

HIGH TEMPERATURE APPLICATIONS OF STRUCTURAL CERAMICS

QUARTERLY PROGRESS REPORT

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I. SUMMARY OF PROGRESS TO DATE

1. High Temperature Fracture of Structural Ceramics

Further studies of Tien's Si_3N_4 materials were conducted to obtain critical stress intensity factors and to clarify some inconsistencies in earlier results. Sialon specimens received from Kobayashi were annealed at 1430 °C for 60 hours with little degradation of the specimen. Billets of SiC materials were ordered from Norton and Carborundum. A literature survey of available data on fracture toughness, crack growth behavior, and creep of SiC, Si_3N_4 , and sialon was completed.

2. Crack Growth Mechanism Maps

A preliminary crack growth mechanism map for commercial, hot pressed SiC materials was constructed from published information. The literature survey of fracture and crack growth mechanisms was completed for silicon carbide, silicon nitride, and sialons. A critical review of these mechanisms is now underway.

3. Thermochemical Data

The experimental results obtained this quarter clearly indicate that it is very necessary to first understand the more simple two, three, and four component systems involved before expecting to obtain useful thermochemical data from specimens in complex five and six component systems. Therefore it will be necessary to first examine such systems as Si-Mo- N_2 , Ce-Ta- N_2 , Si-Ta- N_2 , Si-Ce- N_2 , Si-Ce-Ta- N_2 as well as the corresponding metal plus O_2 systems before studying the metal N_2 - O_2 systems.

4. Kinetics of Oxidation

X-ray analysis has been completed on 17 β - Si_3N_4 plus garnet samples before and after high temperature fracture testing. The surface film thickness after the fracture testing did not show any obvious correlation with the past history of the samples. New phases observed after the high temperature fracture testing include β -cristobalite, β - $\text{Y}_2\text{Si}_2\text{O}_7$, mullite, and a well developed but unidentified phase. There was no correlation between the amounts of the different phases and the processing schedule.

II. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

1. High Temperature Fracture of Structural Ceramics (E. R. Fuller, Jr., R. J. Fields, L. Chuck, and D. Harne)

Progress: The first major milestone for this task (literature survey of available data) has been completed. This literature survey of available data on fracture toughness, crack growth, and creep behavior of SiC, Si₃N₄, and sialon materials was carried out using a computerized literature search facility available at NBS. The results of this search are described in an attached draft of this report. In this report, the lists of papers and reports found by a computerized search were winnowed to extract only that literature having immediate bearing on high-temperature applications of structural ceramics. A critical discussion of these papers is included. This report together with the computer output lists of titles is being prepared for publication as an NBS internal report, and will be submitted to DOE following internal review.

Eighty-eight papers having information relevant to this survey were partially or completely copied. The Fracture and Deformation Division at NBS has this collection available for the use of all interested parties. The major conclusions of the survey were:

1. There is a considerably larger body of literature on the relevant mechanical properties of Si₃N₄ than on SiC.
2. Theoretical studies on fracture mechanisms may be the most active area of current research.
3. The areas where research would be particularly fruitful are:
 - a. Effect of atmosphere on creep rate.
 - b. Creep mechanisms in SiC and Reaction bonded Si₃N₄.
 - c. High temperature v-K plots: the effect of temperature, atmosphere, and structure on all three materials.
 - d. Model experiment on cavitation crack growth in grain boundaries.
 - e. Direct measurement of the physical and chemical properties of grain boundary phases.

Crack lengths at the onset of rapid fracture were determined by microscopic examination of the fracture surfaces of the material obtained from Professor Tien of the University of Michigan. This information together with the load-displacement curves obtained in the last quarter allows the critical stress intensity factor, K_{IC} to be calculated. The results are listed in Table I. The toughness so obtained does not appear to correlate with trends in either the fabrication procedures employed at the University of Michigan or the the x-ray results obtained at NBS. The unreasonably high K_{IC} values

recorded for some of these silicon nitrides indicate that rapid creep deformation is occurring and obscuring the true toughness in some samples. To avoid significant creep deformation, the fracture test must be carried out at a more rapid cross-head speed. However, it is necessary to pre-crack the specimen prior to these rapid tests. A series of tests on Tien's materials are now being performed on pre-cracked specimens to eliminate the effect of creep on toughness in order to check the correlation between a material's composition, fabrication history, and its mechanical properties.

