup c/c composite. From their very brief proposal (that part available to Battelle), the material will have metal oxidation inhibitors added to the resin prior to the cloth pre-impregnation. After the pyrolysis and machining, a separate refractory metal coating will be placed on the surface. No information on metal additive or coating is available.

This material may be very similar to the MDC system if metal carbides or carbides are actually used instead of pure metals.

Union Carbide. No information is available on the nature of the UCC material.

External Insulations

General Characteristics

The characteristics of material candidates which distinguish them as a class of materials are discussed in this section of the report. Specific characteristics necessary to obtain desirable thermophysical and mechanical property data are identified as far as possible.

Morphological Details and Panel Configurations. The design of the Thermal Protection System requires the external insulators to be adhesively bonded to fuselage panels and the wing substructure. Thus, a candidate panel must be fabricated, machined, and/or subsequently formed into a flat or curved configuration depending on the area over which it is to be applied. A material which would be difficult to fabricate in a curved configuration would present manufacturing difficulties. The manufacturing process should be capable of producing panels up to 2-feet square with uniform characteristics within each panel and consistent from panel-to-panel. The material should be reasonably isotropic in properties so as to withstand the complex mechanical loadings expected during launch and re-entry.

Fabrication Procedures. In manufacturing material which satisfies thermal insulation criteria, a very porous structure is necessary to minimize conductive heat transfer. However, radiative heat transfer is even more important, so a finely divided pore or fibrous structure is desired so that radiation is scattered. Ceramic foams and fibrous structures generally satisfy the morphological and thermophysical criteria noted above.

Foams may be made by mechanical or chemical foaming techniques. Mechanical methods such as whipping air into a slurry, using porous aggregate, or by utilizing a fugitive filler such as sawdust or napthalene are rather common laboratory techniques. Foams made mechanically may be bonded chemically at temperatures generally below 1000 F. Ceramics may be utilized as the bond by sintering at temperatures above 2000 F. Chemical foaming involves the reaction of acidic and basic materials, usually in a thick slurry, to form a gas phase which bloats the slurry. Heat released in the foaming process is generally utilized in chemically bonding the material. By the judicious selection of technique and fabrication parameters, foams can be prepared having essentially open or closed porosity as desired. High porosity normally results in open porosity and low porosity usually yields closed pores. Fibrous reinforcement can be incorporated in foams with many of the above fabrication techniques.

Fibrous insulation structures are normally prepared by felting. In this process a slurry of fibers is dewatered by either vacuum, pressure, or centrifugal techniques. Radiation scattering additives or other additives may be added to the slurry, and either chemical or ceramic bonding may be used to increase the strength or rigidity of the insulation.

Weaving may be used to hold a fibrous structure together, but it fails to provide the rigidity a bonded material. Fibrous structures can be made with a higher porosity than foams, but all the porosity of a fibrous structure is open. Because the amount and degree of bonding is minimized in fibrous structures, they are somewhat more flexible (less brittle) than foams. Fine fibers (1 to 10 microns in diameter) are the most effective size for fabrication of insulation materials because they are more effective than larger fibers in scattering radiation.

Mechanical and Thermophysical Properties. The high porosity typical of foamed and fibrous ceramics results in low mechanical and thermophysical property values. For materials in the vicinity of 90 percent porosity, tensile and compressive strengths on the order of 200 psi or less would be expected, and values below 50 psi are not unusual for some materials. The thermal conductivity of fibrous structures typically ranges from 0.3 to 1.0 Btu-in./hr-ft^2-F from ambient temperatures to 1500 F. The value for ceramic foams is somewhat higher, typically on the order of 1.0 to 5.0 Btu-in./hr-ft^2-F in the same temperature range.

An empirical strength-porosity relationship of the type $S = S_o e^{-bp}$, where b is a constant usually between 5 and 10, has been found useful in predicting the strength of foamed ceramics of various total porosities. The total porosity, P, is calculated from the relation $P = 1 - \frac{\rho}{\rho o}$, where ρ and ρo are bulk and true densitites, respectively. Thus, if the strength, bulk density, and true density of a foam is known, a bulk density--strength relation can be estimated. The exponential relationship of strength to porosity explains why small variation in porosity can cause a significant effect on mechanical properties.

Coatings. For the TPS application, a hard surface is necessary to improve the erosion resistance, reduce handling damage, and minimize water absorption. The coating must be as thin as possible to reduce weight, and it must also be thermally compatible with the basic insulation material. It should have a high emissivity to reduce the surface temperatures which develop from aerodynamic heating on re-entry. A coating can be applied to any type of ceramic foam or fibrous structure. However, if the basic structure is flexible, the coating may be damaged readily on handling. In terms of refurbishment, it might be highly desirable to recoat undamaged insulation on the vehicle rather than apply an entirely new TPS. Thus, a chemically bonded or flame or plasma sprayed coating might be more desirable than a ceramic bonded coating which might require a high firing temperature. Of the three, chemical bonding would be the easiest to apply for repairing large areas. All of the coating methods should provide a semipermeable coating so that moisture adsorbed by the insulation can be vented quickly when the material is heated during flight.

Candidate Materials

Data compiled in this section was obtained from proposals and reports of Space Shuttle Programs current as of September, 1970. Only information dealing specifically with candidate external insulation procurement or development contracts has been compiled. Information has been received at Battelle for four of the six proposed external insulation materials. Of the four, two are rigid fiber boards somewhat comparable in characteristics to commercially available insulation boards, one is a flexible 3-dimensional woven composite, and one is a rigid phosphate bonded foam. Characteristics and problem areas of these four candiate materials are discussed in detail in a later section.

Lockheed Missiles and Space Company LI-1500. LI-1500 has been subjected to a significant amount of testing and evaluations. Properties of this material presented in the material procurement proposal resulted from prior in-house or contractual tests which are summarized and discussed in detail in the MSC Workbook. A condensed data summary is given in Table 3. No additional property data were reported under procurement contract NAS 9-10917 as of a biweekly report dated September 15, 1970.

Under contract NAS 9-11222, "Development of a Rigidized, Surface Insulative Thermal Protection System", Lockheed is designing and fabricating prototype panels to demonstrate the TPS concept. A report dated August 24, 1970, indicated the design criteria for the prototype panels had been established, but no data or results were presented. However, mechanical and thermophysical property test details were proposed.

McDonnell-Douglas, Mullite HCF. Properties and performance of this candidate material obtained from the MDAC procurement proposal are compiled in Table 4. The material was considered to be in the development stage and properties should correspondingly be considered tentative.

A biweekly letter report of contract NAS 9-10919 dated September 7, 1970, indicated that panels of mullite HCF being prepared were fired to 2300 F rather than 2000 F as originally proposed. Density variations of the fired panels range from 13.0 to 15.8 lbs/ft^3 because of a change in the processing technique. No additional property data were provided.

AVCO 3D-SX. The structural concept of flexible silica felt insulation, sandwiched between silica fabric, and reinforced normal to the fabric with silica yarn was presented in the proposal. Limited data in the proposal indicated that a sample with a bulk density of 10 lbs/ft^3 had a thermal

TABLE 3. SUMMARY OF DATA ON LI-1500

Property	Units	Results
Thermophysical		
Expansion Coefficient (0-1000 F)	10^{-7}/F	3.0
Thermal Conductivity 500 F	Btu-in./hr ft^{2}F	0.49-0.41
1000 F	Btu-in./hr ft^{2}F	0.63
1500 F	Btu-in./hr ft^{2}F	0.76-0.89
Emissivity, coated	---	0.8
uncoated	---	0.6
Specific heat 200 F	Btu/lb F	0.20
1000 F	Btu/lb F	0.27
1500 F	Btu/lb F	0.29
Shrinkage, parallel 1500 F	percent	0.15
2000 F	percent	---
2500 F	percent	0.6-1.2
Physical		
Bulk Density	lbs/ft^3	15
Mechanical		
Tensile		
Strength*	psi	90-110
Modulus	10^3psi	9-30
Strength/Modulus ratio	in./in.	0.004-0.008
Strength 1200 F	psi	99-141
Strength 1500 F	psi	57-69
Flexural		
Strength	psi	160-220
Modulus	10^3 psi	26-56
Strength/Modulus ratio	in./in.	0.004-0.007
Compressive		
Strength**	psi	35-200
Modulus	10^3 psi	2-18
Strength/Modulus ratio	in./in.	0.02
Shear		
Strength	psi	45

* Parallel to fiber orientation.

** Normal to fiber orientation.

TABLE 4. SUMMARY OF PROPERTIES OF PROPOSED MULLITE HCF

Property	Units	Results
Physical		
Bulk density	lbs/ft^3	13-15
Mechanical		
Tensile strength (parallel to fiber orientation)	psi	60
Compressive strength (perpendicular to fiber oreintation)	psi	51 (at 4% strain)
Acoustic (158db, 5 min)	---	No powdering
Vibration (10.5 g, 5 min)	---	Passed
(45.5 g)	---	Failed in 15 sec
Thermal		
Conductivity (14.7 lb/ft^3 material at one atmosphere)		
at 500 F	Btu·in./hr-ft^2-F	0.53
at 900 F	Btu·in./hr-ft^2-F	0.73
Specific Heat		
at 400 F	Btu/lb F	0.22
at 1600 F	Btu/lb F	0.27
Linear shrinkage (parallel to fiber orientation)		
at 2300 F	percent	0
at 2600 F	percent	2
Expansion coefficient		
at 70 F	10^{-6} in./in.	2.5
at 2400 F	10^{-6} in./in.	2.5
Emittance of coating		
at 2500 F	---	0.95

conductivity of 0.25 Btu-in./hr-ft^2-F at 250 F, was subjected to 2250 F surface temperatures in an arc test at a heat flux of 26.5 Btu/ft^2-sec, and survived a preliminary vibration test.

Biweekly reports on contract NAS 9-10921 through September 8, 1970, revealed no further property data. Development of techniques for applying a high emissivity coating by dip-coating and plasma spraying were under study.

Whittaker Aluminum Phosphate Foam. The proposal by Whittaker described the approaches to be studied in developing a foam to satisfy the materials procurement contract. Advantages of using fillers and reinforcement with the chemical bonding approach were outlined, but no specific data were provided since the materials were in the development stage.

(1) Aluminum phosphate bonded foams could be prepared from silica microballoons with silica fiber reinforcement in the density range of 14-20 lbs/ft^3.

(2) Room temperature compressive strength measurements of these foams were about 80 psi in one direction and 160 psi in the other because of preferential fiber alignment in the molding process.

(3) Torch testing of these foams to surface temperatures of over 2800 F resulted in melting and erosion.

(4) Subsequent furnace tests indicated thermal instability was caused by melting of the silica microballoons at 2400 F.

(5) Replacement of the silica microballoons with carbon microspheres was being pursued to develop a material stable to 3000 F.

(6) Development of coating techniques were being pursued using woven silica fabric integrally cured with the foam.

Thus, little specific data are available at this time.

Union Carbide. No proposal or information has been received.

General Electric. No proposal or information has been received.

COMPILATION AND DESCRIPTIONS OF TEST PROCEDURES

Two distinctly different types of testing are required for the examination and qualification of materials for the thermal protection of the space shuttle. Destructive tests are required for obtaining screening information and design information. Nondestructive testing is important as a quality control tool.

Destructive Testing

Various material properties have been identified as important in the assessment of inorganic, nonmetallic thermal protection systems for space shuttle vehicles in both screening and design functions. The specific properties identified are discussed in more detail in a subsequent section of this report. The properties can be separated into groups associated with the following categories:

(1) Physical (bulk) properties and morphology

(2) Chemical properties

(3) Thermal stability

(4) Mechanical properties

(5) Thermophysical properties

Physical Properties and Morphology. Bulk characteristics of a material are associated normally with the bulk density of the material, which is a measure of the mass per unit volume. It is calculated from total weight and total volume determinations. A knowledge of the density leads to a knowledge of the specific volume of the material. Since the specific volume of constituent materials is usually known, the bulk porosity of the material can then be determined. The integrity of many materials depends directly on the porosity in the material. The bulk porosity determination discussed above does not give the size distribution of pores in that bulk. The most common method for determining the pore size distribution in a material is to monitor the volume of a nonwetting liquid that is being systematically forced into the pores. Gas adsorption can also be used but the method is generally more involved and more suitable for very fine pore structures.

The open nature of the pore system in a material is defined as the permeability of the material. It is important in studying the chemical reactivity of the material in either stagnant or dynamic atmospheres. The permeability is determined by monitoring the volume flow of a fluid through unit volume of the material. The degree of sophistication required for the determination depends on the permeability of the material, lower permeability requiring more sophistication.

The morphology of TPS materials for space shuttle application gives additional, more detailed physical information on the materials. It is important in studies on the placement of second phase materials in the matrix and in studies of bond formation within the matrix. It is also important in the posttest analysis of a material's response to the test environment. Optical methods such as metallography are common. Innovations of optical systems such as image analyzing computers (Quantimet) are helpful in studying surface porosity or phase inversions where an optical change takes place.

Chemical Properties. Chemical analysis is useful in determining the distribution or change in distribution of elements or compounds in TPS materials. The electron probe analysis is a suitable technique in particular with inhibited c/c composites to determine the distribution of elements which can significantly affect, for example, the corrosion resistance of the material and the thermal shock characteristics of the material. Electron probe analysis is a useful tool for this analysis. Wet chemical and spectroscopic analysis is less favored for this application.

X-ray diffraction techniques have been useful in studying the phase changes such as devitrification of fused silica to cristobalite in the ceramic-type surface insulation materials.

Thermal Stability. The term "thermal stability" as used in this study refers to the physical stability of the material on heating to a maximum-use temperature. The physical change could be associated with chemical or phase changes in the material, creep, or internal stress relief. The thermal stability test is a heat treatment under controlled temperature, time, and atmosphere conditions. Both thermogravimetric analysis (TGA) and differential thermal analysis (DTA) may be associated with this test. However, they may also be applied to chemical testing.

An accounting of the physical shape changes after one or multiple heat treatments will provide a qualitative assessment of the thermal stability. Chemical or morphological methods should elucidate the reasons for any physical change.

Mechanical Properties. Mechanical properties including ultimate strength, modulus of elasticity, and failure strain in tension, compression, and shear are important screening and design properties, in particular for the structural c/c composite materials. These properties are probably more important at intermediate temperatures than at room or high temperatures because of the expectation that failure will occur in shear or tension modes by thermally-induced loads. It is, therefore, important to obain screening and design mechanical data at elevated temperatures.

Carbon/carbon composites are recognized as brittle materials at all temperatures of interest in this program. Complications arise in the assessment of their mechanical properties because of the addition of second, third, or fourth phase oxidation inhibiting materials. The complications arise not only from the physical presence of these materials but also because they may be inhomogeneously dispersed and may change their structure or become plastic during high temperature use. The measurement and interpretation of mechanical property data on brittle materials have been the subject of various studies.(4,5) Battelle has access to reports generated in studies being supported by Government agencies including AEC, Air Force, and NASA. Many of these programs are listed in another section of this report.

Surface insulations are not structural materials; therefore, the determination of some of their mechanical properties may not be as critical as that determination with c/c composites. However, properties such as total strain to failure (strain compatibility) are very important for the intended application.

Techniques for determining all mechanical properties are described in various of the reports and programs mentioned. In this program, flexural testing will be extensively utilized because of the nature of the materials (anisotropy, etc.), the nature of the use, and because of the simplicity of testing instrumentation.

Thermophysical Properties. The thermophysical properties that have been identified as pertinent to design with the materials of interest in this program are: thermal conductivity, thermal expansion, thermal diffusivity, specific heat, and thermal emissivity.

Most of the current programs on development of both structural c/c materials and external insulations require measurement of all thermophysical properties mentioned. Techniques are relatively standard because these properties are pure properties. Some of these techniques are described in references (6) and (7).

Battelle uses the self-guarding disk apparatus for thermal conductivity determinations. In this technique, heat is transferred through the specimen and a heat flow meter in series. Temperature and dimension measurements at a number of thermal equilibria throughout the temperature range of interest permit calculation of a conductivity value for the average specimen temperature at each equilibrium. The typical specimen geometry is a three-inch-diameter disk with thickness ranging from 1/4-inch for low-conductivity materials to 1-inch for those of higher conductivity. The thickness is selected to optimize the axial temperature difference. The number of equilibria established depends on the quality of information required, i.e., whether for screening, engineering data, or complete characterization. It also depends on the material and the temperature range.

Where transient measurements are appropriate, thermal diffusivity will be measured by the heat-pulse technique. Battelle's pulsed laser apparatus requires a nominal 1/2-inch-diameter by 1/8-inch-thick specimen;

the thickness is selected on the basis of anticipated heat-pulse transient time in the specimen. Diffusivity is computed on the basis of this specimen thickness-transient-time ratio. Measurements of the transient time (following a heat pulse) are made after equilibrium is established at a number of temperatures throughout the range. For certain instances, it may be sufficient to compare diffusivity values rather than conductivity. It also may be appropriate to calculate conductivity from the diffusivity-specific heat-density relationship rather than to measure conductivity.

Battelle uses the direct view dilatometer (optical method) for thermal expansion determinations. This method is generally recognized as the most accurate for high temperature expansion measurements.

Nondestructive Testing

Nondestructive testing (NDT) of graphite and c/c composites has been the subject of several Government-sponsored programs. Another section of this report identifies appropriate past and current programs. In addition, other investigators have addressed NDT problems that are directly applicable to this program, for example, References (8) and (9). Since the c/c composites are much older materials, considerable more NDT has been performed with these than with the external insulations. NDT methods that may be applicable in this program include: ultrasonics (velocity, through transmission, and pulse echo), X-ray radiography, radiometry, eddy currents, thermal transmission, and holography. Some of these techniques overlap in their functions and obviously, all will not be used. In addition, some (for example, ultrasonics and eddy currents) probably will not apply to insulative materials because of their absorptive and electrical insulative qualities. It is expected that X-ray radiography and holography will be applicable to both types of materials. Techniques for obtaining these data are described in reports from appropriate Government-sponsored programs and the references cited.

