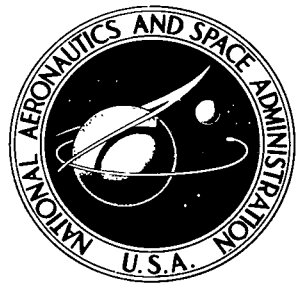
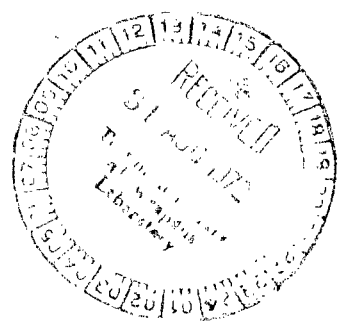
NASA TECHNICAL NOTE

NASA TN D-6890



EVALUATION OF OXIDATION RESISTANT NONMETALLIC MATERIALS AT 1204° C (2200° F) IN A MACH 1 BURNER



by William A. Sanders and Hubert B. Probst

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1972

1. Report No.	2. Government Accession No.	3. Recipie
NASA TN D-6890		

4. Title and Subtitle

EVALUATION OF OXIDATION RESISTANT NONMETALLIC MATERIALS AT 1204° C (2200° F) IN A MACH 1 BURNER

5. Report Date: August 1972

6. Performing Organization Code

7. Author(s)

William A. Sanders and Hubert B. Probst

8. Performing Organization Report No.: E-6918

10. Work Unit No.: 134-03

9. Performing Organization Name and Address

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered: Technical Note

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D. C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Specimens of 23 oxidation resistant, nonmetallic, refractory materials were systematically exposed in a high gas velocity burner to simulate a turbine engine environment. Isothermal and cyclic tests were conducted at a specimen temperature of 1204° C (2200° F) which resulted from exposure to Mach 1 or Mach 0.5 hot gas streams. Specimen behavior was judged on the basis of failure mode, appearance, and weight change. SiC and Si_3N_4 exhibited the most promising behavior surviving all exposures including Mach 1 for 120 cycles (10 hr). Major failure modes identified for other materials were thermal shock, thermal fatigue, and mechanical failure due to gas loading.

17. Key Words (Suggested by Author(s))

Burner rig; Gas turbine; High velocity; Thermal shock; Thermal fatigue; Mechanical failure (gas loading); Ceramics; Refractory compounds; Carbides; Nitrides; Borides; Oxides

18. Distribution Statement: Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	26	$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22151

EVALUATION OF OXIDATION RESISTANT NONMETALLIC MATERIALS AT 1204° C (2200° F) IN A MACH 1 BURNER

by William A. Sanders and Hubert B. Probst

Lewis Research Center

SUMMARY

Cylindrical specimens of 23 oxidation resistant, nonmetallic, refractory materials were systematically exposed in a high gas velocity burner simulating a gas turbine engine environment. Isothermal and cyclic tests were conducted at a specimen temperature of 1204° C (2200° F) which resulted from exposures to Mach 1 or Mach 0.5 hot gas streams. Specimens were examined to determine weight change, appearance, and failure mode. The materials tested were classified according to failure modes such as thermal shock, thermal fatigue, and mechanical failure due to gas loading.

A high density form of silicon carbide (SiC) and two high density forms of silicon nitride (Si_3N_4) exhibited the most promising behavior, surviving all exposures including Mach 1 for 120 cycles (10 hr). These samples showed no signs of cracking or surface degradation, and weight changes were slight.

Two materials not surviving Mach 1 tests because of mechanical failure due to gas loading did survive 120-cycle exposures at Mach 0.5. These materials were a lower density form of Si_3N_4 and boron nitride (BN) containing 60 weight percent silicon dioxide (SiO_2). Neither material showed any signs of cracking or surface damage. The SiO_2 phase in the BN was apparently beneficial in preventing thermal shock failures which occurred in plain BN material.

Some crack arresting features were also observed in aluminum oxide - boron nitride (Al_2O_3-BN) composites. Although these composites were short lived and failed in thermal fatigue in 3 to 9 cycles, the BN flake dispersion in the Al_2O_3 prevented the immediate thermal shock failures noted at Mach 1 and Mach 0.5 for plain Al_2O_3.

A Si-SiC-C fiber composite was found to be resistant to thermal shock and corrosion; however, the material exhibited mechanical fatigue failures due to gas loading.

Mechanical failure due to gas loading was the failure mode for most other materials at Mach 1, with the failure mode at Mach 0.5 often changing to thermal fatigue or thermal shock.

INTRODUCTION

The corrosive attack on turbine vanes and blades by combustion products is a major materials problem in the development of advanced aircraft turbine engines. Although current superalloys are strong enough to permit the use of considerably higher turbine inlet temperatures for better performance, operation at such temperatures is not possible because of the corrosion limitations. The nickel- and cobalt-base superalloys now in use (ref. 1) cannot be used uncoated at metal temperatures above approximately 1000° C (1832° F) because of corrosion and erosion in the severe turbine engine environment (ref. 2). If vanes and blades of superalloys are cooled, higher turbine inlet temperatures can be used, and with coated vanes and blades metal temperatures near 1100° C (2012° F) are permissible (ref. 2). Convective cooling by internal passages, film cooling by air flowing out leading edge cavities, and transpiration cooling by air passing out over the whole vane or blade surface are the techniques employed (ref. 3). But these cooling methods usually involve complicated and expensive casting and machining techniques to achieve the complex cooling configurations required. Although coatings protect superalloy vanes from oxidation at metal temperatures near 1100° C (2012° F), they degrade rapidly and a vane may require 8 to 12 recoatings during its lifetime (ref. 2).

An alternate approach to the attainment of higher turbine inlet temperatures is to employ nonmetallic materials for turbine vane and blade application. Not only certain refractory oxides, but some refractory borides, carbides, and nitrides are of interest for this application because of their demonstrated high resistance to oxidation to at least 1400° C (2552° F) (ref. 4). In addition, these materials have densities less than one-half the densities of the superalloys, and thus the use of these materials could result in significant weight savings. Also, the high hardness of these materials would be beneficial from the standpoint of resistance to erosion due to carbon particles in the combustion gas or ingested particulate matter. Such refractory materials, although brittle, have attracted interest in the past and have been evaluated in the forms then available for possible turbine engine use (e.g., refs. 5 (1957) and 6 (1958)). It was the conclusion of these studies that certain nonmetallic refractory materials had adequate strength and oxidation resistance but that resistance to thermal shock, thermal fatigue, and mechanical shock was inadequate. In an excellent historical review in 1964, Glenny (ref. 7) discussed the application of refractory nonmetallic materials to gas turbine components. Glenny concluded that the key to using such materials was to provide some measure of toughness in the materials and to design the vane or blade component to suit the material. More recently, Godfrey and coauthors (refs. 8 to 10) have reviewed the properties of and compared candidate refractory nonmetallic materials for turbine engine application and have discussed design concepts for the usage of these materials. Also, recently, McLean (ref. 11) has well reviewed the potential and problems of using

ceramics in small gas turbine engines.

The purpose of this investigation was to systematically screen, in a Mach 1 burner simulating an engine environment, several recently introduced, commercial, refractory, nonmetallic materials that were believed to have some potential for gas turbine applications. Materials in the categories carbide, nitride, silicon - silicon carbide - carbon fiber composite, boride, boride composite, oxide, mixed oxide, and oxide composite were evaluated. These materials were selected on the basis of reported good oxidation resistance, high strength, high thermal conductivity, low thermal expansion coefficient, or reasonably low modulus of elasticity. The latter four properties are frequently used to judge the thermal stress resistance of brittle materials (ref. 12). This screening study was made to find the most promising material(s) and to identify failure modes. The study was conducted so that three separate failure modes could be identified; they are thermal shock, thermal fatigue, and mechanical failure due to gas loading. The study results could then be a basis for attempts to improve a few promising materials and for more detailed evaluations of such materials.

The Mach 1 burner used for this screening evaluation was operated at hot gas velocities of both Mach 1 and Mach 0.5 with Jet A, a kerosene-type fuel simular to JP 5 fuel. Materials were tested as right cylinders, 1.3 centimeters (0.5 in.) in diameter by 10.2 centimeters (4 in.) in length. Each material was subjected to a temperature of 1204^{o} C (2200^{o} F) during both isothermal and cyclic exposures in the hot gas stream. Maximum exposures consisted of 120 five-minute cycles, that is, a 10-hour exposure to the hot gas stream. A cycle consisted of 5 minutes at 1204^{o} C (2200^{o} F) in the hot gas stream followed by a 3-minute still air cool. The materials were evaluated on the basis of failure mode, appearance, and weight change.