There is some evidence that long time anneals in air greatly improve the mechanical properties of sialon material. To investigate this possibility, one of Kobayashi's sialon materials ($Z=1$) was aged at 1430 °C for 60 hours to see if it could withstand 1000 hours at this temperature. The oxidation that occurred was not significantly greater than that which occurred in 2 hours at 1500 °C, so it appears that this sialon will remain relatively stable during long time anneals at 1430 °C.

Billets of Crystar, NC 203, and NC 435 were ordered from Norton and billets of Alpha SiC and reaction sintered SiC were ordered from Carborundum.

Plans: Having considered the results of the literature survey, attention will be centered on testing silicon carbide as this material shows excellent combination of creep resistance, crack growth resistance, and toughness. The work on Tien's silicon nitrides will be finished and the results will be communicated to him. Kobayashi's sialons will be tested with and without a 100 hour anneal to see if the effect of heat treatment is as beneficial as preliminary work by other investigators indicate it to be.

Table I

Spec No.	Thickness	Width	Crack Length	Fracture Load	Crit. Stress Intensity*	Fabrication Notes (1)
20-5	3.03 mm	3.44 mm	2.86 mm	5.2 Kg	18.0 MPa(m) ^{1/2}	20 w/o YAG+Pt, HP, PHT
4-5	3.23	4.46	2.63	25.4	14.6	10 w/o YAG, S, HP
17-4	3.22	3.63	2.95	5.6	14.3	10 w/o YAG+Pt, HP, PHT
16-5	3.27	4.37	2.50	25.7	14.1	10 w/o YAG ⁺ , HP
2-4	3.21	4.88	2.86	24.8	12.4	10 w/o YAG+Pt, HP
9-6	2.81	3.94	2.94	6.78	11.2	10 w/o YAG+Pt, HP, PHT
22-4	3.19	4.54	2.95	15.0	10.8	20 w/o YAG, HP, PHT
11-4	3.06	3.75	2.15	13.2	9.8	10 w/o YAG+Pt, HP, PHT
1-5	3.16	4.71	1.65	37.2	9.7	10 w/o YAG, HP, PHT
8-5	3.04	3.63	1.23	20.0	7.8	10 w/o YAG+Pt, S, HP, PH
3-4	3.32	4.41	1.27	27.7	6.5	10 w/o YAG, HP

* These values are high due to creep effects.

+ YAG added as crystalline garnet.

(1) S = sintered, HP = hot pressed, PHT = post heat treated.

2. Crack Growth Mechanism Maps (R. J. Fields and E. R. Fuller, Jr.)

Progress: The first major milestone of this task (compilation of data and construction of crack growth mechanism maps) has been completed. The available crack growth data and fracture toughness data for all types of silicon carbide, silicon nitride, and sialon materials have been collected and are discussed in the attached draft of this literature survey. The greatest amount of data is for hot-pressed silicon nitride, followed by hot-pressed silicon carbide. Crack growth mechanism maps for these two materials have been constructed using the data in Table II and are presented in Figs. 1 and 2.

The purpose of these preliminary maps was to determine areas of fracture behavior in which research was needed and for which research would be most fruitful. The construction of these maps for NC 203 silicon carbide and HS 130 silicon nitride was beneficial in that regard. First, it is clear for both silicon carbide and silicon nitride that more crack growth behavior needs to be examined at higher temperatures (>1400 °C) and at lower crack velocities ($<10^{-8}$ m/s). In the case of silicon carbide, this work should also be carried out at lower temperatures (<1000 °C). Secondly, K_{IC} needs to be measured at higher temperatures as it is still changing rapidly for silicon nitride even at the highest temperatures for which it has been measured. There is some evidence in silicon carbide that there is a minimum K_I below which there is no crack growth. This possibility should be investigated further in both materials. The existence of an intergranular crack growth mechanism change (brittle to viscous) has largely been inferred from gross mechanical behavior and a few isolated microstructural studies. The boundary between mechanisms should be investigated in much more detail to prove the existence of the purported mechanisms. From the map for NC 203, the mechanism change occurs between 1200 and 1300 °C at lower crack velocities.