IDENTIFICATION OF PERTINENT NATIONAL PROGRAMS

Carbon/carbon (c/c) composites are an old class of material relative to the Thermal Protection insulative materials which are associated with the space shuttle program. Development on general c/c composites was begun about 1960, however, the production of these composites is by no means a routine operation at this point in time. Most c/c composites are considered to be in the development stage and any production is, in general, performed in pilot-plant equipment. A program(3) performed in the Defense Ceramic Information Center has provided identification of major contributors to c/c composite technology. The organizations identified in this report generally correspond to those identified as associated with current and recent Government-sponsored programs for both c/c and TPS insulation materials. Table 5 lists recent national programs (those that have a listed completion date earlier than September 1970) and Table 6 lists current National programs (those that have a listed completion date after September 1970). These lists are not meant to be all inclusive but represent some of the more relevant work that has been done in the areas of interest.

TABLE 5.

PERTINENT RECENT GOVERNMENT CONTRACTS RELATIVE TO SPACE SHUTTLE MATERIALS

Title of Program	Gov. Agency	Contractor	Contract No.
Thermal protection systems	Air Force	AVCO	AF33(616)-7483
Evaluation of TPS for advanced Aerospace Vehicle	Air Force	IITRI	AF33(657)-9407
Research Study on development of lightweight Insulation for Rigid Heat Shields	NASA	IITRI	NAS 8-11333
Development of High Temperature Insulation Materials	Air Force	Western Electric	AF-33(615)-2782
Report on Advanced Composites II (RECEP II)	---	LMSC	FO 4701-68-C-0299
Investigation of Heat Transfer Mechanisms Through Insulation Materials	Air Force	AFML	In-house
Reentry Vehicle Thermal Protection System Design Computer Codes	AFML	Aerotherm	F33615-69-C-1412
Material/Process Improvement and Optimization of CVD-Felt C/C Composites for Advanced Reentry Vehicle Applications	AFML	Supertemp	F33615-69-C-1782
Reentry Vehicle Enviornmental Protection (RECEP) Program, Task 2.0 High-Performance Heat Shield Materials, CCN No. 3 C/C Materials	SAMSO	LMSC	A404(694)952
Determination of Relations Between Energy of Sublimation Blow-Off Impulse Mass Loss and Energy Deposition for Reentry Vehicle Heat Shield Materials	Air Force	Space Science	F29601-69-C-0077
Data on Graphite, Carbon, and C/C Composite Materials	AFML	IITRI	F33615-69-C-1454
Improvement and Optimization of CVD Infiltrated Controlled Porosity C/C Fabric Composites for Advanced Reentry Vehicle Applications	AFML	LTV	F33615-69-C-1783

TABLE 5.(Continued)

Title of Program	Gov. Agency	Contractor	Contract No.
Energy Absorbing Ablative Plastic Resins for Reentry Vehicle Missile Heat Shield	AFML	Pennwalt	F33615-69-C-1619
Exploratory Development of High-Performance Ablative Composites for Lifting Vehicle Thermal Protection	AFML	Avco	F33615-68-C-1410
Material/Process Improvements and Optimization of CVD Infiltrated C/C Fabric Composites for Advanced Reentry Vehicle Applications	AFML	Raytheon	F33615-69-C-1629
Improvement and Optimization of Orthogonal 3-D Reinforced C/C Composites for Advanced Reentry Vehicle Applications	AFML	Avco	F33615-69-C-1758
Thermal Stress Behavior of Graphite Materials	AFML	TRW	F33615-69-C-1654
Thermal Protection Systems of Porous Ceramics for Manned Lifting Entry Vehicles	NASA	Bell	NAS-1-5370
Research on High Temperature Thermal Insulations	NASA	Nat. Beryllia	NASw-884
Nondestructive Methods for Evaluation of Ceramic Materials	AFML	Avco	F33615-68-C-1185
Lightweight Thermal Protection System Development	AFML	General Dynamics	AFML-TR-65-26*
Ceramic Systems for Missile Structural Applications	Navy	GIT	NOW-63-0143-d
Study of Ceramic Heat Shields for Lifting Reentry Vehicles	NASA	Bell	NAS-1-5370
Thermal Insulation for Launch Vehicle Radiant Heating Environments	NASA	In-house	NASA TM X-53646*
Develop 1800 F-400 F Fiberous-Type Insulation for Radioisotope Power Systems	AEC	Johns Manville	AT(29-2)-2661
Further Development and Evaluation of M-31 Insulation for Radiant Heating Environments	NASA	In-house	NASA TM X-53267*
Investigation & Development of High Temperature Insulation Systems	AFML	A. D. Little	AFML-TR-65-138*

* Technical Report Number.

TABLE 6. PERTINENT CURRENT GOVERNMENT CONTRACTS RELATIVE TO SPACE SHUTTLE MATERIALS

Title of Program	Gov. Agency	Contractor	Contract No.
High-Temperature Insulation Materials for a Reradiative Thermal Protective System	NASA	McDonnell	NAS 8-26115
Development of Rigidized Surface Insulative Thermal Protective System for Shuttle	NASA	McDonnell	NAS 9-11221
Development of TPS for Shuttle Wing	NASA	LTV	NAS 9-11224
Development of TPS for Shuttle Wing	NASA	McDonnell	NAS 9-11223
Thermal Protection System Study	NASA	General Dynamics	NAS 9-10956
Thermal Study for Space Shuttle	NASA	LTV	NAS 9-11166
Process Improvement and Optimization of Omniweave C/C Composites for Advanced Reentry Vehicle Application	AFML	General Electric	F33615-69-C-1767
Evaluation of Thermal Protection Capability of Thermal Insulation	NASA	---	NAS 9-11238
Evaluation of Analysis Techniques Employed for Ballistic Reentry Nose Tip Design	AFML	Aerotherm	F33615-70-C-1105
Develop and Evaluate Manufacturing Processes for Improved Heat Shield Structures	AFML	Avco	F33615-70-C-1285
Develop and Evaluate Improved Graphite Materials for Reentry Vehicle	AFML	GE	F33615-68-C-1283
Reusable Space Shuttle Vehicle Thermal Protection	NASA	Aerospace	NAS 8-26347
Orthogonal Pyrolyzed Plastic Composites for Reentry Vehicle Missile Nose Tips	AFML	Avco	F33615-70-C-1028
Ablative Materials for High Heat Loads	AFML	GE	F33615-69-C-1503
Analysis Relating Strength to Microstructure for Reentry Vehicles and Rocket Nozzles	AFML	TRW	F33615-70-C-1299
Investigation of NDT Methods for Multidirectional Reinforced Composites	AFML	McDonnell	F33615-69-C-1624

TABLE 6. (Contined)

Title of Program	Gov. Agency	Contractor	Contract No.
NDT Test Methods for Graphite Billets and Shapes	AFML	GE	F33615-69-C-1623
Reinforced Pyrolyzed Plastic Composites for Use in Missile Heat Shields	AFML	Philco-Ford	F33615-69-C-1653
Effect of Environment on Insulation Materials	NASA	Lockheed	NAS 3-14342
Thermal and Mechanical Characterization of Graphite Materials for Advanced Reentry Vehicles	AFML	SRI	F33615-69-C-1796
Investigation of NDT Methods Applicable for Nonmetallic Composite Materials	AFML	Avco	F33615-70-C-1526

In addition to these programs, there are continuing AEC sponsored programs at Sandia Corporation and at Oak Ridge, Tennessee. These programs are concerned principally with c/c composites but some work is also being performed with light-weight external insulative systems similar to those being considered for the space shuttle. An example of the Sandia work is the CVD-infiltrated filament wound and felt materials that are being developed for heat shields. These materials have been developed to the point of being successfully flown as the heat shield on reentry vehicles. Union Carbide's Nuclear Division at Oak Ridge is performing work on insulation type carbon base materials. For example, they have developed carbon forms and honeycomb structures of about 0.2 gm/cc (12-13 lb/ft^3).

It is expected that many of the past programs as well as present programs will aid this program. These programs will provide physical, thermophysical, and mechanical property data on materials that are basically similar to both the c/c composite and the external insulation materials being investigated in this program. These programs will also provide additional information on test procedures for testing and analysis of test data. This is particularly important with both types of materials in this program because of the high anisotropy of the c/c composite and fragile nature of the lightweight insulations. The existing programs are also expected to yield development information that can be relayed to the fabrication involved with this program.

One of the most important aspects of this program is quality control of both leading edge and TPS materials. Some quality control can be exercised by testing pieces cut from the edges of actual pieces used or by destructively testing similarly processed pieces. However, this indirect method can never lead to the confidence necessary for space shuttle materials. Nondestructive methods must be used in determining the quality of 100 percent of the materials used in the space shuttle program.

Some nondestructive test (NDT) results can lead to a calculation of a physical or mechanical property. For example, radiometric NDT dtermination can lead to a calculation of the density in a chemically homogeneous material, and ultrasonic velocity determination can be used with this density to calculate the dynamic modulus through the relationship: $K\rho V_L^2 = E_D$

where

K = constant to adjust units

ρ = density

V_L = longitude wave velocity

E_D = dynamic modulus.

One existing program (see Table 6, NDT test methods for graphite billets and shapes F33615-69-C-1623) is seeking to perfect this approach with bulk graphite. A recently terminated program at AVCO (See Table 5, F33615-68-C-1185) initiated the concept of using NDT data to calculate physical and mechanical properties. This program has been successful with bulk graphites but has not had extensive trials with c/c composites.

The largest proportion of NDT effort as applied to c/c composites has been in detection of defects. Various NDT methods have been used. They include:

(1) Ultrasonic velocity through transmission and pulse echo

(2) Radiometric determination using various energy sources

(3) Infrared and other thermal transmission techniques

(4) Holography

(5) X-radiography, neutron radiography, and radiograph enhancement

(6) Eddy current, multifrequency eddy current, and dielectric property measurements

(7) Surface penetrant, gas adsorption, and general surface phenomenon.

It is expected that the space shuttle program will benefit from NDT methods developed in the two programs mentioned earlier and in the current AFML NDT program: Investigation of NDT methods for multidirectional reinforced composites, F33615-69-C-1624 which is being performed at McDonnell-Douglas. Many of the NDT methods used for c/c composites may be appropriate for oxide insulation systems, especially Items 2, 4, 5, and 7 noted above.

EVALUATION OF PERFORMANCE DATA AND SCREENING TESTS DATA REQUIREMENTS--TASK 1B

CARBON/CARBON COMPOSITE EVALUATIONS

Materials similar to those proposed for leading edges on the space shuttle have been the subject of many R&D programs where the application has been related to one launch and reentry cycle. In these studies the needs for data evaluation techniques, and design procedures have been examined in great detail. Most successful have been the programs where the activities directed towards these subjects have been performed in very close liaison with the material developer. The importance of this liaison cannot be over emphasized. It extends into all facets of the evaluation requirements for design, use, and continuing in-service qualifications.

The requirement to inhibit the oxidation of these c/c composite materials will increase the complexity of the leading edge materials, their evaluation, and appropriate design procedures.

These materials are brittle and very likely to be mechanically, physically, and chemically anisotropic. Therefore, their evaluation will be expensive since they will be conducted in reference to orientations and to integrated use. The determination of properties after use may be particularly important in that the differences in compositions that may result from use are likely to affect both mechanical and physical properties and their corrosion resistance. Further, these changes may switch failure modes and corrosion products may have effects on adjacent structures and thermal protection system components.

Structural Design Considerations

The inhibited c/c composites will behave in a brittle manner. This behavior is accepted because of their attractive attributes such as high specific strength and stiffness and relative inertness in high temperature air. It may also be that the c/c composites which exhibit the most attractive strength and ablation performance characteristics will be anisotropic in mechanical and thermophysical properties.

The brittle nature of the materials makes their tensile strengths a subject of principal concern and components will be so designed that fiber alignment will be, for the most part, in the direction of maximum tensions in service. Therefore, principal attention in screening will be given to assessing their resistance to tension in the direction of fiber alignment.

Performance in Use. The leading edges have the dual purpose of maintaining an aerodynamically viable leading edge shape and accepting the high heating loads associated with their location on the vehicle. The general outline is a thin plate curved to present a continuous, smooth surface from top to leading edge to bottom of roughly the forward 10 percent of the wing chord. This curved plate will generally be stiffened by inward projecting webs and bosses which also support attachment pins. The design of the leading edge which includes the total length of the span, the web or stiffner placement, the attachment method, etc., has not been finalized. Therefore, the performance requirements in these areas must be speculative.

Leading edge candidate materials are structural materials and as such are expected to be little affected by aerodynamic, aeroelastic, or aeroacoustic loads at low temperatures. However, some of the candidate materials, because of the addition of oxidation inhibitors, might become plastic at peak temperatures and permanently deform under load.

Thermally induced stresses are expected to be relatively severe during reentry. Thermal expansion of the hot outer fibers will cause tensile stress on the cooler inner fibers and can induce a tensile fracture on or near the inside surface. The thermal gradient can also induce an interlaminar separation in the material.

At peak heating, the back of the leading edge is expected to attain a high temperature. Attachments must be designed to accommodate this temperature and the attaching mechanism must be compatible with the composite at high temperature.

The response of a c/c composite mechanical and thermophysical properties to high temperatures is known. These materials will provide surprises only in relation to the inhibitor phase in the material. It is expected that each composite chosen for design will have been well characterized before the design is finalized such that the deficiencies brought about by inhibitor addition will be known.

Leading edges are expected to recede via ablation during use. The overall design of the shuttle vehicle depends on rapid replacement of leading edges at regular intervals (for example, 10 cycles). Because of recession, the material will be continuously degraded during use. The effect of this degradation on the overall response of the material must be predictable from inspection routines in order to replace the material before failure is likely to occur in flight.

Structural Failure Definition. While the nature of the brittle failure (as might be expected from these leading edge candidate materials) has been studied and defined in great detail, the definition of failure for filamentary c/c composites is more elusive. In complex composites the presence of pseudotoughness has been observed. This attribute comes from a parting of the materials that bind the fibers together in a manner that does not produce catastrophic failure. This attribute would be highly desirable in terms of fail-safe performance for a structural leading edge and conceivably is a characteristic of (some of) the candidates.

The definition of structural failure must be the inability of the leading edge to perform as an integral part of the structure. The significance of this failure would only be as critical as the designer chose to make it in the performance of the space shuttle at the time of the flight during which the failure occurred.

Characterization Needed for Structural Design Screening. As noted earlier, principal stresses from mechanical loads would be expected to be oriented (by design) in the direction(s) of the carbon fiber alignment(s). This approach does not include consideration of the thermophysical properties and the stresses produced by thermal gradients which can be critical to performance. Therefore, in order to screen materials for structural design potential, the most important information is gained from measurements of strain (ε_t) and fracture stress (σ^*) under tension (σ_t) in the direction of the fiber alignment. These measurements should be conducted so that information is obtained on:

(1) The temperature (up to near service) dependence of

ϵ_t vs σ_t and σ^*_t

(2) Whether the coating contributes significantly to

ϵ_t vs σ_t and σ^*_t

(3) The effect of oxidative heating of the skin on

ϵ_t vs σ_t and σ^*_t

(4) Reproducibility of test results.

Poor characteristics with respect to any one of these four items would constitute a warning against use of the material.

Two types of tests might be used for these measurements--direct tension and bending. However, because of the nature of the subject materials, bend tests would be preferred. This preference is based on consideration of experimental control and test simplicity, and on the need to evaluate the properties of the leading edge materials in terms of surface (inhibitor) layers, thickness, and service. The analytical complications introduced by the use of bending instead of direct tensile tests require appropriate test instrumentation.

For screening, assumptions that the effects of strain rate, stress state, and stress gradient, on strength and elastic moduli are the same for all candidates regardless of composition or direction of stressing can be made.

Tests will be needed to determine effects of surface layers and no assumptions should be made that the back and front surfaces are the same after inhibitor processing. Test data on the effect of orientation of the test specimen to filament or cloth orientations will also be needed.

Thermal Design Considerations

Two kinds of in-service loading need to be considered--thermal and mechanical. Analyses at Battelle, discussed later, conclude that the best (probably only) way to assess resistance of complex c/c composites to thermal loading at this time is analytically, through the use of data from separate mechanical and thermal tests. This requires comparable values of the effective Young's modulus and fracture strength along with thermal expansion and thermal conductivity data.

Thermal stresses accompany temperature differentials in a solid body. The stress system continuously changes during periods of heating or cooling the body, and a stable stress system develops after some period with steady heat flow through the body. The stress system is comprised of combined (biaxial or triaxial) stress states, and is characterized by stress gradations between high- and low-temperature sites such that the hotter areas experience compression and the cooler ones experience tension.

Details of the leading-edge design and flight trajectory along with thermal and elastic properties of the c/c composite material determine the thermal stressing conditions of concern. Thus, design and flight adjustments as well as material choice offer approaches to preventing failures from thermal stresses. Although not treated here, it is recognized that aerodynamic and structural loads will superpose a mechanical stress system on the thermal stress system in service, which might be either favorable or unfavorable.

Beyond simple elastic accommodation, c/c composites might respond to the stresses they will experience in TPS service by fracturing or by localized material flow. Both types of response need to be considered in screening these materials. However, fracture has much more serious consequences and, because of the brittle character of these materials, is probably the most critical limitation.