MATERIALS

Table I lists and categorizes the 23 materials evaluated. Also given in table I are the material vendors and some properties. Test specimens were right cylinders, 1.3 centimeters (0.50 in.) in diameter and 10.2 centimeters (4.0 in.) in length. Specimens were tested in the as-received condition - either as-fired or ground. The specimen surface condition was not a test variable.

TABLE I. - VENDOR PROPERTIES FOR NONMETALLIC MATERIALS EVALUATED IN SIMULATED GAS TURBINE ENVIRONMENT

Material	Vendor	Density, g/cm^3	Porosity, vol %	Room temperature							
				Coefficient of thermal expansion		Thermal conductivity		Bend strength		Modulus of elasticity	
				$cm/cm/^oC$	$in./in./^oF$	$cal/sec-cm-^oC$	$Btu/hr-ft-^oF$	MN/m^2	psi	MN/m^2	psi
Carbides:											
SiC (KT, 9 wt % free Si)	Carborundum	3.10	0	3.38×10^{-6}	1.88×10^{-6}	0.41	99	165	24×10^3	386×10^3	56×10^6
SiC (Refrax, Si_3N_4 bond)	Carborundum	2.65	15	3.24	1.80	------	----	38	5.5	117	17
SiC tube (CVD)	Energy Research Corporation	3.21	[a]0	----------	----------	------	----	>700	>102	-------	-------
Si-SiC-C (fiber composite)	Fansteel	2.71	-----	----------	----------	------	----	----	-------	-------	-------
Nitrides:											
Si_3N_4	Doulton	2.55	[a]20	[b]2.52×10^{-6}	[b]1.40×10^{-6}	[b]0.019	[b]4.6	[c]275	[c]40×10^3	[c]180×10^3	[c]26×10^6
Si_3N_4	Plessey	3.19	.1	2.88	1.60	.043	10.4	551	80	242	35
Si_3N_4	Lucas	3.2	.1	2.7	1.50	.022	5.3	826	120	310	45
BN (60 wt % SiO_2)	Carborundum	2.12	[a]5	1.8	1.0	.042	10.1	102	14.8	100	14.5
BN	Carborundum	1.90	[a]16	(d)	(d)	.120	29	48	6.9	61	8.8
Borides:											
SiB_6 (3 wt % free Si)	Cerac	2.1	[a]14	6.3×10^{-6}	3.5×10^{-6}	[b]0.023	[b]5.5	90	13×10^3	[b]242×10^3	[b]35×10^6
SiB_6 (15 to 20 wt % free Si)	Cerac	2.1	[a]13	----------	----------	------	----	----	-------	-------	-------
Boride composite:											
ZrB_2 (14 wt % SiC-30 wt % C)	Manlabs	4.48	[a]2	6.48×10^{-6}	3.60×10^{-6}	0.18	43	282	41	207	30×10^6
Oxides:											
SiO_2 (fused, Silfrax)	Carborundum	1.9	10	0.54×10^{-6}	0.30×10^{-6}	0.021	5.1	12	1.7×10^3	-------	-------
SiO_2 (fused, O.C.F.)	Owens-Corning Fiberglas	[a]1.5	-----	----------	----------	------	----	----	-------	-------	-------
Al_2O_3 (AD999)	Coors	3.96	[a].5	6.84	3.80	.074	17.8	724	105	386×10^3	56×10^6
ZrO_2 (1706)	Zircoa	5.43	[a]6	[b]6.3	[b]3.5	[b].005	[b]1.2	207	30	103	15
Mixed oxides:											
Alumino silicate (low fired)	Aremcolox	2.3	0.3	2.7×10^{-6}	1.5×10^{-6}	------	----	----	-------	-------	-------
Alumino silicate (high fired)	Aremcolox	2.0	4	(d)	(d)	------	----	69	10×10^3	-------	-------
Pyroceram 9606	Corning Glass	2.6	[a]0	5.76	3.20	0.008	1.9	[b]262	[b]38	120×10^3	17.4×10^6
Pyroceram 9608	Corning Glass	2.5	[a]0	1.98	1.10	.005	1.2	134	19.4	86	12.5
Oxide composites:											
Al_2O_3 (15 vol % BN fiber)	Philco-Ford	3.55	[a]4	6.3×10^{-6}	3.5×10^{-6}	------	----	128	18.6×10^3	403×10^3	58.5×10^6
Al_2O_3 (15 vol % BN flake)	Philco-Ford	3.55	[a]4	6.66	3.70	------	----	94	13.6	238	34.5
$MgAl_2O_4$ (15 vol % BN flake)	Philco-Ford	2.80	[a]17	7.2	4.1	------	----	23	3.3	104	15

[a]Calculated.
[b]Ref. 4.
[c]Ref. 17.
[d]Negligible.

APPARATUS AND PROCEDURE

A schematic of the burner rig described in detail in reference 13 is shown in figure 1. The apparatus was operated with Jet A fuel at combustion gas velocities of Mach 0.5 or Mach 1 at the conditions given in table II. The cylindrical specimens were tested singly, and each specimen was held in a holder which rotated the specimen about its own axis at 200 rpm. The purpose of this rotation was to ensure uniform heating. The holder accepted the specimen and a two-piece stainless-steel specimen collar secured with a bolt and locknut. A schematic of the specimen in the holder in exposure position with respect to the burner rig nozzle is shown in figure 2.

For temperature calibration, a slip-ring assembly mounted in the lower end of the specimen holder shaft was used to provide an electrical circuit to a thermocouple mounted on a nickel base superalloy rod which was used for this calibration purpose only. During tests, the temperature of the rotating specimen was monitored with an optical pyrometer. The same burner running conditions established for the calibration temperature of 1204^{o} C (2200^{o} F) were used for all material tests. All materials were observed to reach and maintain the 1204^{o} C (2200^{o} F) test temperature within 20 to 25 seconds of exposure at Mach 1 and within 30 to 35 seconds of exposure at Mach 0.5. The radiation shields close to the specimen were very effective in promoting rapid heating. These shields provided a radiating cavity such that for the same burner rig operating conditions, the temperature measured by optical pyrometer did not vary from material to material. Thus, no corrections for emissivities were made. The burner gas temperature was controlled by a thermocouple downstream of the specimen position (see fig. 1). At test temperature, all specimens exhibited uniform hot zones for a distance of approximately 1.3 centimeters (0.5 in.) on both sides of the centerline of the nozzle. Within this zone surface temperature was maintained within $\pm 8^{o}$ C ($\pm 15^{o}$ F). Under normal operating conditions the temperature of the specimen just above the point where the specimen entered the collar was in the 816^{o} to 927^{o} C (1500^{o} to 1700^{o} F) range.

Materials were tested in a stepwise fashion according to the schedule given in figure 3. The first step in testing any material at 1204^{o} C (2200^{o} F) consisted of exposing the specimen to the Mach 1 hot gas stream for 60 minutes without cycling - a still air cool ended this step. If the material survived this step, a fresh specimen was given 12 cycles for a total exposure time of 1 hour. A cycle consisted of 5 minutes at 1204^{o} C (2200^{o} F) in the hot gas stream followed by a 3-minute still air cool to black heat. If the material survived this step, a fresh specimen was then given a maximum of 120 cycles for a total exposure of 10 hours. If a material failed in any step at Mach 1, that step was repeated but at a hot gas stream velocity of Mach 0.5 which provided a somewhat less severe heating rate and significantly lower gas loading conditions. In some cases, due to a limited number of samples, this procedure could not be followed completely. Maximum exposure was limited to 10 hours because it was felt that all the ma-

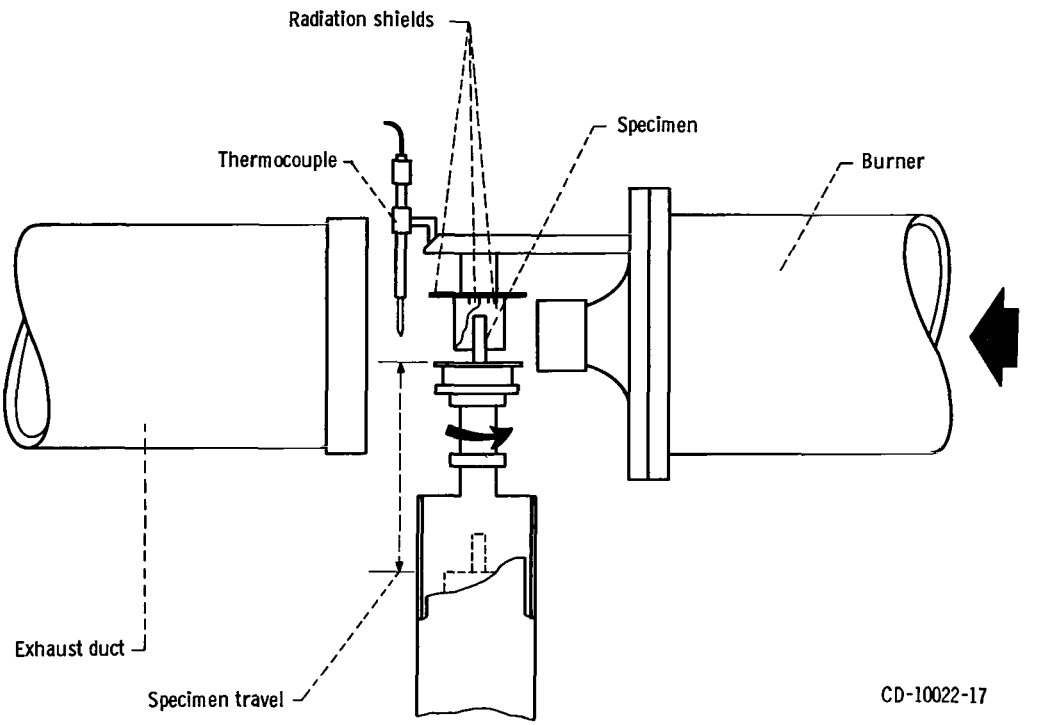


Figure 1. - Burner rig for simulated gas turbine environment.