The literature survey for the second major milestone of this task (i.e., literature survey and critical review of crack growth mechanisms in structural ceramics) has been completed and a draft is attached. The formal report is being prepared.

Plans: Complete the critical review of fracture and crack growth mechanisms in structural ceramics. This review will focus on three main mechanisms in crack growth: 1) diffusional crack growth; 2) crack growth by viscous flow; and 3) lattice trapping and stress corrosion cracking. Data from Task 1 will be analyzed to generate v - K diagrams and crack growth mechanism maps. In light of the preliminary map for SiC, crack growth in NC 203 will be investigated below 1000 and above 1400 °C. Also, microstructural analyses will be made on specimens broken at 1200 and at 1300 °C to verify the existence of the possible mechanism change.

TABLE II

Silicon Nitride (HS 130), tested in air				Silicon Carbide (NB203), tested in air			
Temperature (°C)	Velocity (m/s)	K_I (MPa \sqrt{m})	Reference	Temperature (°C)	Vel. (m/s)	K_I (MPa \sqrt{m})	Reference
1400	10^{-2}	7.8	1	1400	10^{-2}	2.5	1
	10^{-4}	5.0			10^{-4}	2.1	
	10^{-6}	3.1			10^{-6}	1.7	
1350	10^{-2}	9.5	1	1300	10^{-8}	1.4	1
	10^{-4}	6.0			10^{-4}	4.2	
	10^{-6}	3.7			10^{-6}	3.0	
1300	10^{-2}	9.1	2	1100	10^{-8}	2.2	2
	10^{-4}	7.4			10^{-4}	5.0	
	10^{-6}	4.7			10^{-6}	4.1	
1250	10^{-2}	6.8	2	1000	10^{-8}	3.3	2
	10^{-4}	6.4			10^{-4}	5.2	
	10^{-6}	5.6			10^{-6}	4.5	
1200	10^{-2}	5.7	2		10^{-8}	4.2	2
	10^{-4}	5.5			10^{-10}	3.7	
	10^{-6}	5.1					
Temperature (°C)	Velocity (m/s)	K_I (MPa \sqrt{m})	Reference	Temperature (°C)	Vel. (m/s)	K_{IC} (MPa \sqrt{m})	Reference
1350	10^{-6}	12.0	2	1500	4	4	2
				1400	4.6	4.6	2
1300	9.5	4.3	2	1300	4.3	4.3	2
1200	6.0	4.6	2	1250	4.6	4.6	2
1000	5.1	4.3	2	1200	4.3	4.3	2
		5.0	2	1100	5.0	5.0	2
		6.4	2	700	6.4	6.4	2
		6.0	2	25	6.0	6.0	2

Ref.

1. Evans, A.G. and Lange, F.F., *J. Matl. Sci.* **10**, p. 1659, (1975).
2. Henshall, J.L., Rowcliffe, D.J., and Edington, J.W., *J. Amer. Cer. Soc.*, **62**, p. 36, (1979).

Ref.: Evans, A.G. and S. M. Wiederhorn, *J. of Matl. Sci.* **9**, p. 270, (1974).