Carbon-base materials tend to become plastic at temperatures around 4300 F, and the additives or coatings used for oxidation protection would be expected to lower the softening temperature. Such flow will tend to relieve thermal stresses throughout the body, and allow thermal loading to proceed without fracturing the body. However, such flow could lower appreciably the material's resistance to subsequent thermal stressing, by freezing-in a deleterious stress system on cooling from the plastic state. The severity of the residual stresses would depend on the rate of cooling through the temperature regime where the material changes from plastic to elastic.

This suggests that for screening one would need to know likely peak temperatures in service, and rate materials on the basis of tendency to flow at these temperatures by an appropriate screening test; e.g., hot hardness or an unsophisticated creep (hot-load) test might be adequate for a first look.

Stress-induced material transport also is observed in bulk graphites at room temperature, as evidenced by a small residual strain on unloading before fracture in mechanical tests. This flow also would tend to relieve thermal stresses throughout the body. However, it would probably be exhausted on repeated thermal stressing, and any dependence on it would limit the number of thermal loadings that a c/c composite could survive.

Any adjusting flow in the material, whether thermally activated or simply stress induced, will change the c/c composite's resistance to fracture. This suggests that resistance to fracture (strength) should be determined both before and after deforming each composite as part of the initial screening program. In the case of thermally activated flow, care should be taken to insure that specimens are thoroughly annealed before testing. In this screening, one is concerned about whether the material is weakened or strengthened by each type of flow and the extent of change. It should be kept in mind that during a single flight, areas of the leading edge will be subjected first to flow stresses (shear) and later to fracture stresses (tension) by the thermal loading. Thus, screening tests of only virgin material for fracture resistance could be misleading even if reuse capability is neglected.

As indicated above, screening for resistance to fracture by the service-imposed thermal-stress system is of primary concern. In order to assess this resistance, it is essential to observe fracture and, in some way, to assess the stress (or strain) that caused the fracture crack to develop. If screening is by a thermal-stress test, it is essential to measure some quantity at fracture that is related in a reasonably known way to stress (or strain) at fracture.

In considering what to measure, no thermal-stress test is known in which the strain causing fracture has been successfully monitored. Tests have been used in which the instantaneous surface temperature change to cause fracture is measured, and in which the steady heat flow (or temperature difference) at fracture in the specimen is measured.

The rationale behind each type of test being that fracture stress is directly proportional to the measured quantity in that particular test. This proportionality is obtained from analytical descriptions for the conditions to initiate fracture in a Hookean isotropic solid. A basic assumption in the analyses is that fracture occurs when a critical tensile stress is reached in the solid. Also, it is assumed that coefficients of thermal conductivity and thermal expansion and elastic moduli do not vary with temperature in the body. On this basis, the following proportionalities have been found:

$$\Delta T_f = R_1 S = \frac{\sigma_f}{E\alpha} \cdot S \quad ,$$

$$W_f = R_2 S' = \frac{\sigma_f k}{E\alpha} \cdot S'$$

where:

ΔT_f = instantaneous surface temperature change to cause fracture

σ_f = tensile fracture stress

E = Young's modulus

k and α = coefficients of thermal conductivity and expansion, respectively

S and S' = shape factors, parameters dependent only on specimen geometry*

W_f = steady heat flow that will cause fracture.

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* Poisson's ratio is included in the shape factors, since the nature and extent of its influence depend on the shape under consideration. So doing, involves the assumption that Poisson's ratio does not vary significantly among different brittle materials.

These analytical considerations provide the basis for assessing resistance to thermal fracture. If the shape is constant and the shape factor unknown, either ΔT_f or W_f would be the screening criterion, depending on the test conditions selected. Different shapes could be used in screening only if the shape factor can be evaluated. A different value of ΔT_f or W_f will be obtained on specimens of the same material having different geometries. Size, per se, may or may not have an effect on shape factor theoretically.

The relationship, $\Delta T_f = R_1 S$, requires an <u>instantaneous surface</u> temperature change for use in evaluating materials. This means that Biot's modulus, β, must be large (a limiting minimum value of about 20 has been reported).

$$\beta = \frac{r_m h}{k} ,$$

where:

r_m = distance from center to surface of specimen
h = heat-transfer coefficient between surface and surroundings
k = thermal conductivity coefficient.

ΔT_f is not directly proportional to fracture stress in tests where β is not small yet is below the minimum value, and the basis for rating materials that are fractured in such tests is not scraightforward. It might be possible, however, with exact knowledge of h.

Since fracture occurs from tensile stresses, tests based on the relationship, $\Delta T_f = R_1 S$, could only be accomplished with sudden quenching from a uniform high temperature. Sudden heating places the surface in compression, and any fracture would initiate at a nonsurface site, invalidating use of the ΔT_f criterion.

There are no available tests in which c/c composite specimens might be fractured by an instantaneous surface temperature drop. In general, such shock tests are difficult to conduct and involve a considerable number of experiments to obtain a data point. Not much effort has been devoted to their development for materials evaluation purposes. This leaves the possibility of using the relationship, $W_f = R_2 S'$, as a basis for a screening test in which the material is actually fractured from an imposed thermal stress.

A review of efforts on thermal-stress testing of graphite indicates the dominant concern has been on finding laboratory conditions severe enough to cause fracture. In the development of these tests, little attention has been given to whether the quantity measured is proportional to the stress at fracture. On the several tests reviewed, only one has been developed (at ORNL) that seems to offer much hope for fracturing c/c composite specimens. In it, a poorly defined, generally radial outward heat flux is imposed in a solid disk specimen by arc heating at a central point on one surface. The power to the arc that causes fracture is measured. It appears that the test might give a rough approximation of the heat-flow conditions where $W_f = R_2S'$ are applicable, with the measured power indicative of W_f. The stress causing fracture is probably a tangential tension at the outer surface which reaches a maximum at steady state for each power setting of the arc. In general, results from this test at its present stage of development are not considered sufficiently meaningful for its use as a screening test in our program.

A somewhat more refined test has been developed at Los Alamos, which also seems to approximate the heat-flow conditions necessary for use of the relationship, $W_f = R_2S'$. However, the possibility of fracturing c/c composites in it appears to be rather remote. Further consideration should be given to the potential of this test, however; particularly the feasibility of achieving greater thermal loadings. The same general conclusion applies to a test developed at TRW. As added concerns to be checked, it may not be possible to prepare suitable specimens for it from available panels of c/c composite materials.

The BCL test is by far the most refined one available. In it, R_2 values are measured directly (i.e., the value of S' is known) and with considerable precision because the thermal-stress system has been well defined and is under good control. With this test, the dependency of R_2 on temperature also can be assessed. However, at its present state, it is quite unlikely that sufficient thermal loading can be obtained to fracture c/c composites. Two ways to modify the test so that materials like graphite can be fractured have been proposed, but at least a 6-month program would be required to qualify either modification. Thus, the use of the BCL test at its present state in the screening program is limited to determinations of effects of thermal stressing on properties or microstructure and, perhaps, to fracturing laminar composites on weak planes between plies.

In view of this apparent lack of any adequate test method in which the c/c composite specimens could be fractured by thermal stressing, screening can only be accomplished from data on individual elastic, thermal, and strength (fracture stress) properties. For this approach, one can take the position that fracture occurs when a critical condition of stress is reached without regard to whether the stress system results from mechanical or thermal loading. If appropriate data are used, this position is sound, and one can determine R_1 and R_2 values as the screening criteria. Further, by use of a model material(s) that can be fractured in the BCL thermal-stress test, one could obtain a good indication of whether the data being used are appropriate. Also, it is to be expected that much of the same data needed will also be required for design purposes, so that its generation need not be considered as solely for materials screening.

The kinds of properties needed are fixed by the R_1 and R_2 parameters (E, α, k, and σ_f). However, the requirements in testing to obtain suitable data are not a simple matter, involving such considerations as needed accuracy in all data; how to treat temperature, anisotropy, and coating effects; and specification of what σ_f to use and the best way to measure it with recognition of possible strain-rate, test hardness, stress-distribution, and combined stress effects.

Quality Control and NDT Considerations

Even the best behaved carbon-base materials such as the bulk graphites present difficulties in design. This difficulty arises because of anisotropy and the brittle nature of the materials that is a result of the multiphase nature of all structural bulk graphites. Carbon/carbon composites are special cases in that greater differences exist in their constituents and anisotropy both on micro and macro scales. In addition, c/c composites are much newer in development than the bulk graphites. It is imperative, therefore, that all practical quality control practices be used in producing these materials.

One important aspect of quality control is careful and deliberate reproduction of all processing parameters. This requires that good records must be kept during the development of the material. Processing equipment must be capable of rigid control in all operations. All of the candidate materials require a pyrolyzing heat treatment which provides the foundation for further treatment of the material. NDT techniques must be incorporated as soon as possible to assess the quality of the material.

Some quality control can be exercised by careful adherence to processing specifications, more information on the importance of this control can be gained by the destructive examination of similarly processes pieces or of edge areas in the production piece. However, the most direct method is NDT of the piece itself. NDT can be applied to material for two different types of assessment: (1) determination of data for calculation of physical and mechanical properties, and (2) determination of data for the assessment of defects.

Fair success has been achieved in using NDT data for the calculation of density, modulus, and tensile strength of individual bulk graphite pieces. However, assumptions must be made that require considerable detailed experience with the material, much more than is available on any c/c composite. The only NDT procedure that might be used to assess a c/c composite property is radiometry for the determination of density. Even this technique would probably not apply for inhibited c/c structures.

Various NDT procedures are available for defect determination in the subject materials. They are:

(1) Ultrasonics (velocity, through transmission, back echo)
(2) Radiography
(3) Eddy currents
(4) Thermal transmission
(5) Radiometry
(6) Holography.

None of these methods have been developed to the point of complete reliability. Radiography has had the widest usage and must be a part of this quality control program. Ultrasonics has been demonstrated in detecting defects in c/c composites. Either through-transmission or back-echo "C" scans are applicable but the technique requires a great deal of experience in instrumentation. Eddy currents are limited to surface or near surface inspections and cannot be applied to a surface that is an electrical insulator. Multifrequency eddy currents can be used to identify and position a near-surface defect more accurately than the conventional method.

Radiometry is a valuable tool in detecting density variations in well characterized homogeneous materials. It may not be applicable to inhibited c/c composites. Holography and thermal transmission techniques are the newest of the NDT methods. Both have demonstrated capability in NDT of c/c composites. Thermal transmission results in a plot similar to an ultrasonic "C" scan for detecting defects. Holography detects the change in strain on a surface of a material which has been stressed in another area. Defects within the material will cause the surface to strain nonuniformly and likely areas of failure can be detected.

Techniques that may have application for in-service inspection will depend on the design of the component (wing, fin, etc.). Techniques that require access to the inside surface are: radiography and radiometry, thermal transmission. Those that require a coupling to the surface are: through transmission and back-echo ultrasonics. The one technique that can be performed from outside the surface and without a coupling to the surface is eddy currents. Therefore, multifrequency eddy currents may prove to be a valuable technique in in-service NDT inspection of leading edge materials.

Candidate Materials Descriptions and Assessments

This discussion provides an assessment of some of the problem areas likely to be associated with each of the leading edge candidate materials for which processing information has been received. All of the materials proposed are development-type materials and little characteristics information is available. The Union Carbide material will not be discussed since the nature of the material has not been revealed.

General Electric. The omniweave method proposed by G.E. appears to offer a good method for increasing the interlaminar strength of c/c composites. Because of its physical flexibility after weaving, processing into leading edge forms should be relatively easy. This is not to say, however, that the mismatch in matrix-filament will not be a problem. The combination of resin and CVD binder system should result in a better matrix than either alone. The reason for using silica fibers is not clear. The total volume of fibers in the material will certainly be less than 50 percent. If any carbon fibers are replaced with silica, the structure can only be weakened, particularly at high temperature where silica softens. There would appear to be adequate room in the structure for addition of the protective materials without replacing carbon fibers. For example, if the c/c composite (not including other materials) is 1.3 gm/cc density, about 42 percent porosity is present. Possibly 80 percent of this or over 30 percent of the structure is available (without penalty) for the insertion of protective materials.

The specific carbon filament to be used is not specified in the General Electric proposal. The designation of high strength and low modulus leads to the thought they may be contemplating a carb ized PAN fiber. This fiber is generally easier to bond in a matrix than the graphitized version; therefore, the choice of fiber appears to be correct. In addition, the lower modulus filament may be easier to weave than very stiff filaments would be.

The proposed material may have the highest density (in c/c composite) of those proposed because of the dual binder application system and because the 3-dimensional weave pattern does tend to give a permeable network for binder application. Therefore, the c/c composite should have good resistance to oxidation. Providing the oxidation protection system is acceptable, the material should be one of the most promising for leading edge application.

AVCO. The orthogonal 3-dimensional weave that could be performed by AVCO should be included in the program for completeness. It is the only orthogonally woven material among the six being prepared for this program and could provide answers to questions concerning the need for good interlaminar strength in the leading edge material. It appears from their proposal, however, that only the 3-inch diameter x 0.250-inch thick disks will be 3-dimensionally woven. Their proposal, in this case, is nothing more than a test of their protective system, since 2-dimensional laminated structures with essentially the same properties will be available in the program from other suppliers.

Orthogonally woven 3-dimensional composites offer upgraded third dimension properties over that of the braided omniweave construction proposed by General Electric. AVCO has performed considerable government-sponsored research with 3-dimensional woven structures. This work has shown that the mechanical and thermophysical properties can be about equivalent in each direction. This results in a tremendous increase in the "Z" direction (what would be interlaminar of 2-dimensional material) properties. For example, the tensile strength may be increased from < 1000 psi to > 4000 psi without significant sacrifice in properties of the other two dimensions. However, the thermal conductivity in this direction will also be increased by a small amount.

The 2-dimensional materials which appear to be proposed by AVCO will not give an assessment which can be used to judge 3-dimensional material. The six 3-inch diameter disks can only serve as ablation and thermal conductivity specimens; therefore, the screening program cannot adequately judge orthogonally woven composites.

Problems may arise in the oxidation protection system proposed by AVCO. There will certainly be some mismatch between the proposed SiC coating and the composite, at least on a microscale. This mismatch usually results in a debonding of the coating in successively bigger areas as the material is temperature cycled. The result is spalled coatings eventually and a loss of protection.

McDonnell-Douglas. The structure of the MDC material will be typical of 2-dimensional composites. It will exhibit good mechanical properties along the length and width of the material and relatively poor properties in the "Z" direction (through the material). Apparently, they will use only the pyrolyzed resin bond system. Even if the material is reimpregnated to increase the density, the matrix will likely be inferior in certain respects to a combination (coke and pyrolytic carbon) matrix system. The basis c/c composite can therefore be poor with regard to oxidation which results in a greater demand on the oxidation protection system. MDC will apparently use the internal oxidation protection system with some combination of the elements--boron, silicon, and zirconium. The oxidation protection system should be similar to that proposed by General Electric; therefore, a good comparison of c/c composite structure should be possible.

LTV System. The c/c composite proposed by LTV is nearly identical to that proposed by MDC. There may be a difference in both the carbon cloth and the precursor resin matrix, but the materials are likely to be very similar basically. Both will be subject to delamination during processing, probably more so than woven structures. Each will have relatively poor interlaminar mechanical properties.

LTV proposes a unique (for this program) oxidation protection system. This protection system involves a "diffusion coating" technique to apply silicon and tantalum presumably in the carbide form. Some experience has been obtained with LTV's silicon carbide protection system. In the materials examined, the silicon carbide appeared to impregnate more than to coat, i.e., the carbon present in certain areas was simply converted to the carbide and no intact, impervious coating was evident. The graphite fibers as structural entities in the composite are destroyed by this system and, in addition, considerable weight pickup is necessary to protect the remainder of the carbon. If the Si-Ta system to be used produces "coatings" similar to the Si "coating" in the preliminary material, there are several areas that deserve close scrutiny:

(1) The coatings tend to be inhomogeneous, both across the piece and through the piece.

(2) Carbon filaments are destroyed, at least in the surface areas, and replaced with the carbide which is much weaker because it is not a single crystal whisker.

(3) The strength of the material is apparently greatly degraded when sufficient oxidation protection is afforded.

(4) Starkly different phases within the material (carbide and carbon) may not be compatible structurally or thermophysically.

Hitco. Hitco is apparently proposing a typical cloth laminate using prepreg graphite cloth and their standard Pyro-Carb processing cycle. Because the material is as close to a production item as any c/c composite, it may be more reproducible than, for example, the omniweave or 3-dimensional weave.

The information on the oxidation protection system proposed by Hitco is very limited. It states only that the material will be machined to shape prior to coating with refractory metal. Apparently the protection system will incorporate both interstitially placed refractories and an external coating. Providing the coating is identical or chemically compatible with the internal oxidation protection material, the combined protection system should be superior to either internal or external alone. However, the weight of the material may be increased significantly over the single system.

The basic c/c composites proposed by Hitco, LTV, and MDC are similar, 2-dimensional cloth laminates. They will all be relatively weak in the interlaminar direction and subject to delaminations during processing.

Union Carbide. No information was available as to the nature of this material.

Screening Test Plan

The objective of the screening test plan for the oxidation-inhibited c/c composites is the generation of data and information that will permit the ranking of candidate materials in their proposed application as leading edges for the space shuttle.

The approach to be used in the evaluation of oxidation-inhibited c/c composite materials for application as leading edges for the very hot surfaces of the space shuttle differs significantly from the screening test plan for the external insulation materials candidates.