TABLE II. - BURNER CONDITIONS FOR EVALUATION OF NONMETALLIC MATERIALS

[Specimen test cycle: 5 min at 1204° C (2200° F); 3 min still air cool.]

Burner gas temperature, °C (°F)	1538 (2800)
Specimen rotational speed, rpm	200
Burner nozzle diameter, cm (in.)	5.1 (2.0)
Air to fuel ratio	20:1
Burner air flow, kg/sec (lbm/sec):	
At Mach 0.5	0.2 to 0.1 (0.4 to 0.3)
At Mach 1	0.4 to 0.5 (0.9 to 1.0)
Burner pressure, MN/m^2 (psia):	
At Mach 0.5	0.12 (18)
At Mach 1	0.23 (33)

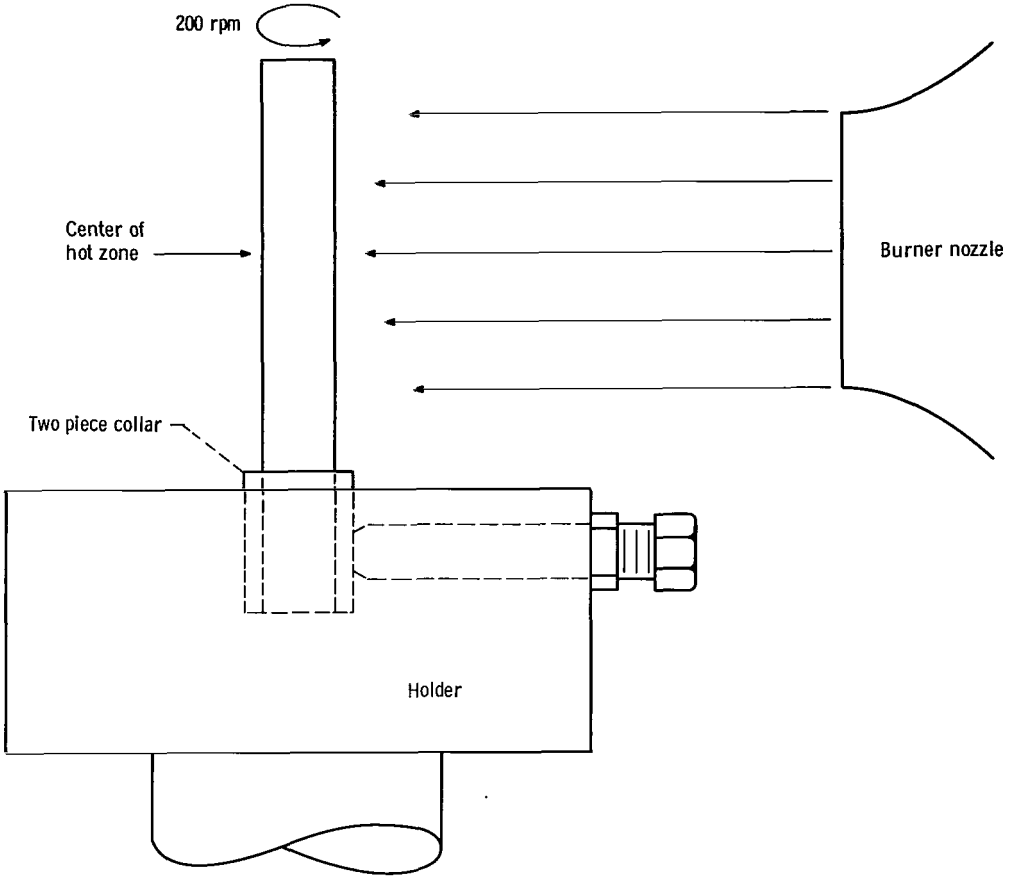


Figure 2. - Schematic of specimen-holder-nozzle arrangement for exposing test specimen to simulated gas turbine environment.

	Test step		
	One	Two	Three
Total exposure time at 1204° C (2200° F), hr	1	1	10
Target cycles	Not cycled	12	120
Mach 1 hot gas velocity	Pass → * Pass → * Pass Fail Fail Fail		
Mach 0.5 hot gas velocity	Pass → * Pass → * Pass Fail Fail Fail		
	No further testing		

* Fresh sample

Figure 3. - Test schedule for nonmetallic materials in simulated gas turbine environment. Test cycle: 5 minutes at 1204° C (2200° F); 3 minutes still air cool.

terials had sufficient oxidation resistance so that long time exposure was of secondary importance compared to the accumulation of a relatively large number of thermal cycles. Duplicate tests were not generally run.

Specimens were weighed before and after testing, and they were examined at ×30 with a binocular microscope for surface degradation and cracks. Selected specimens were photographed. Some specimens were mounted in epoxy resin, sectioned longitudinally in the hot zone crack area, and polished for metallographic analyses. Some of the better materials were also examined metallographically in the as-received condition to determine the general microstructure. No etchants were used.

RESULTS AND DISCUSSION

The behavior of the test materials in the burner rig will be discussed in the order of the material categories given in table I. The results consist of visual observations made during specimen heatup and cooldown, post-test observations of cracking and surface deterioration, and changes in weight (rubbing and chipping in the holder sometimes prevented determining weight change). Results in the form of microstructures of specimens containing cracks and representative microstructures of the better materials are also presented.

Three major specimen failure modes were noted during the course of testing:

1. Mechanical failure due to gas loading. - In this failure mode the specimen broke at the point where it entered the holder immediately on insertion into the hot gas stream. Such fractures are the result of aerodynamic gas loading. Maximum outer fiber tensile stresses for the rod specimens were calculated to be approximately 19 meganewtons per square meter (2700 psi) at Mach 1 and approximately 3 meganewtons per square meter (400 psi) at Mach 0.5 (ref. 14).

2. Thermal shock. - The specimen broke in the hot zone (area of hot gas impingement) immediately on insertion into the hot gas stream.

3. Thermal fatigue. - The specimen broke in the hot zone during cyclic exposure after having survived at least one cycle - a cycle consisting of a 5-minute exposure at 1204° C (2200° F) in the hot gas stream, followed by a 3-minute still air cool.

Less prevalent failure modes such as mechanical fatigue due to gas loading (a failure at the holder entrance point and dependent on cycling), heavy oxidation, and softening were also noted. No samples failed during the 3-minute still air cooling portion of the test cycle, and therefore, thermal shock failure on cooling is not included as a failure mode. A summary of failure mode test results is given in table III.

