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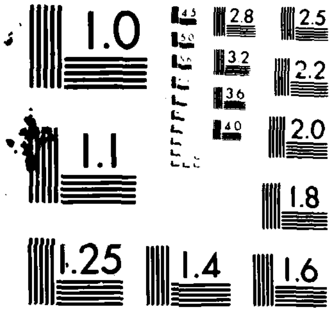

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PROCESS DEVELOPMENT AND PROPERTY EVALUATION OF ORGANOSILICON INFILTRATED REACTION SINTERED SILICON NITRIDE (RSSN)

Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

January 1982

FINAL REPORT FOR PERIOD JUNE 1980 - SEPTEMBER 1981

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

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The porous nature of RSSN limits its performance as a structural material because the pores act as strength limiting flaws and facilitate internal oxidation. The objective of this program was to develop an impregnation and pyrolysis process to fill these pores with silicon carbide and/or nitride derived from organosilicon precursors.

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Seven organosilicon precursors were evaluated as infiltrants using reaction bonded silicon nitride (RSSN) ceramics of different densities. Methylsilazane in decalin solvent was the best infiltrant.

Pyrolysis of methylsilazane resulted in a fine-grained microstructure containing 1μ closed pores. This grainy deposit bonded well to the pore walls in RSSN, and for this reason the methylsilazane is considered to be the best candidate organosilicon for improving the properties of RSSN.

During pyrolysis all organosilicon precursors exhibit a considerable volume of shrinkage and weight loss causing residual surface material to flake off the RSSN surface. Thin coatings were applied to RSSN samples to effectively plug the surface porosity. This resulted in significant improvements in oxidation resistance in both high and medium density RSSN materials. A 70% ~~percent~~ increase in the strength of low density foam RSSN was obtained.

FOREWORD

This final report was prepared by Dr. R.R. Wills, Mr. R.A. Markle, and Mr. W.E. Hauth of Battelle Columbus Laboratories, Columbus, Ohio under contract F33615-80-C-5007 with the Air Force Wright Aeronautical Laboratories, Materials Laboratory, Wright Patterson Air Force Base, Ohio. Mr. K.S. Mazdiyasni AFWAL/MLLM was the project monitor for the latter phases of the research.

The authors gratefully acknowledge the helpful suggestions of Mr. K.S. Masdiyasni of AFWAL/MLLM and Professor R. West of the University of Wisconsin who acted as a consultant during the program.

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SUMMARY

The porous nature of RSSN currently limits its performance as a structural material because the pores act as strength limiting flaws and facilitate internal oxidation. The objective of this program was to develop an impregnation and pyrolysis process to fill these pores with silicon carbide and/or silicon nitride derived from organosilicon precursors.

Seven organosilicon precursors were initially selected as candidate infiltrants. These were silazane, carbosilane, and chlorosilane derivatives. Impregnation and pyrolysis experiments were performed with three grades of RSSN ceramics ranging from a low density foam material (density 0.55 - 0.85 g/cm^3) to a high density slip cast material (2.79 g/cm^3).

The only precursor suitable for impregnation as a neat liquid was hexaphenylcyclotrisilazane. A methylsilazane precursor, in a decalin solvent was the only other candidate system that could be used as an infiltrant. Other selected precursors either were too unstable or could not easily be prepared. After three impregnation/pyrolysis cycles with hexaphenylcyclotrisilazane the density of low density Boeing RSSN increased 63.6 percent, medium density (2.09 g/cm^3) AME RSSN increased by 14.8 percent and high density AiResearch RSSN showed virtually no change in density. A larger density increase was obtained per impregnation/pyrolysis cycle with the methylsilazane solution than for the hexaphenylcyclotrisilazane. The ability to impregnate a given void volume decreased with each impregnation and pyrolysis cycle.

Conversion of hexaphenylcyclotrisilazane to silicon nitride occured by a vapor phase mechanism resulting in the formation of fibers which are not bonded to the host RSSN microstructure. Pyrolysis of methylsilazane resulted in a fine-grained microstructure containing 1μ closed pores. This grainy deposit bonded well to the walls of the pores in RSSN, and for this reason the methylsilazane precursor is considered to be the best candidate for improving the properties of RSSN.

During pyrolysis all organosilicon precursors exhibit a considerable volume shrinkage as well as weight loss so that after pyrolysis residual surface material flakes off the surface of the RSSN. Thin coatings were applied to RSSN samples to effectively plug the surface porosity. This

resulted in significant improvements in oxidation resistance in both high density and medium density RSSN materials. A 70 percent increase in the strength of low density Boeing Foam RSSN was obtained.

INTRODUCTION

The United States Air Force has an increasing interest in high performance ceramics, primarily for nonman rated vehicles such as RPV's, domes, and missile systems. Reaction sintered silicon nitride (RSSN) has emerged as a strong candidate material for many of these applications because of cost, performance, and shape-forming advantages.

RSSN is fabricated by the nitridation of silicon metal powder. The use of a variety of ceramic fabrication processes permits forming of a range of component shapes since less than 1 percent change in dimensions occurs during the nitridation process. RSSN is a relatively low cost structural ceramic with favorable room temperature and good high temperature properties which merits its consideration for use in advanced United States Air Force systems.

The porous nature of RSSN currently limits its performance as a structural material because the pores act as strength limiting flaws. This problem is enhanced at high temperatures where oxidation of free surfaces occurs. Closure and sealing of surface pores is thus highly desirable, particularly when this is performed with organosilicon precursors that decompose to silicon nitride or silicon carbide. The objective of this program was to develop an impregnation and pyrolysis process to fill these pores with silicon carbide and/or silicon nitride derived from organosilicon precursors.

To achieve the desired program goals of good room temperature strength and improved oxidation resistance, the surface porosity must be completely filled with ceramic to a depth greater than the critical flaw size. The ceramic deposit must be strongly bonded to the host RSSN, and must ideally contain no voids or cracks generated by evolution of volatiles and/or volume reduction during decomposition. The size and location of defects in the deposit will determine the degree of improvement in strength and oxidation resistance of the impregnated RSSN.

The general approach used in pursuing this program included: (1) the selection/development and characterization of low weight-loss organosilicon precursors; (2) determination of impregnation/coating conditions; (3) determination of pyrolysis conditions; and (4) post-treatment evaluation of RSSN materials.

DISCUSSION

Selection and Preparation of Organosilicon Precursors

Selection Criteria

Organosilicon precursors must satisfy several criteria to be acceptable infiltration materials for upgrading of RSSN properties. Candidate precursors must be stable under infiltration conditions, and undergo pyrolytic conversion to either Si_3N_4 or SiC at some higher temperature. That is, upon heating from ambient temperature to temperatures in the range of 700 to 2000 C, the organosilicon material must be converted to Si_3N_4 and/or SiC. Candidate organosilicon precursors should ideally have the following general properties:

- Be a low-viscosity liquid or melt, without the use of solvents, at infiltration temperature.
- Wet the RSSN well, i.e. show a low contact angle on an RSSN surface.
- Exhibit low, or nil, weight loss due to direct volatilization of the monomer of prepolymer itself, i.e. the infiltration compound should have a low vapor pressure.

- Show high solubility in a suitable infiltration solvent if the viscosity of the liquid or molten material is too great for satisfactory impregnation.
- Produce volatile leaving groups during thermal convertion to Si_3N_4 or SiC, with as much weight loss as possible occurring before the polymer crosslinks to avoid formation of secondary pores, or holes in the surface coating layers.
- Exhibit low weight loss on decomposition/conversion to Si_3N_4.

The main selection criteria employed were: (1) the precursor must have a viscosity of <100 centipose at the impregnation temperature, and, (2) the weight loss on pyrolysis should be minimal (less than 40 percent and preferably less than 20 percent).

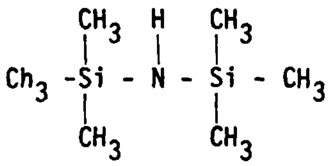
Chemical Classes

Two principal classes of materials were considered to be important candidates for possible use. One pyrolyzes to Si_3N_4/SiC mixtures of varying ratio that may approach Si_3N_4 as a limit, while the second class produces mainly SiC. At the present state-of-the-art, both classes can produce ceramic products containing varying amounts (typically up to about 20 percent) of carbon. If any moisture is absorbed by the prepolymers, oxygen will be present and some silica (SiO_2) will also form.

The first group of materials is the silazanes, or carbosilazanes. These are organosilicon compounds which have both carbon and nitrogen bonded to silicon, with the nitrogen attached as a secondary or tertiary amine. The second group includes the carbodisilanes, with central linear chain or ring silicon-silicon bonds in which one or both silicons also are bonded to carbon, and the carbosilanes which contain silicon-carbon chain or ring bonds. Either one of these general types of organosilicon infiltration compounds can be a low molecular weight noncyclic compound (i.e. an acyclic compound), a cyclic monomer, or a low molecular weight polymer, or prepolymer. Prepolymers can, in turn, contain either cyclic, or acyclic units, or both types connected together. These structural features are briefly discussed below under polycarbosilazane prepolymer infiltration candidates.

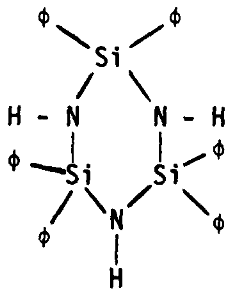
Carbosilazanes or Silazanes

The following discussion presents the background information and rationale for using cyclic silazane compounds and prepolymers to produce Si_3N_4/SiC infiltrated RSSN. Shown below are examples of acyclic (a), cyclic (b), linear acyclic prepolymer (c), and polycyclosilazanes (d). All these material types pyrolyze to produce mixtures of Si_3N_4 and SiC and varying minor amounts of encapsulated carbon with the relative amounts dependent on the actual precursor material and the processing conditions. Gases such as NH_3, CH_4, and H_2 are also produced.

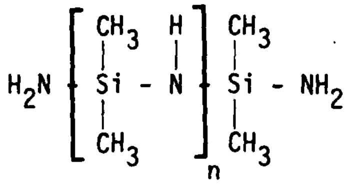


$$Ch_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-\overset{H}{\overset{|}{N}}-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3$$

(a) Hexamethyldisilazane

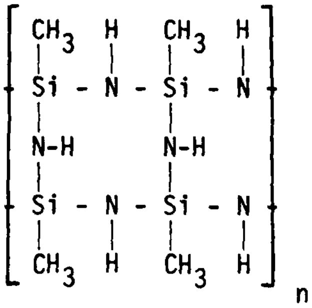


(b) Hexaphenylcyclotrisilazane



$$H_2N\left[\begin{matrix}CH_3 & H\\ | & |\\ Si & - N\\ | & \\ CH_3 & \end{matrix}\right]_n\begin{matrix}CH_3\\ |\\ Si - NH_2\\ |\\ CH_3\end{matrix}$$

(c) Polydimethylsilazane



(d) Polymethylsesquisilazane

The materials used in prior infiltration and ceramic powder binder studies$^{(1)}$ were cyclic monomers (Type b) or prepolymers of cyclic structures (Type d). This is primarily because both six- and eight-member ring cyclosilazanes are quite stable thermodynamically and tend to form spontaneously during synthesis or link together into prepolymer-linked cyclics when they are heated. The simple cyclics are usually very low viscosity liquids at room temperature, or just above their melting points. The viscosity of prepolymers depends primarily on molecular weight. Low molecular weight prepolymers (n = 2-6) would be expected to be low viscosity liquids at acceptable infiltration temperatures, and that would probably most nearly meet the selection criteria given earlier, provided structures with low pyrolytic weight loss are obtained.

The best known examples of the cyclic compounds are the six-membered ring trimer hexamethylcyclotrisilazane (boiling point, 187 C) and the eight-membered ring tetramer octamethylcyclotetrasilazane (boiling point, 224 C). These compounds are commercially available and are possible candidate infiltration materials if a sealed or pressurized infiltration chamber is used to prevent evaporation before conversion to polymer is effected. Some pertinent data are listed in Tables 1 and 2 which demonstrate the high thermodynamic stability of these compounds$^{(2)}$. Fairly rapid decomposition of hexamethylcyclotrisilazane starts between 300 and 350 C with more rapid breakdown starting between 450 and 500 C. The products at 500 C are a high yield of infusible polymer and NH_3 and CH_4 gases. Octamethylcyclotetrasilazane converts to the trimer and polymer

TABLE 1. THERMOSTABILITY OF HEXAMETHYLCYCLOTRISILAZANE(a,b)

Temperature, C	Products Found		
	Hexamethylcyclotrisilazane	Polymer	Gas, ml(c)
200	100	0	0
300	96.3	3.7	10
350	67.0	33.0	245
400	62.0	38.0	370
450	60.0	39.8	467
500	27.2	72.8(d)	1,887

(a) D. Ya. Zhinkin, E. A. Semenova, M. V. Sobolevskii, and K. A. Andrianov, Plasticheski Massy, (12), 1963, p. 16-17, reference 1.

(b) 100 g hexamethylcyclotrisilazane heated 3 hours in a 250-ml autoclave at indicated temperature, then the decomposition products were analyzed and the results listed as percentages of total recovered.

(c) At 300-400 C, mostly NH_3; at 400-500 C, mostly NH_3 and CH_4.

(d) 72.8 percent solid and 11.9 percent liquid.

TABLE 2. THERMOSTABILITY OF OCTAMETHYLCYCLOTETRASILAZANE (a,b)

Temperature, C	Products Found			
	Hexamethylcyclo-trisilazane	Octamethylcyclo-tetrasilazane	Polymer	Gas,ml (c)
200	0	0	0	0
300	0	100	0	0
350	60.25	0.55	39.2	174
400	63.1	1.9	35.0	212
450	59.5	0.5	40.0	415
500	0	0	63.3 (d)	1,710

(a) D. Ya. Zhinkin, E. A. Semenova, M. V. Sobolevski, and K. A. Andrianov, Plasticheski Massy, (12), 1963, p. 16-17, reference

(b) 100 g octamethylcyclotetrasilazane heated 3 hours in a 250-ml autoclave at the indicated temperature, then the decomposition products were analyzed and the results listed as percentages of total recovered.

(c) At 300-400 C, mostly NH_3; at 400-500 C, mostly NH_3 and CH_4.

(d) 63.3 percent solid.

between 300 and 350 C indicating the higher thermodynamic stability of the trimer. This also shows that trimer or tetramer cyclics, and most likely polymers containing these rings, can be considered equivalent as far as RSSN infiltration is concerned.

Data for a third cyclic monomer, tetramethylcyclotetrasilazane (b.p., 54 C)(3) are listed in Table 3(2). This compound is also quite stable up to at least 200 C. Between 200 and 300 C some decomposition occurs, but between 300 and 350 C rapid, and apparently complete conversion to polymer and gases occurs. This compound, which is not commercially available, is of great interest because it has a lower methyl group, or carbon, content and therefore has a lower theoretical weight loss when pyrolyzed to Si_3N_4/SiC, and would presumably result in a lower encapsulated carbon content in the ceramic residue. This is shown in Table 4 which lists theoretical weight losses for a series of cyclosilazanes. The maximum Si_3N_4/SiC residues that can be produced from each compound were identified and the corresponding amount of volatiles expected were calculated. In most cases an upper and lower level of volatiles is possible depending on whether the pyrolysis leads to the maximum possible yield of Si_3N_4 or SiC. These ranges are shown, based on the assumption that all other material except Si metal, if produced, will volatilize. Excess carbon is assumed to be volatilized, for example as methane, in arriving at the calculated volatile losses, although it is known that varying amounts of carbon are retained. Tetramethylcyclotetrasilazane volatile losses should be between 23.7 and 32.1 percent as opposed to 38.3-49.2 percent for the fully methyl substituted cyclics, which are listed above it in Table 4.

Silazane, or carbosilazane, materials have already been studied for infiltration of porous RSSN(1). Hexaphenylcyclotrisilazane was heated to 250 to 300° C to infiltrate RSSN samples under vacuum. The samples were then pyrolyzed to 1400 C under N_2. Pronounced changes in microstructure, increased densities, and improved room-temperature strength RSSN were achieved. However, most of the porosity remained unfilled by this approach. It is not surprising that hexaphenylcyclotrisilazane produced only moderate pore infiltration in view of the very high weight loss potential (78 percent, Table 4).

TABLE 3. THERMOSTABILITY OF TETRAMETHYLCYCLOTETRASILAZANE[a,b]

Temperature, C	Products Found		
	Tetramethylcyclotetrasilazane	Polymer	Gas, ml
200	100	0	0
300	Not given	some	some NH_3, H_2
350	0	high yield[c]	NH_3,H_2,CH_4
450	0	high yield	NH_3,H_2,CH_4

(a) D. Ya. Zhinkin, E. A. Semenova, M. V. Sobolevski, and K. A. Andrianov, Plasticheski Massy, (12), 1963, p. 16-17, reference

(b) Tetramethylcyclotetrasilazane heated in a 100-ml autoclave from 200 to 450 C and held at 450 C for 30 minutes.

(c) At 350 C most of the material becomes a solid foam.

TABLE 4. THEORETICAL WEIGHT LOSS FROM CYCLOSILAZANES(a)

Compound	Molecular Weight	Empirical Formula				Residue Assumed	Volatiles Assumed	Theoretical Loss, weight percent
		C	H	Si	N			
Hexaphenylcyclotrisilazane	591.5	72	66	6	6	Si_3N_4 + 3 SiC	$C_{69}H_{66}N_2$	78.0
Octamethylcyclotetrasilazane	292.6	8	28	4	4	Si_3N_4 + SiC	C_7H_{28}	38.3
						-- 4 SiC	$C_4H_{28}N_4$	45.2
Hexamethylcyclotrisilazane	219.5	6	21	3	3	Ibid(b)	Ibid	38.3
Tetramethylcyclotetrasilazane	236.64	4	20	4	4	Si_3N_4 + SiC	C_3H_{20}	23.7
Trimethylcyclotetrasilazane	222.61	3	18	4	4	Si_3N_4 + SiC	C_2H_{18}	18.9
	667.83	9	54	12	12	Si_3N_4 + 9 SiC	$H_{54}N_8$(c)	24.9
Dimethylcyclotetrasilazane	208.59	2	16	4	4	Si_3N_4 + SiC	CH_{16}	13.5
	625.77	6	48	12	12	Si_3N_4 + 9 SiC	$H_{48}N_8$(c)	25.6
Methylcyclotetrasilazane	194.56	1	14	4	4	Si_3N_4 + SiC	H_{14}	7.3
Cyclotetrasilazane	180.54	--	12	4	4	Si_3N_4 + Si	H_{12}	6.7(d)

(a) After pyrolysis to 1200-200 C in inert atmosphere.