The differences in this test plan's approach and details are necessitated by two important considerations:

(1) The c/c composite materials will be used as a structural leading edge; therefore, the external shape, dimensions, and the internal configuration details of the structures will be a product of a design based on thermal and mechanical properties and the expected thermal and mechanical loads.

(2) The simple shapes of the candidate materials that are available are, or should be, representative of the external skin structure and sections of internal structure such as stiffening webs.

These above considerations preclude the value of conducting tests that would quantitatively measure the effects of environmental or structural loads. Rather, it becomes more appropriate to conduct evaluations: to estimate the state of development of the materials, to measure simple properties, to record how the materials respond or fail in environmental tests, to interpret by analysis the cause of the failures, and to comment on how much freedom will be available to the designer.

It is apparent that the evaluations will be much more subjective than the evaluations to be performed on the external insulation materials. In spite of this, a total appraisal and a positive ranking of the candidates can be made. This positive ranking will be the product of an evaluation test plan "logic tree". This tree will consider the differences and the similarities of the c/c composite material candidates and give weight to the special requirements of leading edge applications.

Figures 1 and 2 illustrate the evaluations and tests that will be performed in sequence and in concert. The materials received would all be nondestructive test (NDT) in order to estimate the uniformity of the samples and to aid in the selection of specimens for each of the evaluations or tests.

The evaluations and tests to be performed will be accomplished in four parallel programs: Morphological (and chemical), Environmental response, Mechanical properties, and Thermophysical properties. The morphological and environmental evaluations will be performed first, closely followed by the mechanical and thermophysical property determinations. Pretreatments (thermal cycling) of the specimens used for property tests may be imposed if the environmental tests indicate such treatments would be appropriate.

The early evaluations (Part One, Figure 1) of the candidate material for morphological details (compositions, homogeneity, isostrophy, microstructure, etc.) and response to arc jet environmental heatings is justified by the necessity to obtain information on which to base a decision to initiate

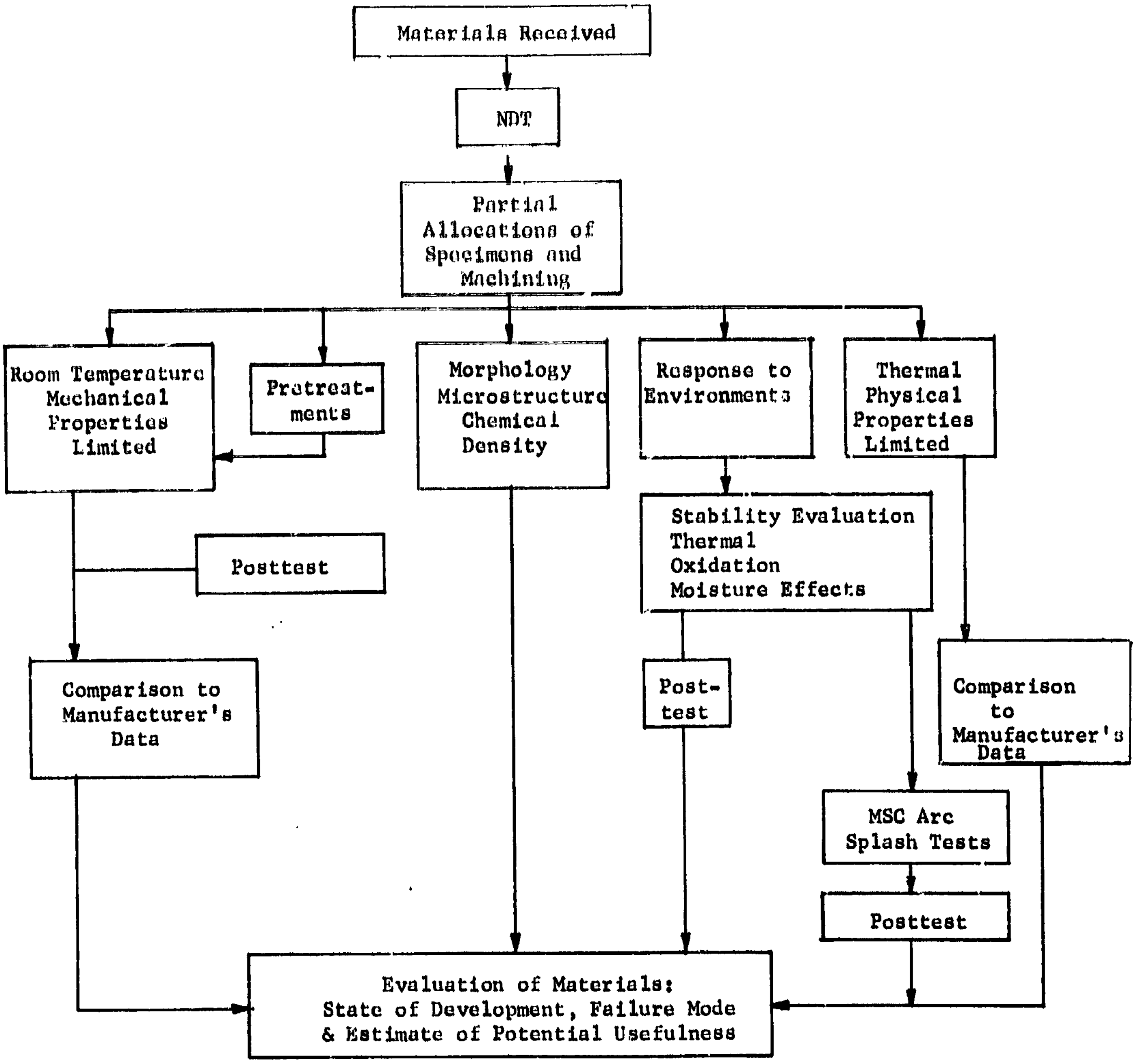

FIGURE 1 . PART ONE OF SCREENING TEST PLAN FOR CARBON/CARBON COMPOSITES

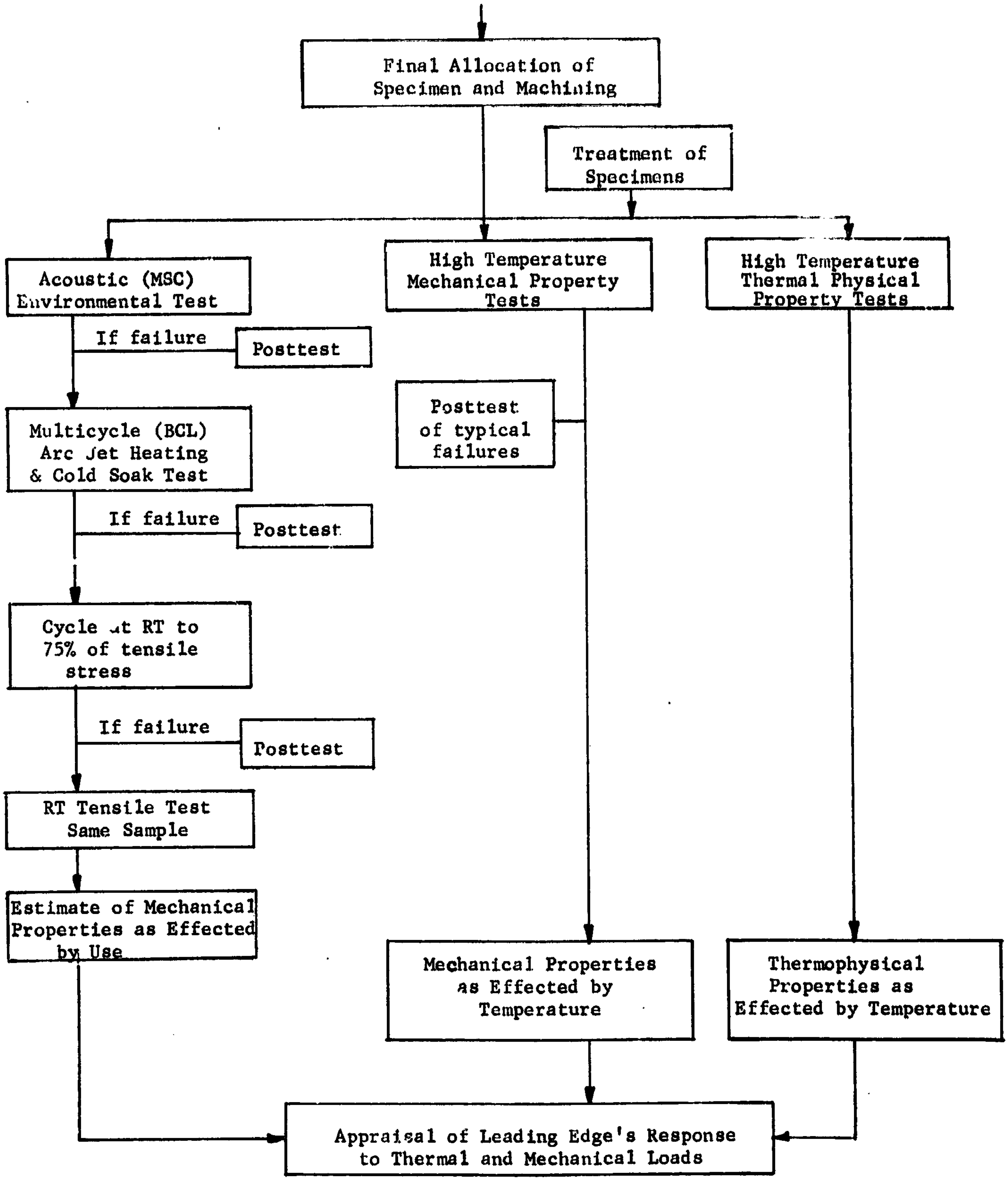

FIGURE 2. PART TWO OF SCREENING TEST PLAN FOR CARBON/CARBON COMPOSITES

the costly high temperature thermophysical and mechanical property testing. If sufficient documentation is obtained on the state of the materials' development and if the material exhibits good (low recession and no thermal stress fracture) response in the arc jet heating test, the high temperature thermal physical and mechanical properties tests (Part Two, Figure 2) would be initiated.

External Insulation Evaluations

The external insulations cover that large portion of the vehicle exposed to intermediate reentry heating loads--less severe than the concentrated areas of high heating rates such as the leading edges, but more than can be tolerated by acceptable structural materials. Compromises between estimates of acceptable temperatures and the amount of the vehicle surface requiring special "leading edge" type material design led to the selection of 2500 F as the maximum surface temperature for the external insulators.

The insulation thickness is defined by the 500 F temperature limit on the adhesives bonding the insulation panels to its supporting substructure. Nonablative external insulations must be capable of withstanding the exterior influences of rain, snow, dust, and handling without degradation so future flights without refurbishing are possible. In addition, the external insulations should not fail catastrophically under extreme use such as might be associated with an abort reentry. It is expected that acceptable external insulators will degrade controlledly during over-design exposure giving a fail-safe behavior whenever reuse is sacrificed.

Structural Design Considerations

The failure criteria for the design of external insulators are related primarily to strain compatibility of the insulator material with the substrate structure to which it is bonded. The external insulation material is to be bonded directly to the lower portions of the wing surfaces and also is to be bonded to light weight structural panels, roughly two feet on a side, spanning the fuselage framing members. Consequently, two somewhat different strain compatibility situations exist: (1) on the bottom of the wing boxes where the section is deep and the strains are imposed quite independently from the insulation; and (2) on the fuselage panels where the support structure to which the insulation is bonded serves only the function of carrying the loads imposed on the panel.

In both cases it can be assumed that the insulation adds a negligible stiffening to the structural material to which it is bonded. Consequently, the loading of the structure defines the strain at the structural surface which will be the boundary condition strain imposed on the insulation. If the loading on the structure is pure tension, the same strain should ideally be applied to the outer fiber of the insulation as to the bondline. If, however, the bondline strain is caused by flexure, a constant strain gradient will exist in the structure which will locate a "neutral axis" a distance, c, from the bondline. Ideally, the strain imposed on the outer fibers will be increased by the amplification ratio, A, where

$$A = \frac{c + t}{c} ,$$

and t = insulation thickness

c = distance from bondline to neutral axis.

This can be illustrated in Figure 3 which shows the strains in a differential length at midspan of a "long" beam....one where planes in the unstrained material remain planes when loaded.

The amplification,

$$A = \epsilon_2/\epsilon_1 ,$$

is not applicable at the ends of the beam for here $\epsilon_2 \longrightarrow 0$. Moreover, near the ends, the stress state is quite complex in response to the loading condition at the bondline, even when ϵ_1 is constant over the full insulation span. Because of the bonding, the strain in the insulation at the bondline is identical with that of the support structure; but the insulation is loaded only through shear stresses adjacent to the bondline. For an extremely short insulation span, the bondline shear increases from zero at the end to a large value at midspan; but the maximum tension strain in the outer surface of the insulation may be less than the amplified value, $A\epsilon_1$, and in actuality could be less than the bondline tension strain ϵ_1.

As the insulation span increases (relative to its thickness), the shear stress increases from zero at the end to a maximum, then decreases

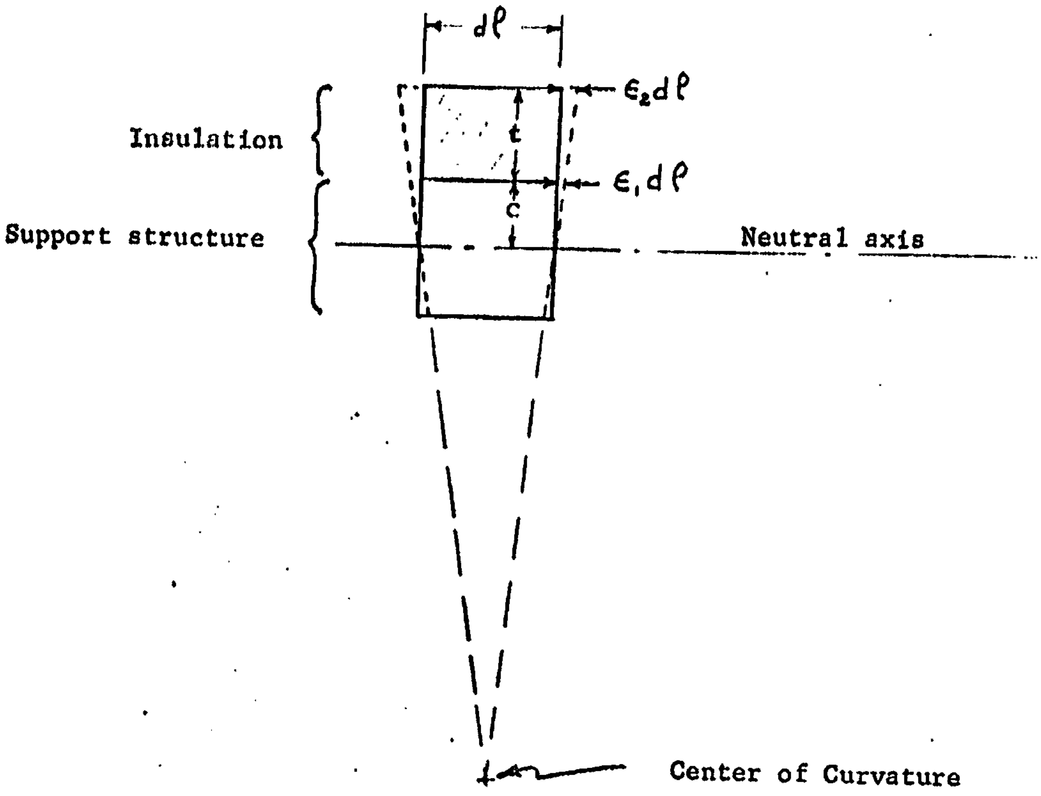

FIGURE 3. IDEAL STRAIN AMPLIFICATION

toward midspan. For a long enough span, the shear stress pattern near the end stabilizes, going from zero at the end to a maximum about one thickness in from the end, then decreasing toward zero at midspan. The tensile strain at midspan approaches the ideally amplified value. Further increases in insulation span merely increase the central span that experiences the ideal strain amplification but the edge zone stresses are unchanged.

The shear stress near the end could lead to a failure in the fibers adjacent to the bondline that is quite common and is often referred to as a delamination failure. Also associated with this shear pattern is a tensile stress, normal to the bondline, which reaches a maximum at the end of the panel. This is commonly called a "peel" stress and is partly responsible for delaminations.

The two design locations are representative both of different ideal strain amplifications and different bondline strain patterns. For the wing box, $c \gg t$ and "A" is not much larger than 1. For the fuselage panels, however, c and t are apt to be similar numbers and $A \simeq 2$ is not unreasonable. The wing box is also long compared with the insulation panels so that the bondline strain changes little across a given panel just as the "moment diagram" changes little over that portion of the wing span covered by a single insulation panel.

The fuselage insulation panels, however, could be considered to be supported by structural panels the same size as the insulation. Regardless of how the edges are supported, the bending moment diagram is variable over the span and a complex condition exists, particularly near the edges. If the span is "long" and the moment diagram less rapidly changing, ideal amplification of tension (or compression) strains will occur at midspan. The changing bondline tensile strain near the ends should be expected to reduce the size of both the peak bondline shear stress and the peeling tensile stress at the end, relative to the midspan bondline strain.

The critical failure stress state could be outer surface tension, tension perpendicular to the bondline at the end of the panel, and/or bondline shear, depending upon the way in which the insulation takes up the strain imposed at the bondline. The design problem, then, requires the determination of the limiting bondline strain profiles that will not exceed any of these critical stress states. It is further complicated by the effects of the bond itself on the distribution of stress between substrate and insulation. A thin, hard (inelastic) bond represents one limit, while a thick, softer bond can reduce the stress patterns at the edges but adds weight to the system.