No attempt was made in this study to correlate test results with the thermal stress parameters for the instantaneous surface temperature change and for steady-state heat

TABLE III. - SUMMARY OF TEST RESULTS FOR NONMETALLIC MATERIALS EVALUATED AT 1204° C (2200° F)

IN SIMULATED GAS TURBINE ENVIRONMENT

Gas velocity	Materials surviving all tests	Failure modes for other materials			
		Thermal fatigue (Break in hot zone)	Thermal shock (Immediate break in hot zone)	Low strength (Immediate break at base)	Other
Mach 1	SiC (KT) Si_3N_4 (Pressey) Si_3N_4 (Lucas)	Pyrocerам 9606, 2nd cycle Alumina (15 vol % BN flake), 3rd cycle	BN SiB_6 (3 wt % free Si) Al_2O_3 (AD999) ZrO_2 (1706) Alumino silicate (low fired) Alumina (15 vol % BN fiber), failure delayed 15 sec	SiB_6 (3 wt % free Si) SiB_6 (15 to 20 wt % free Si) SiO_2 (fused, Silitrax) SiO_2 (fused, O.C.F.) Alumino silicate (high fired) Pyrocerам 9608 $MgAl_2O_4$ (15 vol % BN flake) BN (60 wt % SiO_2)	Mechanical fatigue (break at base): SiC (Refrax), 116th cycle Si_3N_4 (Doulton), 2nd cycle Si-SiC-C, 8th cycle Heavy oxidation: ZrB_2-14 wt % SiC-30 wt % C
Mach 0.5	Si_3N_4 (Doulton) BN (60 wt % SiO_2)	SiO_2 (fused, Silitrax), 37th cycle ZrO_2 (1706), 2nd cycle Pyrocerам 9606, 11th cycle Alumina (15 vol % BN flake), 9th cycle	BN SiB_6 (3 wt % free Si) SiB_6 (15 to 20 wt % free Si) Al_2O_3 (AD999) Alumino silicate (low fired) Alumino silicate (high fired) Alumina (15 vol % BN fiber), failure delayed 1 min $MgAl_2O_4$ (15 vol % BN flake), failure delayed 28 sec	SiB_6 (3 wt % free Si) SiB_6 (15 to 20 wt % free Si) SiO_2 (fused, O.C.F.), break in hot zone	Softening: Pyrocerам 9608

flow. These parameters relate the ability of a material to withstand thermal stresses to such properties as strength, thermal conductivity, elastic modulus, and coefficient of expansion (ref. 12). For the proper use of such parameters, the material properties must be known at the temperature at which thermal stress failure occurs. Because of the lack of such complete property data for this wide variety of materials, comparisons of such parameters were not made. However, available room temperature properties are listed in table I to provide an approximate comparison of materials and illustrate the range of properties.

Carbides

All of the materials in this category contain SiC. One of the materials is a composite consisting of silicon, SiC, and carbon fibers. The other three materials (KT SiC, Refrax SiC, and SiC tube CVD) contain SiC as a major phase with minor phases dependent on the manufacturing process.

The KT and Refrax SiC bodies withstood Mach 1 exposures for 120 (10 hr) and 115 cycles (9.6 hr), respectively. After 120 cycles, the arbitrary testing limit, the KT SiC specimen was not cracked nor had it sustained any surface degradation. This specimen is shown in figure 4. Chipping of this KT SiC specimen inside the holder, due to the sample becoming loose during the test, precluded a weight change measurement. However, another KT SiC sample gained only 2.8 milligrams after 12 cycles (1 hr) at Mach 1. On an area basis, this slight weight gain amounts to approximately 0.14 milligram per square centimeter, assuming an affected cylindrical sample surface area of 20 square centimeters. In comparison, a thoriated nickel - 20 percent chromium alloy blade-type specimen similarly exposed in the burner rig for 1 hour at 1204° C (2200° F) without cycling suffered a 1.5 milligram per square centimeter weight loss (ref. 15). The weight loss of the nickel-chromium alloy is associated with the vaporization of the chromium oxide (Cr_2O_3) scale which forms on such alloys. By contrast, the small weight gain observed for KT SiC suggests that its scale, which is reported to be SiO_2 (ref. 16), is stable and protective. The Refrax SiC specimen failed where it entered the holder during the 116th cycle because of mechanical fatigue due to gas loading. Representative microstructures of the KT SiC and Refrax SiC materials are presented in figure 5. The failure of the Refrax SiC may be related to its porosity which is evident in figure 5.

The SiC tube CVD (chemical vapor deposition) specimens had a 0.13-centimeter (0.050-in.) wall thickness and were closed at the free end. These tube specimens were received from the vendor fitted at the holder end with stainless-steel sleeves which included a crushable metal inner sleeve to absorb compressive loads due to differences

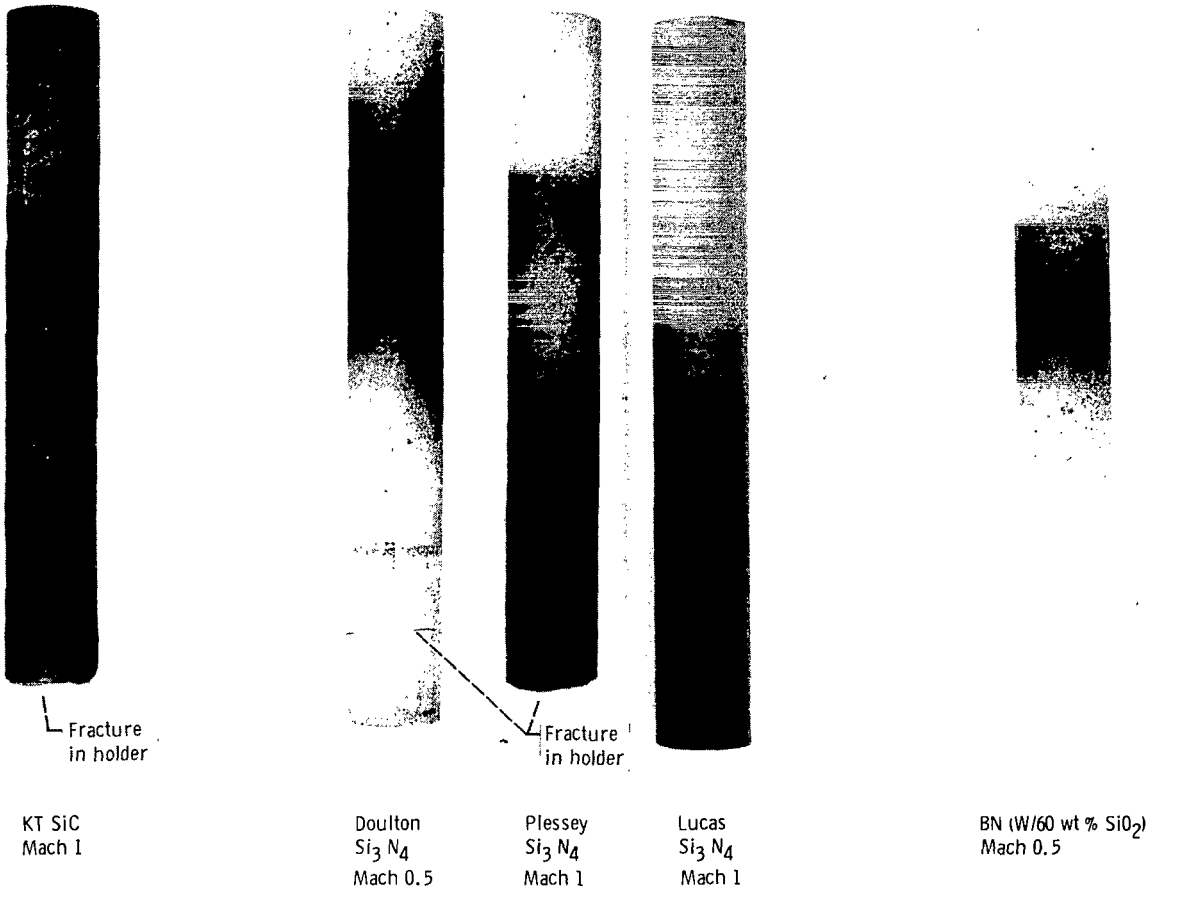
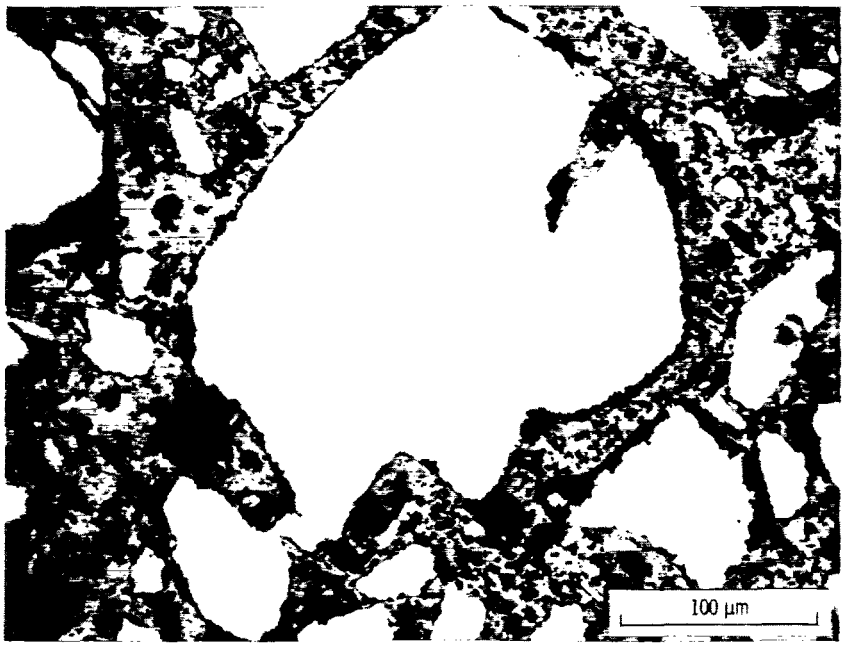


Figure 4. - Materials surviving 120 cycles (10 hr) in simulated gas turbine environment. Test cycle: 5 minutes at 1204° C (2200° F); 3 minutes still air cool.

in thermal expansion. In spite of these fittings, only limited exposures were possible because of the specimens loosening in the holder and coming out of the holder during exposures. However, SiC tube CVD specimens did survive 22- and 60-minute isothermal exposures at Mach 1 and Mach 0.5, respectively, and survived 12 cycles at Mach 0.5. These specimens did not show any signs of cracking or surface degradation. Exposure attempts with four other specimens failed because the specimens loosened in the holder and were lost. Without the holding problem the SiC tube CVD material might well have performed as well as the KT SiC.