(b) Multiply empirical formula by 1.333.

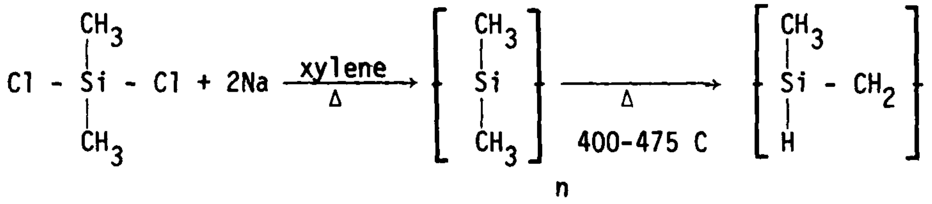
(c) Multiply empirical formula by 3. Assume extra Si will remain as SiC.

(d) Silicon is left as a 20 percent by weight residue based on Si_3N_4, or 16.7 percent by weight residue based on Si_3N_4 + Si.

Work has also been done at Bayer AG in West Germany on the preparation of prepolymers like Type d(4,5). The materials produced were all solid resins which were soluble in organic solvents(4) or meltable to moderately viscous (quantitative viscosity data not given) liquids(5). Although RSSN infiltration studies were not done, it was stated that the carbosilazane resins can be melt processed mixed with silicon carbide and/or silicon nitride powders to produce bodies of arbitrary shape, such as plates, tubes, bricks, tiles, rods, etc. The primary objective of the work was the spinning of carbosilazane fibers for pyrolytic processing into high-strength Si_3N_4/SiC fibers. The products were claimed to be solely Si_3N_4/SiC mixtures in about a 50/50 weight ratio, that are achieved at weight losses below 30 percent by weight.

Carbosilanes and Disilanes

The carbosilanes are typified by the polymer synthesized from dimethyldichlorosilane by reaction with metallic sodium in hot xylene to produce insoluble polydimethylsilane. This polymer is then thermally rearranged at 400 to 475 C to produce polymethylcarbosilane.

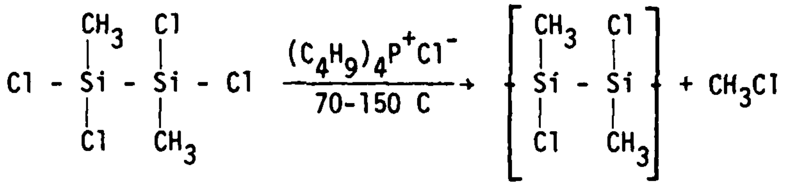


$$\mathrm{Cl}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{Cl} + 2\mathrm{Na} \xrightarrow[\Delta]{\text{xylene}} \left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right]_n \xrightarrow[\substack{\Delta \\ \text{400-475 C}}]{} \left[\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}\right]_n$$

This reaction and the use of the polymer to prepare films and spin fibers which can be pyrolyzed to SiC are the subject of a series of papers and patents by S. Yajima and J. Hayashi and coworkers(6-11). The workhorse polymer produced by Yajima's group is polymethylcarbosilane.

However, it has been known for some time that the SiC fibers produced by this process typically contain 10 to 20 percent residual carbon and the pyrolytic weight loss is >40 percent. Yajima has recently confirmed this and reported data indicating 15 percent carbon retained in SiC fiber heat treated to 1300 C(12). However, this carbon appears to be entirely enclosed or encapsulated in the SiC because the fiber can be placed directly in a gas flame for 1 day or more with no change in weight or loss of strength(13). Also, the prepolymers are relatively viscous (>100 centipose) at temperatures >250 C. This would make it very difficult to infiltrate RSSN without using a solvent.

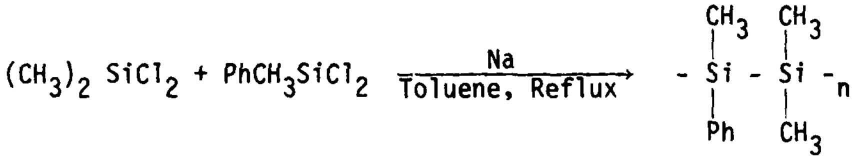
Dow Corning (R. H. Baney). Dow Corning has recently been issued patents(14-15) on a new, improved process for preparing a polymer which is somewhat like the Yajima polymethylsilane. It is a polymethylchlorosilane produced by a low temperature (70 to 150 C), quaternary salt catalyzed, process, as follows (oversimplified):



$$Cl - \underset{Cl}{\overset{CH_3}{Si}} - \underset{CH_3}{\overset{Cl}{Si}} - Cl \xrightarrow[\text{70-150 C}]{(C_4H_9)_4P^+Cl^-} \left[\underset{Cl}{\overset{CH_3}{Si}} - \underset{CH_3}{\overset{Cl}{Si}} \right] + CH_3Cl$$

Dr. R. H. Baney and associates at Dow Corning have prepared prepolymers with weight losses ranging from about 30 to 40 percent to about 10 percent by weight(16). Also, these prepolymers have a potentially lower commercial production cost since they are made from a raw material that is a by-product of the process by which Dow Corning manufactures chlorosilanes for the production of silicone resins, and the production process is low temperature and essentially one step. Consequently, Dow Corning was engaged as a subcontractor to supply some of these new SiC precursors for use on this program, and Dr. Baney became a consultant to Battelle concerning the use of these new materials.

Polysilastyrene (R. West). The reaction of equimolar quantities of dimethyldichlorosilane and phenylmethyldichlorosilane with sodium dispersion in hot toluene produces a readily soluble and meltable polymer which Professor West (University of Wisconsin) has named polysilastyrene(17) as shown below:



$$(CH_3)_2\,SiCl_2 + PhCH_3SiCl_2 \xrightarrow[\text{Toluene, Reflux}]{\text{Na}} -\overset{CH_3}{\underset{Ph}{Si}}-\overset{CH_3}{\underset{CH_3}{Si}}-_n$$

Polysilastyrene

This polymer degrades to a SiC residue when heated above 300 C. It is easily made but has some drawbacks for use as an RSSN infiltrant. The melt viscosity of a low molecular weight polymer ($\bar{M}_w \sim 7000$) is appreciably greater than 100 centipoise even at 250 C. Also, the theoretical weight loss is higher than desired (55 weight percent). However, some of this low molecular weight polymer was readily available to us and was given limited attention. Professor West was a consultant to Battelle during the program.

Infiltration Candidates

Based on the above information and availability of materials, an initial list of candidate organosilicon RSSN infiltration materials was selected. It consisted of the following materials:

(1) Moderate yield SiC prepolymer (Dow Corning)
(2) High yield SiC prepolymer (Dow Corning)
(3) *Tetramethylcyclotetrasilazane Dimer* (Battelle)
(4) Prepolymer of tetramethylcyclotetrasilazane (Battelle)
(5) Prepolymer based on methyltrichlorosilane and ammonia (Battelle)
(6) Polysilastyrene (Professor West, University of Wisconsin)
(7) Hexaphenylcyclotrisilazane. (Commercial)

Candidates (1) and (2) are based on the work done at Dow Corning over the past several years to prepare precursors for high yield SiC fiber described above.

Candidates (3) and (4) are based on the cyclic monomer tetramethylcyclotetrasilazane described above. These types of materials are not commercially available, but are produced from commercial intermediates (methyldichlorosilane and ammonia) and have been described in two literature reports(2,18). They have the potential to provide up to 76 percent ceramic yield (mixture of Si_3N_4 and SiC), when obtained in an appropriate prepolymer form and were thus considered good candidates.

Candidate (5) consists of prepolymers based on work done by Bayer AG in West Germany. These prepolymers are not commercially available but have been made at Battelle during prior work(19). The product based on methyltrichlorosilane and ammonia is a low melting, solid resin which has been shown to yield 72 percent residue by thermogravimetric analysis (TGA) in our work. Unfortunately, this resin was known to crosslink when heated above its melting point of about 50 C and would therefore have to be used in solution to infiltrate RSSN.

Candidate (6), the polysilastyrene, has been described above. Candidate (7) was hexaphenycyclotrisilazane. Although the ceramic yield potential is only 22 percent for this material, it was considered to be a good reference material for preliminary studies because of its prior use(1) and a large amount (>1 kg) of pure material was available.

Dow Corning SiC Precursor Prepolymers

A 200 gram sample of the moderate yield SiC prepolymer and 50 grams of the high yield SiC prepolymer were obtained from Dow Corning for evaluation.

Carbosilazane or Silazane Prepolymers

Three candidates selected for study from this class included items 3 (tetramethylcyclotretrasilazane dimer), 4 (prepolymer of tetramethylcyclotetrasilazane), and 5 (methylsilazane prepolymer based on methyltrichlorosilane and ammonia). These materials had to be prepared in the laboratory since they are not commercially available.

Tetramethylsilazane Dimer and Prepolymer. The initial work was done on the preparation of tetramethylsilazane dimer and prepolymer since these products have been previously reported by two groups of workers, Semenova et.al.(2) in Russia and Brewer and Haber(18) at General Electric in the United States. Semenova et.al. reported an 81 percent yield of crude methylcyclosilazane liquid from which they isolated tetramethylcyclotetrasilazane in 20 percent yield and a compound believed to be a simple 8,6-fused ring bicyclic compound (dimer) in 8 percent yield, by vacuum distillation at 40 to 200 C. Brewer and Haber obtained a 52 percent yield of a "viscous oil" from which they isolated a 5 percent yield of a distillate boiling at 166 to 168 C at atmospheric pressure which they believed consisted primarily of the cyclic trimer.

It was of great interest in the present work that both of these prior reports produced more prepolymer (undistillable product) than monomer. It was felt that this prepolymer might be usable as prepared, either by removing the highly volatile monomers by vacuum stripping or by solvent precipitation, or by modifying the preparations to reduce or eliminate the monomer content. In fact, a small amount of monomer (e.g. ~10 percent) might be acceptable as a solvent for the prepolymer, allowing effective infiltration of RSSN to be accomplished. Even if all this monomer evaporated during pyrolysis, a theoretical ceramic yield of 58 to 66 percent would result. Furthermore, if the pyrolysis were done under pressure, especially under ammonia, volatile loss of monomer might be eliminated through pressure and through thermally induced crosslinking of the monomer via reaction of the SiH groups with the ammonia before volatilization occurs.

A total of five reactions were carried out, two following Semenova's procedures in which ammonia gas was bubbled through a dilute solution of methyldichlorosilane in benzene at room temperature, and three following Brewer and Harber's procedure in which methyldichlorosilane dissolved in diethyl ether was added to a mixture of diethyl ether and liquid ammonia at low temperatures (-78 C or lower). All solvents were dried over CaH_2 to remove water quantitatively. The reaction flask was flame dried and cooled under dry argon which was passed through the reaction flask continuously to keep out water. The ammonia, and argon were dried by passing through a CaH_2 tower and methyldichlorosilane was distilled just before use or was a freshly obtained high purity sample. In two of the five reactions about a 20 percent yield of a moderately viscous liquid or meltable solid was obtained while the rest of the product was insoluble and infusible. The other three products were all crosslinked solids. The two products that were tractable were both found to be unstable. The liquid crosslinked to an insoluble gel after 2 weeks storage at 5 C. The originally soluble solid product partially melted at 80-90 C to a slightly viscous melt containing an unmelted fraction. The melted sample crosslinked rapidly at 110 to 120 C to an insoluble, friable solid. This product was also found to be largely insoluble in methylene chloride after just 1 day as a recovered solid. It was concluded that this product was too unstable for use as an infiltration candidate.

These results are not consistent with those reported by the prior workers. The reasons for this are unknown. Since some indication that liquid or meltable solid products can in fact be obtained this approach may still have merit for further study.

Methylsilazane Resin. The reaction of methyltrichlorosilane with ammonia produces a soluble resin (reaction shown in Figure 1) which is stable in solution if kept dilute and dry. The structure of the resin

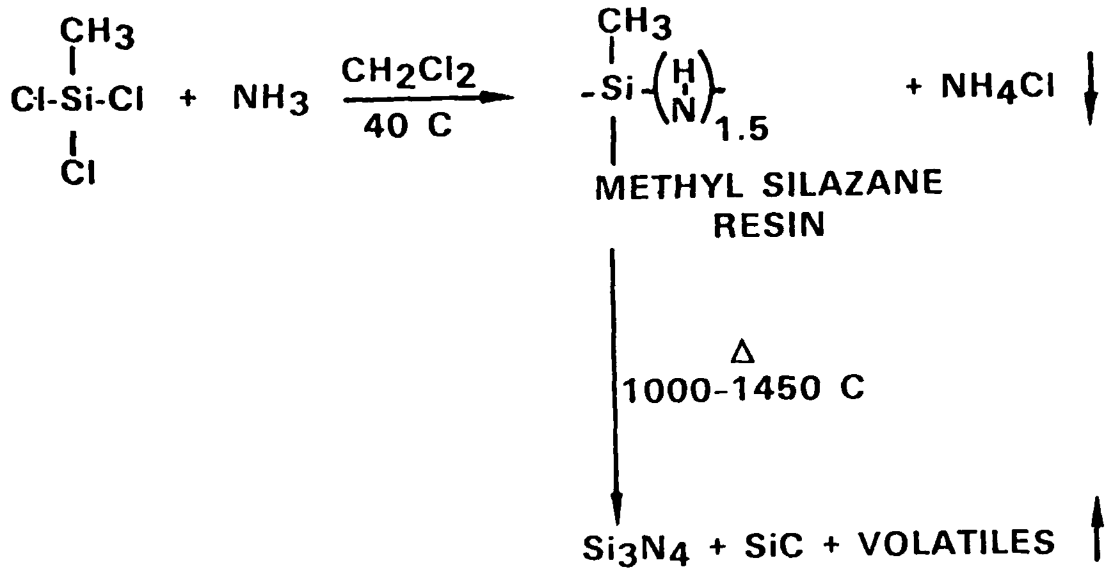


FIGURE 1. METHYLSILAZANE RESIN ACCORDING TO U.S. PATENT 3,892,583 (Bayer, A.G., July 1, 1975)

product is not known but structure b on page 4 is one possible idealized representation. A number of other reports concerning the reaction of methyltrichlorosilane with ammonia have appeared in the literature(20-37). In addition there are also reports in the Russian literature which describe various uses of a "methylsilazane" resin solution which is not further described but which is believed to be based on the reaction of methyltrichlorosilane and ammonia(38-49). Three of these articles are concerned with the impregnation of boron nitride with "MS-7 polymethylsilazane" to improve strength and oxidation resistance(38-40). This literature, as a whole, shows that a solution stable resin usable to coat or impregnate various substrate materials has been made by a number of different groups since about 1947. All uses of the product involve a solution of the resin in solvents like methylene chloride, benzene or toluene, indicating that stable solutions can be prepared readily. Where the subject of neat resin, isolated from solution, is discussed, it is stated or implied that the solid resin is not stable and cannot be used as such. This is in agreement with our prior experience in handling this product, since it crosslinks slowly when isolated as the neat resin, with the reaction speeding up greatly when the resin is melted(19). In this prior work, the melting point was recorded as 200-215 C, with the viscous liquid obtained rapidly decomposing, releasing ammonia, and crosslinking. However, the resin prepared on the present program and described below (product 35996-35)* melts at much lower temperatures (40-50 C) to a moderately viscous liquid. It is now believed that the earliest high melting point was anomalous and was due to absorption of water resulting in condensation to a higher molecular weight or lightly crosslinked resin. Nevertheless, lower melting product 35996-35 still slowly decomposes and crosslinks when melted. It was not known at the outset whether it was possible to obtain a stable usable infiltration solution of this resin. However, the known high ceramic yield (72 percent) and the fact it had been prepared before as a stable solution were evidence in favor of preparing and studying this polymer. About 55 grams of this resin were therefore synthesized. This resin, when isolated as a solid by stripping away the methylene chloride solvent, is a friable tan solid.

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* Experimental details are given in Appendix A

An infrared (IR) spectrum of the freshly prepared methyl silazane resin in methylene chloride solution is shown in Figure 2. A medium intensity, relatively narrow absorption band is consistent with a secondary aminosilazane N-H stretching absorption at 3380 cm^{-1}(50). Moderately strong absorptions at 1550 cm^{-1}, 1150 cm^{-1} and 950 cm^{-1} are consistent with silazane NH_2 and N-H deformation and Si-N-Si stretch absorptions. The absence of an absorption in the 1020-1130 cm^{-1} range shows that there is no significant amount of Si-O-Si structure present. Thus, a methyl silazane resin with no absorbed water is indicated.