<u>Performance in Use</u>. Aerodynamic loads cause direct compression loads [illegible] the surface of the insulation that it must transfer to the substructure. The loads are small, generally less than 1 psi, and can be neglected as direct contributors to the stress state of the insulation. Their loads, however, do strain the substrate as a uniformly loaded beam (or panel) and cause deflection accordingly. The beam loading of the substrate would normally be related to the allowable level of stress at its surface which corresponds (through the elastic modulus) to an allowable surface strain. An ideal external insulator would tolerate this strain and the associated amplification. An acceptable external insulator would not limit the acceptable bondline strain/strain-amplification levels significantly, for to do so would be to require very rigid construction that would be intolerably heavy.

Aeroelastic loads and vibration loads would impose beam loading on the substrates as uniform loads providing the resonant response is in the first mode. Regardless of mode, the substrate behavior is like a beam and the insulation must respond to the particular bondline strain/strain-amplification conditions imposed without failure. The insulation adds only a small mass and possibly a slight damping to vibration responses.

Aeroacoustic loads will deposit energy in the external insulation material directly in the high frequencies and will drive the substructure in the extreme lows. Materials properties will define the response to the highs, so direct tests are necessary; whereas system flexural resources will define the limits to the lows and design analysis of resonant responses will suffice.

Attachment is related solely to the adhesive used. As discussed previously, elastic bonds can reduce the severity of the stress patterns near the panel edge but would probably not affect the central portions.

In the design procedure, the insulation thickness is reduced in relation to the peak temperature so that the same maximum bondline temperature results from the local thermal pulse at the surface of that panel. Two critical modes of thermal stress can be defined:

(1) At the earliest point of peak heating

(2) When the bondline reaches its maximum value.

At peak heating, the temperature gradient will be restricted mostly to the insulation, with the structure changed very little in temperature. This large temperature difference would cause the outer surface to try to elongate while being restrained by the flat, unstrained bondline. Because the thermal expansion coefficient of LI-1500 is about an order of magnitude less than most common materials and because the elastic modulus is at least three orders smaller (than steel, for example), the stress imposed by the large temperature difference is not critical. (Example: at $\Delta T = 2000$ F the induced stress would only be about 18 psi, well below the low ultimate strength values reported for this material.) However, it could be sufficient to fracture other candidate materials.

When the bondline is at its maximum temperature, the outer fiber of the insulation is relatively cool. The insulation, however, would be highly strained because its bondline is strained by the thermal expansion of the structure. To make matters worse, the bondline strain is a flexural because of the temperature gradient in the structure; consequently, the strain at the outer fiber of the insulation is amplified from that at the bondline.

In this case, the support structure next to the bondline may be virtually unstressed because it will be axially unrestrained, whereas hot LI-1500 insulation next to the bondline should be in tension because the thermal expansion of the insulation is expected to be much smaller than that of the understructure. The tensile strain in the insulation will increase to a maximum at the outer fibers of the insulation. As in bending, the bondline of the insulation is strained by the support structure, the outer fibers experience an amplification of strain, and this strain loading is transferred through shear near the bondline in the insulation. This shear peaks near the end, as in the flexure situation, and is accompanied by a high tensile stress at the end normal to the bondline plane.

The shape of the temperature gradient in the support structure merely affects the ideal strain amplification to the outer insulation fiber. So also, would bending imposed by a simultaneous structural loading. The outer fiber of the insulation, which is relatively cool, should experience the same strain limitation as under bending if it were the critical failure point. If, however, the limiting strain that could be imposed on the outer fiber were defined by a failure at the edge (delamination or peeling), that limiting outer fiber strain will be dependent on both the ideal strain amplification and on the changes in properties of the insulation at the bondline temperature.

Exactly the same stress states occur in the thermal strain loading as in the wing loading, for the moment is essentially constant along the panel....although amplification factors may be different between them. The fuselage panels, however, can experience a parabolic bending moment from aerodynamic loading and from "g" loads, either steady or cyclic. This may reduce the severity of the stress state at the edge and lead to larger allowable maximum bondline strains in the middle of the panel.

Structural Failure Definition. Whereas a permanent deflection or a crack are obvious failure conditions for a structural material, the situation for a relatively weak strain loaded material is less clear. Previous discussions centered around objective criteria such as failure stresses but subjective re-evaluations will be significant. Any crack that leads to the loss of chunks of material and obvious degradation of the structural shape and integrity must be avoided. Similarly, an edge (delamination and/or peeling) crack that allows the insulation to lift from the surface during load and present an uneven surface (particularly for aerodynamic heating) must be avoided.

But what about a stable crack in the coating? If such cracks can live in the arc (reentry) environment and don't get worse, it is likely they should be considered similar to the microcracks that exist in some of the materials from manufacture and should not be considered as design limits or as "failures". Separation between panels must exist, so cracks progressing the full depth of the insulation could even be acceptable if such a crack is stable and doesn't branch into a delamination or affect heat transfer.

Interior (delamination) shear cracks that are stable and don't lead to surface irregularities may also be acceptable. Consequently, bond perfection in the interior of the panel may be unnecessary....or, at least, the interior bond could be less critical than that at the edge.

Such factors must eventually enter strongly into the design process. Bonds different at the panel edges from the panel interior are rational. Deliberate cracking along prescribed patterns during manufacture could be attractive, so reducing the "length" of any continuous portion of a panel that its strain response is significantly improved.

Characterization Needed for Structural Design Screening. Assuming candidate materials are comparable in terms of the pure "thermal protection" function, the primary source of design interaction comes from the flexural strains at the bondline that the insulation can tolerate. It is believed that the most useful form of critical information would be in bondline strains at failure....ignoring differences in the actual mode of failure stress within the insulation. This becomes quite attractive as a potential screening mechanism for it is directly interpretable to the designer.

This is in direct contrast with testing to derive material properties such as the elastic moduli and ultimate stresses in the appropriate direction for both the insulation proper and the coating and, in addition, Poisson's ratio for the insulation proper and estimates of the coating thickness. These general properties would support test conclusions when they are ultimately utilized in design computer codes.

It is not clear at this time whether the response of these composite materials should be reduced to classically general analyses or should be treated as experimentally determined empirical correlations throughout development. It should be anticipated, however, that the most efficient design characterizations would come from a combination. Most analytical techniques involve assumptions such as the constancy or linear variation of properties, isotropy, and elasticity that need experimental correlation and verification. It would seem mandatory to bound the material loading regimes experimentally and then use analytical techniques to "interpolate" results to actual design conditions.

It is estimated that a square panel 25 inches on a side and on the order of one-inch thick would behave as a "long" structure and that a beam representing a central, full-span strip is a reasonable proxy for the full panel in screening tests. As the insulation span is reduced from that of the true span, the assurance is lessened that the stress patterns produced are representative of the critical patterns in the panel. Past experience with strain controlled laminate problems would lead to "rule-of-thumb" estimates that the beam would behave like a "long" beam at span lengths greater than ten times the coating thickness. For screening, however, reasonable first-order approximations of the relative behavior of the candidates are believed possible with reasonable length specimens.

Thermal Design Considerations

The external insulator, during the high heating rates, conducts only a small portion of the incident heat toward the vehicle, reradiating most of the heat from its surface. The emissivity of the surface must be as high as possible to limit the surface temperature which approaches the radiation equilibrium temperatures for any given heating rates.

The thermal conductivity must be low to minimize the heat flow into the vehicle and the thermal diffusivity (k/ρc) should be low to so attenuate the temperature pulse resulting from the peak heating pulse that the bondline temperature is limited to 500 F--the allowable limit for the adhesive. The bondline temperature defines the insulation thickness for this 500 F limit and is to be maintained for all portions covered with external insulation TPS. Since the weight restrictions of the vehicle dictate low densities, low values of thermal diffusivity are associated primarily with the low thermal conductivity but are benefited by large specific heats. The minimum practical thickness of insulation may also be important since vehicle sections needing insulation less than the minimum manufacturable thickness are, by definition, overweight if the material cannot be cut or ground thinner.

The thermal stress situation has already been discussed as part of the structural section.

Quality Control and NDT Considerations

An important part of the preliminary understanding of the external insulative materials involves Non-Destructive Testing (NDT) techniques for ascertaining the acceptability of any given specimen for use. Actually, three aspects are involved: (1) insight into the material to better understand the response of specimens to test loadings, (2) evaluation of the closeness "to standard" of given panels, and (3) evaluation of the degree of production control attained with given batches of specimens.

X-ray radiographs show net density patterns which can be related to some types of failure patterns. Variations within a given panel and interior flaws that would be indicative of poor production control should be readily determined by X-ray. Holographic techniques exist in which a panel can be lightly loaded to produce an optically recorded interference pattern that would be indicative of the way this panel responds to a "standard" load. Interior imperfections of significance should show readily but panel-to-panel comparisons may be too subjective to be reliable.

Depending on morphology, other nondestructive techniques with potential for providing information that would correlate with properties and/or performance include acoustic emission, dielectric measurements, and infrared heat transmission. The latter technique could be particularly significant in evaluating cracks and discontinuities in bonded panels for low temperature heating of the substrate would show discontinuities in an infrared scan wherever different heat conduction resistances should occur.

Candidate Materials Description and Assessment

The following discussion identified certain characteristics of each of the four known candidate insulation materials which could present specific problems or have certain advantages as a Thermal Protection System. Except for LI-1500 and mullite HCF, little specific information was available for the other candidate materials, so much of the assessments were made on the basis of expected characteristics of each candidate. Problems common to all of the candidate materials such as dimensional stability of the bulk material and coating compatibility cannot be evaluated due, for the most part, to the lack of data on laboratory-stage materials. Information on which this discussion is based was obtained primarily from company proposals which resulted in the following NASA contracts:

NAS 9-10917 (Lockheed)
NAS 9-10919 (McDonnell-Douglas)
NAS 9-10920 (Whittaker)
NAS 9-10921 (AVCO).

Additional information on LI-1500 and mullite HCF was available prior to the time the above contracts were received. No information was available on the materials Union Carbide and General Electric proposed for the TPS.

Lockheed (LI-1500). Lockheed has proposed using a chromia-silica coated variation of LI-1500 designated as LI-1525 for the Space Shuttle Thermal Protection System (TPS). This material is basically a fused silica fiberboard which would have a potential problem of devitrification of the fibers and/or bond phase. Devitrification (crystallization of the glass) of the material to cristobalite could be accompanied by a loss in strength, especially after repetitive cycling through the 300 to 600 F range where cristobalite exhibits a phase transformation characterized by a large volume change of the material. Alkali contamination (from coastal environments) would tend to accelerate devitrification and have to be avoided. Because the material must be fired at temperatures in the vicinity of 2200 F or below to avoid devitrification, cyclic heating to higher temperatures can cause dimensional stability problems from additional shrinkage that occurs.

Bond migration is a general problem with chemical bonding which must be minimized to avoid forming bodies with weak interiors and hard surfaces. This phenomenon is associated with surface tension movement of the bond solution through a material because of the moisture gradient which develops on drying. Excessive shrinkage which could occur at areas where the bond phase is concentrated is a detrimental feature of bond migration. Lockheed's LI-1525 examined at Battelle showed no indications of bond migration but did exhibit higher shrinkage near the coating compared to the bulk of the material.

The material is claimed to have a random distribution of fibers, but Battelle examinations have indicated the material is anisotropic, with the fibers predominately oriented in one plane. However, there is a 3-dimensional microstructural network linking the structure. Generally, the absence of large voids is a desirable feature of this material, but laminations which curved upward near the ends of panels examined at Battelle are undesirable macroscopic inhomogeneities probably related to the manufacturing process. These could lower the resistance of the material to shear stresses.

The most attractive feature of the "as manufactured" LI-1500 would be its excellent thermal shock resistance because of the low thermal expansion coefficient of the fused silica fibers. However, the expansion coefficient of a chromia-silica coating is likely to be an order of magnitude higher than that of the basic insulation, which may cause problems with coating adherence. Coating integrity is of major importance if this type of material is expected to withstand erosion on reentry.

Because silica dust is considered hazardous, dust collecting equipment should be used for cutting and grinding operations.

<u>McDonnell-Douglas (Mullite HCF)</u>. The insulation system proposed by McDonnell-Douglas is a mullite variety of Hardened Compacted Fiber. Mullite is a crystalline alumina-silica material which has an expansion

coefficient about an order of magnitude higher than fused silica, but even so is considered to be a relatively thermal shock resistant ceramic material. It does not have crystalline inversions which degrade mechanical properties on thermal cycling and should be more dimensionally stable than fused silica in the vicinity of 2500 F. However, the use of a silica bond from ethyl silicate as proposed would lower the thermal stability of the pure fiber and introduce some characteristics of silica, namely, phase inversions. Since the silica probably would not form a continuous network, its effects on mechanical and physical properties would be less predominant than for a material composed entirely of fused silica. Data in the MDAC proposal (NAS 9-10919) indicated only 2 percent shrinkage occurred parallel to the fiber orientation after 1-hour at 2600 F.

The use of crystalline material does not impose severe restrictions on the firing process to avoid devitrification problems--the material could be processed at or above the anticipated use temperatures to minimize dimensional change on subsequent use. However, MDAC proposed to fire their mullite HCF to 2000 F although data in the proposal indicated about 2 percent additional shrinkage would be expected on heating to 2500 F. Since the bonding phase derived from ethyl silicate is probably amorphous silica, the lower firing temperature may be designed to prevent crystallization of the silica bond. The use of ethyl silicate eliminates alkali contamination of the bond which would be a problem with colloidal silicas, and microwave curing should aid in minimizing bond migration problems.

A proposed high emissivity iron titantate coating is to be applied to the mullite HCF in a 3-step process to provide a graded coating. This may eliminate thermal expansion mis-match problems but thermal stability of the coating composite would be of concern to see if coating shrinkage causes delamination on thermal cycling. Coating adherence is considered a major problem for all of the candidate materials.

In general, the available physical and mechanical properties of mullite HCF, many of which are estimated (i.e., thermal expansion coefficient), are close to those of Lockheed's LI-1500. These two candidate insulation materials are believed quite similar in state-of-development and in general characteristics compared to the other candidate materials. However, mullite fiber is believed to be available only from Babcock and Wilcox on a limited basis while fused silica fiber is well developed commercially, J. P. Stevens being the principal source. MDAC does indicate that HCF is anisotropic, a characteristic which will be examined carefully for each of the candidate materials.

AVCO (3D-SX). This candidate material is unique in that it appears to be rather flexible and would offer a high degree of strain compatibility (and thermal shock resistance) compared to any of the other candidate systems. However, the fused silica body would have devitrification problems similar to LI-1500.

Other potential problems associated with the use of this material are (1) its relatively low state of development, (2) its susceptibility to damage from cutting, and (3) difficulty in joining (and/or bonding) and possible joint erosion from the side-wall "cotton bale" characteristic. Coating development does not seem to have progressed beyond the planning stage and could be a major problem because of the inherent flexibility of the insulation substructure. However, the surface fabric of the basic insulation may provide sufficient erosion resistance in itself, although water absorption would still be a problem. Deformation of the material under aerodynamic loading would be another potential problem.

Although a lack of mechanical property data prevents further assessment of this candidate, it does seem to have potential in meeting strain compatibility criteria without the need for a thick, soft bond. Thus, it might offer a weight advantage in that a thin bond could be used.

Whittaker (Aluminum Phosphate Foam). Chemically bonded ceramic foams have received considerable interest in the last decade as a filler for metal-honeycomb type heat shields. However, for the proposed insulation concept there seems to be no particular advantage to chemical bonding the material as it could be pre-fired (sintered) before use. Bond migration, thermal stability ($AlPO_4$ is isostructural with SiO_2 and has comparable phase inversions), solubility (with water), compatibility (with fillers or reinforcement), and quality control difficulties are problems associated with phosphate bonding techniques.

Methods of producing a porous foam may be classified as either chemical or mechanical, and chemical bonding can be used with both methods. Whittaker is evaluating both types and will select one from which screening specimens are to be fabricated. Limited data presented for the reaction (chemically foamed) foam indicates a high (1 percent) solubility in water, possibly because the foam was cured at too low of a temperature. Control of pore size and distribution is difficult with this method. Both burn-out and filler techniques were considered for their syntactic foam, although another method of mechanically introducing porosity is by whipping air into a slurry. The former two methods offer quality control advantages over whipping and chemical foaming techniques.

Anticipated characteristics of either type of foam related to TPS usage are (1) a low strength-to-modulus ratio (less than 0.1 percent) typical of brittle ceramics, (2) low strength unless reinforcements are used, (3) nonuniformity of properties if porosity is high (because larger pore sizes are necessary for high porosity), (4) possible better thermal stability compared to silica bonded material, (5) less surface area and consequently less moisture absorption compared to fiberous insulation, (6) possibly less ansiotropy of properties, and (7) comparable to LI-1500 in ease of cutting, fitting, and bonding. The material seems to be in the laboratory stage of development compared to rigid fibrous insulation systems.

Union Carbide. No information is available on the insulation material proposed by Union Carbide for the Space Shuttle TPS. However, the company currently markets zirconia felts, cloth, blocks, and rigid cloth composites on a limited basis, which represents the state of the art of insulation for use in excess of 2500 F. Availability of zirconia fibrous products, possible destabilization, and the high cost and density of the material would be of concern for external insulation applications. The high thermal stability of zirconia would permit higher surface temperatures and consequently longer vehicle cross-range if it were used.

General Electric. No details on the material proposed by G.E. have been released by NASA.

Screening Test Plan

The objective of the screening test plan for candidate external insulation materials is the generation of both data and subjective information that will contribute to their relative ranking. This must include allowances for the current state of development of each candidate in terms of probable ultimate potential.