Silicon-SiC-carbon composite specimens survived Mach 1 exposures for 1 hour isothermal and for 60 cycles (5 hr). The specimens had no cracks in the hot zone and the 60-cycle specimen showed only slight pitting. However, the 60-cycle specimen was found to have cracked inside the holder. In two subsequent tests at Mach 1, specimens

(a) KT. Gray grains, SiC; white intergranular material, free Si; unetched; X250.



(b) Refrax. White grains, SiC; porous gray intergranular material, - silicon nitride (Si_3N_4) bond; unetched; X250.

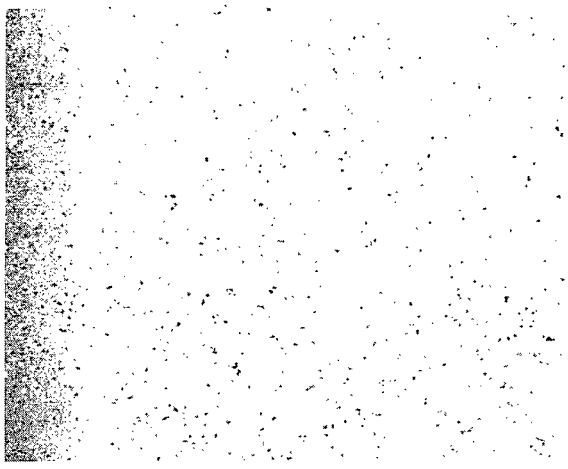
Figure 5. - Microstructures of KT and Refrax types of silicon carbide (SiC).

failed in the eighth cycle at the holder entrance point because of mechanical fatigue due to gas loading. Thus, this material can resist thermal shock and corrosion but is deficient in fatigue strength.

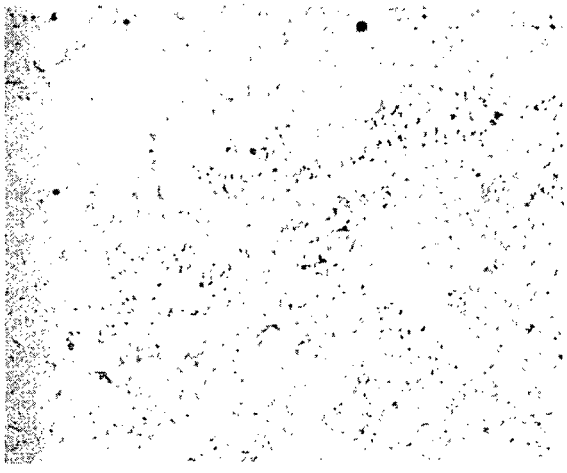
Nitrides

The two very high density forms of Si_3N_4 supplied by Lucas and Plessey withstood all Mach 1 exposures through 120 cycles (10 hr). No cracks or surface deterioration were noted. These specimens are shown in figure 4. The fracture of the Plessey Si_3N_4 specimen inside the holder precluded a weight change measurement. After 120 cycles (10 hr) the Lucas Si_3N_4 had gained only 5.2 milligrams (0.26 mg/cm^2). For 12 cycles (1 hr) the Lucas Si_3N_4 weight gain was 2.5 milligrams (0.13 mg/cm^2) - very similar to that for KT SiC. This result is not surprising since both SiC and Si_3N_4 oxidize to form thin protective films of SiO_2 (ref. 16). The good oxidation resistance of the silicon nitride is reflected by the fact that the 120-cycle (10-hr) weight gain was only slightly more than twice the 12-cycle (1-hr) weight gain. This suggests the formation of a protective silica film which thickens with time leading to lower oxidation rates. The similar microstructures of the high density, fine grained, Lucas Si_3N_4 and Plessey Si_3N_4 are shown in figure 6.

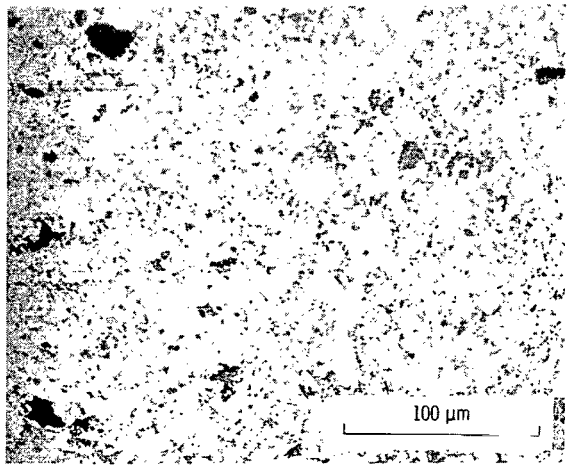
The Doulton Si_3N_4 with 20-percent porosity could withstand only the 1-hour isothermal exposure at Mach 1. When cycling was attempted, the specimen broke at the holder in the second cycle due to mechanical fatigue. At Mach 0.5, however, the Doulton Si_3N_4 survived the 120-cycle exposure (10 hr) with no cracking or surface damage. But the sample had cracked inside the holder as shown in figure 4. This fracture, halfway down in the holder, is felt to be the result of overtightening on installation and not the result of exposure. The microstructure of the Doulton Si_3N_4 is shown in figure 6. Compared to the Lucas high density Si_3N_4, the Doulton Si_3N_4 (20 percent porosity) gained 14 times as much weight for the 120-cycle (10-hr) exposure. This difference is undoubtedly due to the greater surface area of the Doulton Si_3N_4 with a porosity of 20 percent in comparison to the lesser surface area of the almost 100-percent-dense Lucas Si_3N_4. The weight gain for the porous Si_3N_4, although greater than the weight gain for dense Si_3N_4, is not considered to be excessive. The ability of the Doulton Si_3N_4 to survive the Mach 0.5 cycling but not the Mach 1 cycling reflected the difference in the gas loading for the two hot gas velocities. As previously noted, the outer fiber tensile stresses for the rod specimens at the point where the specimen enters the holder were calculated to be approximately 19 meganewtons per square meter (2700 psi) at Mach 1 and approximately 3 meganewtons per square meter (400 psi) at Mach 0.5.



(a) Lucas; porosity, 0.1 percent.



(b) Plessey; porosity, 0.1 percent.



(c) Doulton; porosity, 20 percent.

Figure 6. - Microstructures of Lucas, Plessey, and Doulton types of silicon nitride (Si_3N_4). All unetched; X250.

In the case of the BN materials, neither plain BN nor the BN - 60 weight percent SiO_2 specimens could survive Mach 1 exposures - the BN failing by thermal shock and the BN - 60 weight percent SiO_2 failing mechanically due to gas loading. However, at Mach 0.5, the SiO_2 phase in the BN - 60 weight percent SiO_2 was beneficial in increasing thermal shock resistance. At Mach 0.5, the BN - 60 weight percent SiO_2 survived the 120-cycle exposure (10 hr) with no cracking or apparent surface degradation, while the plain BN again failed by thermal shock. The specimen surviving the 120-cycle exposure is shown in figure 4. However, this BN - 60 weight percent SiO_2 specimen did suffer a rather high weight loss of 13.4 milligrams per square centimeter which contrasts with Lucas Si_3N_4 which gained only a slight amount of weight, 0.26 milligram per square centimeter, as a result of 120-cycle Mach 1 exposure. The weight loss for the BN - 60 weight percent SiO_2 material suggests that the oxidation products are volatile or are lost by spalling. The microstructure of the BN - 60 weight percent SiO_2 material is shown in figure 7.

Figure 7. - Microstructure of boron nitride (BN) - 60 weight percent silicon dioxide (SiO_2) material. Light gray matrix, BN; dark phase, SiO_2; fine light phase, unidentified. Unetched; X250.

Borides and Boride Composite

Both the silicon boride (SiB_6) materials behaved the same at Mach 1 and at Mach 0.5. For both materials thermal shock failures and mechanical failures due to gas loading were noted on initial exposure and no cycling tests were attempted.