A thermogravimetric analysis (TGA) of the freshly prepared dry resin is shown in Figure 3. The TGA was run at 4 C/min under Ar to 1440 C. There are four major breaks in the weight loss curve, at approximately 280, 400, 700, and 900 C. Weight loss starts at about 50-60 C and continues at a constant rate up to about 280 C (~2 percent weight loss). This weight loss is probably partly due to volatilization of some low molecular weight products and partly due to slow onset of degradation, with loss of ammonia. Between 280 and 400 C, the weight loss rate increases sharply and another 7 percent weight loss occurs. By analogy with the degradation characteristics of hexamethylcyclotetrasilazane (Table 1, page) this weight loss is probably mostly ammonia, with some organosilazane volatiles. Between 400 and 700 C weight loss continues at a slightly slower rate with another 8.5 percent (18.5 percent total at this point) recorded. Again by analogy with the Table 1 data, this weight loss would be expected to include ammonia and methane, along with organosilazane volatiles. Above 700 C, the weight loss rate again accelerates and another 9.5 percent loss is observed (total 28 percent). The nature of the loss occurring in this region is unknown. It would be of great value to determine the identity, rate of evolution and total amount of the major volatile products across the entire range of the TGA, for example by mass spectrometry of volatiles after chromatographic separation. This information, along with spectroscopic, elemental and microscopic analysis of the residue at each stage of the thermal conversion process would allow for identification of the chemical degradation mechanisms and microstructure evolution of the ceramic end product. This type of

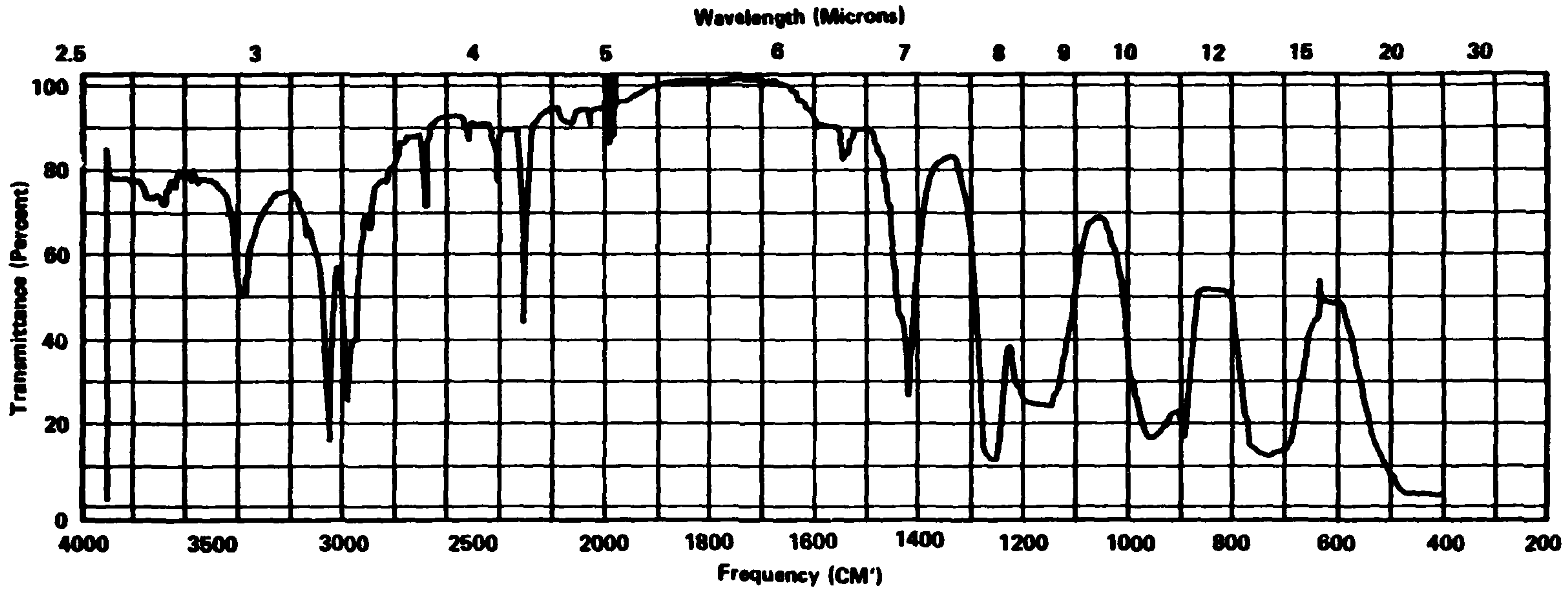


FIGURE 2. INFRARED SPECTRUM OF METHYL SILAZANE RESIN (in CH_2Cl_2)

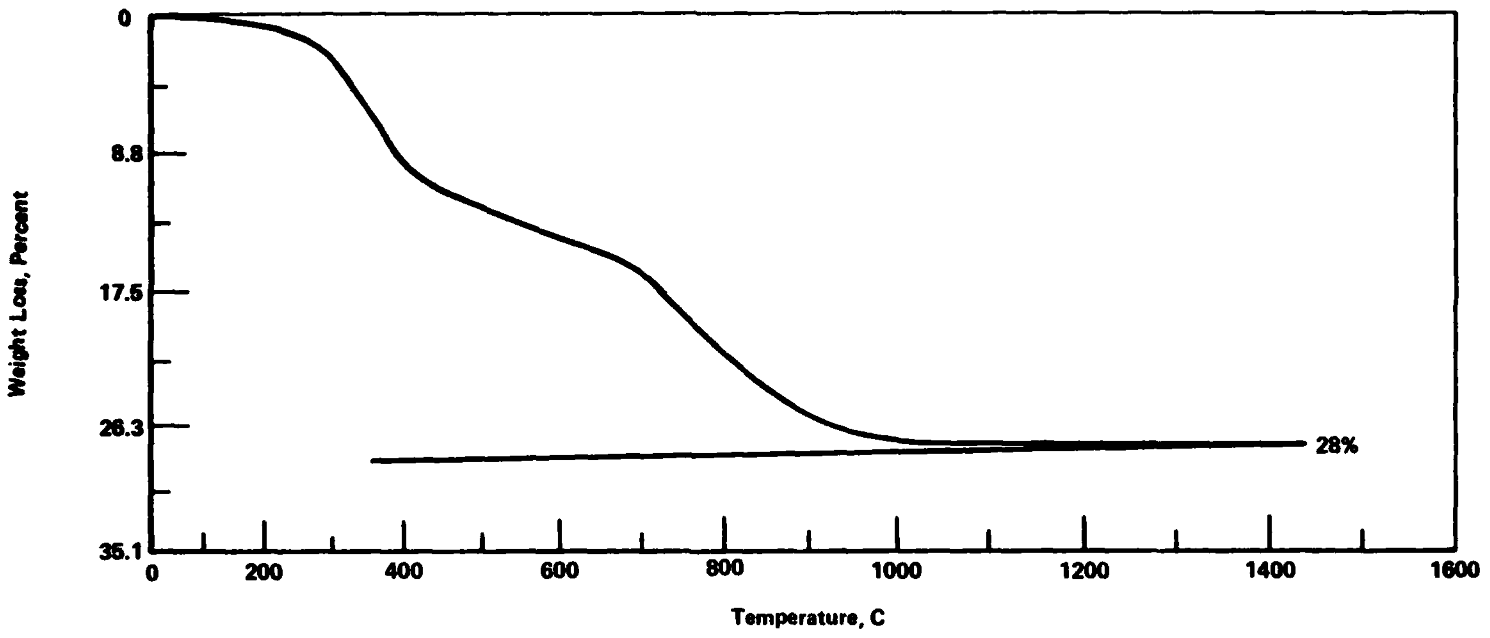


FIGURE 3. METHYLSILAZANE RESIN 35996-35 TGA

information is ultimately needed to understand and control the thermal conversion process in order to optimize the amount and nature of the ceramic end product.

Soon after it was prepared, the methylsilazane resin was found to be slowly degrading in the methylene chloride solution, forming an insoluble precipitate. This solution instability may be due to either thermal or trace-moisture-induced crosslinking through $Si\text{-}NH_2$ groups or to precipitation of a high molecular weight fraction. The solution was refiltered five times through a 0.2μ millipore filter using argon pressure. Each time about 0.5 grams of insoluble, silazane resin was obtained. The freshly filtered solution was initially clear, but precipitate slowly began to form again. Small samples of resin obtained immediately after filtration, by carefully evaporating the methylene chloride solvent under dry conditions, were found to be clear, colorless, very slightly tacky solids melting at 40 to 50 C. This is much lower than the previously found melting temperature(19). The higher melting point (approximately 210 C), found initially, is believed to be due to a partial hydrolytic reaction of the recovered solid before the melting point was determined.

It was also observed that a small portion of the resin solution remained clear (no precipitate) during removal of all of the methylene chloride. Further instability or precipitation was prevented by treatment of the resin in solution with N,O-bis (trimethylsilyl) trifluoracetamide, a very powerful trimethylsilating reagent. This reagent quantitatively converts $SiHN_2$ or SiOH groups to stable $\overset{H}{N}$ - or $-O\text{-}Si(CH_3)_3$ groups. Room temperature treatment of the resin solution with 10 grams of this silylation reagent immediately stabilized it.

Several potential solvents for the stablized methylsilazane resin were studied for their ability to produce a solution suitable for infiltration trials. It was found that the resin was quite soluble in hydrocarbon solvents including toluene, xylene and decahydronaphthalene (decalin), but insoluble in more polar solvents like cellosolve acetate and butyl cellosolve acetate. Decalin was selected as the solvent because it boils at about 200 C and it has an acceptable vapor pressure for use as an impregnation solvent under vacuum conditions. The vapor pressure is about 0.2 mm Hg at 25 C and about 6 mm Hg at 50 C. The viscosity of a solution with 57 percent solids of the methylsilazane resin in decalin containing about 11 percent of the silylating reagent appeared to be water-like at about 70 C. The entire stock of methyl silazane resin 35996-35 in decalin solution (51.4 grams in 90 grams of solution containing 10 grams silylating reagent and 28.6 grams of decalin prepared by adding the decalin and vacuum stripping the methylene chloride) was then placed in the special glove box which contained the RSSN vacuum impregnation equipment and kept there under argon at ambient temperature. This solution proved to be stable and useful for vacuum impregnation of RSSN. However, after 6 weeks the unused portion of this infiltration solution became unstable and formed a heavy precipitate over a period of several days making it unfit for further use. This only occured, however, after this solution had been heated up to 50-70 C for approximately 2 hours during infiltration experiments.

Attempts were then made to prepare another batch of methyl silazane resin to replace 35996-35. Twice reactions were run nearly to completion but at some point near the end of the reactions, the products crosslinked to an insoluble, useless solid. The reason this occurred is unknown. At this point, funds for preparation of silazane resins were exhausted and no further work could be done. However, work being carried out under in-house sponsorship at Battelle on a new approach to the preparation of a methyl silazane resin that would be melt stable succeeded in producing such a product. A portion of this prepolymer code named R-41, was made available for use in this program to coat and/or infiltrate RSSN. This modified methyl silazane resin is a brittle, clear, amber solid with a melting point of 50-60 C. It is melt stable up to about 250 C under Ar. At 200 C it is a viscous honey-like melt, stable for at least 24 hours.

The TGA of R-41, ran at 10° C/minute under argon atmosphere, is shown in Figure 4. The much greater thermal stability of R-41 is shown by the fact that there is no weight loss until 400 C. There are two major slope changes in the TGA curve, at 480 C and at 800 C, and two minor changes, at 600 and 700 C. There is a 20 percent weight loss between 400 and 480 C, a 7 percent loss between 480 and 600 C, a 7 percent loss between 600 and 700 C and a final 6 percent loss between 700 and 900C, for a total weight loss of 40 percent (ceramic yield 60 percent). Thus, R-41 is much more stable than 35996-35 but shows a 12 percent lower ceramic yield.

A 75 μm (3 mil) thick ceramic free film was produced from R-41 neat resin by placing a small sample (about 0.3 gram) in a flat bottom molybdenum cup in the glove box under Ar and subjecting the sample to pyrolysis in the furnace to 1400 C (250 C/hour heating rate). Photomicrographs of the film obtained are shown in Figures 5 and 6. Figure 5 is a 1000X picture of the top surface of the film. Pits with diameters ∿1 μm are visible on the surface. The fracture surface of the film at 350X (Figure 6) shows clearly that the film is predominately solid ceramic material with sparsely and randomly distributed voids that are <1 μm in diameter. This indicates that R-41 has the potential for providing a ceramic material with microstructural features capable of providing improved oxidation resistance and strength improvements in RSSN.

Polydimethylsilazane Synthesis. Polydimethylsilazane (Experiment 35996-30) was made by the Rochow equilibrium process in which hexamethylcyclotrisilazane (commercially available liquid monomer derived from dimethyldichlorosilane and ammonia) was rearranged by heating to ∿150 C in the presence of eight atmospheres of ammonia (see Figure 7). The reaction gave a 13 percent yield (20 percent reported by Rochow) of liquid polymer with a viscosity comparable to 30-40 weight motor oil at room temperature. The rest of the product was recyclable cyclic monomers.

Infrared spectra of the hexamethylcyclotrisilazane (HCMTS) starting material (Figure 8) and the polydimethylsilazane product (Figure 9) are consistent with these structures. Absorptions due to Si-NH-Si, NH stretch (3400 and 3380 cm^{-1}), respectively), NH bend (1175 and 1160 cm^{-1}, respectively), $SiCH_3$ asymmetric deformation (1400 cm^{-1}, both), $SiCH_3$

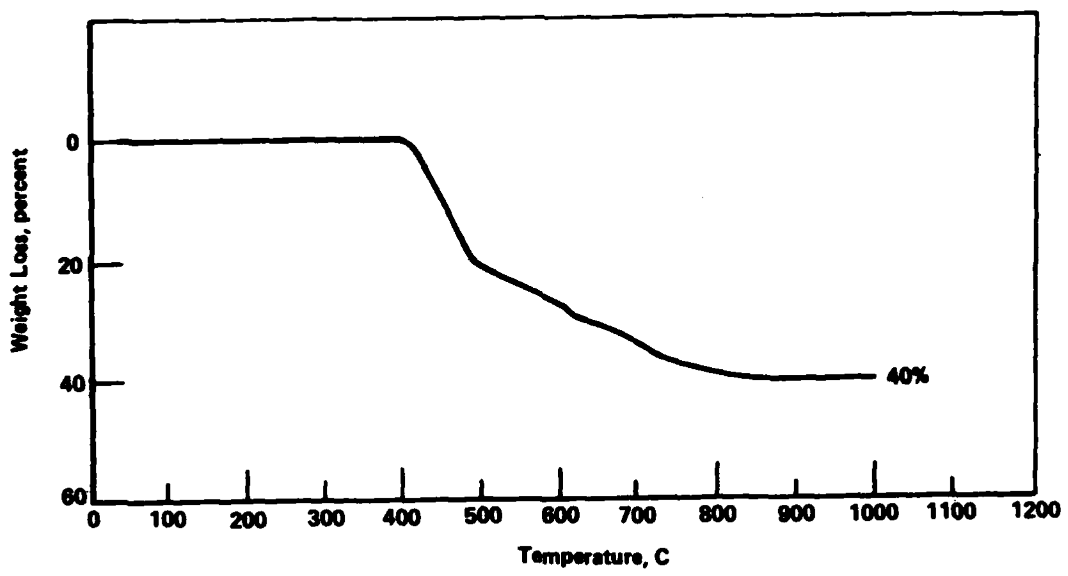


FIGURE 4. METHYLSILAZANE RESIN (R-41) TGA

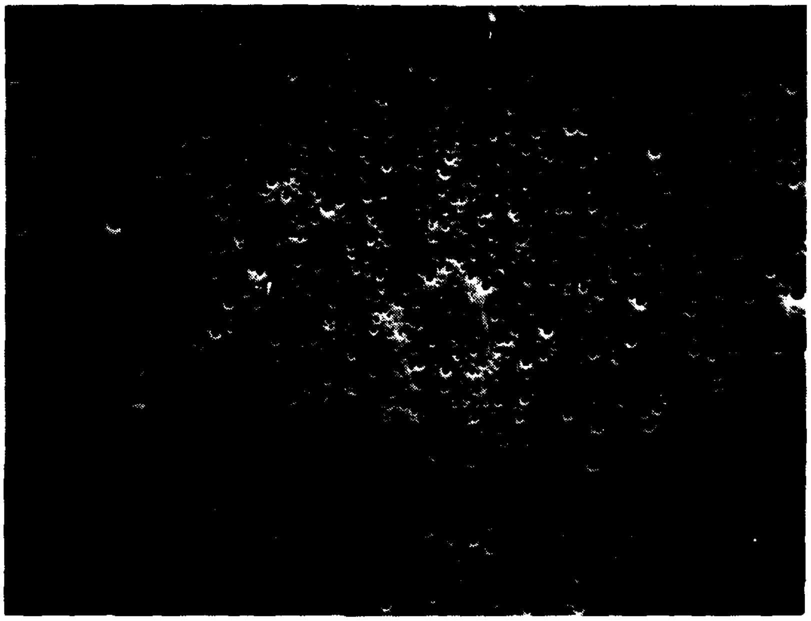


FIGURE 5. TOP SURFACE OF PYROLYZED R-41 FILM (1000X)

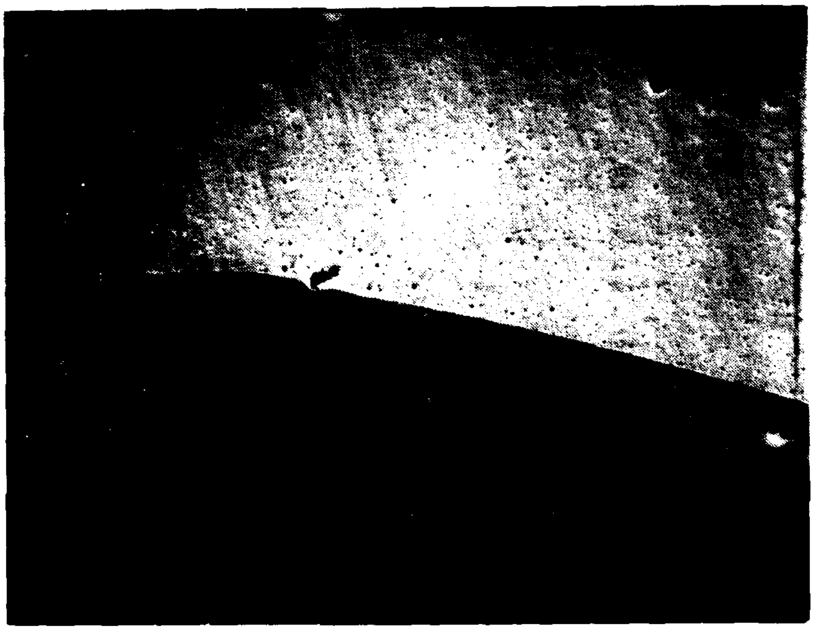
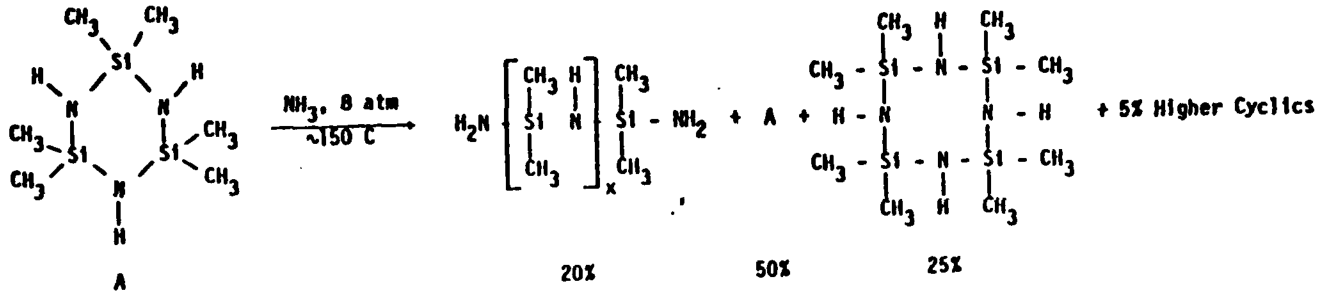