Figure 1

CRACK GROWTH MECHANISM MAP

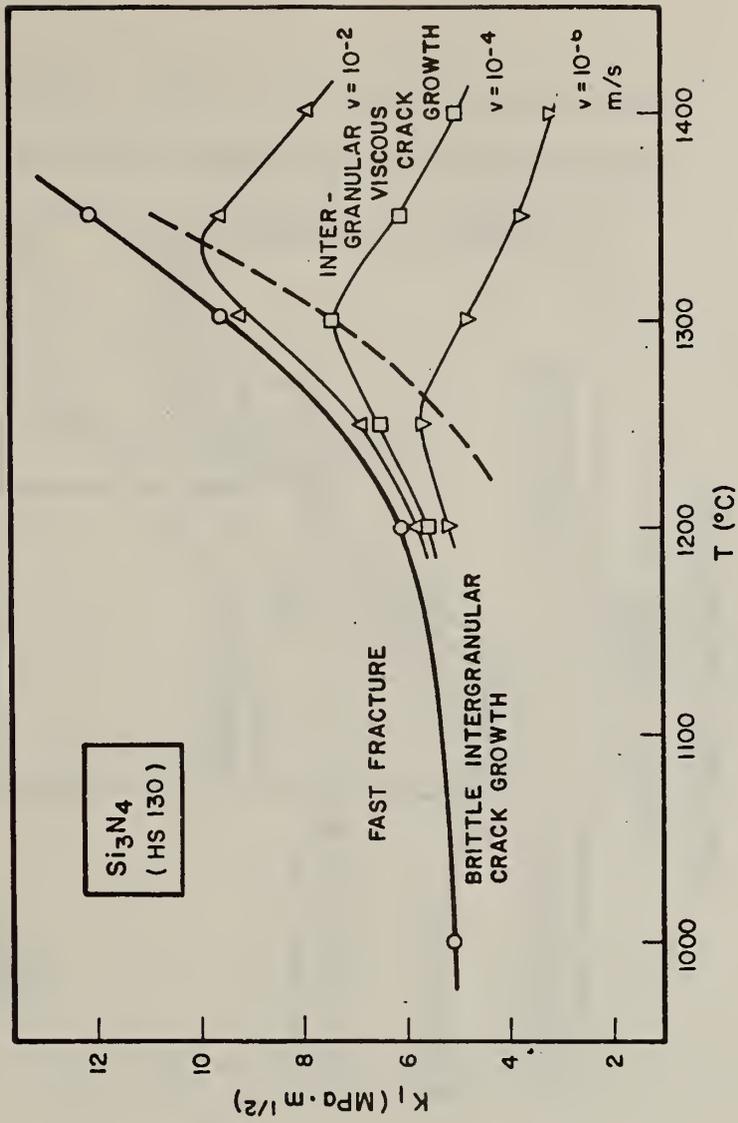
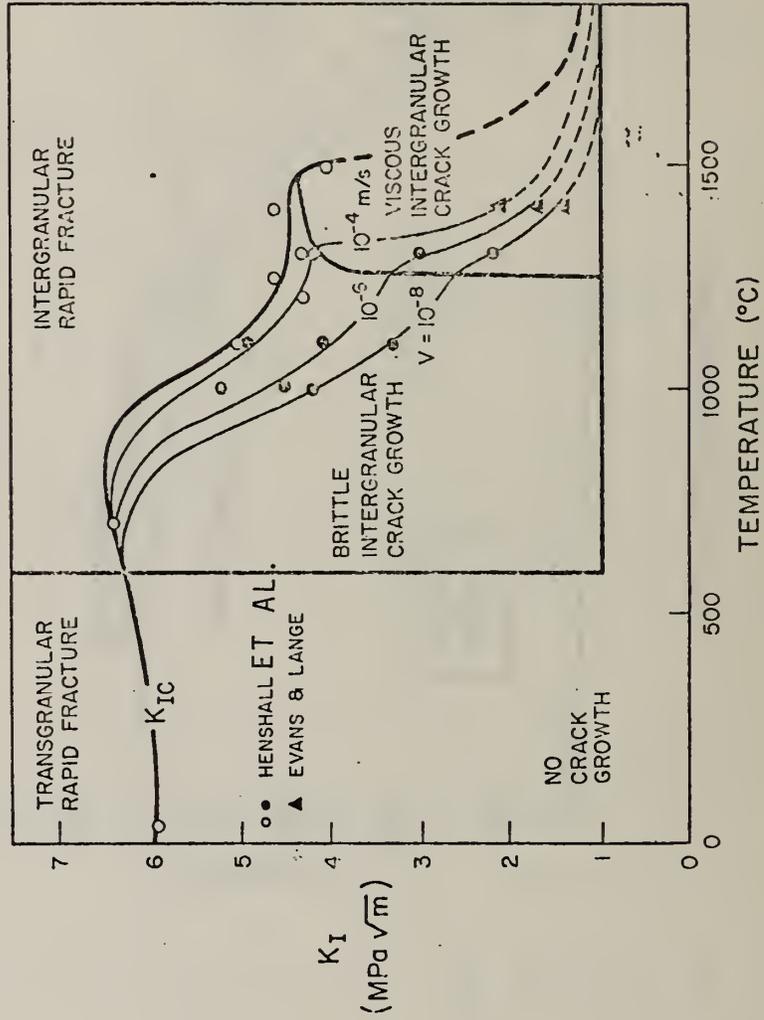