The boride composite, zirconium diboride (ZrB_2) - 14 weight percent SiC - 30 weight percent C, could withstand the Mach 1 exposure from the thermal shock standpoint, but it was found to oxidize and spall to such extent that Mach 1 exposure was discontinued after 36 cycles (3 hr). At this point, the ZrB_2 - 14 weight percent SiC - 30 weight percent C specimen had lost 86.2 milligrams per square centimeter and was obviously degraded as shown in figure 8.

Figure 8. - Great material loss for zirconium diboride (ZrB_2) - 14 weight percent silicon carbide (SiC) - 30 weight percent carbon (C) composite specimen by oxidation and spalling resulting from 36-cycle (3 hr) exposure in Mach 1 simulated gas turbine environment. Test cycle: 5 minutes at 1204° C (2200° F); 3 minutes still air cool.

Oxides

The two fused silica materials Silfrax and O.C.F. (Owens Corning Fiberglas) were too weak to sustain the Mach 1 loading and exhibited mechanical failures due to gas loading. At Mach 0.5, the O.C.F. material broke in the hot zone within 3 minutes. This hot zone failure is believed to be due to a low density low strength region in the center of the O.C.F. specimens as reported by the supplier. The Silfrax material, however, survived Mach 0.5 exposures of 1 hour isothermal and of 12 cycles without cracking or damage and failed because of thermal fatigue only after 37 cycles.

At Mach 1 both the Al_2O_3 and the zirconium dioxide (ZrO_2) materials failed by thermal shock immediately on first exposure. At Mach 0.5, Al_2O_3 again failed by thermal shock while ZrO_2 failed by thermal fatigue in only the second cycle.

Mixed Oxides

The low-fired and high-fired alumino-silicates both failed at the first step at Mach 1 and Mach 0.5. Failure mode was thermal shock for the low fired alumino-silicate for both Mach numbers. The high fired alumino-silicate showed mechanical failure due to gas loading at Mach 1, but at Mach 0.5 failure was by thermal shock.

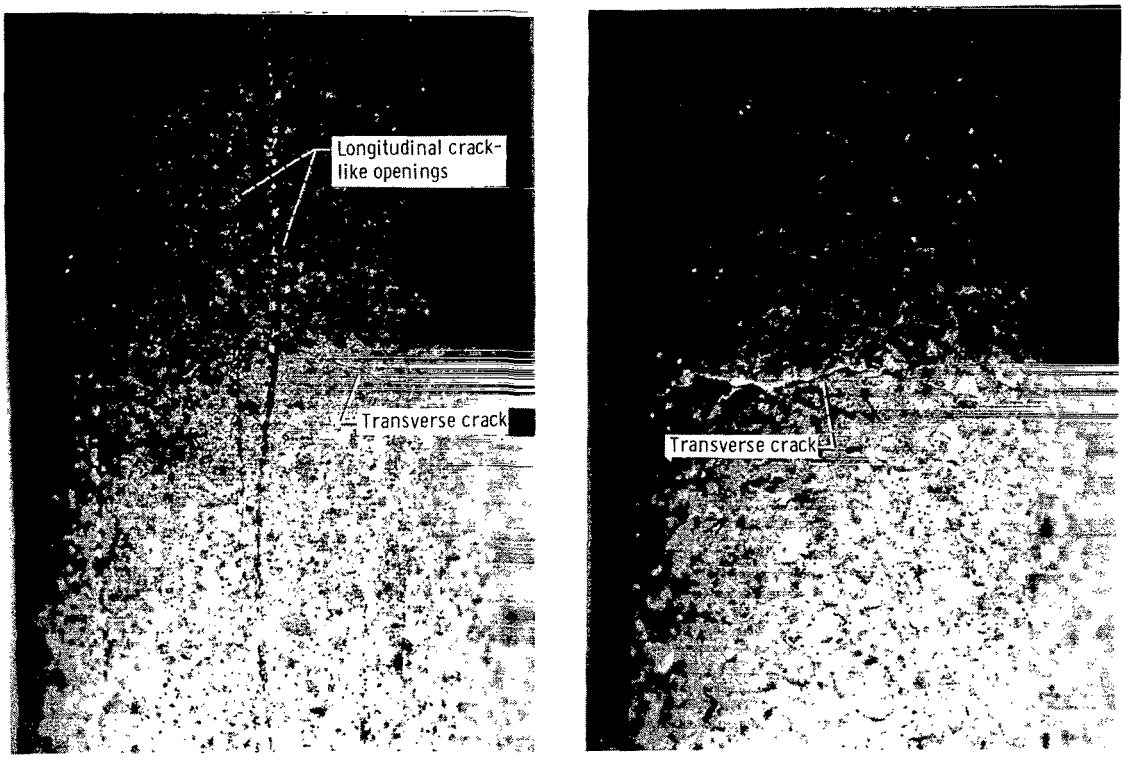
Pyroceram 9606, a magnesia-alumina-silicate, behaved somewhat better than the plain alumino-silicate materials just covered. Pyroceram 9606 survived the 1-hour isothermal exposure at Mach 1 without damage but failed in thermal fatigue at Mach 1 in the second cycle. At Mach 0.5, Pyroceram 9606 failed in thermal fatigue in the 11th cycle. The other Pyroceram, type 9608, exhibited mechanical failure due to gas loading at Mach 1, and it softened and distorted to such a degree in Mach 0.5 exposure that testing was stopped after a 4-minute exposure. The reported softening point for Pyroceram 9608 is given as 1249° C (2280° F) (ref. 4).

Oxide Composites

The BN additions to Al_2O_3 resulted in improved performance for the Al_2O_3-BN composites in comparison to the plain Al_2O_3 material which failed by thermal shock at both Mach 1 and Mach 0.5. At Mach 1, the Al_2O_3 - 15 volume percent BN flake material survived the 1-hour isothermal exposure without cracking, while the Al_2O_3 - 15 volume percent BN fiber material experienced a delayed thermal shock failure. Failure was delayed in the sense that the specimen broke in the hot zone after a 15-second exposure, while, with one exception to be mentioned, all other material thermal shock failures occurred immediately on insertion into the hot gas stream.

In cycling tests at Mach 1, the Al_2O_3 - 15 volume percent BN flake composite

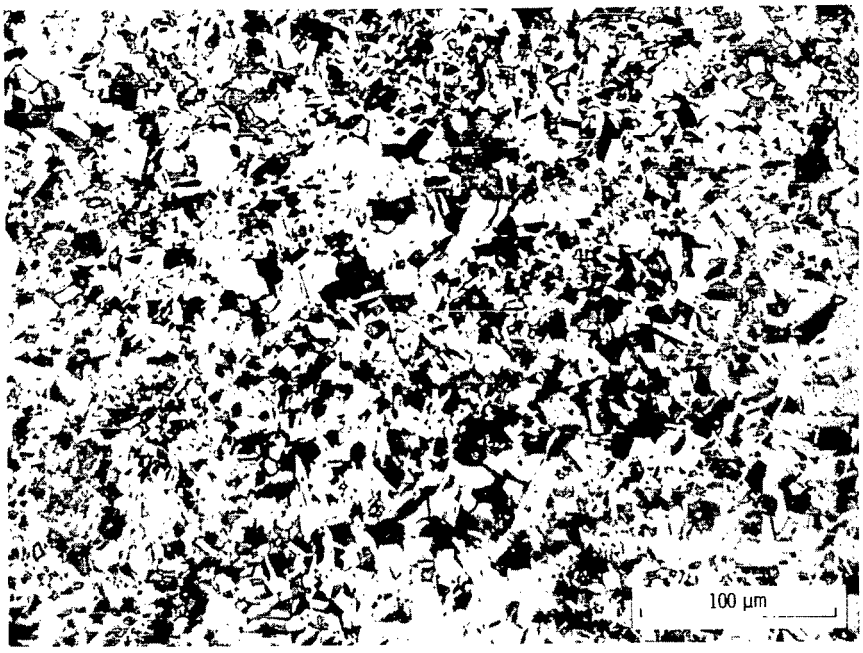
failed by thermal fatigue in the third cycle. And in Mach 0.5 cyclic testing, the Al_2O_3 - 15 volume percent BN flake composite failed in the 9th cycle due to thermal fatigue. However, in another cyclic exposure at Mach 0.5, an Al_2O_3 - 15 volume percent BN flake composite, although cracked, survived a 12-cycle exposure. And, also at Mach 0.5, Al_2O_3 - 15 volume percent BN fiber composites survived the 1-hour isothermal exposure in one test but exhibited a 1-minute delayed thermal shock failure in another test. Both of these specimens which survived were cracked transversely as a result of exposure but remained whole as shown in figure 9. In figure 9, the longitudinal crack-like openings in the Al_2O_3 - 15 volume percent BN fiber specimen and the angular pits in the Al_2O_3 - 15 volume percent BN flake specimen resulted from the loss of BN phase from the surface due to oxidation. The fact that the specimens were able to sustain cracks without complete failure is thought to reflect a crack arresting property of the BN phase, particularly the BN flake. Some metallographic evidence of crack arresting is shown in figures 10 and 11 along with representative microstructures for the Al_2O_3 -