FIGURE 6. FRACTURE SURFACE OF PYROLYZED R-41 FILM (350X)



E. G. Rochow, "Polymeric Methylsilazanes", Pure and Applied Chemistry, 13, 247-262 (1962)

FIGURE 7. PREPARATION OF POLYDIMETHYLSILAZANE

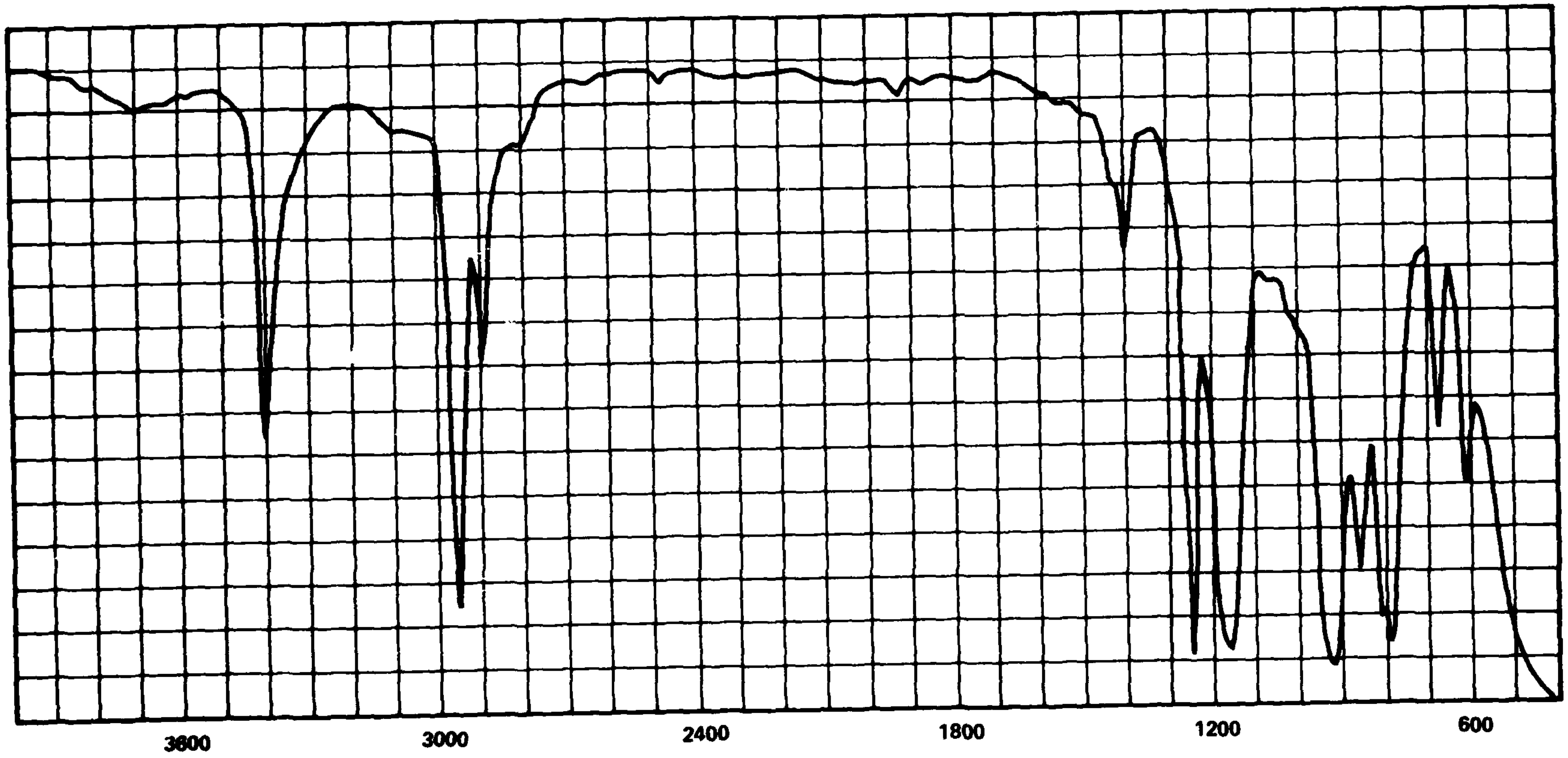


FIGURE 8. INFRARED SPECTRUM OF HEXAMETHYLCYCLOTRISILAZANE

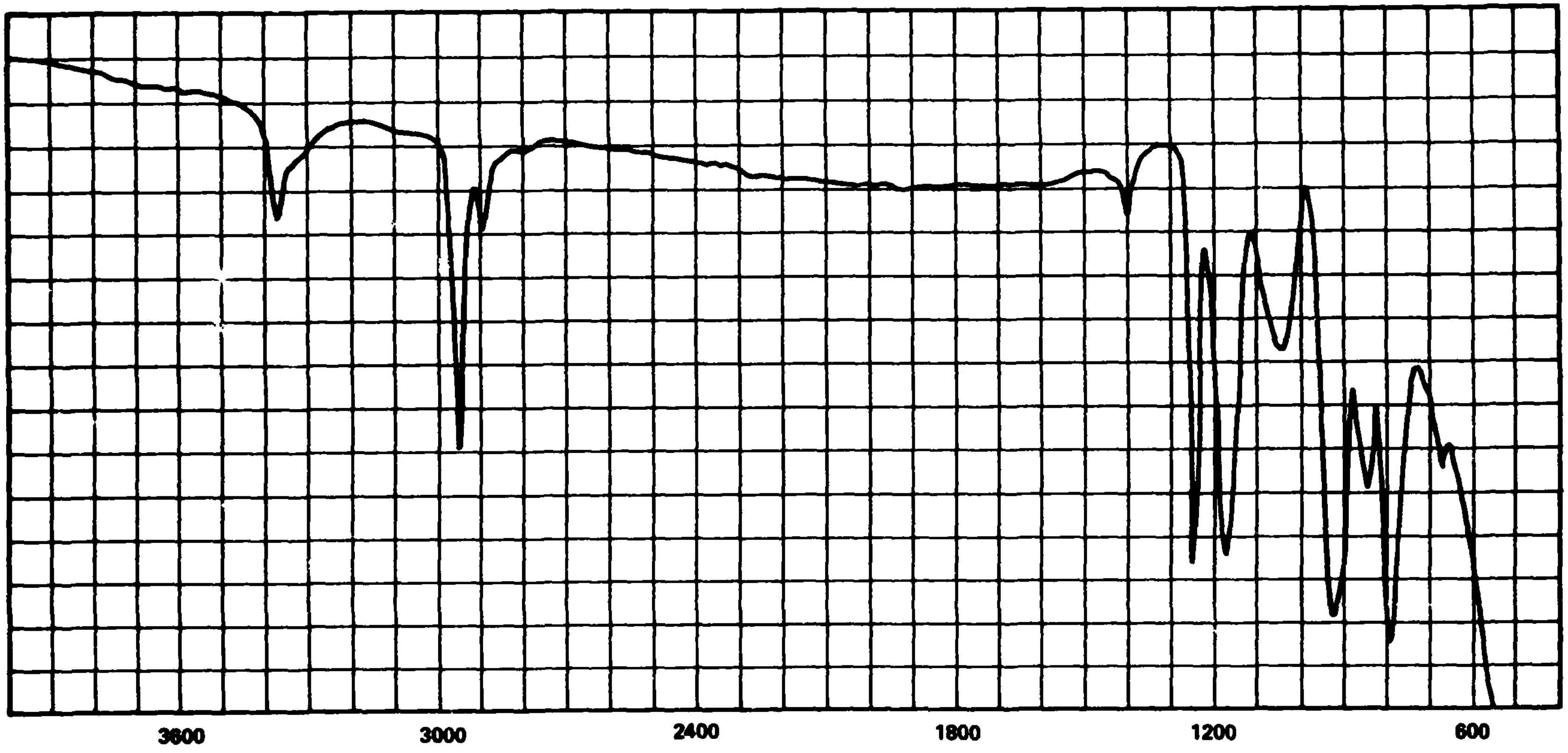
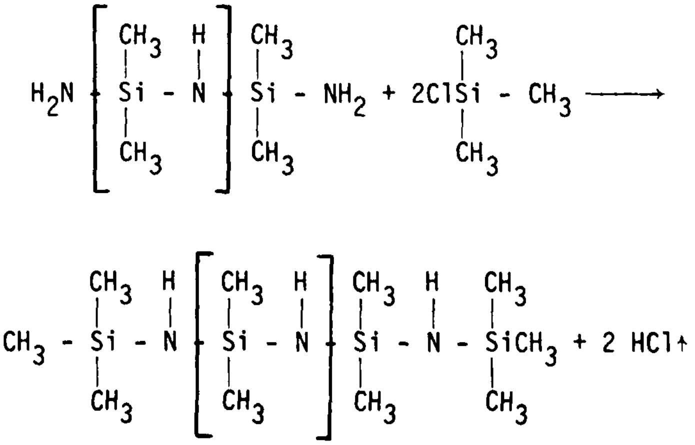


FIGURE 9. INFRARED SPECTRUM OF POLYDIMETHYLSILAZANE

symmetric deformation (1255 cm^{-1}, both), and Si-N rock (1050 cm^{-1}, polydimethylsilazane only) are present. The 1050 cm^{-1} absorption found in the polymer spectrum, but not the HCMTS spectrum could be due to Si-O-Si absorption or to an Si-N rocking absorption with a high degree of freedom to move, as opposed to the fairly rigid cyclic compound. Otherwise, the spectra are very similar, as expected, except for a small (15-20 cm^{-1}) shift to lower frequencies for some absorptions in the polymer as compared to the cyclic starting material.

The prepolymer thinned to near water-like viscosity at 140 to 150 C and was quite stable (at least 24 hours) under Ar at that temperature. However, the TGA of this material was found to be very poor (Figure 10). The prepolymer lost 91 percent weight between 200 and 900 C. It is believed that the most likely explanation for this very high weight loss is a "back-biting" mechanism which the terminal primary amino groups attack the silicon atom at the third (or fourth) position from the end of the chain reforming the cyclic trimer (or tetramer) starting material, which then volatilizes. If this is true, the polymer can be greatly stabilized by reacting the end groups with trimethylchlorosilane, to form unreactive trimethylsilazane, i.e. $(CH_3)_3Si\text{-}\overset{H}{\overset{|}{N}}\text{-}$, ends.

<u>End Group Stabilized Polydimethylsilazane</u>. A portion of the polydimethylsilazane was treated with trimethylchlorosilane (TMCS) to stabilize the primary amine end groups that are presumed to be present in the structure, as shown below:



$$H_2N\left[\underset{CH_3}{\overset{CH_3}{Si}} - \overset{H}{N}\right]\underset{CH_3}{\overset{CH_3}{Si}} - NH_2 + 2Cl\underset{CH_3}{\overset{CH_3}{Si}} - CH_3 \longrightarrow$$

$$CH_3 - \underset{CH_3}{\overset{CH_3}{Si}} - \overset{H}{N}\left[\underset{CH_3}{\overset{CH_3}{Si}} - \overset{H}{N}\right]\underset{CH_3}{\overset{CH_3}{Si}} - \overset{H}{N} - \underset{CH_3}{\overset{CH_3}{Si}}CH_3 + 2\ HCl\uparrow$$

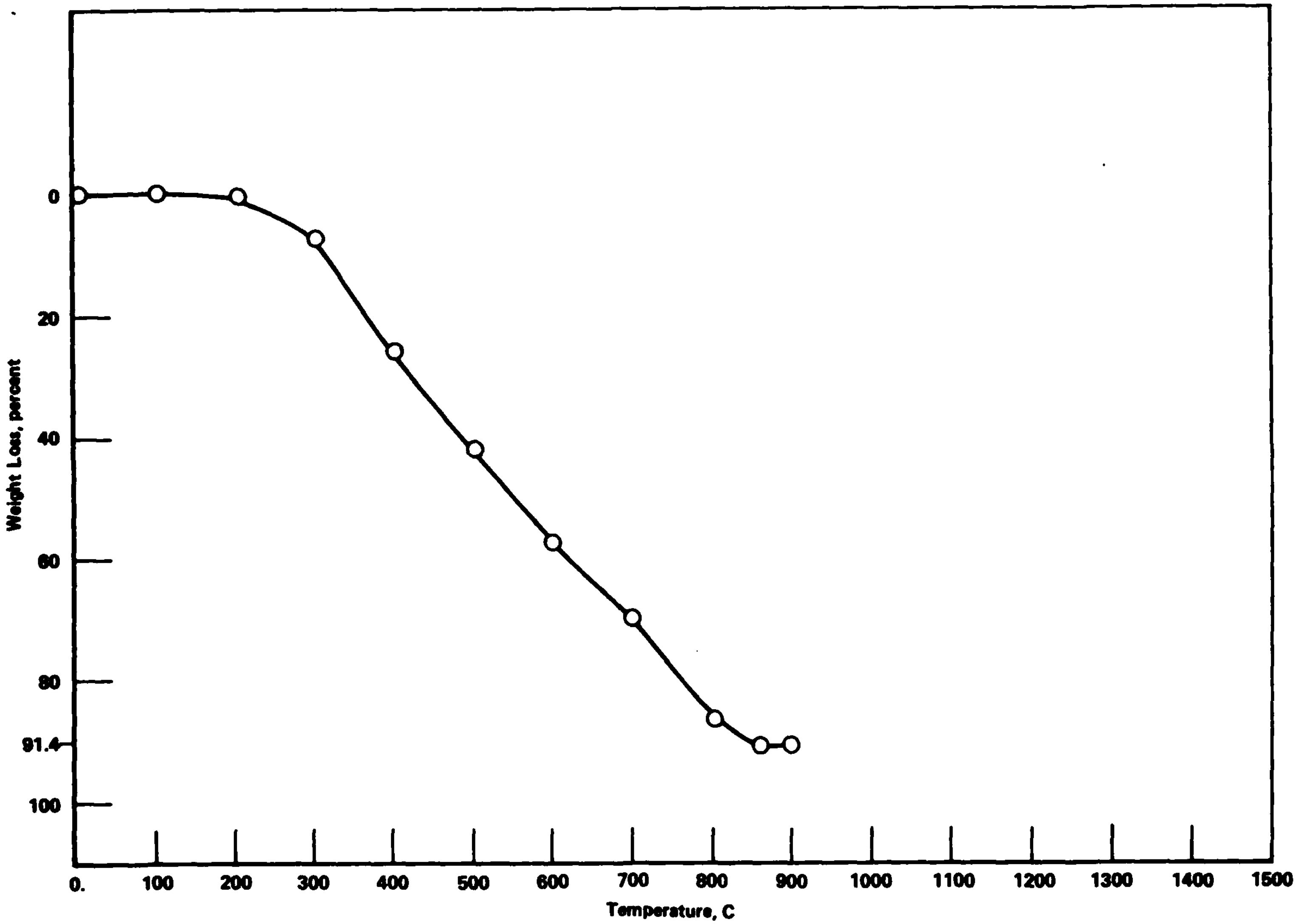


FIGURE 10. TGA OF POLYDIMETHYLSILAZANE MADE BY THE ROCHOW PROCESS

The reaction was done by heating the prepolymer with excess TMCS at reflux (~58 C) for about 1 hour, then vacuum distilling all volatiles.

A TGA of the trimethylsilylated polydimethylsilazane was then carried out. The TGA curve obtained (Figure 11) showed an almost threefold improvement in ceramic yield (24 percent weight retention above 900 C), although weight loss started at a somewhat lower temperature (170 C). This was considered quite promising, even though 62 percent is theoretically possible and a much greater weight retention had been sought. The lower temperature at which degradation started in the trimethylsilylated product may be due to HCl salts formed _in situ_. These salts are known to act as degradation catalysts for polydimethylsilazane. Use of silylating reagents should avoid this problem. This should allow retention of the excellent physical properties for infiltration shown by polydimethylsilazane, including the following very important properties at 150 C:

- Very low viscosity (water-like)
- High thermal stability
- Nonvolatility.

Also, blocking of the NH_2 end groups with vinyldimethylsilyl groups should allow the prepolymer to be crosslinked by treating with peroxides and heat or microwave energy. This should also improve the pyrolysis ceramic yield.

A new batch of polydimethylsilazane resin (35996-38) was made by equilibrating 80 grams of hexamethylcyclotrisilazane under approximately four atmospheres of ammonia. A 16 gram yield of clear, light straw-colored liquid polydimethylsilazane was produced after removal (distillation) of cyclic silazanes. Six grams were treated with 3 grams of N,O-bis (trimethylsilyl) trifluoroacetamide at 20 to 50 C to prepare the trimethylsily end-capped prepolymer. The volatile components were removed under vacuum at 50 C. This prepolymer also lost 75 percent weight in TGA.