Figure 2
 CRACK GROWTH MECHANISM MAP

SILICON CARBIDE (NC 203)
 IN AIR



DRAFT

LITERATURE SURVEY OF THE HIGH-TEMPERATURE CREEP
AND FRACTURE PROPERTIES OF SILICON NITRIDE,
SILICON CARBIDE AND SIALONS

John S. Nadeau

1. Objectives of Survey:

1.1 To obtain all available literature on subcritical crack-growth and creep at high temperatures for the compounds SiC, Si₃N₄ and Sialons.

1.2 To extract from the literature all information on V-K plots (crack velocity versus stress intensity) for SiC, Si₃N₄ and sialon, for the purpose of constructing fracture mechanism maps.

1.3 To obtain all relevant literature on fracture mechanisms in ceramics at high temperatures.

1.4 To provide a critical evaluation of the literature on high temperature creep and fracture of SiC, Si₃N₄ and sialons, in order to identify areas where additional experiments would be fruitful or where the understanding of mechanisms is lacking.

2. Scope of Survey:

The following abstract sources were used:

- 2.1 Compendex (Engineering Index) - 1970 to present.
- 2.2 Chemical Abstracts - 1970 to present.
- 2.3 National Technical Information Service (NTIS) - 1964 to present.
- 2.4 Ceramic Abstracts 1970 to present.
- 2.5 An Annotated Bibliography on Silicon Nitride for Structural Applications: D.Messier and M.M. Murphy, MCIC Battelle, Columbus, 1979. 1961 to 1978.

The first three sources were surveyed by computer, while the remaining two were surveyed directly. Reference lists in individual articles and reports were also examined to see if they contained references not otherwise identified.

3. Survey Method:

In the computer searches, the computer was asked to identify all references to SiC, Si₃N₄, sialons, creep, fracture or crack growth. A typical result, that from Chemical Abstracts, was as follows:

Table 1. Results of Computer Search in Chemical Abstracts.

Description	Number of Items
1. Silicon Carbide	2148
2. Silicon Nitride	1161
3. Sialon	6
4. Crack growth or fracture or creep	7254
5. (1+1)	41
6. (2+4)	38
7. (3+4)	0

Thus the last three items, constituting 79 papers, contained information on both the materials and the properties of interest. The computer was then directed to print the titles of the 79 articles so identified.

The list of identified items from the three computer sources contained a total of 375 references as shown below:

Table 2. Items identified by Computer Search.

NTIS	135
Compendex	161
Chemical Abstracts	<u>79</u>
Total	375

Unfortunately, there was no way of rejecting from one source items that had already been identified in another source. Thus, there were many cases where a single article was identified by

all three sources. This was also true of the two non-computer sources and it became incumbent upon the searcher to recognize articles that had been previously examined.

The raw materials for this literature survey thus consisted of five lists of titles, the three computer produced lists, the annotated bibliography of Messier and Murphy (1,386 entries) and the list obtained by searching the index of Ceramic Abstracts (44 items). These lists were then examined and winnowed to yield the titles of articles fitting the criteria of this search. The resulting winnowed lists were then examined directly by going to the library shelves. Those items which upon direct examination were found to have information that satisfied the criteria of this survey were partially or completely copied.

4. Results of the Survey:

The main product of the survey is a collection of copies of titles, abstracts, data and entire papers and reports, fitting the criteria of the search. A list of the titles of these items is appended to this report. They are comprised as follows:

Table 3. Number of published articles fully or partly copied or on hand.*

	<u>Articles and Reports</u>
Si ₃ N ₄	51
SiC	18
Sialons	3
Fracture Mechanisms	<u>16</u>
Total	88

* Items containing information on both SiC and Si₃N₄ are counted twice.