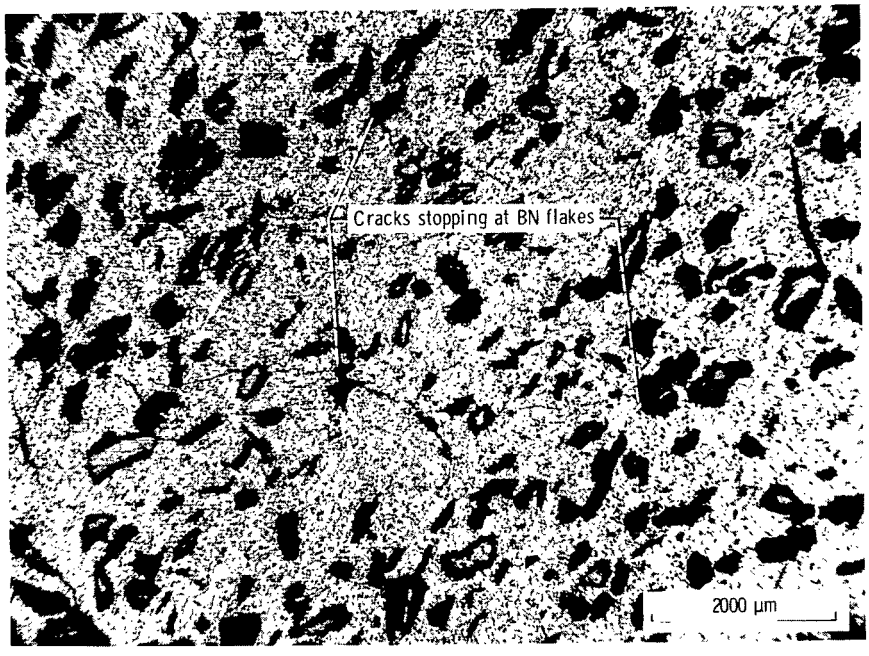
(a) Al_2O_3 - 15 volume percent BN fiber; isothermal; 1 hour.

(b) Al_2O_3 - 15 volume percent BN flake; cyclic (12 cycles = 1 hr).

Figure 9. - Surfaces of aluminum oxide (Al_2O_3) - 15 volume percent boron nitride (BN) fiber and Al_2O_3 - 15 volume percent BN flake specimens sustaining cracks after exposure at 1204° C (2200° F) in Mach 0.5 simulated gas turbine environment. Test cycle: 5 minutes at 1204° C (2200° F); 3 minutes still air cool. X6.

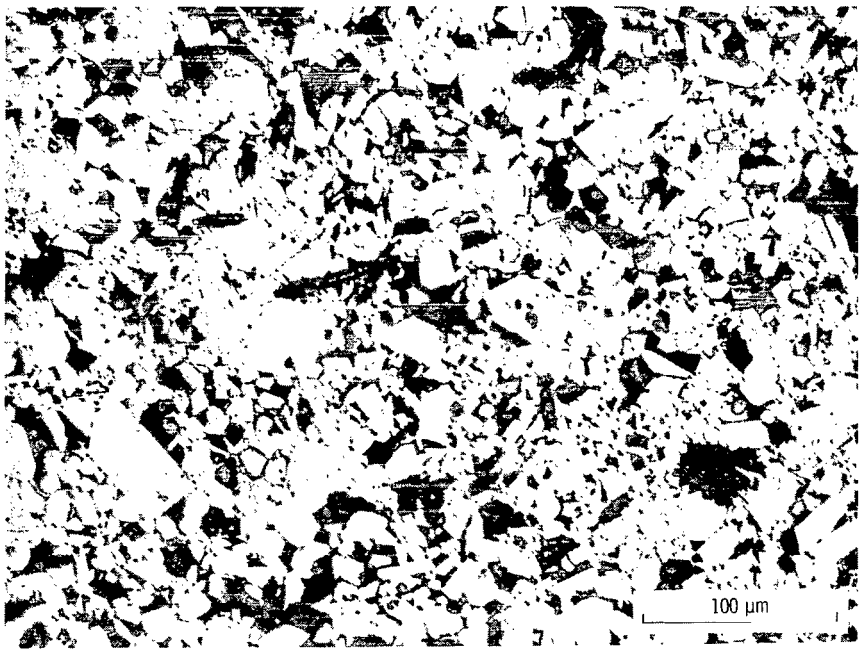


(a) Voids due to grain pullout. X250.

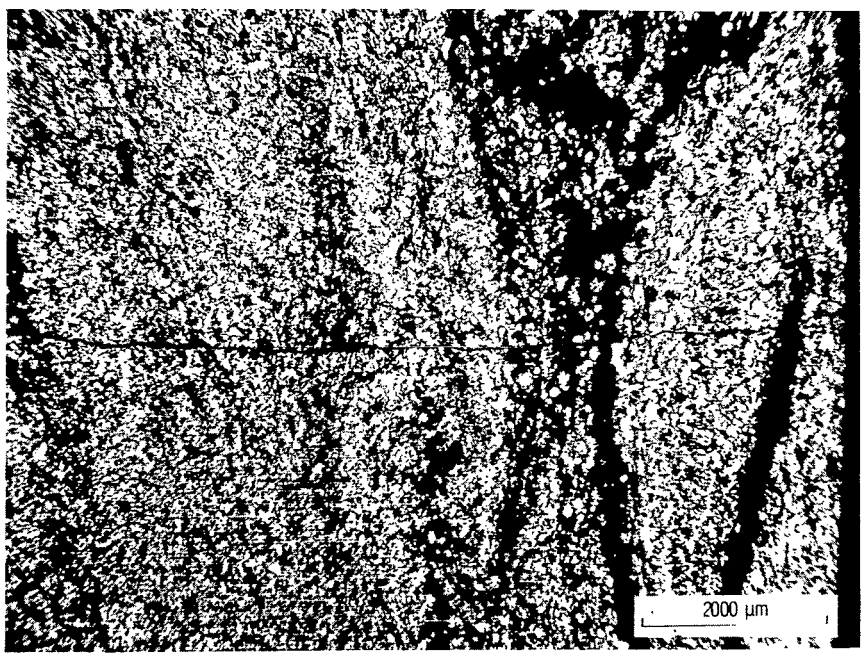


(b) Angular particles are BN flake (some pullout). Note cracks stopping at BN flakes. X12.

Figure 10. - Microstructure of aluminum oxide (Al_2O_3) - 15 volume percent boron nitride (BN) flake material. Unetched.



(a) Voids due to grain pullout. X250.



(b) Vertical voids reflect BN fiber locations. Note crack stopping at void near right edge. X12.

Figure 11. - Microstructure of aluminum oxide (Al_2O_3) - 15 volume percent boron nitride (BN) fiber material. Unetched.

15 volume percent BN flake and Al_2O_3 - 15 volume percent BN fiber composites. In figure 10, some cracks in the matrix of the Al_2O_3 - 15 volume percent BN flake composite can be seen terminating at BN flake locations. And, in figure 11, it appears that the transverse crack has been stopped at the vertical void where BN fiber was located. The absence of the BN phase in the figure 10 and 11 microstructures is due to the loss of the softer BN during metallographic polishing.

It should be recalled that some crack arresting ability was also indicated by the previously noted 15-second delayed thermal shock failure at Mach 1 for the Al_2O_3 - 15 volume percent BN fiber composite and a 1-minute delayed thermal shock failure at Mach 0.5 for this same material.

The magnesium aluminum spinel ($MgAl_2O_4$) - 15 volume percent BN flake composite, which had a porosity of 17 percent, was too weak to survive the Mach 1 gas loading and broke at the holder. At Mach 0.5 this composite showed a delayed thermal shock failure. Although a plain $MgAl_2O_4$ material was not tested, it can be inferred from the results on the alumina-base materials that the BN flake in $MgAl_2O_4$ also acted briefly as a crack arrestor.

SUMMARY OF RESULTS

In this investigation, cylindrical specimens of 23 oxidation resistant, nonmetallic, refractory materials were systematically exposed in a high gas velocity burner simulating a gas turbine engine environment. Isothermal and cyclic tests were conducted at a specimen temperature of 1204° C (2200° F) which resulted from exposure to Mach 1 or Mach 0.5 velocity hot gas streams. Specimens were exposed first to the Mach 1 environment; if they failed here, specimens were then exposed to the Mach 0.5 environment. Test specimen behavior was judged on the basis of failure mode, appearance, and weight change. The results for the materials are summarized in four categories; most promising, good, possible potential, and other.