A 3 gram sample was treated similarly with vinyldimethylchlorosilane (1 gram) to put vinyl groups on the ends of the prepolymer molecules. One gram or 0.5 gram samples of each of these three polydimethylsilazanes were sealed in evacuated glass ampoules and 1.5 weight percent Vulcup R (α,α-bis (t-butylperoxy) diisopropylbenzene) or tert-butyl perbenzoate peroxide curing agents added. In a second set of ampoules 3.0 weight percent pentaerythritol tetraacrylate was also added with the peroxide. One

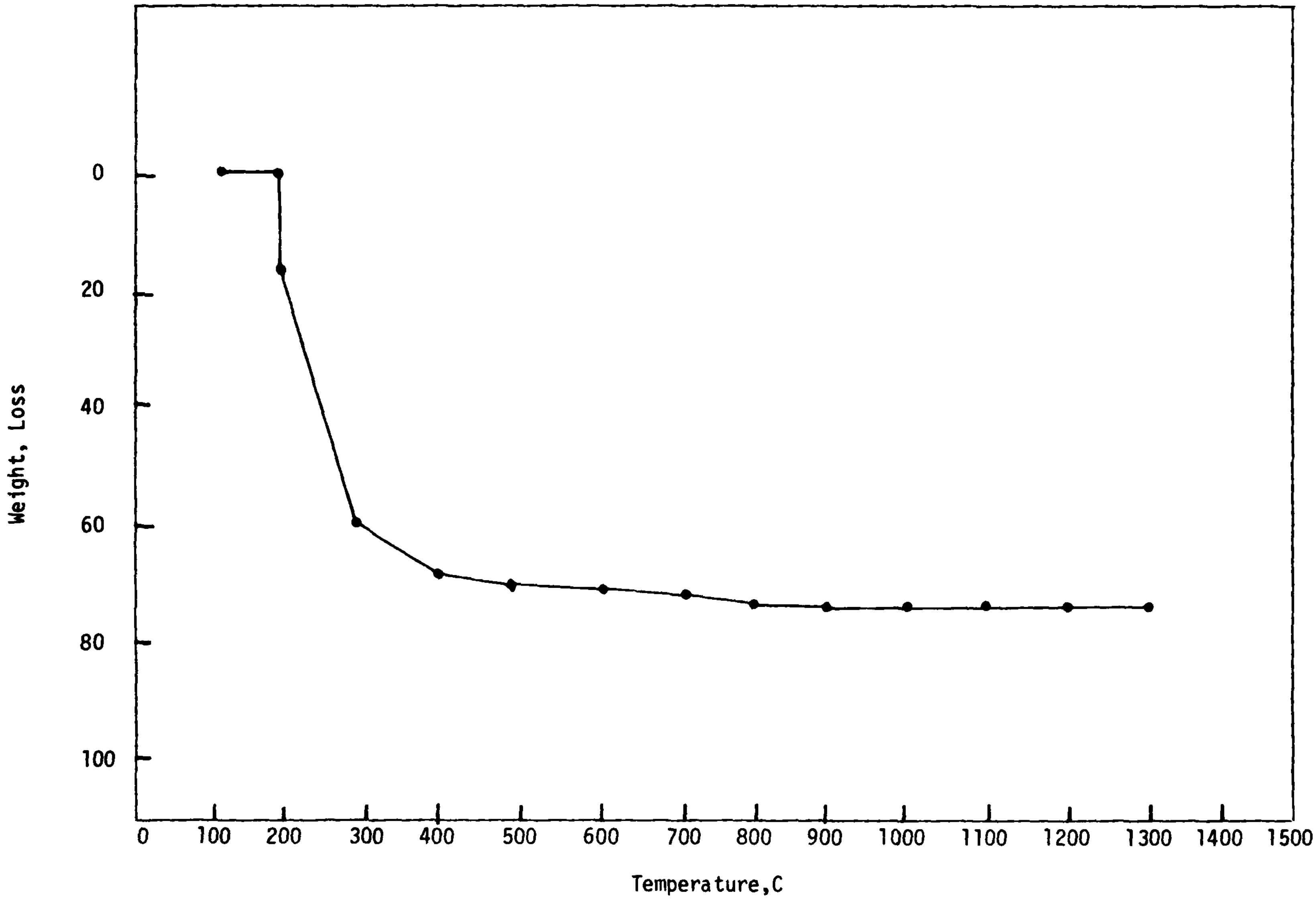


FIGURE 11. TGA OF TRIMETHYLSILYL END-BLOCKED POLYDIMETHYLSILAZANE

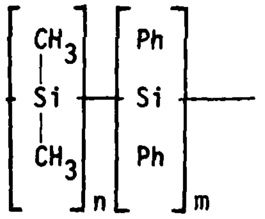
set of samples was oven-cured 4 hours at the temperature where the peroxide half-life was 0.5 hour (Vulcup R, 160 C; t-butyl perbenzoate, 120 C). No cures were observed for any sample. The whole series was repeated using microwave energy (600 watts - 1 kw, 20 to 60 second exposures for a total of 2 minutes). No cures were obtained. It is concluded that the reason polydimethylsilazane does not cure is due to one or more of the following factors:

(a) Molecular weight is too low (about 1000 to 3000) for efficient crosslinking

(b) Vinyl group concentration needs to be considerably greater than end-groups only

(c) The silazane/hydrogen (N-H) group is a radical trap (i.e. amino free radical interceptor).

Polysilastyrene. A polysilastyrene candidate was supplied by Professor West for study in approximately 10 gram quantity. This polymer has the following structure:



$$\left[\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} \right]_n \left[\begin{array}{c} Ph \\ Si \\ Ph \end{array} \right]_m , \quad \begin{array}{l} n = 0.83 \\ m = 1.00 \end{array}$$

This product, where Ph = phenyl (or benzene ring) has a number average molecular wegiht ($\overline{M}_n$) of 7000. It softens at 85 C and melts at 160 C. This product shows a TGA weight loss (Figure 12) of 75 percent. However, it is important to note that this prepolymer is quite stable to at least 300 C. This could ultimately prove very beneficial in using controlled low molecular weight prepolymers for infiltration, since the melts would presumably be low viscosity and stable for reasonable times at these high infiltration temperatures. However, the theoretical ceramic yield (maximum SiC possible) of this polymer is only 32-33 percent, i.e. the theoretical weight loss is 68-67 percent. Hence this polymer was not considered a prime SiC infiltration candidate in view of the 70 and 90

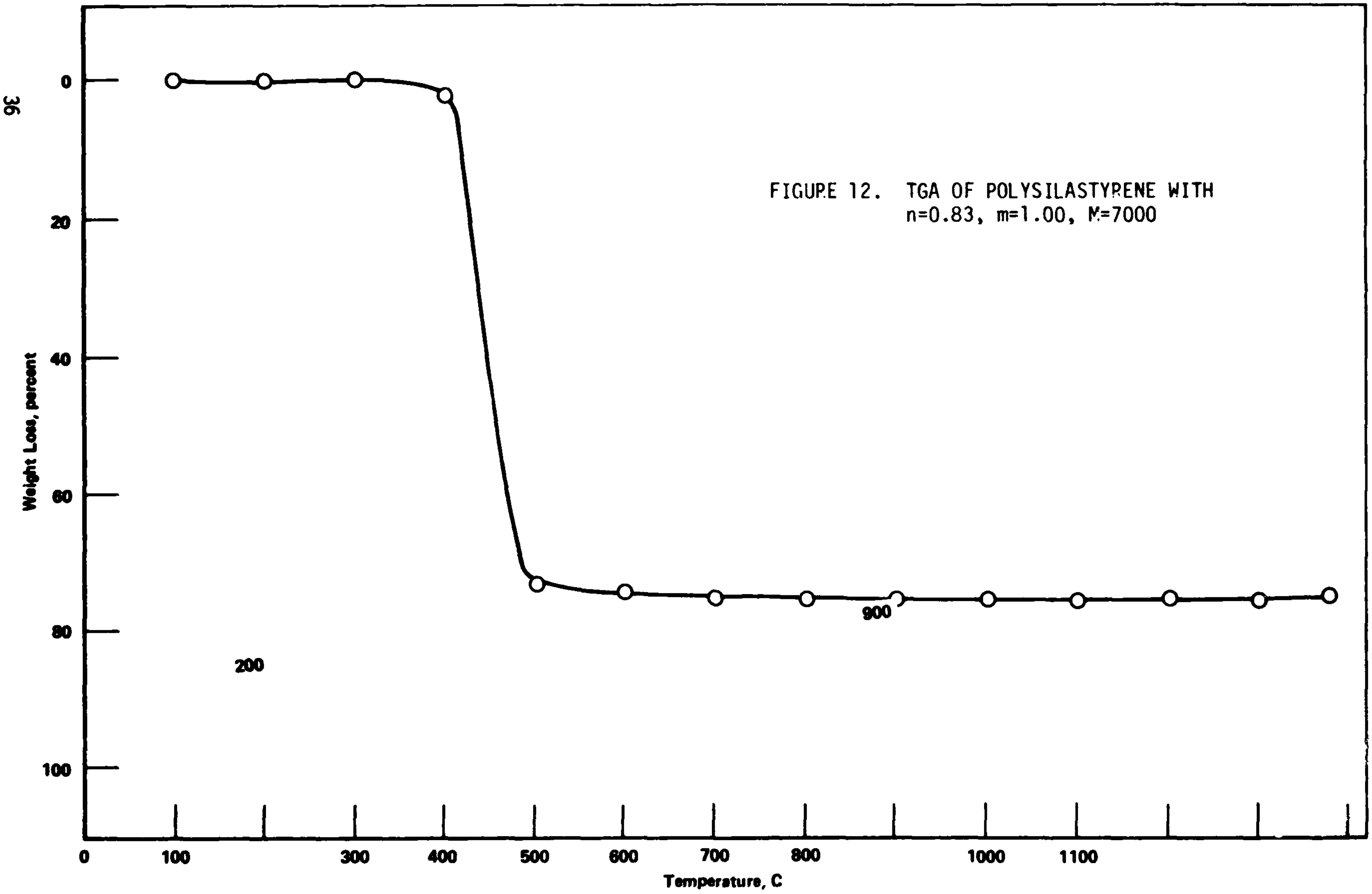


FIGURE 12. TGA OF POLYSILASTYRENE WITH n=0.83, m=1.00, M=7000

percent SiC ceramic yield products which were prepared for this program at Dow Corning.

Selection and Characterization of RSSN

Reaction sintered silicon nitride (RSSN) is made by the nitridation of a silicon metal powder compact by a multistage process in the temperature range 1000 C to 1400 C. Additions of iron silica and other additives are frequently made to enhance the reaction rate and affect the α/β ratio of the result compact. The microstructure of this porous ceramic is thus influenced by these processing variables, which tend to differ from supplier to supplier.

The RSSN materials examined in this program (see Table 5), exhibit a wide range of total porosity and open porosity values. Four suppliers of RSSN materials, AiResearch Casting Company, Norton Company, Advanced Materials Engineering, Ltd. and Kyocera International, Inc. all indicated their willingness to provide bend bar samples. However, due to cost and availability considerations only samples from AiResearch and AME were procurred. The samples of Boeing Foam materials referred to in Table 5 were provided for evaluation by Mr. K.S. Mazdiyasni. Additional as-received testing of these materials included flexural strength testing and microstructural observations at IITRI* for the AME and AiResearch RSSN materials and similar testing performed at BCL for the Boeing Foam RSSN #2. Samples of the AiResearch RSSN have a room temperature strength of 40 Ksi. Fracture origins for samples of this material were primarily processing defects such as subsurface inclusions and porosity. The AME samples had a room temperature strength of about 7.5 Ksi. The fracture features for this material were ill-defined and the rough intergranular nature of the material precluded identification of fracture origins. The Boeing Foam material was also difficult to characterize microstructurally and had a strength of about 1.8 Ksi.

As expected with these RSSN materials the level of porosity is inversely related to flexural strength. The primary fracture origins for the AiResearch RSSN were subsurface defects and in view of the high density of this RSSN were material impregnation/pyrolysis would not be expected to improve the materials strength dramatically. It

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* See ITTRI Report - Appendix B

is expected that the higher porosity RSSN materials would have a higher potential for strength improvement.

TABLE 5.
REACTION BONDED SILICON NITRIDE MATERIALS
AS-RECEIVED DENSITY AND POROSITY CHARACTERISTICS

Material	Density (g/cc)	Total Porosity(%)	Open Porosity(%)	Closed Porosity(%)	Flexural Strength (Ksi)
AiResearch 104	2.79	13	7.5	5.5	40.0
AME	2.12	34	31.5	2.5	7.5
Boeing Foam #1	0.55	83	>82	<1	---
Boeing Foam #2	0.85	73	>72	<1	1.8

Impregnation/Pyrolysis Experiments

Infiltration

Infiltration in a porous ceramic can be achieved by two basic mechanisms:

(1) Capillary action
(2) Permeability.

Capillary action depends upon the movement of liquid through the interconnected porosity of the ceramic according to the following equation:

$$V = K \left(\frac{r}{\eta}\right) t^{\frac{1}{2}}$$

where V is the volume flow of a liquid of viscosity η through a capillary or radius r at time t. The soak time and viscosity are the key parameters.

The permeability coefficient of a material describes its resistance to flow of a viscous flow by the relation

$$K = \frac{QL_{\eta}}{A\Delta P}$$

where

K = Permeability coefficient
Q = Flow rate
L = Length of flow path
η = Viscosity of liquid
A = Specimen area
P = Pressure drop.

For a given material, the key parameters are the viscosity of the liquid and the applied pressure.

Past experience has indicated that good infiltration can be achieved when the impregnant has a viscosity at the impregnation temperature that is about the same as that of water at room temperature (about 100 centipoise). It is also important that the maximum possible amount of organosilicon precursor is infiltrated into the macrostructure of the RSSN because of the large volume of impregnant volatilized during pyrolysis.

In-Situ Decomposition of Organosilicon Precursors

Previous work by Mazdiyasni, et al(1) indicates that various organosilicon precursors will decompose to form silicon nitride and silicon carbide. The structures of these organic materials give rise to high weight losses on pyrolysis. This did not affect the strength of the RSSN in the referenced work, but evolution of large amounts of volatiles could be a significant factor in developing an impregnated RSSN with a strength approaching that of dense Si_3N_4 because of the small flaw sizes that must be reached. Evolution of gases when the organosilicon has become a rigid structure could, at the very least, initiate micro fissures, which act as strength limiting flaws. It is important, therefore, to consider using organosilicons with a low weight loss on decomposition. Preference has been given to identifying organosilicons which decompose by evolving small molecules, such as hydrogen and methane, which can diffuse through the RSSN without damaging it.

In addition, the structures of candidate monomer/polymer organosilicons will effect the pyrolysis products from the viewpoint that some side groups, such as phenyl, leave the main backbone of the organosilicon structure more readily than others. This is important since such groups will tend to evolve during the early stages of the decomposition while the compound is still in the liquid state. Large weight losses occurring at this stage of the decomposition will not cause microfissure formation because the organosilicon is still a liquid, and the gases can move through it.

As discussed earlier, the viscosity of the organosilicons should be low enough (∿100 centipoise) to readily facilitate infiltration, but the viscosity-weight loss characteristics of the organosilicons may be very critical if the temperature difference between the infiltration temperature and the temperature at which a rigid polymer/decomposition occurs, is small.

Impregnation Equipment and Sample Preparation

All of the AiResearch and AME RSSN samples were cleaned prior to their use in impregnation experiments. These materials were ultrasonically cleaned for 1 hour in distilled water, for 10 minutes in methanol, and for 10 minutes in dry acetone prior to being dried at 110°C in vacuum for 24 hours. Initial attempts to clean the Boeing Foam samples by the same procedure resulted in degradation of the foam structure under the action of the ultrasonic cleaner. Instead of this these samples were cleaned with dry air, washed in dry acetone and dried at 110°C in vacuum for 24 hours.

In order to facilitate infiltration and contain the cleaned RSSN samples and the heated organosilicon impregnants, a glass vessel, shown in Figure 12 was designed and built. The glass vessel is a large desiccator that has been modified to facilitate atmosphere and temperature control, and RSSN sample manipulation while providing for process observation through the transparent walls. Using this system requires loading the RSSN samples in the wire basket which is suspended above the organosilicon in the beaker. After evacuating, the organosilicon is melted and heated to a suitable fluidity before the RSSN samples are immersed and the vessel back-filled with inert gas. The impregnated RSSN samples are removed from the liquid prior to cooling of the system. This equipment was located inside an inert-atmosphere dry box which was connected to a high temperature, moist atmosphere furnace system. The use of this dry box system was required to permit safe handling of and impregnation of RSSN with organosilicon precursors that are pyrophoric and/or hygroscopic.

Impregnation/Pyrolysis with Hexaphenylcyclotrisilazane

The impregnation trials were initiated by experimentally determining the temperature range necessary to produce a liquid of suitable viscosity using one of the candidate organosilicon precursors. The first precursor to be evaluated was hexaphenylcyclotrisilazane resin. Although the ceramic yield upon pyrolysis for this material is only 22 percent, it has a usable temperature-viscosity relationship and is available in sufficient quantity to serve as a reference material for these processing studies. These infiltration trials were performed using the same basic procedure described by Mazdiyasni(1). Impregnation of AME and AiResearch RSSN bend bars and Boeing Foam RSSN samples were performed in the range of 225 C to 250 C under argon gas. After impregnation the excess hexaphenylcyclotrisilazane was removed from sample surfaces to permit evaluation of the ability to infiltrate the surface and sub-surface voids. The samples were then fired to 1400°C (40°C/Min. to 600°C and 8°C/Min. from 600° to 1400°C) under static nitrogen gas in order to polymerize and pyrolyze the organosilicon precursor, and to bond the pyrolysis products to the RSSN host material. This process cycle was repeated several times with two groups of samples. The first group contained bend bars of AME and AiResearch RSSN and a sample of Boeing Foam #1 RSSN bend bars. Bulk density for each sample was determined at each stage of the process cycle:

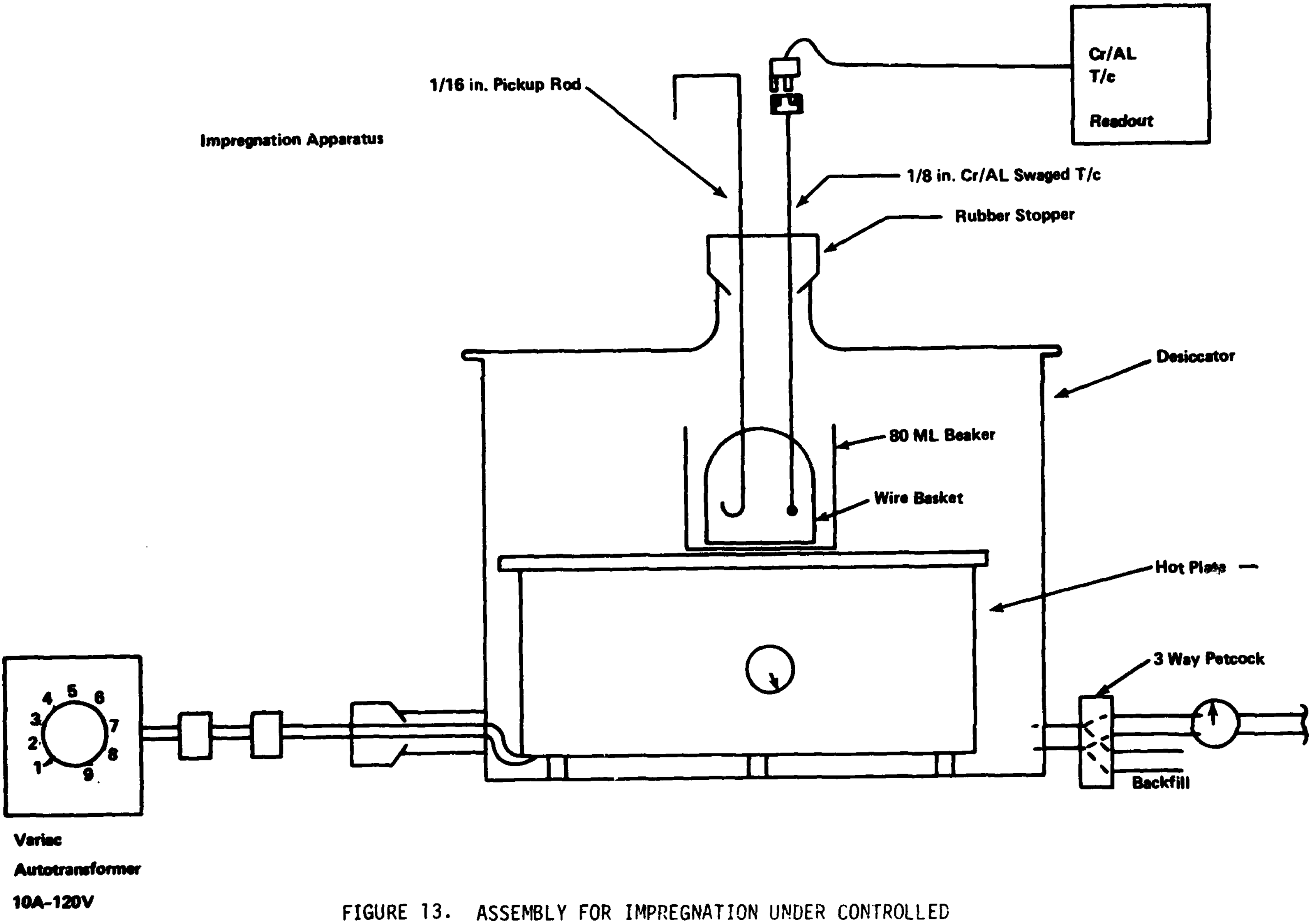

FIGURE 13. ASSEMBLY FOR IMPREGNATION UNDER CONTROLLED TEMPERATURE, ATMOSPHERE AND PRESSURE

as-received, post-impregnation and post-pyrolysis. These data have been analyzed with respect to density change as related to each process step, and are reported for the AME RSSN samples in Table 6. As expected, the sample density increased during each processing cycle (See Figure 14) as a result of the pyrolysis products being left in the voids after each cycle. For the same reason the percent density change during impregnation decreased for each cycle. The data for sample density change as a result of each process cycle shows no clear trend. However, a measure of process efficiency is to determine what percentage of impregnant deposited is remaining after pyrolysis. Table 6 shows a marked improvement in process efficiency, even significantly above the theoretical yield level, for processing cycles after cycle 1. It is apparent from these data that there is some means by which the reduction of void volume contributes to retaining of pyrolysis products during firing. This same trend was noted in the AiResearch and Boeing Foam samples although the absolute efficiency values for these samples appears to be effected by the abundance of interconnected, permeable porosity in the foam samples and the virtual absence of such porosity in the AiResearch samples. In order to verify the reproducibility of these data AME samples were impregnated and pyrolyzed with AiResearch samples but without coincident processing of foam samples. The data resulting from three impregnation/pyrolysis trials are summarized in Table 7. These data show entirely different effects of the processing with little density improvement and very low process efficiencies. However, it should be noted that the process efficiency and density change through the process increase with each cycle. Comparison to these data with those in Table 6 indicate that the presence of the foam samples, or more probably the large amount of gas produced from them during pyrolysis, serves in some way to enhance the process efficiency in all of the RSSN samples, particularly the AME samples. This observation coupled with the enhanced efficiency observed with reduced void volume suggests that an "over pressure" of gaseous pyrolysis products or organometallic precursor is formed by pyrolysis with the foam samples and, although much less efficiently, is formed in the reduced volume of the voids containing solid pyrolysis products. This "over pressure" probably enhances process efficiency

TABLE 6. SUMMARY OF SAMPLE DENSITY BY PROCESS STEP FOR IMPREGNATION OF AME RSSN WITH HEXAPHENYLCYCLOTRISILAZANE AND PYROLYZED IN THE PRESENCE OF BOEING FOAM SAMPLES

	Cycle Number			
	1	2	3	4
A. Starting Density-g/cc	2.09	2.16	2.29	2.40
B. Impregnated Density-g/cc	2.42	2.46	2.51	2.49
C. Density Change During Impregnation-%	16.40	13.70	9.70	4.10
D. Pyrolyzed Density-g/cc	2.16	2.29	2.40	2.44
E. Density Change During Cycle-%	3.50	6.00	4.90	1.90
F. Cycle Efficiency ($^E/C$)-%	21.00	44.00	51.00	46.00
G. Density Change Thru Process	3.50	9.70	15.10	17.30

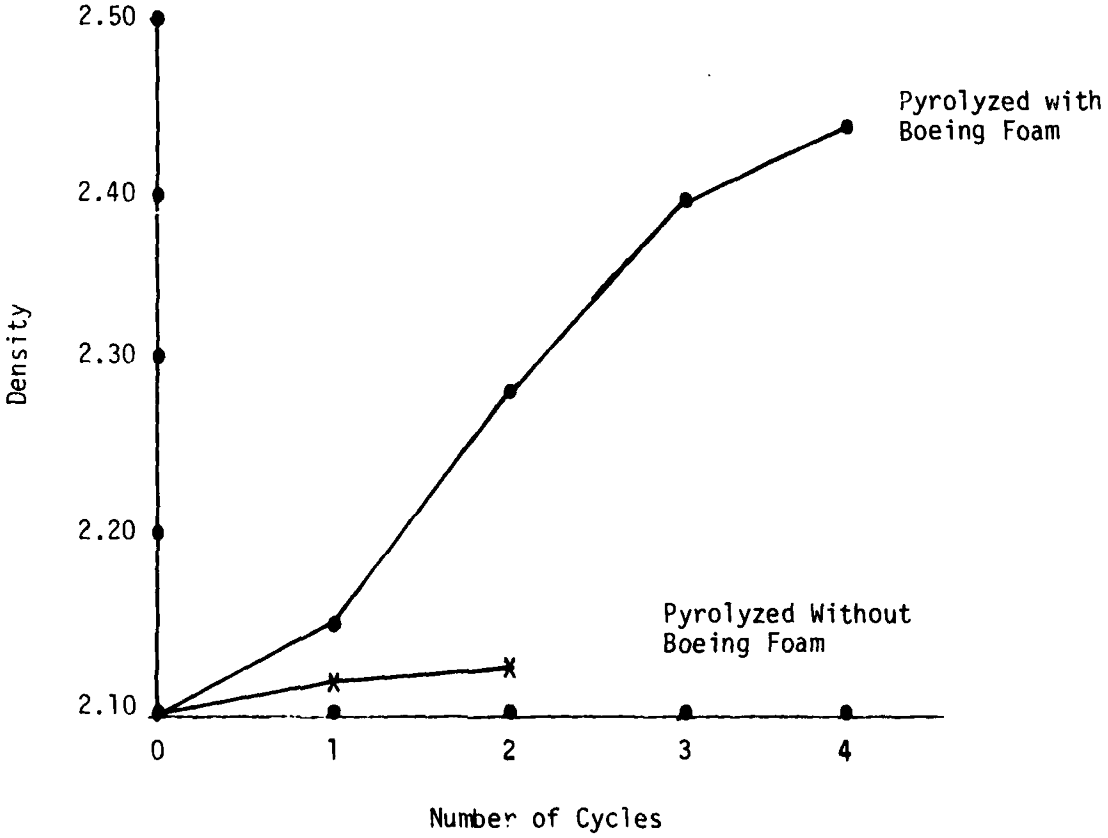

FIGURE 14. SAMPLE DENSITY OF IMPREGNATED AND PYROLYZED AME RSSN WITH HEXAPHENYLCYCLOTRISILAZANE FOR EACH PROCESS CYCLE

TABLE 7. SUMMARY OF SAMPLE DENSITY BY PROCESS STEP FOR IMPREGNATION OF AME RSSN WITH HEXAPHENYLCYCLOTRISILAZANE AND PYROLYZED IN THE ABSENCE OF BOEING FOAM SAMPLES

	Cycle Number		
	1	2	3
A. Starting Density-g/cc	2.09	2.09	2.11
B. Impregnated Density-g/cc	2.42	2.43	2.43
C. Density Change During Impregnation-%	16.40	15.90	15.00
D. Pyrolyzed Density-g/cc	2.09	2.11	2.13
E. Density Change During Cycle-%	0.30	0.80	1.10
F. Cycle Efficiency ($^E/C$)-%	1.60	4.60	7.30
G. Density Change Thru Process	0.30	1.00	2.10

by making the escape of gases during pyrolysis progressively more difficult causing: (a) char formation (i.e., production of carbon containing compounds); or (b) precursor polymerization and pyrolysis in the voids at elevated pressures. Any char formed should be removed by the firing process which achieves temperatures well in excess of the pyrolysis range. The data and observations suggest that an over pressure of hexaphenylcyclotrisilazane and/or control of the atmosphere during pyrolysis is an important process variable. This theory is supported by observations of others during the plasma polymerization of silazanes(52,53). It is also supported by the observation during microstructural evaluation that fibers are formed in the pores during processing (see Microstructural Evaluations). Silicon nitride fibers are typically formed the vapor state.

Other observations made during these impregnation/pyrolysis trials are worthy of noting. Five types of RSSN materials, with five different densities, were processed during these trials. It was observed that the order of increasing weight gain during the first impregnation cycle is as shown in Table 8. Although sample infiltratability is inversely proportional to sample density, there is no apparent difference in wettability of the RSSN materials by the impregnant, and no apparent effect of increasing the time of exposure to the infiltrant (see Table 9).

All of the RSSN materials had a noticeably darker color both after the impregnation and pyrolysis steps. This dark grey color was uniform throughout the AME and Boeing Foam materials. This observation is consistant with the large amount of permeable porosity in these materials. The AiResearch RSSN was slightly darker on the surface that the interior after pyrolysis, as expected. It should be noted that a loose, flaky residue was found in the bottom of the molybdenum boat containing the RSSN material after pyrolysis. It is apparent that this material is evolved from the RSSN samples during pyrolysis, presumably in the form of a liquid at low temperatures. The presence of this deposit reveals two problems: (1) the pyrolysis yield is being reduced by an amount equivalent to the deposit amount; and (2) the heating rate and atmosphere during pyrolysis must be identified and used to permit decomposition and gas evolution to proceed without causing expulsion of precursor or pyrolysis products during processing.

TABLE 8. WEIGHT GAIN DURING THE FIRST IMPREGNATION CYCLE FOR CANDIDATE RSSN MATERIALS USING HPCTS

RSSN Material	Sample Density(g/cc)	Weight Gain (%)
AiResearch 104	2.8	1.0
Norton NC350	2.6	3.5
AME #1	2.1	16.0
AME #2	1.7	28.0
Boeing Foam #1	0.6	150.0
Boeing Foam #2	0.9	86.0

TABLE 9. WEIGHT GAIN OF AME RSSN MATERIAL DURING IMPREGNATION AS A FUNCTION OF TIME

Density	Impregnation Time (Hr)
2.09	0
2.42	0.5
2.43	1.0
2.42	2.0

The resulting data from multiple impregnation/pyrolysis trials of AiResearch RSSN bend bars and Boeing Foam RSSN samples with hexaphenyl cyclotrisilazane (HPCTS) are presented in Table 10. The AiResearch RSSN samples have only about 7.5 percent open porosity which severely limits the ability to impregnate. The total density change through three process cycles was less than 1 percent of the starting density. The Boeing Foam RSSN samples contain more than 80 percent open porosity which greatly facilitates impregnation but provides no restriction to evolution of vaporized impregnant during pyrolysis. It should be noted that the density of this material can be increased by more than 70 percent as a result of four process cycles. The density of the Boeing Foam #2 RSSN can be increased by similar amounts. Both of these materials, like the AME RSSN, show a reduced capacity for impregnation after three or four cycles presumably due to a reduction in the size and quantity of permeable voids. It also appears that the process efficiency for these materials is effected by the abundance of interconnected, permeable porosity in the Foam samples and the virtual absence of such porosity in the AiResearch samples.

Multiple impregnation/pyrolysis processing of RSSN materials using hexaphenylcyclotrisilazane is controlled by the ability to completely fill the available void volume, to retain as much of the pyrolysis products as possible during thermal treatment, and to product a microstructure that is conducive to both strength and oxidation resistance improvement while facilitating further processing. These processing trials have revealed that multiple cycling with HPCTS is limited after only three to four cycles because the rate at which infiltration density gain is achieved is reduced. This occurs despite the continued precence of a significant amount of permeable porosity. As less material is placed in the pores with each successive cycle, less pyrolyzed material is available to fill the available porosity and further reduce the average flaw size.

Chlorosilanes

Two candidate precursors produced by Dow Corning that were anticipated to be suitable infiltration materials are methylchloropolysilanes referred to as Moderate Yield Preceramic Polymer (MYPP) and High Yield Preceramic Polymer (HYPP). These materials were evaluated using

TABLE 10. SUMMARY OF SAMPLE DENSITY BY PROCESS STEP FOR IMPREGNATION OF RSSN MATERIALS WITH HEXAPHENYLCYCLOTRISILAZANE* (HPCTS)

AiResearch RSSN	Cycle Number 1	 2	 3
A. Starting Density-g/cc	2.76	2.77	2.78
B. Impregnated Density-g/cc	2.78	2.78	2.78
C. Density Change During Impregnation-%	0.87	0.55	0.11
D. Pyrolyzed Density-g/cc	2.77	2.78	2.78
E. Density Change During Cycle-%	0.26	0.27	-0-
F. Cycle Efficiency (E/C)-%	29.90	49.10	-0-
G. Density Change Thru Process-%	0.26	0.58	0.61

Boeing Foam #1 RSSN	Cycle Number 1	 2	 3	 4
A. Starting Density-g/cc	0.55	0.63	0.75	0.90
B. Impregnated Density-g/cc	1.39	1.34	1.47	1.53
C. Density Change During Impregnation-%	152.70	112.70	96.00	70.30
D. Pyrolyzed Density-g/cc	0.63	0.75	0.90	0.95
E. Density Change During Cycle-%	14.60	19.10	20.00	5.60
F. Cycle Efficiency (E/C)-%	9.60	17.00	20.80	8.00
G. Density Change Thru Process-%	14.60	36.40	63.60	72.70

*Theoretical cycle efficiency for HPCTS based on TGA in a static, inert atmosphere is approximately 20 percent.

physical property data supplied by Dow Corning and by performing melting experiments to determine viscosity and wetting characteristics.

The MYPP material has a theoretical weight loss of about 50 percent. TGA data accompanying this yellow-gold lump resin material reveals a 42 percent weight loss by 1150°C with weight loss continuing at a significant rate up to this temperature. During melting trials this material proved too viscous for infiltration, it did not wet the RSSN, and it was prone to outgassing and foaming. This material is also very hygroscopic. The HYPP material has a theoretical pyrolytic weight loss of 10 to 15 percent. Data received with this granular yellow-white powder revealed a 25 percent weight loss by 700°C with weight loss continuing at a significant rate up to this temperature. It must be handled very carefully because it is highly pyrophoric. During melting trials this material outgassed badly and did not achieve a melt of viscosity suitable for infiltrating prior to forming a tough, sticky film. Further testing showed that both Dow Corning materials are soluble in Decalin, but that the outgassing character observed earlier continues to preclude the use of the MYPP at temperatures for which the viscosity would provide for adequate wetting of the RSSN materials. Further discussion of the use of the HYPP material is presented in the discussion of Coating Activities.

Methylsilazane

Impregnation/pyrolysis processing was also performed using methylsilazane to infiltrate AME RSSN and AiResearch samples. The solution used for impregnation contained 55 percent solids of methylsilazane resin in Decalin solvent described earlier. This solution would be expected to have a ceramic yield theoretical value of about 40 percent based on a 72 percent yield of the solvent free resin. Although the AiResearch samples showed no significant change in density, the AME RSSN samples showed a marked density improvement as a result of this processing by comparison to results obtained using HPCTS for infiltration (see Table 11). Although the samples have the same starting density, the higher ceramic yield, 40 percent for methylsilazane versus 22 percent for HPCTS, provides a higher

TABLE 11. SUMMARY OF SAMPLE DENSITY BY PROCESS STEP FOR IMPREGNATION OF AME RSSN WITH HEXAPHENYLCYCLOTRISILAZANE OR METHYLSILAZANE*

	Cycle Number				
	Hexaphenylcyclotrisilazane			Methylsilazane	
Process Step	1	2	3	1	2
Starting Density-g/cc	2.09	2.16	2.29	2.09	2.22
Pyrolyzed Density-g/cc	2.16	2.29	2.40	2.22	2.32
Density Change During Cycle-%	3.50	6.00	4.90	6.22	4.50
Cycle Efficiency-%	21.00	44.00	51.00	37.30	34.40
Density Change Thru Process-%	3.50	9.70	15.10	6.20	11.00

*Theoretical cycle efficiency for methylsilazane based on TGA in a static, inert atmosphere is approximately 40 percent.

sample density for each of the first two cycles. The density change through the process continues to be significant but the density change during the process cycle dropped off after the first cycle. This is presumably caused by the reduction in permeable void volume resulting from this process. It should also be noted that the cycle efficiency was essentially constant and approximated the theoretical yield expected. There is also a significant reduction in the ability to impregnate while 20 to 25 percent of the RSSN body is still permeable voids.

The methylsilazane resin in solution used for this process was observed to precipitate out of solution upon standing for several weeks at room temperature. Further processing trials with this impregnant were troubled by lower infiltration levels and lower cycle efficiency. A sample of Boeing Foam RSSN that was part of these processing trials showed a 41 percent density improvement in the first cycle again reflecting the high theoretical yield of this impregnant.

Microstructural Evaluations

The ability to produce pyrolysis products with specific macro- and microstructural attributes is critical to achieving strength and oxidation resistance improvements. The macrostructural requirements for these products include: (1) formation of a dense, continuous pyrolysis deposit of at least two dimensions; (2) development of an organosilicon deposit that does not form large cracks and voids as a result of volume shrinkage and volatiles evolution during pyrolysis.

The microstructural requirements for these materials include: (1) deposit of the pyrolysis products in the areas of voids and cracks so as to fill small defects that could serve as crack tips; (2) filling of voids should be accomplished to reduce the size of both large and small flaws; and (3) deposition should occur in such a manner as to reduce the average surface area of all exposed surfaces to reduce the area over which oxidation will occur.