According to Table 3, silicon nitride has received much more attention than silicon carbide (within the framework of this study). This attention has been fairly recent. Table 4 shows that the output of papers on the high temperature creep and fracture of silicon carbide has been more or less constant for the past decade, averaging about one to two papers per year. Similar papers on silicon nitride began to appear in 1972, and the output quickly increased to ten per year in 1975. It appears that the production of papers on silicon nitride is now falling, but the data for 1980 are incomplete.

The publications in which papers relevant to this study have appeared are shown in Table 5. The major journals are Journal of the American Ceramic Society and Journal of Materials Science. Papers on fracture mechanisms tend to be in the metallurgical literature rather than in the ceramics literature. All of the

articles are in the English language except for four in German. Two articles in Japanese were rejected from the search because of the searcher's inability to deal with that language. The penalty for confining the search essentially to English appears to be negligible, since most non-English speaking workers seem to publish some of their results in English.

Table 4. Dates of Copied Articles:

<u>Date</u>	<u>Si₃N₄*</u>	<u>SiC</u>	<u>Sialon</u>	<u>Mechanisms</u>
Before 1970	-	2	-	-
1970	-	-	-	-
1971	-	2	-	-
1972	1	-	-	-
1973	6	1	-	-
1974	4	-	-	-
1975	10	4	1	3
1976	5	2	-	1
1977	5	3	-	-
1978	9	1	-	4
1979	8	1	-	2
1980 ⁺	<u>3</u>	<u>2</u>	<u>2</u>	<u>6</u>
Total	51	18	3	16

⁺Incomplete

*Articles having information on both SiC and Si₃N₄ are counted twice.

Table 5. Sources of Published Articles Having Data Relevant
to this Survey:

<u>Publication:</u>	<u>Materials:</u>			
	<u>Si₃N₄</u>	<u>SiC</u>	<u>Sialon</u>	<u>Mechanisms</u>
J. Amer. Ceram Soc.	13	6	-	-
Bull. Amer. Ceram. Soc.	6	1	-	-
J. Mater. Sci.	14	3	1	-
Powder Met. Int.	3	3	1	-
Ber. Deut. Keram. Ges.	4	1	-	-
Met. Trans. A.I.M.E.	1	-	-	2
Special Ceramics	1	-	-	-
Matls. Sci. and Eng.	-	1	-	-
Symposia	6	3	-	-
Acta Met.	-	-	-	5
Phil. Mag.	-	-	-	1
Reports and unpubl. man.	3	1	1	6
Scripta Met.	-	-	-	2

5. Critical Evaluation of the Available Literature:

The purpose of this evaluation is to summarize the amount and type of information that is available, to identify areas in which more complete knowledge would aid the understanding of creep and fracture mechanisms, and to examine critically the prevailing views on high temperature failure mechanisms.

It must be pointed out, however, that the materials of interest in this survey are still under development. There are several methods of producing them and a host of possible compositions. Thus, in making generalizations about them, it is usually necessary to treat broad classes, and only occasionally is it possible to refer to a particular material with a well-characterized structure and set of properties. A simple nomenclature that seems to pervade the literature defines the following materials:

Silicon Nitride

- A. Reaction-bonded (RBSN) - parts are made by cold-pressing or injection-molding silicon powder and reacting it with nitrogen at approximately 1200°C.
- B. Hot-pressed (HPSN) - billets are made by hot-pressing Si_3N_4 powder with a few percent of MgO , Al_2O_3 or other oxides as sintering aids.
- C. Sintered - this is a fairly recent development of G.T.E. laboratories. The material contains 6% Y_2O_3 as a sintering aid.

Silicon Carbide

- A. Hot-pressed (HPSC) - sintering aids, such as boron or oxides, are required.
- B. Sintered (SSC) - boron and carbon additions permit pressureless sintering.
- C. Direct-bonded (DBSC) ("KT" or "Refel" are trade names) - a porous, partially sintered body of SiC is infiltrated with molten Si and reacted with carbon.

Sialons

These materials can be made by hot-pressing or sintering, and a wide range of compositions is possible. The starting materials are Si_3N_4 , Al_2O_3 , AlN and sintering aids such as MgO

5.1 Creep

The creep test is a simple and direct measure of the rate of deformation of a specimen under stress. The "creep strength" is usually the controlling engineering property of materials used at high temperatures. The two objectives of creep testing are to answer the questions:

- a) What is the life expectancy of a structure under load? and
- b) What is the deformation mechanism?