Because strain compatibility was identified as the dominant structural property and the appropriate tests were nonstandard, it was suggested by both MSC and Battelle that the screening program initially proposed in our letter of July 7, 1970, should be verified by experimentation. Task 2, therefore, was defined as a pilot exercise of the Screening Test Plan using available samples of Lockheed's LI-1525. This task is the subject of a separate report*. The following test plan is the outgrowth of that task incorporating the indicated modifications.

Recognizing that it is both economically desirable and technically feasible to make early selections of preferred materials, the Screening Test Plan has been divided into two parts as shown in Figures 4 and 5, respectively. The first part of the Screening Test Plan logic tree shown in Figure 4 is divided into four main branches--Mechanical Properties, Morphology, Response to Environments, and Thermal Physical Properties--into which the specimens are fed after initial NDT and specimen machining as needed.

X-ray examination of all as-received specimens would be performed as a primary base for specimen allocation but also as a primary discriminator on the production control of each candidate. Unreasonable variations within a candidate lot could be adequate grounds for (at least temporary) rejection considering the desirability of minimizing the higher risk developmental investments.

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* Kistler, C. W., Wilkinson, W. H., Ungar, E. W., Foster, E. L., "Task 2, Assessment of Material for Space Shuttle", Contract NAS 9-10853, BMI Summary Report, October 2, 1970.

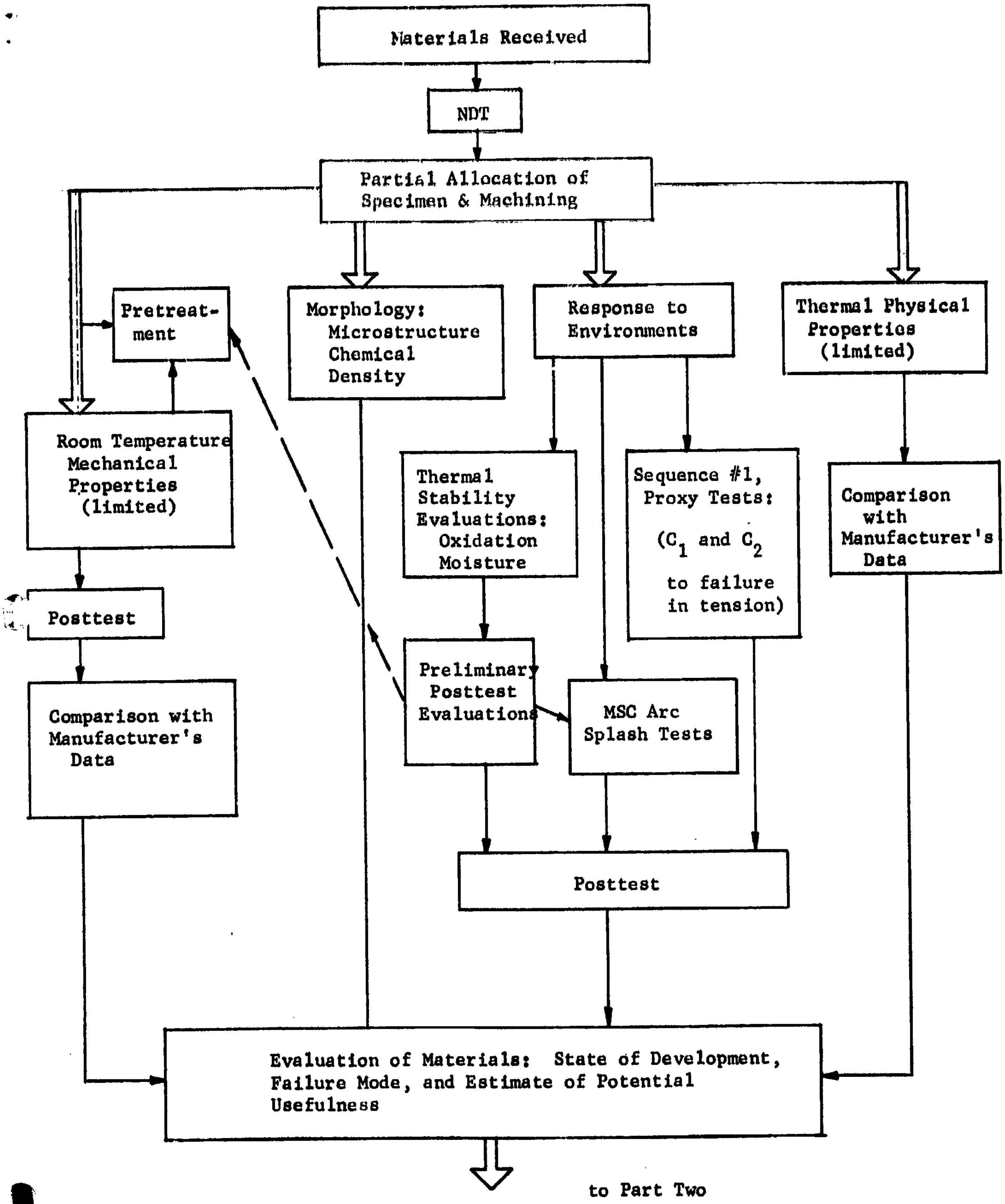

FIGURE 4. PART ONE OF SCREENING TEST PLAN FOR SURFACE INSULATION CANDIDATES

Any other tests on the as-received panels must be considered at this time before they are machined into specimens. Holographic examination of the full panels, for instance, would have to be done at this point or deferred until subsequent sample panels would become available. Consideration of developmental priorities will have to be made before specimen machining. This concern is not appropriate for materials which cannot be machined and will be manufactured in test bars.

The first branch to be investigated should be the Thermal Stability portion of the Response to Environments in that it defines appropriate test conditions for subsequent Arc Plasma tests and actually performs the pretreatment for some of the Mechanical Property tests. Large specimens--bars at least 1 x 1 x 6 inches--will be heated in air to 2500 F (the nominal design specification), held for five minutes, cooled slowly, and examined for dimensional or other changes. This heating/cooling cycle will be repeated five times or until gross failure is observed. If necessary, lower peak temperatures will be used to find a satisfactory reduced thermal stability limit. These specimens will be saved for mechanical strength tests (where possible) and will be given microstructural and selected chemical composition analyses. Unexpectedly poor thermal stability also could be grounds for shelving a candidate material.

Also included in the thermal stability examinations is an examination of the effects of salt water on the candidate material because of the likelihood of exposure of the vehicle to air borne salt spray (at least). To exaggerate the effects it is anticipated that the specimen be soaked in salt water, dried carefully, and then thermally cycled. Comparison with comparable thermal cycling of an as-received specimen gives an indication of the susceptability of the material to salt water.

The next portion of the Part One Screening would be the determination of the more readily obtainable Thermal Physical properties primarily to check the manufacturer's data. The coefficient of thermal expansion is probably the most important property in that it has strong mechanical overtones, both for design and for testing. Emissivity also is of early interest because it is desirable for the arc tests.

The Morphology investigations are restricted to the Part One in that they provide a data base for the entire screening program. Microstructure examinations will be performed both by conventional metallographic and photographic techniques and by scanning electron microscope (SEM) examinations as needed.

Chemical composition of the critical portions of the specimens before and after treatments are expected to be very meaningful. Chemical analysis will include limited X-ray diffraction techniques where appropriate.

Density measurements will be made as a matter of course in specimen preparation where external dimensions and gross weights define average bulk densities. The effects of water absorption are important as a modifier both to density and to chemical composition. Rates of moisture pickup, rate of drying, and permeability are of interest.

Mechanical property tests will be limited to room temperature and to tension and flexure to determine effective characteristics of the composites. Since the primary interest is in strain compatibility, strain-to-failure data for test bars in tension and in flexure are the primary results. The effective elastic modulus and modulus of rupture are also important in verifying the stiffness contribution of the insulation to the substrata structures. Derived values of failure stress are primarily of value as a check against the manufacturer's data.

With temperature limits guided by thermal stability experiments, the arc splash tests at MSC provide a cross check on the high temperature viability of the candidate. Posttest analyses will be correlated with the posttest evaluations of the Thermal Stability specimens and with the base line information developed by the Morphology studies.

Also included in the Part One Screening Program is Sequence 1 of the strain compatibility tests. In test C_1, 12 in.-long specimens, 1 in.-wide and 1 in.-thick are mounted to 1-in.-thick substrates, and 4-point loaded so that the specimen bondline is at constant strain (constant moment) in tension to failure. Test C_2 mounts identical specimens on 2-in.-thick substrates and loads them identically to failure. This sequence not only defines baseline values for acceptable bondline strain for relatively "long" specimens, but also gives an indication of how the strain-imposed load is distributed through the sensitivity of the material to strain amplification (from bondline to surface). Further insight into the material response under strain loading comes from comparisons with the strain-to-failure results from modulus of rupture and tensile tests.

Aided by appropriate posttest investigations and review of the test data, a preliminary evaluation of each of the material candidates can be made. Judicious blends of objective comparisons between such data as strain-to-failure limits for each of the candidates with subjective consideration of the failure modes, state-of-development, and process control will lead to a relative ranking of the materials and also to a preliminary evaluation of the potential of the surface insulation concept in general.

Part Two of the Screening Test Plan as shown in Figure 5 should be reserved for only the most promising candidates. Its function is both a deepening of insight into external insulation materials and a more finely tuned comparison between the remaining candidates.

Additional room temperature mechanical property tests will be performed on both as-received and pretreated specimens as needed. Many of the Thermal Physical Properties determinations were delayed until this time because of their relatively high cost. Before the screening is completed adequate data will be obtained on thermal expansion, surface emissivity, specific heat, thermal diffusivity, and thermal conductivity.

The dominant portion of Part Two of the Screening Program is the Strain Compatibility Tests--Sequences 2, 3, and 4. Sequence 2 is primarily a baseline test, qualifying 6-inch long specimens with reference to the 12-inch long specimens used in Sequence 1. In this test the 6-inch long specimens, 1-inch wide and 1-inch thick, will be bonded to a 1-inch thick substrate and subjected to a 4-point flexure loading which imposes a uniform tensile strain at the bondline. Specimens in this sequence will be loaded to failure or 1/2 percent substrate strain, whichever comes first.

Sequence 3 is identical with Sequence 2 except that the bondline strain is in compression and is limited to 0.4 percent strain if no failure is observed. In this latter case, the beam is unloaded, the specimen examined, and then reloaded in tension the same as in Test C. Differences in the mode

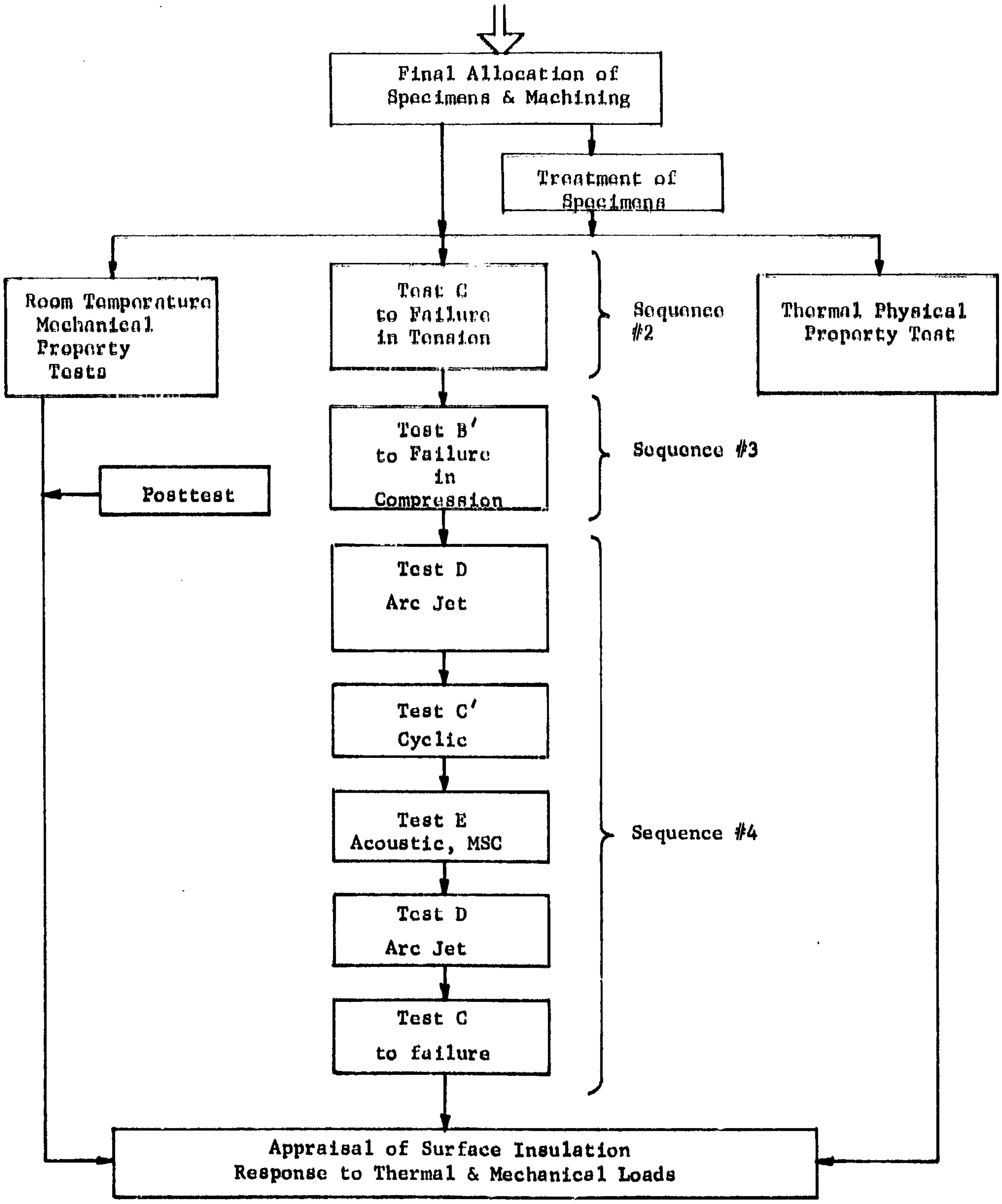

FIGURE 5 . PART TWO OF SCREENING TEST PLAN FOR SURFACE INSULATION CANDIDATES

of failure associated with the compression pretreatment become significant if failure during the compression process is not observed or indicated.

Sequence 4 includes tests that are designed to indicate preliminary weaknesses associated with reuse. A 6-inch long specimen, 1-inch wide and 1-inch thick, is mounted as in previous sequences by adhesive bonding to a 1-inch thick titanium substrate and then subjected to tests D, C', E, D and C in sequence.

In Test D, the specimen is mounted in a flat plate holder designed also for resistance heating of the substrate and its thermal growth. Resistance heating is begun, followed by arc exposure for about five minutes at constant heating to bring the surface of the specimen to the desired test temperatures. This temperature is nominally 2500 F but will be reduced if the thermal stability tests from Part One indicate a lower temperature to be appropriate. After the arc is turned off the substrate continues to be heated as the attenuated heat pulse from the surface approaches the bondline. The surface is now being cooled and when the bondline reaches its desired maximum of 500 F, the substrate heaters are turned off. This should be the condition of severest thermal stress and cracks must be recorded in the strained state for, upon cooling for removal from the arc test chamber, any cracks may close up and be hard to find.

Test C' is a cyclic repetition of flexure loading in the same fixture as in Test C but in both tension and compression and to a maximum value assumed from previous tests to be within usable limits. The limiting strain may not necessarily be one where no cracks have formed but it certainly should be one where they have not progressed deep into the specimen or begun to branch laterally. The incidence of cracks, associated with the thermal stress history and the growth and/or stability of flexure cracks during the 10 cycles are critical results.

Each of these specimens will now be given an acoustic exposure, Test E, in the facilities at MSC, Houston. This exposure is to be representative of launch conditions and is reuse oriented because of the previous heating, cooling, and cyclic loading history. Our experience with LI-1525 also indicated marked insensitivity to acoustic exposure so we have chosen to make the test more severe (and more discriminating) by delaying the test until some potential damage may have occurred.

The arc jet heating/cooling (Test D) is repeated also with preliminary interest in reuse. This test is particularly important where the stability and influence of surface cracks is an issue.

The final flexure to failure in tension is identical with Test C, the base line test of Sequence 2. Differences in the crack growth to failure are the critical aspect, indicating, among other things, the potential acceptability of the limiting condition of the specimens' exposure history.

With all of these results available, the ranking of the candidates can be done with reasonable assurance of their relative performance after normal development and design. Sufficient testing will have been done that some preferrable design options will be indicated and the practicality of the external insulation concept can be estimated.

EVALUATION OF DESIGN DATA REQUIREMENTS FOR FIRST FLIGHT--TASK 1B

This discussion is directed towards introducing data requirements for mechanical loading. However, it is illustrative of the concerns for the thermophysical property data needed. Both requirements are coupled closely with the design procedure details. Some of the special concerns for these types of brittle materials are addressed. The seriousness of these concerns will be specific and depend upon the nature of the materials finally selected for preliminary and final design activities.

In the aerospace industry the establishment of a design allowable such as F_{tu} or F_{ty} is an important step in the process of developing safe and reliable aerospace vehicles. These are the strength values upon which are based ultimate and limit load for static strength and which are factored downward by experience when considering fatigue, creep, and fracture arising from intentional or unintentional flaws. An important key to the establishment of design allowables lies in the word reliability. The concept is growing in aerospace procurement that vehicles be designed according to some level of reliability. Therefore, in selecting a procedure for establishing design allowables (for example, a minimum level for tensile strength), the computations not only have to be concerned with establishing this minimum strength with a probability that X percent of a large population will exceed that figure, but the computations also have to establish the level of confidence (Y percent) at which this will occur.