The microstructural features of fracture surfaces of AME RSSN samples processed using HPCTS or methylsilazane were examined to attempt to determine the morphological character of the ceramic residue remaining in the RSSN after pyrolysis. Figure 15 shows the typical fracture surface of this RSSN material with a fiber loaded void at 2500X magnification. This sample had been processed through three infiltration/pyrolysis cycles using HPCTS. The fibers in the void are a result of vapor stage pyrolysis of the ceramic precursor. It should be noted in this photomicrograph and in Figure 16(10,000X) that these fibers have a large-length to-diameter ratio and are relatively smooth and symmetric. They are apparently not bonded or only weakly bonded to the void wall or to each other, but rather resemble rods standing in a hole. This observation of the fibrous form of the pyrolysed product supports the data which indicated that the process cycle efficiency was related to the presence of an gaseous over-pressure during pyrolysis. The work of Masdiyasni(1) does not suggest that bonding between the Norton NC350 RSSN grains and the hexaphenylcyclotrisilazane is a problem (good bonding is essential to improve the strength of RSSN), but bonding character could also be affected by low-level impurities such as iron found in certain RSSN materials as suggested by Mazdiyasni(54). These presumably form an iron silicate glass which facilitates bonding of the fibers to the host RSSN. The presence of non-bonded silicon nitride fibers is not considered likely to improve the strength and oxidation resistance (of the host RSSN).

Figure 17 shows a fracture surface of AME RSSN at 2500X magnification after two impregnation/pyrolysis cycles with methylsilazane. This photomicrograph reveals the grainy character of the pyrolyzed product which appears to be bonded to the void walls. This deposit is composed of very fine densely packed grains that the parent RSSN structure. It is felt that the methylsilazane pyrolysis product has a much higher potential for improving the strength and oxidation resistance for RSSN than does the HPCTS pyrolysis product.

FIGURE 15. AME RSSM WITH HPCTS AFTER THREE
CYCLES (2500X)

FIGURE 16. AME RSSN WITH HPCTS AFTER THREE CYCLES (10,000X)

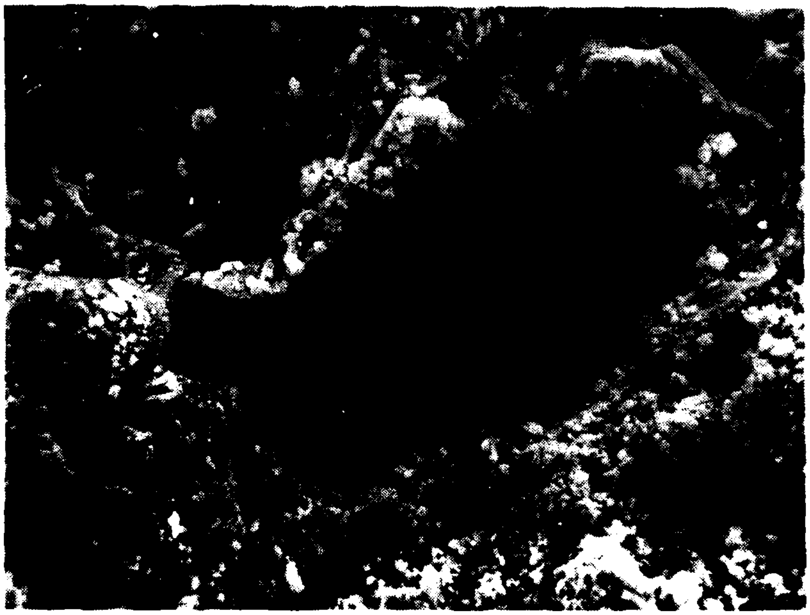

FIGURE 17. AME RSSN WITH METHYLSILAZANE AFTER TWO CYCLES (2500X)

The primary experimental approach for this program has been to obtain/develop an organosilicon precursor with suitable viscosity and wetting characteristics coupled with impregnation of RSSN materials to fill voids and flaws, and pyrolysis to produce a bonded, all ceramic deposit. A brief summary of the project work to this stage reveals several significant problems. The wetting and viscosity characteristics of the precursors with reasonably low pyrolytic weight loss are not suitable for infiltration without the use of a solvent. Dilution of these precursors with a solvent significantly increases the pyrolytic weight loss. Additionally, the ability to impregnate a given void volume decreases with each process cycle as the void volumn is diminished and the void access route becomes impermeable due to its size reduction below the precursor wetting angle. Pyrolysis of the precursor and the activity of the pyrolysis products are significantly effected both by the response of the precursor to heat and to the confining action of evolved and residual species by the void that has been impregnated. In order to overcome some of these problems attempts were made to coat the RSSN minimizing the amount of impregnation.

Coating Experiments

The objective of these coating experiments was to form a high density coating while minimizing bulk impregnation. These experiments were designed to evaluate the utility of the available precursors for meeting even the minimum requirements for enhancing the properties of the host RSSN materials. The initial approach to forming a high quality coating on the RSSN materials was to produce a precursor liquid with appropriate viscosity and wetting characteristics to thinly coat the entire surface of the RSSN samples. Two organosilicon precursors that have shown significant potential for providing these characteristics and providing for high ceramic yield upon pyrolysis are methylsilazane and Dow Corning High Yield Preceramic Polymer.

The procedure used to perform these experiments entailed immersing the preheated RSSN samples in the fluid organosilicon precursor while exposed to an inert gas atmosphere, heating and/or exposure to air to polymerize and/or hydrolyze the precursor, and firing of the coated RSSN samples to pyrolyze and bond the coating in contact with the RSSN. The objective of these trials was to develop an adherent surface layer that is bonded to the surface and immediate subsurface of the RSSN.

Several experiments were performed to attempt to coat AME and AiResearch RSSN samples with melt-processable methylsilazane, a high solids content solution of methylsilazane in toluene, a high solids content solution of High Yield Pre-Ceramic Polymer in decalin, or a high solids content solution of polysilastyrene in toluene. Coating attempts using the polysilastyrene were unsuccessful because of insufficient wetting and bonding of this material to the RSSN materials during coating or pyrolysis processing. Coating trials using methylsilazane were more successful and provided the opportunity to evaluate the effects of several processing variations. Data found in Table 12 shows the information gained during these trials. It is apparent from these data that using this processing cycle does not generate a coating containing much material. Also it is obvious that the higher permeable void volumn in the AME RSSN contributes to the ability to deposit and retain such a coating. The slight difference in sample density change after one cycle between the methylsilazane and HYPP precursor coatings is presumed to be due to processing parameters rather than materials characteristics. Generally processing the RSSN samples through a second coating cycle provides no significant coating enhancement. It was observed, however, that the solution of methylsilazane in toluene produced a similar sample density change during both coating cycles. It was also noted that exposure to air and heat to hydrolyze and cross-link the coating had no discernable effect on the coating. All of the coated RSSN samples lost the majority of material applied as a coating as a result of volume shrinkages during pyrolysis. Improvements resulting from this processing appear to be a result of "surface stuffing". The higher surface contact between the host RSSN and the organosilicon precursor in the substructure apparently prevents loss of material during the volume shrinkage occurring during pyrolysis.

TABLE 12.
RSSN SAMPLE

Precursor/RSSN	Sample Density Change (%) Cycle 1	Cycle 2
Methylsilazane		
/AiResearch	0.2	0.02
/AME	3.9	0.1
Methylsilazane/		
/AiResearch	0.2	0.02
/AME	3.9	3.2
High Yield Preceramic Polymer/Decalin		
/AiResearch	0.4	0.04
/AME	6.1	0.9

It was felt that the best way to evaluate the effectiveness of using these coating materials was to determine the oxidation resistance improvement of the resulting coated RSSN samples. These samples were exposed at 1000°C under 0.2 atmosphere oxygen for 24 hours and evaluated for change in weight per unit surface area as a function of time. Figures 18 and 19 are graphical presentations of the data resulting from these evaluations. Each figure provides curves for weight per unit area as a function of time for one of the RSSN materials as-received, and two post processing conditions. It is apparent from this data that the weight gain during these oxidation experiments can be reduced more than 75% by these coatings compared to the as-received RSSN material. It should be noted, however, that HYPP was apparently more effective in the case of AiResearch RSSN and the methylsilazane was apparently more effective in the case of AME RSSN. It is felt that effectiveness of these coatings is controlled more by the fabricability of the "coatings" than by the composition. However, a marked enhancement in oxidation resistance has been achieved using both coating systems on these RSSN materials.

An experiment was also performed to attempt to evaluate the utility of this coating system for increasing the strength of RSSN materials by reduction in the average surface flaw size. Boeing Foam #2 RSSN was selected as the host material because its high void content would make this a more rigorous test. Bend bars of this RSSN material were tested for three point bend strength to compare the uncoated strength to the strength produced by coating with melt-processable methylsilazane. The data resulting from this testing is provided in Table 13. An improvement in average strength of 70 percent was observed. It was also noted that the standard deviation and coefficient of variation increased after coating. It is felt that this observation supports the conclusion drawn from the oxidation resistance testing that coating processing has not been optimized but that a significant improvement can be achieved via this coating system.

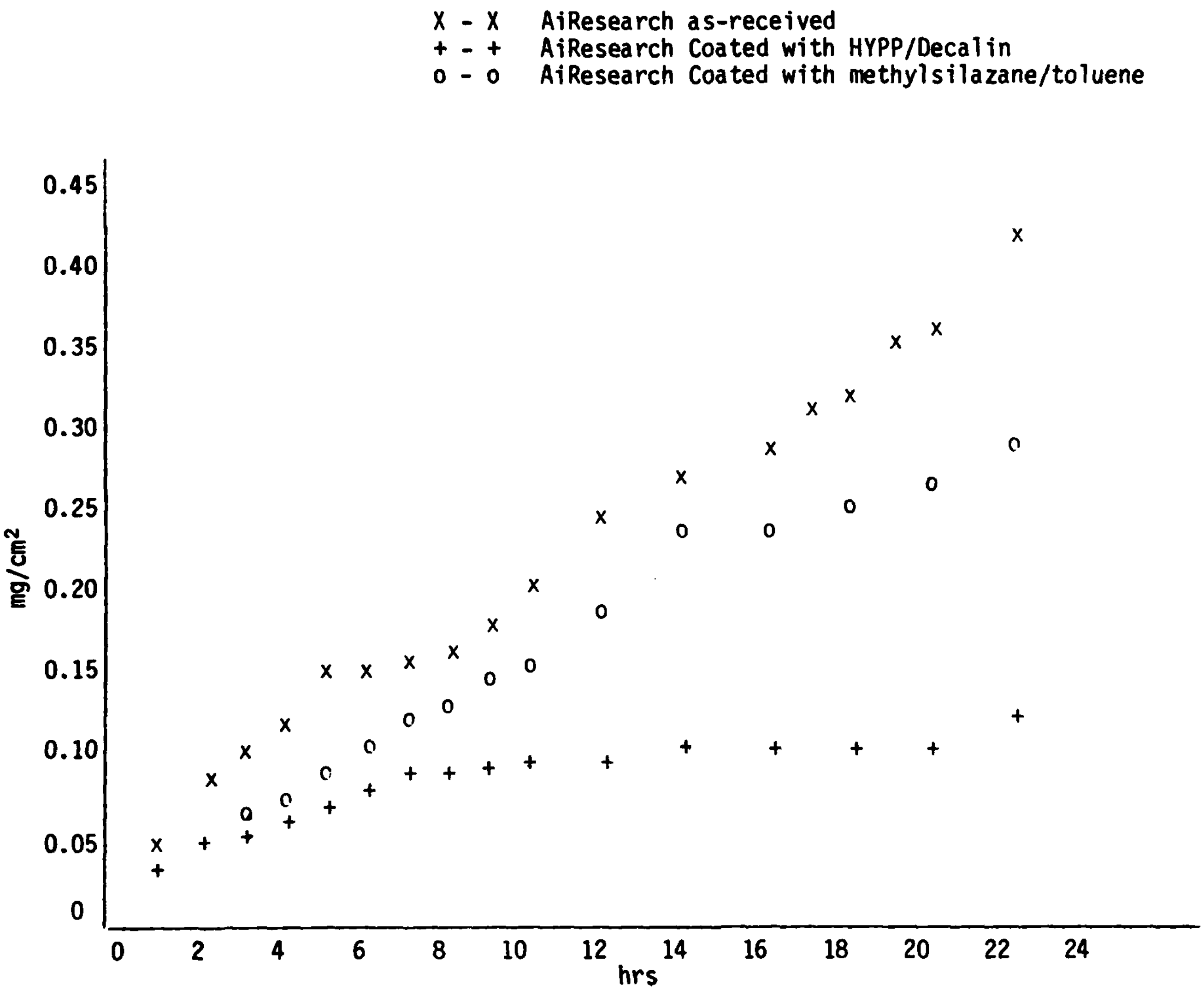

FIGURE 18. OXIDATION* WEIGHT CHANGE FOR AIRESEARCH RSSN AS A FUNCTION OF TIME

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* Oxidation Conditions: 1000°C under 0.2 ATM O_2

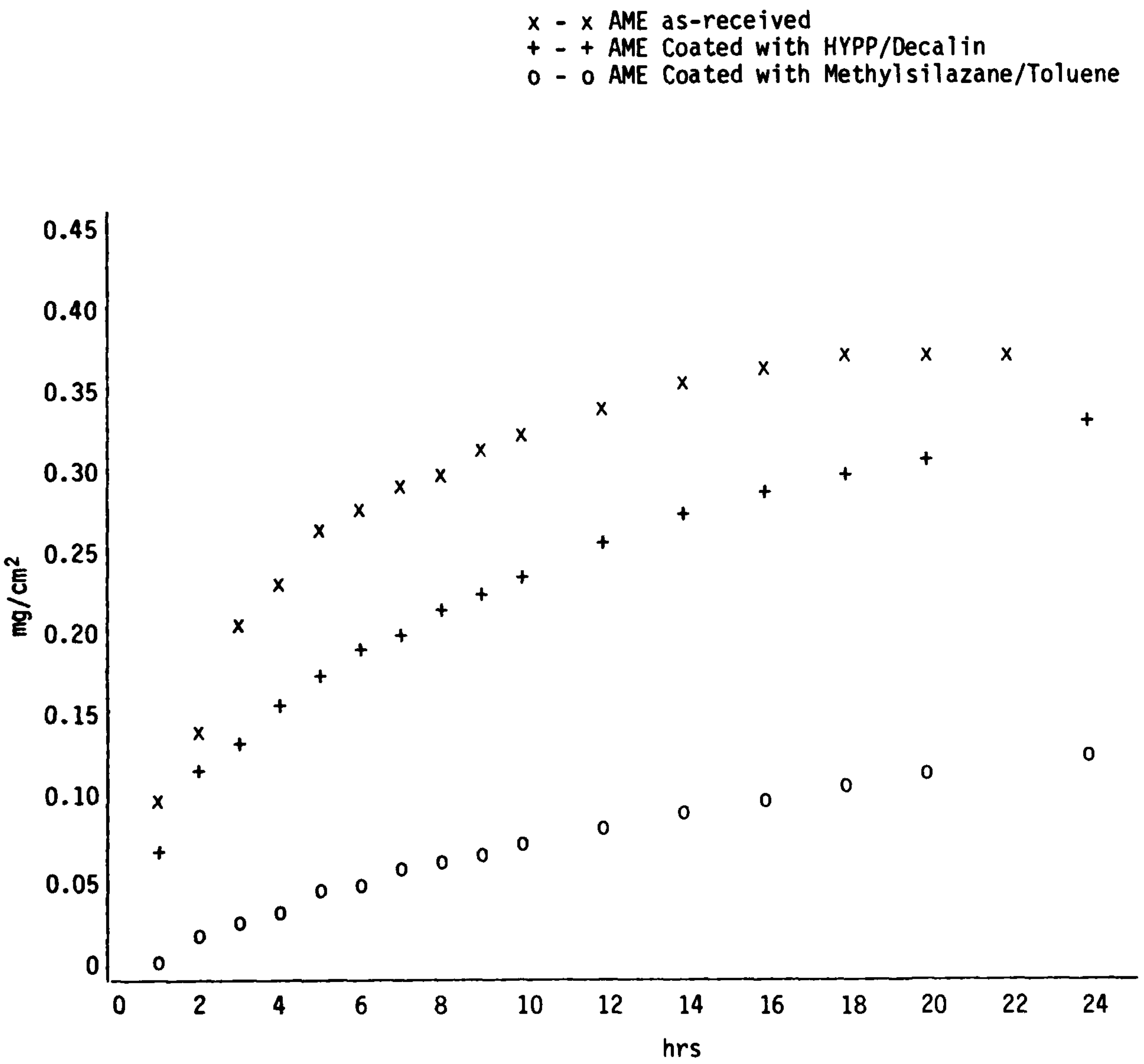

FIGURE 19. OXIDATION* WEIGHT CHANGE FOR AME RSSN AS A FUNCTION OF TIME

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*Oxidation Conditions: 1000°C under 0.2 ATM O_2

TABLE 13.

STRENGTH OF BOEING FOAM #2 RSSN UNCOATED VERSUS COATED WITH METHYLSILAZANE

	Uncoated	Coated
Number of Samples	9	8
Mean Strength (3-point bend)	1750 psi	2990 psi
Standard Deviation	150 psi	590 psi
Coefficient of Variation	8.6%	20%

Improvement in Average Strength - 70%

CONCLUSIONS

The following conclusions can be drawn from the work performed in this program:

1. Multiple impregnation/pyrolysis of hexaphenylcyclotrisilazane and methylsilazane in decalin results in an increase in density of both low density and high density RSSN materials. After about 3 cycles the capacity for further density improvements decreases.

2. On pyrolysis hexaphenylcyclotrisilazane converts to silicon nitride fibers which do not bond to the RSSN material. Pyrolysis of methylsilazane results in a fine grained microstructure containing 1μ closed voids. This microstructure is more desirable for effecting the desired property improvements.

3. Improvements in oxidation resistance were obtained by stuffing the surface of RSSN. Due to the large volume shrinkage occurring in these organosilicon precursors during pyrolysis a portion of the coating flakes off during heat treatment. A 70 percent increase in average strength was obtained for Boeing RSSN.