Most Promising

One type of SiC(KT) and two types of Si_3N_4 (Lucas and Plessey) survived the Mach 1, 1204° C (2200° F), 1-hour isothermal, 12-cycle, and 120-cycle tests without any signs of cracking, surface degradation, or great weight change. Refrax SiC failed at the base during the 116th cycle at Mach 1. The Refrax material was not damaged in the 1-hour isothermal or 12-cycle exposures. The failure in the 116th cycle is believed to have been due to mechanical fatigue.

Good

Although not surviving Mach 1 testing, a lower density form of Si_3N_4 (Doulton) and BN containing 60 weight percent SiO_2 did survive the Mach 0.5, 1204° C (2200° F), 1-hour isothermal, 12-cycle, and 120-cycle tests without any signs of cracking or surface degradation. The weight gain experienced by the porous Doulton Si_3N_4, although greater than the weight gain for the high density Lucas Si_3N_4, is not considered excessive. At Mach 1, the Doulton Si_3N_4 survived the 1-hour isothermal exposure, but failed at the base in the second cycle by mechanical fatigue due to gas loading.

For BN, the SiO_2 phase was apparently beneficial in preventing thermal shock at Mach 0.5, since a plain BN material failed in thermal shock at Mach 0.5 (as well as at Mach 1). At Mach 1, the BN material containing 60 weight percent SiO_2 exhibited mechanical failure due to gas loading on first exposure to the hot gas stream.

Possible Potential

Although short lived, the alumina composite materials showed some interesting behavior in that their performance was better than that of plain alumina which failed immediately by thermal shock on insertion into Mach 1 or Mach 0.5 hot gas streams. The alumina with BN flake material survived the 1-hour isothermal Mach 1 test, but it failed by thermal fatigue in the third cycle at Mach 1. At Mach 0.5 this material survived 12 cycles in one test, and in a second test another sample failed by thermal fatigue during the 9th cycle. We feel this improvement in behavior over the plain alumina material is due to the crack arresting properties of the BN flake second phase. Although not as beneficial, the BN fiber additions slightly delayed thermal shock failures and permitted a 1-hour isothermal exposure at Mach 0.5.

A slightly delayed thermal shock failure was also observed for the $MgAl_2O_4$ material which contained BN flake. This result suggests some crack arresting action in light of what was observed for the alumina base materials.

The silicon - silicon carbide - carbon fiber composite passed the 1-hour Mach 1 isothermal exposure but failed in two tests after seven and eight cycles at Mach 1 in mechanical fatigue due to gas loading. In another test at Mach 1, the sample failed mechanically in the holder but remained in the holder and received 60 thermal cycles. Examination of the hot zone surface of this sample showed only slight pitting but no cracking or great loss of material. Thus, this material appears to resist thermal shock and corrosion but needs greater mechanical strength.

Other

Most of the remaining materials exhibited mechanical failure due to gas loading at Mach 1: both varieties of SiB_6, both varieties of SiO_2, the high fired alumino silicate, and Pyroceram 9608. In some cases, testing these poor performance materials at Mach 0.5 resulted in a change in the failure mode from mechanical failure due to gas loading to thermal shock or thermal fatigue. For example, although SiO_2-Silfrax failed mechanically due to gas loading at Mach 1, the material survived a 1-hour exposure at Mach 0.5 and failed in thermal fatigue in the 37th cycle.

Although the ZrB_2-SiC-C composite was able to withstand the Mach 1 gas loading and cycling, the material suffered from great oxidation weight loss after only 36 cycles.

The SiC tube (CVD) specimens might well have displayed the endurance of the KT SiC but difficulties in holding the specimens resulted in lost specimens and very limited exposures.

CONCLUDING REMARKS

As a result of this screening study some nonmetallic materials with great promise for gas turbine application were identified. Also, the failure modes of the other materials were identified. Thus, the major problem area associated with each material was identified, and this knowledge can serve as a guide for any future efforts to improve a specific material.

Silicon carbide and silicon nitride materials were found to be outstanding in their resistance to 1204° C (2200° F) cyclic exposures to a Mach 1 hot gas stream. These materials certainly warrant efforts to improve their already good properties; for example, surface treatment to remove flaws and/or to impart beneficial residual stresses might be profitable areas of endeavor. Evaluation of these materials in more realistic turbine blade or vane shapes is also warranted. These materials are also the most likely candidates to which to apply toughness improvement techniques such as refined root designs and the incorporation of second phases to prevent catastrophic failure.

A boron nitride material containing 60 weight percent SiO_2, although weak and not able to survive the stress generated by the Mach 1 gas loading, could be cycled at Mach 0.5 for 120 cycles without becoming cracked or otherwise damaged. This behavior might warrant attempts to improve the strength of this material, possibly by density improvements or some oxidation resistant second phase additions.

Although the alumina composite materials were short lived, their behavior was superior to that of plain alumina. This difference is thought to be due to the presence of the BN flake or fiber second phase. The BN second phase is believed to arrest cracks that form quickly in the alumina matrix on first exposure to the hot gas stream. This

demonstrated crack arresting property of these composites suggests that the concept of improving fracture toughness of brittle materials by brittle second phase additions is worth pursuing, that is, by optimizing second phase additions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 22, 1972,
134-03.

REFERENCES

1. Simmons, W. F.; and Wagner, H. J.: Current and Future Usage of Materials in Aircraft Gas Turbine Engines. Rep. DMIC Memo 245, Battelle Memorial Inst. (AS-701371), Feb. 1, 1970.

2. Myers, J. R.; and Geyer, N. M.: Coatings for Superalloys in Gas-Turbine Engines. Materials. J., vol. 1, no. 1, Fall 1969, pp. 18-28.

3. Bradley, E. F.; and Donachie, M. J., Jr.: The Role of Materials in Flight Propulsion Systems. J. Metals, vol. 22, no. 10, Oct. 1970, pp. 25-30.

4. Lynch, J. F.; Ruderer, C. G.; and Duckworth, W. H.: Engineering Properties of Ceramics', Databook to Guide Materials Selection for Structural Application. Battelle Memorial Inst. (AFML-TR-66-52), June 1966.

5. Blakely, T. H.; and Darling, R. F.: The Development of Refractory Nozzle Blades for Use in High-Temperature Gas Turbines. Trans. Northeast Coast Inst. Eng. Shipbuilders, vol. 73, pt. 5, Mar. 1957, pp. 231-252.

6. Glenny, E.; and Taylor, T. A.: The High-Temperature Properties of Ceramics and Cermets. Powder Metallurgy, no. 1/2, 1958, pp. 189-226.

7. Glenny, E.: Ceramics and the Gas Turbine. Special Ceramics 1964. P. Popper, ed., Academic Press, 1965, pp. 301-315.

8. Godfrey, D. J.; and Mitchell, K. W.: Statistical and Practical Approaches to the Development of Design Criteria for Brittle Materials. The Engineer, vol. 224, no. 5836, Dec. 1, 1967, pp. 737-738.

9. Godfrey, D. J.: The Use of Ceramics in High Temperature Engineering. Metals and Materials, vol. 2, no. 10, Oct. 1968, pp. 305-311.

10. Godfrey, D. J.; and Taylor, P. G.: Designing with Brittle Materials. Eng. Mat. Des., vol. 12, no. 9, Sept. 1969, pp. 1339-1342.

11. McLean, A. F.: The Application of Ceramics to the Small Gas Turbine. Paper 70-GT-105, ASME, May 1970.

12. Kingery, W. D.: Factors Affecting Thermal Stress Resistance of Ceramic Materials. J. Am. Ceram. Soc., vol. 38, no. 1, Jan. 1955, pp. 3-15.

13. Johnston, James R.; and Ashbrook, Richard L.: Oxidation and Thermal Fatigue Cracking of Nickel- and Cobalt-Base Alloys in a High Velocity Gas Stream. NASA TN D-5376, 1969.

14. Hoerner, Sighard F.: Fluid-Dynamic Drag. S. F. Hoener, Midland Park, N.J., 1965.

15. Lowell, Carl E.; and Sanders, William A.: Mach 1 Oxidation of Thoriated Nickel Chromium at 1204° C (2200° F). NASA TN D-6562, 1971.

16. Antill, J. E.; and Warburton, J. B.: Active to Passive Transition in the Oxidation of SiC. Corrosion Sci., vol. 11, no. 6, June 1971, pp. 337-342.

17. Evans, A. G.; and Davidge, R. W.: The Strength and Oxidation of Reaction-Sintered Silicon Nitride. J. Materials Sci., vol. 5, 1970, pp. 314-325.

NASA-Langley, 1972 —— 17 E-6918

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546