The techniques to accomplish these types of computations are commonplace when it comes to the establishment of design allowables for metallic materials--some quite brittle. They have evolved over a series of years in discussions between design allowables specialists of aerospace companies and material suppliers.

The concern is to test these techniques with the more brittle materials of this program. However, some indications presently exist that suggest that structures-oriented people already are thinking this way. The advanced report "Structural Design Guide for Advanced Composite Applications", prepared by the Los Angeles Division of North American Rockwell on AF33615-

68-C-1489, indicates that design allowables for composite materials will be established by techniques described in AFML-TR-66-386 when sufficient data become available.

Normally the first step in the establishment of design allowables or design data requirements is done by obtaining a quantity of tensile property data from producers and users. Variables considered are producer, product, form, thickness, and testing direction. The objective is to determine whether the property values come from a single population or whether there are various subpopulations and to determine whether significant differences exist among the variables.

The next step is to establish the nature of the distribution of values. In the event the distribution is normal, the mean strength and standard deviation is computed.

With few data as would be expected with a material under development, two cautions are needed. Few data mean a small number of data points, and one may question whether the estimates of the population parameters actually represent the parameters of the real population. The other caution is that with a smaller population of values, the design allowables could be reduced from those computed with a large population of values (if they existed) if the same confidence level is used.

Probably the most important features of the brittle materials to be evaluated on this program will be the limited quantity of material for test, the data available to analyze and the dispersion of the data. Primary attention needs to be focused on reaching some decision concerning the further definition of a design allowable and the design data requirements.

Two characteristics of these materials also bear some mention. One of these is the size effect generally attributed to brittle materials. Thus, with a large size sample, the strength becomes lower. The second characteristic, also associated with size effect, is stress distribution. With this characteristic, data indicate that the maximum tensile stress that can be supported in bending is on the average greater than that which can be supported in tension, which, in turn, is greater than that which can be supported in a tension test.

Both of these characteristics have been examined in a variety of ways and some success has been achieved in devising statistical models to rationalize observations. The more successful of these treatments takes cognizance of the fact that these materials contain real and numerous flaws that qualitatively by a weakest link mechanism can explain the two characteristics. These models, for example, the Weibull distribution, have been altered to provide the best fit with experimental data and may be useful in providing a unified theory to relate size and stress distribution dependence. The advantage of a Weibull distribution is in describing the "tails" of the distribution; however, data availability may limit its use as has been the case with other statistical treatments involving the definition of the distribution shape. The intention of the program is to examine most available statistical techniques to determine their suitability for presenting design allowables. Of course, until one is more certain how much data will become available, it is possible the only recourse will be to use average values or some fraction thereof agreed upon with the project monitor.

The problem of flaws has not been treated in this discussion too completely. Over the past ten years or more there has been evolving a growing confidence that linear elastic fracture mechanics can be a useful analytical tool for predicting strength of flawed parts. Oddly enough, most of the experimental work has been done on metallic materials having appreciably more ductility than the materials of this program. The model in this case is the Griffith flaw model as modified by Irwin. The simplest rationale of this approach is that there is a material index for each material that is a constant. This index , the fracture toughness of a material, is represented symbolically as K/c and, in turn, is related to gross stress on a member and flaw size. With metallic materials, the ductility has complicated the simple Irwin formulation, in that there has to be plastic zone size corrections and width correction factors to rationalize many of the data.

Since the entire concept initially was formulated by Griffith to explain the fracture behavior of glass, it would appear that data from this program should be examined with linear elastic fracture mechanics studies to determine whether this type of modeling will provide a useful framework to describe strength characteristics. In addition to gross fracture stress information, each tested specimen should be evaluated metallographically to determine the size of the critical flaw associated with the failure and that datum.

Therefore, the ultimate needs of the designer must be interacted with the material supplier to develop a material to its most advantageous form for the space shuttle applications. Two test plans are outlined that are general enough to be applicable for both classes of developing materials--those for external insulation and those for leading edges. The Preliminary Design Data Test Plan accommodates the developing nature of the materials and the need for design interaction and feedback. The subsequent Design Data Test Plan focuses on the needs for final design and flight qualification.

Carbon/Carbon Composites

A satisfactory leading-edge material must perform as an integral part of the Space Shuttle structure. This integration means that loads will be transmitted to and from the leading-edge materials from and to the primary structure. These loads will be associated with deflections and strains produced from launch, separation, in-orbit thermal cycles, reentry, crossrange flight, landing, and ferrying.

To determine how well a material will perform, preliminary design analysis activities must be performed. Prior to the performance of the design, confidence in the materials is obtained by evaluating it to prove that it is in control and its response to service is in accordance with the requirements.

For the leading-edge materials it is the mechanical and thermophysical properties that are needed most for designing for first flight. These properties are needed, but only if they represent a stable material or one in which the effect of service on properties is accurately known.

The leading-edge materials would be expected to be more tolerant of the more demanding environments that might be met during flight such as high acoustic noise levels, vibration, dust, rain, etc.

External Insulation

A satisfactory external insulative material must tolerate a series of environmental loadings before it is exposed to reentry heating--its prime reason for existence--and it must continue to present an unperturbed surface throughout cross-ranging flight and landing. During launch the insulation panels experience acoustic loadings and also cyclic and steady acceleration loadings leading to strain of the substrates to which they are bonded. Response to acoustic environment must be tested directly. Satisfactory strain compatibility relates only roughly to modulus of rupture data or tensile or compression data in terms of strain-to-failure; the true criterion involves the stress distribution within the insulation considering the actual use boundary problem including bondline strain and curvature, effects of bond elasticity, and shear transfer of load within the panel.

Outgassing of adsorbed liquids as the ambient pressure is reduced is a critical material property only if a unique behavior exists. A highly hygroscopic material, for instance, would require (at least) design allowances for nondestructive venting. Outgassing of the adhesive must be considered. In the hard vacuum conditions of space, the material must be stable. Except for impact loads from micrometeorites the structural response is still substrate strain controlled and the strain compatibility is the dominant material response data requirement. As part of the strain compatibility, however, verification of the structural dominance of the substrate must be obtained for flexure (low elastic modulus of insulation) and for thermal load (both low elastic modulus and low thermal expansion coefficient).

During reentry, data on thermal diffusivity are needed to qualify the thermal protection performance. Conductivity may be needed as a separate parameter along with the contact resistance of the insulation/substrate bonds to permit accurate thermal analysis. The insensitivity of heat transfer to surface conditions (including panel-to-panel joints) must be proved because, although this is a design aspect, practical material characteristics will limit the design options. Strain compatibility again is the dominant aspect with particular emphasis on thermal strain loading.

The integrity of the bond at its maximum temperature must be considered as a potential insulation characteristic for one material may bond better with a given adhesive.

The insulation must also be capable of withstanding dust and rain erosion during cross-ranging flight and landing without gross loss of material. Combinations of erosion and flexure should be expected so this aspect could be a limitation on the acceptability of strain-induced surface microcracks that otherwise appear stable.

Outside of the obvious verification of the thermal protection function, the prime performance factors are the limitations on bondline strain that the insulation requires to avoid catastrophic cracking. First flight qualification considers a specific sequence of events in evaluating the stability and acceptability of strain-induced microcracks associated with critical bondline strain limits. Some flexural loadings will be repetitive and (at least low cycle) fatigue and crack stability are important; but thermal stresses associated with reentry occur only once per flight.

Proposed Preliminary Design Data Test Plan

Objective

The objectives of the preliminary design data test plan are the generation of data for preliminary design activities and confirmation that appropriate procedures have been selected for property measurements, nondestructive testing, and design.

Discussion

It is anticipated that preliminary design data will be generated on at least two TPS materials each from the external insulation and leading-edge candidates.

The approach presented is general enough to provide for the evaluation of both external insulation and c/c composite (leading-edge) TPS materials. However, for the first time prime consideration is given to what design procedures are to be used. From this consideration the preliminary design data requirements can be defined. The data requirements will vary depending upon whether an external insulation or leading-edge candidate is being appraised. For example, in this plan the evaluation of bonding and joint concepts for external insulation would be conducted or the design freedoms allowed with stiffeners or cutouts for the leading edges would be measured in performance tests.

Property measurements at low and high temperatures and as a function of integrated use would be performed and chemical and microstructural characterizations would be conducted. The measurements and characterizations would be made on sample lots produced in the materials process development activities. Iterations, as necessary to show quality control over performance or properties and to demonstrate correlation with NDT results, would be performed. Such iterations would be repeated until a basis for the confirmation (or rejection) of the candidate was accomplished and a preliminary property and performance specification would be written.

In this generation of preliminary design data opportunities to confirm or change the design procedures would also be available.

The performance of extended thermal and chemical stability tests, together with thermodynamic analysis, would provide a detailed description of failure criteria and a phenomenological model of the failure mode in terms of temperature and integrated use.

Confirmation of the appropriateness of property test procedures, instrumentation details for property tests and performance tests, and nondestructive tests would be obtained. In particular reference to NDT, opportunities available within the plan would be taken to gather data on the appropriateness of possible service inspections and nondestructive evaluations.

The considerations controlling the Preliminary Design Data activities can be summarized as follows:

- Materials Processing Development will be continuing
- Property Data from Screening tests not of significant or sufficient quality for Preliminary Design Activities
- Results of Screening test plan will identify:
    - (a) NDT techniques to be applied
    - (b) Appropriate property test procedures with instrumentation
    - (c) Potentially significant effects of pretreatments or cyclic use on properties.

Outline of Test Plan

Figure 6 shows the logic tree outline of the Preliminary Design Data Test Plan. The results of the Screening Tests not only are a selection of candidates but the highlighting of critical development areas for the manufacture, or priorities for additional test results for the materials analyst, and of the more promising design options for the designer. The development effort of the materials supplier is represented by the left-hand branch where he applies the immediate results of the screening plan and the Preliminary Identification of Design Data Requirements to the development of his material. The material output would be in terms of simple shapes for the basic testing specified.

The right-hand branch represents the joint efforts of materials and design analysis. The prime effort is the definition of meaningful tests both as to material characterization and to design usefulness. It is at this stage that the proper blend of pure property testing, sophisticated analysis, and empirical correlation of composite performance will be defined. It would be poor judgment either to assume that the material is too complex, too anisotropic, and/or too nonlinear for anything but empirical correlation or, on the other hand, to assume that adequately general characterization and understanding can only result from determining the separate properties of the macroscopic components and developing analysis codes for determining the system response.

The central portion of the plan is essentially an extension of the part of the screening test plan, investigating in more detail Morphological Aspects and Thermal, Physical, Chemical, and Mechanical Properties. The Performance Test branch is a variation of the proxy test concept into specific area of design concern as specifically applicable for both classes of materials. The strain compatibility aspects of the surface insulators would probably be continued. The effects of such aspects as bosses, cutouts, pin-loading holes, and stiffness would probably be best answered by special tests leading to design and stress concentration factors for the leading edge materials.

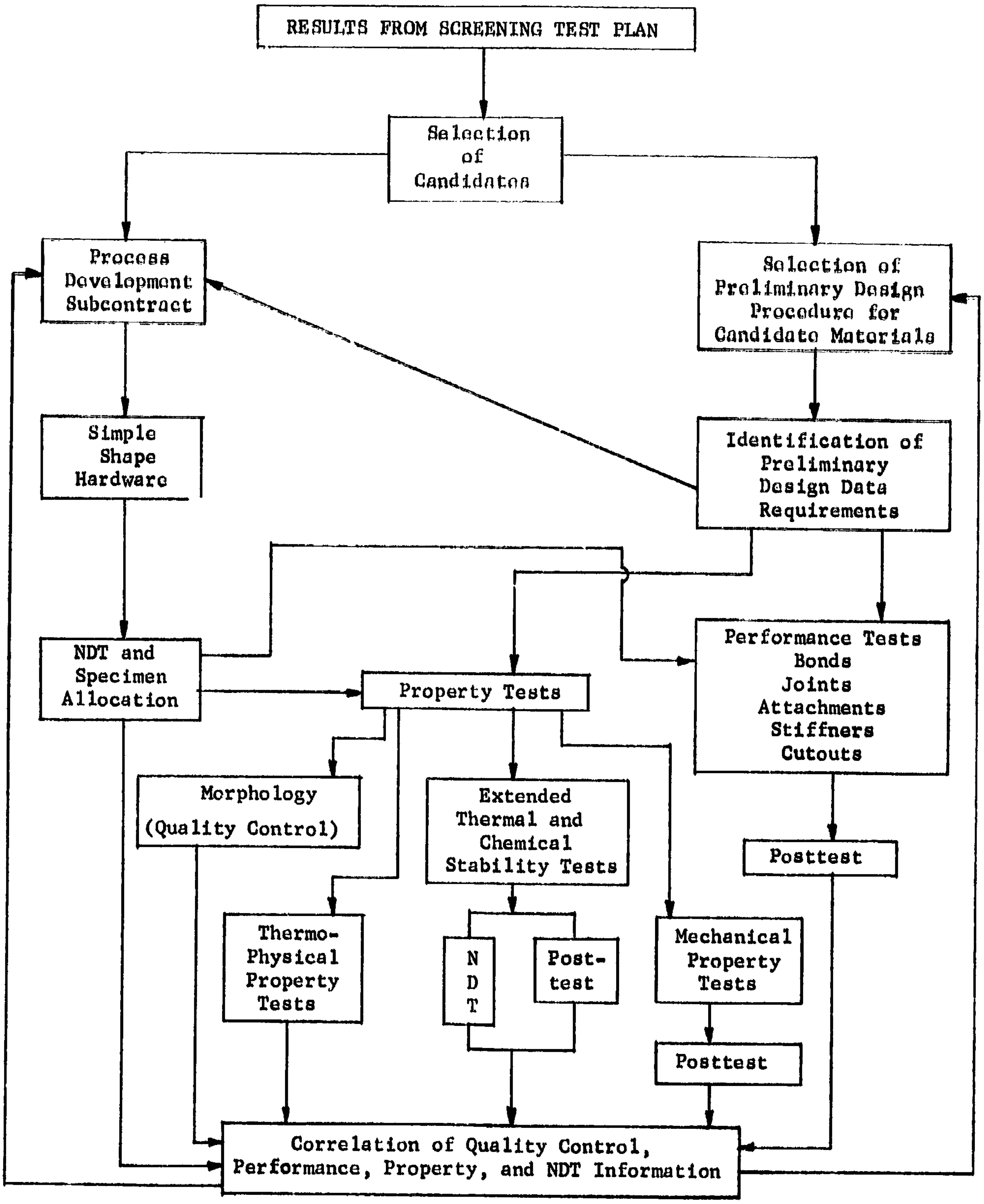

FIGURE 6. PRELIMINARY DESIGN DATA TEST PLAN

Significant note should be made of the feedback processes from the ultimate correlation phase to both the process developer and to the materials and design analysts. Not only will the material itself be developing but the design itself will be being modified in response to unique aspects of the material uncovered in the testing.

The results, or output, of this effort can be summarized as follows:

- Information on performance criteria--Mechanical Properties as a function of temperature and integrated use, and Thermal Properties as a function of temperature and integrated use.
- Information on failure modes--identification of failure modes as a function of temperature and integrated use.
- Appraisal of degree of correlation possible between data from (prior and in-service) NDT and performance criteria and failure modes (Quality Control).
- Appraisal of Design Freedoms associated with bonds, joints, attachments, stiffeners, and cutouts.

Proposed Design Data Test Plan

Objective

The objectives of the Design Data Test Plan are the generation of design data with the limitations of configuration features as functions of temperature, use, and environment and age, and the identification of NDT in-service requirements and final property and performance specifications.

Discussion

It is assumed that design data for only one TPS candidate each for the surface insulation and leading-edge application requirements will be generated.

The ability to generate design data is based on the availability of a well-known and well-behaved material that can and will be prepared in prototype and simple forms. Familiarity with the materials will be established and tentative property and performance specifications will be written during the process developments associated with the generation of the preliminary design data. These specifications and their acceptance by the manufacturing organization represent a product that was produced in the past and whose properties and performances and their relationships to manufacturing processes are well in hand.

From this viewpoint, design property data are the main concern and the performance of morphological evaluations and thermal and environmental tests are done only in order to confirm quality control and the significance of NDT evaluations.

The significance of NDT evaluations is reflected in the ability to correlate manufacturing faults with effects on properties and performance and to demonstrate the validity of their correlations with the NDT evaluations of prototype TPS structures.

It is envisioned that the material used for property tests specimens in the generation of the design data will be manufactured in simple shape hardware parts, in prototype hardware for performance tests, and in sections or cutouts or trim from prototype hardware.

Information on the effect of service on design data will be obtained on pretreated test specimens or specimens cut from prototype hardware after aging or after performance tests. This prototype hardware will be examined after performance cycles and before sectioning by selected in-service NDT evaluation procedures. Such NDT evaluations will include the restraints present in flight hardware.

Iteration of the results of property and NDT evaluation to the manufacturer and to the designer will be done to improve manufacturing methods, to confirm tractability of the hardware, and to improve correlations between design analyses and test results.

The considerations fundamental to the acquistion of Design Data are:

- Process development will be complete but manufacturing and quality control developments will be continued.
- Property testing procedures will have been established in Preliminary Design Data Tests.

- NDT procedures will have been established or the needs for (prior) NDT developments identified.
- Information on statistical sample (numbers) will be in hand.

Outline of Test Plan

The general Design Data Plan, as outlined in Figure 7, follows a logic development similar to the previous test plans. The designer's interests, however, are now dominant for he will be defining hardware specifications for two types of testing: one developing design properties from tests on special simple shapes, and the other giving the performance results of laboratory prototype designs. Figure 7 shows these two efforts and the related interrelations and iterations culminating in the detailed information necessary for performing the actual vehicle design.