4. Optimum organosilicon precursors for efficiently improving the properties of RSSN materials are not available. Desired precursor characterisitcs include: (a) stability when subjected to conditions under which viscosity and wetting characteristics are suitable for impregnation/coating; (b) minimal weight loss and shrinkage during pyrolysis; and (c) handleable in air. The precursor should preferably be liquid at a low temperature, or be handleable in high concentrations in suitable solvents.

5. The use of organosilicon precursors for the preparation of ceramics or for achieving improvements in existing ceramics offers great promise for silicon based ceramics, but until a better understanding of structure-property relationships in the conversion of polymers to ceramics is obtained, attempts to use this technology to obtain useful ceramic products and properties will be thwarted or at best delayed.

RECOMMENDATIONS FOR FUTURE WORK

1) While it has been demonstrated that the oxidation resistance of RSSN can be improved by filling the surface porosity the engineering of this process needs to be optimized in order to maximize the oxidation resistance and flexural strength of RSSN.

2) The methylsilazane organosilicon system shows the best promise for upgrading the properties of RSSN, but work needs to be done to enable a methylsilazane with optimum physical and chemical properties to be reproducibly prepared.

3) A better understanding of the mechanism of pyrolysis of methylsilazane is needed so that processing candidates can be optimized to produce a high density fine grained ceramic.

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APPENDIX A

PREPARATION OF ORGANOSILICON PRECURSORS

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Polydimethylsiliazane 35996-30

Hexamethylcyclotrisilazane (HMCTS) liquid (45.8 g, 0.209 moles, as received from Chemical Procurements, Inc.) was added to a dry 16-ounce beverage bottle at room temperature. The bottle, containing a magnetic stir bar, was predried in an oven at 110 C. All additions were done under dry argon gas. The bottle, containing the HMCTS, was slowly chilled to -55 C, while it was continually flushed with dry argon. Ammonia (1.2 g, 0.070 moles) was then added as a dry liquid by passing ammonia gas through a drying tower of CaH_2 and condensing in a dry ice-cooled aluminum coil. The liquid ammonia was passed into the bottle via a 16-gage hypodermic needle through a neoprene septum on the bottle. The bottle was capped and the contents stirred continually while heating in an oil bath at 140-155 C for 48 hours. The bottle was cooled, the pressure vented, and the clear, thin liquid product placed in a dry Pyrex distillation apparatus.

The HMCTS and octamethylcyclotetrasilazane present were distilled off at ∿20 torr (39 C and 79-80 C, respectively). A total of 35.2 g of distillate was recovered. The undistilled product (5.82 g, 12.9 percent yield) was the desired polydimethylsilazane prepolymer. It was a clear, moderately viscous (30-40 weight motor oil), golden colored liquid. When heated to 150 C the liquid became water-thin and was qualitatively unchanged after 24 hours at this temperature under dry argon. As infrared spectrum (Figure 3) of the product was consistent with the presumed dimethylsilazane polymeric structure. However, a thermogravimetric analysis (TGA, 10 C per minute under argon, Figure 4) showed a 91 percent weight loss between 200 C and 900 C.

Trimethylsilyl-Blocked Polydimethylsilazane 35996-34

Polydimethylsilazane (0.5 g, 0.0068 mole) was treated with a large excess (∿2 cc) of trimethylchlorosilane under dry argon gas in a predried 10-cc Pyrex flask fitted with a reflux condenser. The reaction mixture was held at reflux temperature (∿58 C) for 1 hour to convert all primary amino end groups to trimethylsilyl amino groups. The excess trimethylchlorosilane was then removed under vacuum at ambient temperature and the polydimethylsilazane recovered. The originally clear, golden-colored liquid had become a slightly turbid light brown liquid of similar viscosity. TGA (10 C minute, under argon, Figure 11) showed a 75 percent weight loss between 200 C and 900 C.

Polymethylsilazane Resin 35996-35

Methyltrichlorosilane (150 cc, 191.2 g, 1.284 moles) was added to three liters of methylene chloride (dried over CaH_2) in a flame-dried five-liter reaction flask fitted with a Trubore stirrer, reflux condenser, and gas inlet and outlet tubes. The reaction mixture was blanketed at all times with dry argon. The rapidly stirred reaction mixture was held at reflux temperature (∿40 C) using an oil bath while ammonia gas, dried by passing through a CaH_2 tower, was passed through it. Ammonia was passed at a rate of about 27 cc/minute until the reaction mixture was no longer acidic (pH of small aliquot in water >7). This took approximately 6 days. The ammonium chloride precipitate was then removed by filtration through an oven-dried (110 C) medium porosity sintered glass funnel under dry argon. A clear, colorless solution containing polymethylsilazane product was obtained. A 1-cc aliquot of the approximately 1800 cc of product solution was taken to dryness (0.0500 g). Thus the product solution contains 5 percent polymethylsilazane and the yield of polymer on a dry basis is ∿55 g. This is about a 65 percent yield based on an expected yield of about 85 grams, depending on the molecular weight of the polymer produced. The dry product is a light tan or off-white solid which melts at about 40-50 C. The melt is unstalbe and cross-links slowly. Above about 100 C the melt rapidly gels, forming a hard solid. After about two weeks insoluble precipitate began to form. This was filtered out with a 0.2 μm micropore filter under Ar five times (about 2.5 grams lost). The solution was then stabilized by adding 10 grams of N,O-bis (trimethylsilyl)-removed at ambient temperature and reduced pressure.

APPENDIX B

REPORT FROM IITRI

RECD JAN 28 1981

IITRI
IIT Research Institute
10 West 35 Street, Chicago, Illinois 60616
312/567-4000

15 January 1981
IITRI-M6054-18

U.S. Air Force
Wright Aeronautical Laboratory
Contract No. F33615-79-C-5100
Wright-Patterson AFB, Ohio 45433

Attention: Dr. Robert Ruh
AFWAL/MLLM

Subject: Monthly Letter Report No. IITRI-M6054-18, "Property Screening and Evaluation of Ceramic Turbine Materials" for the period 1 December through 31 December 1980

Dear Sir:

During this reporting period room-temperature flexure data and fractographic analysis were completed for (1) Associated Engineering Developments, Ltd. RS-Si_3N_4 (Batch 5), (2) Kyocera SC-201 sintered SiC, (3) Westinghouse HP-Si_3N_4 (experimental), and (4) two types of Battelle/AFWAL organo-silicon-infiltrated RS-Si_3N_4 in the non-infiltrated condition: AME RS-Si_3N_4 and AiResearch RBN-104 RS-Si_3N_4.

The 4-point bend strength of AED RS-Si_3N_4 is presented in Table 1. The mean strength of 26 ksi is comparable to that of the first four batches of this material. Although the porosity has been slightly decreased, this material still exhibits very rough intergranular fractures with poorly defined features. Fracture origins were the same as for previous batches: large dark, shiny inclusions or bands of unreacted material. Refer to Fig. 13 of ITR 8 for a representative macrograph of a room-temperature fracture surface.

Flexure results for Kyocera SC-201 sintered SiC are shown in Table 2. The 4-point bend strength of 56 ksi is comparable to that of current vintage Carborundum sintered α-SiC (SASC), which is being used in the DOE/NASA AGT program, conducted by teams from DDA/Pontiac and AiResearch/Ford. We have evaluated an earlier version of Carborundum SASC, for which the strength was ∿45 ksi. The present Kyocera SC-201 sintered SiC fractures transgranularly which makes the location of fracture origins difficult. For almost half of the flexure bars the critical flaw could not be determined, Four (4) of the remaining bars failed at small surface or subsurface pores, one failed due to a deep machining groove and one at a large subsurface particle.

Flexure strengths for the experimental Westinghouse HP-Si_3N_4 material are presented in Table 3. The 91 ksi bend strength and 44 x 10^6 psi elastic modulus are typical of fine-grain hot-pressed Si_3N_4 materials. It is believed that this material is doped with Y_2O_3. Westinghouse personnel will be contacted for information regarding processing history and nominal composition. Fracture sources for this material were almost exclusively subsurface, shiny, light-colored particles. Only one bar failed due to a deep surface scratch. Figure 1 shows a typical fracture surface.

Baseline flexure strengths at room temperature were determined for non-infiltrated AME RS-Si_3N_4 (shown in Table 4) and AiResearch RBN-104 RS-Si_3N_4 (shown in Table 5). These materials are to be supplied in the organosilicon-infiltrated condition by Battelle/AFWAL at a future date.

The AME RS-Si_3N_4 is an extremely coarse material with 33% porosity. Its room-temperature strength is ∿7 ksi. Fracture features were ill-defined,and the rough intergranular nature of the material defied the identification of fracture origins. A representative fracture surface is shown in Fig. 2.

Fracture origins for AiResearch RBN-104 RS-Si_3N_4 were primarily processing defects; subsurface inclusions and porosity. There was one instance of a machining defect. Fracture features were well defined, which is consistent with the relatively high room-temperature strength of 40 ksi. A typical fracture is shown in Fig. 2.

Spectrographic, X-ray diffraction, oxygen content, and microstructure samples of all new materials are in the process of being submitted for analysis. Results will be presented in a future MLR, Flexure testing at elevated temperatures continues on these materials.

The total expenditures to date on Contract F33615-79-C-5100 are presented in Fig. 3,

Respectfully submitted,
IIT RESEARCH INSTITUTE

Jane Adams

J. W. Adams
Senior Experimentalist

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APPROVED:

S. A. Bortz
Senior Engineering Advisor
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Table 1

FLEXURAL TEST RESULTS (4 Point)

Supplier: ASSOC ENG DEVEL

Material: RS Si_3N_4 **(Nitrasil) Diamond Ground**

Temperature: 25°C

Atmosphere: AIR

Sample	Bulk Density (gm/cc)	Strength (psi)	Strength (MPa)	Strain-To-Failure (in/in x 10^{-3})	Secant Modulus (10^6 psi)	Secant Modulus (GPa)
P5F 01	2.620	27,480	189.5	.94	28.6	197.4
P5F 02	2.651	22,930	158.1	.85	27.1	186.9
P5F 03	2.625	29,480	203.3	1.03	28.8	198.3
P5F 04	2.623	27,230	187.8	.95	28.3	194.9
P5F 05	2.620	30,360	209.3	1.07	28.4	195.7
P5F 06	2.619	19,010	131.1	.66	28.7	197.6
MEAN	2.626	26,080	179.8	.92	28.3	195.1
ST.DEV						
MAX.						
MIN.						

* * Mean Values * *

Surf. Finish = 11 Microinches (RMS)

Theo. Density (3.200) = 82.1%

Total Porosity = 17.9%

Open Porosity (Meas.) = 11.3%

Closed Porosity (By Difference) = 6.6%

Table 2

FLEXURAL TEST RESULTS (4 Point)

Supplier: KYOCERA

Material: SC-201 SINTERED SiC

Temperature: 25°C

Atmosphere: AIR

Sample	Bulk Density (gm/cc)	Strength (psi)	(MPa)	Strain-To-Failure (in/in x 10^{-3})	Secant Modulus (10^6 psi)	(GPa)
KK1F 01	3.137	60,850	419.6	1.00	59.4	409.5
KK1F 02	3.144	60,170	414.9	1.00	59.2	408.0
KK1F 03	3.136	45,350	312.7	.74	60.2	414.9
KK1F 04	3.218	35,440	244.4	.58	60.4	416.4
KK1F 05	3.138	73,190	504.6	1.20	60.4	416.2
KK1F 06	3.141	39,990	275.7	.66	60.2	415.3
KK1F 07	3.136	68,030	469.1	1.10	61.5	423.7
KK1F 08	3.138	49,320	340.1	.79	62.0	427.7
KK1F 09	3.149	62,260	429.3	1.01	60.3	416.0
KK1F 10	3.139	66,150	456.1	1.08	61.4	423.5
MEAN	3.148	56,080	386.7	.92	60.5	417.1
ST.DEV	.025	12,740	87.8	.21	.9	6.2
MAX.	3.218	73,190	504.6	1.20	62.0	427.7
MIN.	3.136	35,440	244.4	.58	59.2	427.7

Weibull Modulus(Strength) = 4.0

* * Mean Values * *

Surf. Finish = 27 Microinches (RMS)

Theo. Density (3.217) = 97.8%

Total Porosity = 2.2%

Open Porosity (Meas.) = .0%

Closed Porosity (By Difference) = 2.2%

Table 3

FLEXURAL TEST RESULTS (4 Point)

Supplier: WESTINGHOUSE

Material: HP-Si_3N_4.(EXPERIMENTAL)

Temperature: 25°C

Atmosphere: AIR

Sample	Bulk Density (gm/cc)	Strength		Strain-To-Failure (in/in x 10^{-3})	Secant Modulus	
		(psi)	(MPa)		(10^6 psi)	(GPa)
WB1F 01	3.180	100,700	694.3	2.43	41.1	283.6
WB1F 02	3.269	75,490	520.5	1.68	44.9	309.5
WB1F 03	3.174	89,540	617.4	2.15	41.8	288.0
WB1F 04	3.323	114,800	791.5	2.45	46.7	321.9
WB1F 05	3.267	103,200	711.6	2.30	44.5	307.1
WB1F 06	3.249	105,600	728.1	2.36	44.5	306.6
WB1F 07	3.267	84,120	580.0	1.87	44.8	309.1
WB1F 08	3.314	79,840	550.5	1.71	46.2	318.6
WB1F 09	3.169	61,440	423.6	1.50	40.9	281.7
WB1F 10	3.286	95,050	655.4	2.04	46.6	321.4
MEAN	3.250	90,980	627.3	2.05	44.2	304.7
ST.DEV	.057	16,080	110.9	.34	2.2	15.2
MAX.	3.323	114,800	791.5	2.45	46.7	321.9
MIN.	3.169	61,440	423.6	1.50	40.9	321.9

Weibull Modulus(Strength) = 5.3

* * Mean Values * *

Surf. Finish = 8 Microinches (RMS)

Theo. Density (3.200) =

Total Porosity =

Open Porosity (Meas.) = .1%

Closed Porosity (By Difference) =

Table 4

FLEXURAL TEST RESULTS (4 Point)

Supplier: **BATTELLE/AFWAL/Organosilicon-Infiltrated RSSN**

Material: **AME RS-Si_3N_4 (Non-infiltrated)**

Temperature: 25°C

Atmosphere: AIR

Sample	Bulk Density (gm/cc)	Strength (psi)	Strength (MPa)
BI1F 01	2.130	7,970	55.0
BI1F 02	2.115	7,450	51.4
BI1F 03	2.113	7,920	54.6
BI1F 04	2.115	6,530	45.0
MEAN	2.118	7,470	51.5

* * Mean Values * *

Surf. Finish= >100 Microinches (RMS)

Theo. Density (3.200) = 66.2%

Total Porosity = 33.8%

Open Porosity (Meas.) = 31.5%

Closed Porosity (By Difference) = 2.3%

Table 5

FLEXURAL TEST RESULTS (4 Point)

Supplier: **BATTELLE/AFWAL/Organosilicon-Infiltrated RSSN**

Material: **AiResearch RBN-104 RS-Si_3N_4 (Non-infiltrated)**

Temperature: 25°C

Atmosphere: AIR

Sample	Bulk Density (gm/cc)	Strength (psi)	Strength (MPa)
BI2F 01	2.789	44,840	309.2
BI2F 02	2.783	37,110	255.9
BI2F 03	2.775	31,830	219.5
BI2F 04	2.792	47,310	326.2
MEAN	2.785	40,270	277.7

* * Mean Values * *

Surf. Finish = 54 Microinches (RMS)

Theo. Density (3.200) = 87.0%

Total Porosity = 13.0%

Open Porosity (Meas.) = 7.6%

Closed Porosity (By Difference) = 5.4%

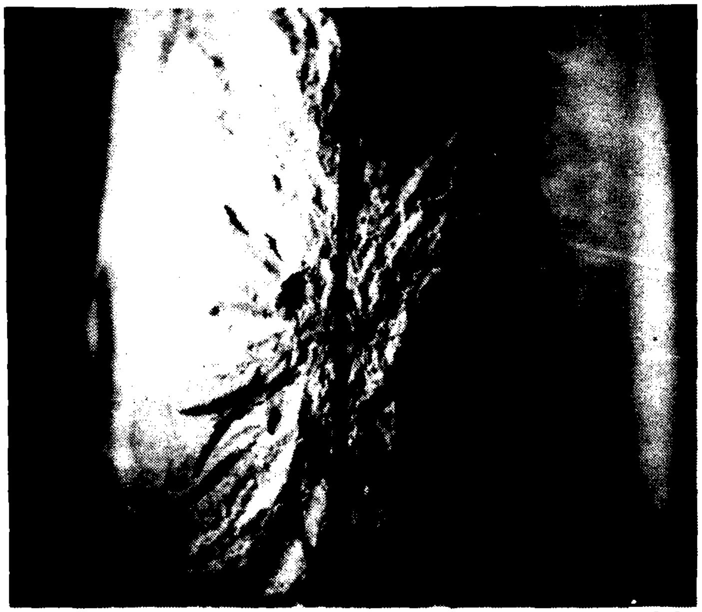
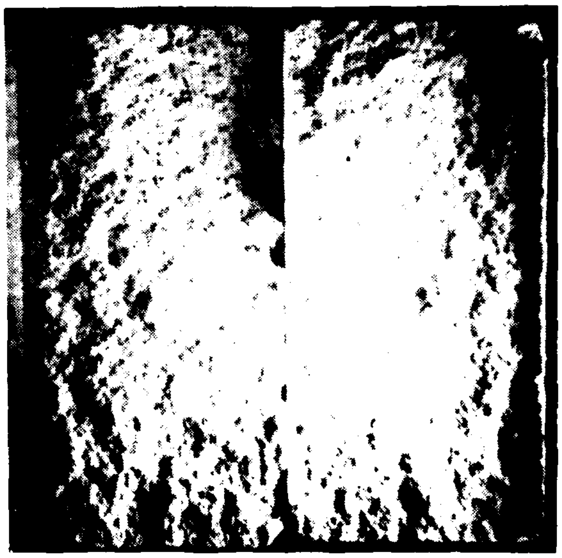


Figure 1

Fracture Surface (Tensile Surfaces Together) of Westinghouse HP-Si_3N_4 (Experimental) Tested at Room Temperature



12X

(a) AME RS-Si_3N_4 (non-infiltrated)

16X

(b) AiResearch RBN-104 RS-Si_3N_4 (non-infiltrated)

Figure 2

Fracture Surfaces (Tensile Surfaces Together) of Battelle/AFWAL Organosilicon-Infiltrated RS-Si_3N_4 Tested at Room Temperature

[illegible]