The results of this effort would be:

- Complete design curves.
- Environmental and aging effects on design curves.
- Design limitations associated with configuration features of prototype hardware.
- Identification of NDT in-service data requirements.
- Final property and performance specifications.

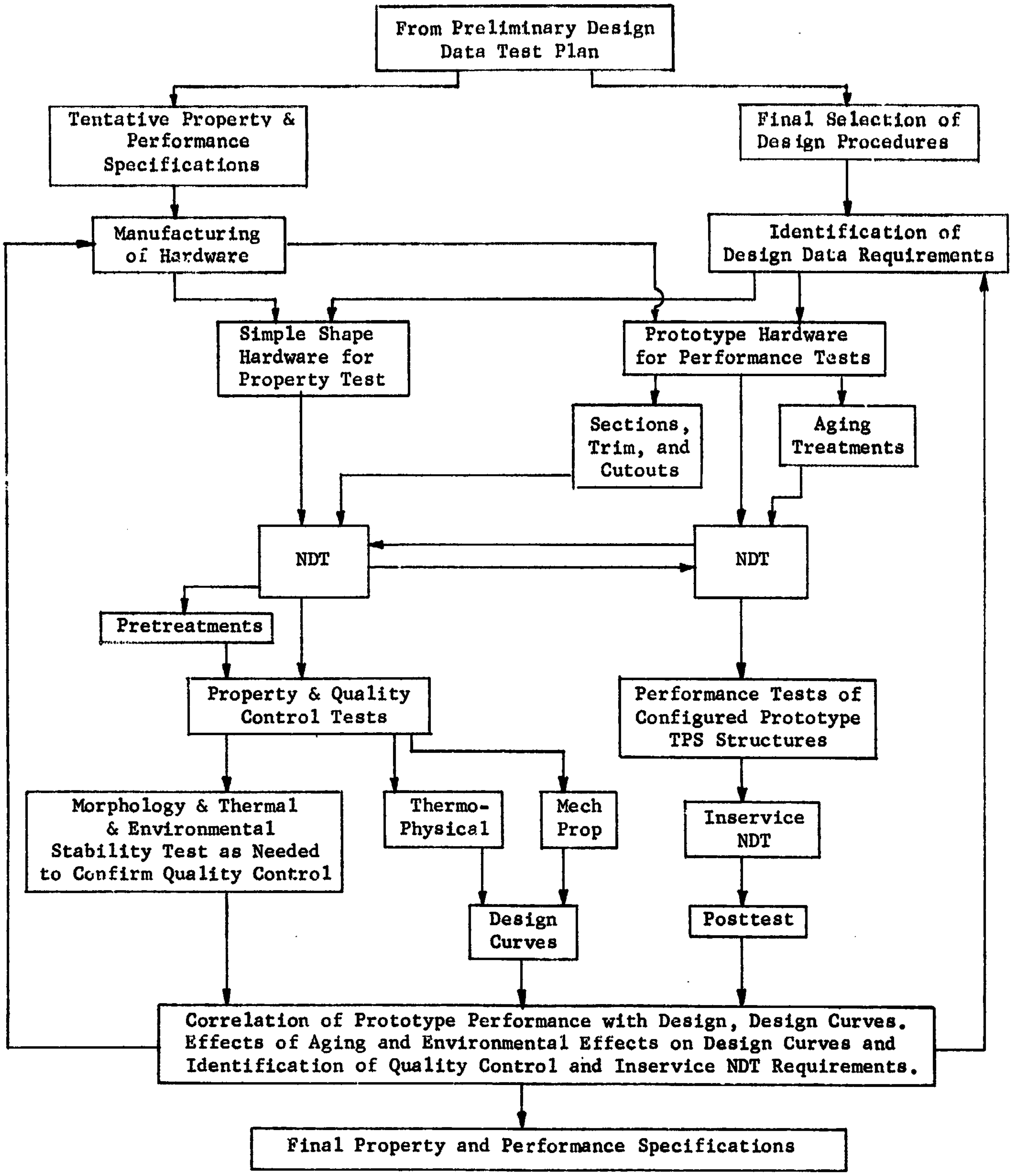

FIGURE 7. DESIGN DATA TEST PLAN

EVALUATION OF DESIGN DATA REQUIREMENTS FOR SUBSEQUENT FLIGHTS--TASK 1C

For subsequent flights only four modifications are important: (1) the loss of one-flight sequence in exposures, (2) the repetitive nature of all loadings, (3) the addition of ground handling as a source of damage, and (4) the necessity of inspection for subsequent flight certification.

In the first case, each environmental condition must now be considered to have already been preceded by all conditions as a pretreatment to the specimen so such things as microcracks and locked-in thermal stress must be taken into account. The acoustic exposure, for instance, now must be imposed upon a specimen eroded by dust, drenched by rain or sleet, and subject to infiltration of moisture into cracks and interstices with associated phase changes. The reentry heating is controlled by a radiation coating possibly degraded by dust or rain erosion and subsequent evaporation residues and by possible chemical change in the coating from previous high-temperature exposure.

The repetitive nature of all loadings means that fatigue and crack-growth concerns become more critical. A crack must now remain stable over long periods of time and the faying surfaces of a crack must not abrade one another. Thermal stability limits also become more critical for the high-temperature transformations (such as devitrification of fused silica to cristobalite) are generally time dependent. A material insignificantly affected by one reentry heating should be expected to accumulate damage with each flight.

Ground handling at a launch site can be more carefully monitored and controlled than that upon landing, ferrying, and storage. The probability of an accident increases with each handling process. A particularly brittle coating or a particularly soft and permanently deformable material should be viewed with concern as to its practicality for reuse.

Reuse certification could be classed as a major material characteristic in that NDT of panels, in place, may be more reasonable for one material than another. Or one material may be more subject to the initiation of nonstable subsurface cracks. The ability to be sure that the vehicle has "one more flight" after an inspection is mandatory; the expense and complexity of the inspection process will be related to the way the material can fail in the design.

Significance of Reuse on (Properties) Performance

Since the actual exposures now occur with material pretreated by all other exposures, this aspect must be reflected in the definition of design limits and the determining tests. Fatigue tests and crack stability investigations are obvious but considerations of such things as thermal exposure prior to definition of mechanical property limits or to acoustic testing are just as important though more subtle in their specification of reasonable qualification tests. The result is a need for as much experience as possible relating exposure to the end condition of a material and relating, in turn, an abnormal initial condition with flight operation limits.

Significance of Reuse on Failure Modes

Properly structured testing programs will have considered the effects of various pretreatment exposures on the modes of failure. This can be related to accumulated damage considerations which will be only as reliable as postflight inspection can correlate material with test experience with that particular material condition.

Special Requirements of TPS Materials for In-Service NDT

Next-flight certification would seem to be particularly unreliable if no practical methods were available for actually measuring the condition of various critical portions of the vehicle TPS. An excellent data base for subsequent usability based on accumulated damage is not particularly useful unless the actual condition can be monitored periodically. NDT techniques, therefore, are fundamental to reuse. Consequently, careful correlation of NDT measurements on test samples related to accumulated damage must be included in the programs.

CONCLUSIONS

The primary conclusion that can be drawn from this program is that detailed consideration of both screening and ultimate design data acquisition is critical to practical risk assessment of developing materials for a developing design. The reduction of virtually all structural situations for the surface insulators to the composite strain compatibility response is one example; the definition of critical pretreatments is another.

The program has been successful in defining tests and test priorities and orders. It has developed insight into the design requirements for test results. Critical areas such as the sensitivity of the fused silicas to combinations of seawater residues and extended times at high temperature have been identified. Although a number of areas of concern have been identified, the potential of both the external insulation and the inhibited c/c composites (for leading edges) still seems reasonable.

Based on available (lack of) information on the candidate materials, with the exception of LI-1525 (as studied and reported in Task 2 Report), it is not possible to identify the most appropriate thermophysical or mechanical property test procedures or the exact number of samples that would constitute a statistical sample. This is due to the developmental nature of the material candidates. However, based upon the wealth of evaluation procedures available, no serious difficulty in arriving at suitable choices and accurate estimates is anticipated.

This same general conclusion stated above can be drawn for simulated testing for the environments to be met in ground handling, launch, reentry, and ferry.

For some of the candidate materials, and because of the high interest of the technical community in this subject, the availability of NDT procedures to qualify a material for first flight also is foreseen and good correlation with properties and performance is to be expected in a selected and fully developed material. The future availability of in-service NDT procedures is much more difficult to estimate. These estimates will become accurate as the performance characteristics and failure modes of the candidates are established by the Screening Test Plans.

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APPENDIX A

WORKBOOK TABLE OF CONTENTS

APPENDIX A

WORKBOOK TABLE OF CONTENTS

A Thermal Protection Systems Materials Workbook has been compiled. The intent of this Workbook was to gather under one cover useful and not-for-publication information on the pertinent mission requirements and material parameters needed to appreciate the development of the Thermal Protection System (TPS). The contents of this Workbook are given in outline form to illustrate the scope of the coverage.

WORKBOOK CONTENTS

I. Mission Requirements

    Reentry

    References

II. External Insulation

- IIA. Material Candidates
  - IIA1. Lockheed LI-1500 Insulation
    - General Description
    - Processing and Manufacturing Information
    - Material Evaluations
    - Attachment Features
  - IIA2. McDonnell-Douglas - Mullite HCF
    - General Description
    - Processing and Manufacturing Information
    - Material Evaluations
    - Attachment Features
  - IIA3. Whittaker - Oxide Foam
    - General Description
    - Processing and Manufacturing Information
    - Material Evaluations
    - Attachment Features

IIA4. AVCO - 3D-SX

- General Description
- Processing and Manufacturing Information
- Material Evaluations
- Attachment Features

IIA5. Union Carbide - Composite

- General Description
- Processing and Manufacturing Information
- Material Evaluations
- Attachment Features

IIA6. General Electric - Carbon Foam

- General Description
- Processing and Manufacturing Information
- Material Evaluations
- Attachment Features

IIB. References

III. Carbon-Carbon Composites

IIIA. Material Candidates

- General Electric Omniweave
  - General Description
  - Property Data

Avco Orthogonal

General Description

Property Data

Hitco Pyrocarb

General Description

Property Data

McDonnell-Douglas System No. 1

General Description

Property Data

LTV System TS

General Description

Property Data

UCC-Carbon Products Division

Repyrolized Plastic (RPP)

General Description

Processing and Manufacturing Information

Property Data

IIIB. References

IV. Metallics

V. Internal Memos

APPENDIX B

SOURCES OF INFORMATION

APPENDIX B

SOURCES OF INFORMATION

Document No.	Description	Title	Date
SS-1	Technical Proposal Vol I, Part 1	Evaluation of Nonmetallic Thermal Protection Materials for the Manned Space Shuttle	February 24, 1970
SS-2	Technical Capabilities Vol I, Part 2	Ditto	Ditto
SS-3	Cost Proposal, Vol II	"	"
SS-4	BMI Capabilities	Nondestructive Testing at BMI	
SS-5	BMI Memorandum	A Cursory Examination of the Use of the Space Shuttle to Deliver OSSA Payloads	October 27, 1969
SS-7	BMI Memorandum	Inclusion of the Space Shuttle Concept in the Launch Vehicle Estimating Factors Book	January 28, 1970
SS-8	BMI Memorandum	Space Shuttle Technology	January 28, 1970
SS-9	BMI Memorandum	Space Shuttle Configurations and Performance	January 30, 1970
SS-10	BMI Memorandum	Space Shuttle--Synopsis of Early Economic Data	February 2, 1970
SS-11	BMI Memorandum	NASA Shuttle Reuse, Refurbishment, Safety, Turnaround Time and Nondestructive Testing (NDT)	April 15, 1970
SS-12	BMI Write-up	Space Shuttle Thermal Protection Systems	
SS-15	NASA-Langley Minutes	Advisory Subcommittee on Materials	October 7-8, 1969
SS-16	AIAA Paper	Structures and Materials for Manned Reentry Vehicles	November 29 - December 2, 1966
SS-24	NASA Memorandum	Thermal Evaluation Tests of RPP Materials in the MSC 1.5 MW and 10 MW Arc-Heated Facilities	
SS-25	NASA Memorandum	Thermal Evaluation Tests of LI-1500 Insulative/Nonablative Materials in the MSC 1.5 MW Arc-Heated Facility	
SS-26	Specimen List	MSC Procurements (one page)	

Document No.	Description	Title	Date
SS-28	Statement of Work	Development of Insulative, Non-Ablative Materials for Reusable Thermal Protective System Applications	
SS-29	Statement of Work	Development of Oxidation--Inhibited Carbonaceous Materials for Reusable Thermal Protection Systems Applications	
SS-30	NASA MSC RFP No. MSC-JC-421-M68-0-112P	Development of a Rigidized, Surface Insulative, Thermal Protection System	April 13, 1970
SS-31	NASA Hqs. RFP No. DHC/10-8717	Economic Benefits of a New Launch System	April 7, 1970
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SS-36	TRW Memorandum	LI-1500 Thermal Properties Evaluation	February 17, 1970
SS-37	NASA Memorandum	Nominal Reentry Trajectory for the April Baseline Space Shuttle Vehicle	March 30, 1970
SS-38	BMI-NLVP Report to NASA (Part I)	An Analysis of the Allocation of Federal Budget Resources as an Indicator of National Goals and Priorities	February 10, 1969
SS-39	BMI-NLVP Report to NASA (Part II)	Ditto	Ditto
SS-40	NASA Status Report	Status of MSC Shuttle Study	May 21, 1969
SS-41	NASA Status Report	MSC ILRV--Space Shuttle	August 13, 1969
SS-42	NASA Paper presented at IEEE EASCON Session	Logistics Transportation for Space Station Support	October 29, 1969
SS-43	LTV Final Laboratory Data Report	Oxidation Inhibited Carbon-Carbon Composites	November 15, 1969
SS-44	McD-D Report Summaries	(1) A Two-Stage Fixed Wing Space Transportation System	December 15, 1969

Document No.	Description	Title	Date
	(1) Final Report, Vol I (2) Executive Summary	(2) Integral Launch & Reentry Vehicle System	November, 1969
SS-45	Lockheed Final Report	Integral Launch & Reentry Vehicle	December 22, 1969
SS-46	McD-D Final Report, Vol II, Preliminary Design	A Two-Stage Fixed Wing Space Transportation System	December 15, 1969
SS-47	Photograph	Gulfstream Flight LI-1500	
SS-48	Photograph	LI-15 Gulfstream Test Panel	
SS-49	Drawing	II Engine Booster Configuration 002	March 27, 1970
SS-50	Drawing	Orbiter Configuration 002	April 3, 1970
SS-51	Excerpts from NASA Staff Study	Manned Space Flight--Present and Future	February 12, 1970
SS-52	Magazine Article	Design of High Temperature Structural Systems	
SS-53	Article from Space/ Aeronautics	Man in Space--Stations and Bases	September, 1969
SS-54	Articles from Aviation Week	NASA Budget Hits 7-Year Low	February 2, 1970
		Integrated System Studies Decided Upon for Shuttle	"
SS-55	Article from Aviation Week	Space in the 1970's	February 9, 1970
SS-56	Article from Aviation Week	NASA Plans Fiscal 1972 Increase	February 16, 1970
SS-58	Phase A Report	Thermal Protection Systems	November, 1969
SS-59	Work Statement (DCN 1-0-50-09659)	Development of Design Data for Grphite Fiber Reinforced Epoxy and Polyimide Composites	
SS-60	NASA-MSFC RFQ No. DCN 1-0-50-09667	Development of Techniques and Associated Instrumentation for High Temperature Emissivity Measurements	April 24, 1970

Document No.	Description	Title	Date
SS-62	BMI Memorandum with Charts attached	MSC Testing Procedures	May 7, 1970
SS-63	BMI Program Prospectus by E. S. Bartlett	Development of Fail-Safe Coated Columbium Alloy System	April 13, 1970
SS-64	BMI Proposal to NASA-MSFC (DCN 1-0-50-09638)	Degradation and Reuse of Radiative Thermal Protection System Materials for the Space Shuttle	May 14, 1970
SS-66	Memorandum from R. W. Scott	NASA Shuttle Reuse, Refurbishment, Safety, Turnaround Time, and Nondestructive Testing (NDT)	May 4, 1970
SS-67	NASA Press Conference	NASA Planning Procedures Dr. Wernher von Braun Mr. O. B. Lloyd, Jr.	March 31, 1970
SS-74	NASA Memorandum	Thermal Evaluation Tests of Oxidation Inhibited Carbonaceous Materials in the MSC 1.5 MW Arc-Heated Tunnel	May 20, 1970
SS-75	Hitco Data Sheet	Pyro-Carb	
	Paper by Dr. Gavert	Carbon Composite Pyro-Carb 406 for Isotope Reentry Protection	
SS-77	Exhibit Material	SAMPE Convention Miami Beach, Florida	May 19-21-1970
SS-78	Preliminary Test Data	MSC 10 MW ARMSEF Facility	February 14, 1968
SS-80	Article from Aviation Week	Crew Describes Apollo 13 Crisis	April 27, 1970
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SS-87	NASA-MSC Volume I	DC 3- Space Shuttle Study	April 27, 1970
SS-88	NASA-MSC Volume II	DC 3- Space Shuttle Study	April 27, 1970
SS-89	Memorandum by Kistler	Characterization of LI-1525 Insulation	June 8, 1970
SS-90	Memorandum by Kirkhart	Reinforced Pyrolyzed Plastic (RPP) Material from LTV	June 8, 1970