Both questions can usually be answered by a combination of the simple creep test, a well established analytical method and an

elaborate theory rooted in absolute reaction-rate theory. The analytical method, in its simplest form, employs two ways of plotting creep data. The first plot (on logarithmic axes), of creep-rate versus stress with temperature as a parameter, usually gives straight lines, the slopes of which are related to the deformation mechanism. These plots also clearly display the relative creep resistance of different materials and are therefore an indispensable part of engineering design.

The second plot, of creep rate versus reciprocal temperature with stress as the parameter, reveals the activation energy of the rate-controlling process and thereby helps to identify the deformation mechanism.

The analysis of creep data is a time-honoured activity and has resulted in good empirical methods for characterizing the effects of temperature, stress and some of the microstructural variables, such as grain-size and porosity, on creep-rate. The theory of creep has evolved steadily over the past thirty years and has become more complex and detailed as it tried to embrace the growing wealth of experimental data. It has provided mechanistic models for the processes of creep and analytical methods for testing a set of creep-data to identify the mechanisms. It is when the theories are validated by comparison with experiments, that certain misgivings arise. The validation process involves comparison of measured thermodynamic quantities, such as activation-

enthalpies and activation-volumes, and of course creep-rates, with those predicted by calculation from a model. The basic physical mechanism is seldom observed directly, it is only perceived through its thermodynamic properties. The model may be too simple or even wrong and still have approximately the correct thermodynamic behaviour. For the materials of this report, the analysis is even more awkward, because the basic thermodynamic properties (activation-enthalpies and volumes for self-diffusion) are not known. Furthermore, while the models assume essentially homogeneous microscopic processes, direct observations seem to reveal heterogeneous, macroscopic phenomena. Nevertheless, careful metallographic studies in conjunction with creep-tests have developed a consensus that creep in silicon nitride (particularly HPSN) is controlled by a glassy phase in the grain boundaries. This has led to elaborate efforts to remove or to crystallize the glassy phase and to devise theoretical models for creep in materials that deform in this manner. There has been some success in both areas, although it would appear that success in the first might render the second unnecessary.

The actual mechanism of creep in HPSN (and to varying degrees in the other materials covered by this report) is rather complex. The creep deformation may be due largely to extensive cracking and cavity formation, processes that are difficult to model. The creep rate is almost ten times faster in tension than in compression

(in HPSN), suggesting the need for tensile stress to open cavities. The creep rate of HPSN is about five times faster in air than in argon or vacuum, which is very difficult to reconcile with a bulk process. (Sialons also creep faster in air than in argon.) No tests of the effects of environment on the creep of SiC were discovered in this survey. Since HPSC has good creep-resistance, this might be a fruitful area for research.

The following generalizations can be made about creep in the materials considered in this study.

A. The order of creep resistance is roughly as follows:

1. HPSC
2. Sintered SiC
3. RBSN
4. Sialons
5. HPSN - Y_2O_3
6. HPSN - MgO

However, there is considerable variation among materials of a particular class.

B. The deformation mechanism involves boundary sliding,

cavitation and possibly a small amount of plastic

deformation at triple points.

C. The rate of creep in some of these materials is sensi-

tive to environment.

5.2 Subcritical Crack-Growth.

One of the early disappointments with the silicon compounds was that they were not as refractory as expected. The strength fell precipitously in the temperature range 1200° to 1400°C . Even then it was recognized that the weakening was probably due to an intergranular phase. Now it is widely accepted that the drop in strength as well as the low creep resistance of some grades of these materials is due to subcritical crack-growth (SCG) in the boundary phase. As a result, the relatively new techniques of fracture mechanics have been mobilized to study this phenomenon. The objectives of such studies are to develop an understanding of this type of subcritical crack-growth and to use the analytical failure-prediction methods that fracture mechanics provides.

Fracture mechanics tests yield two types of data, V-K plots and K_{IC} values. The first is just a plot of crack velocity versus stress intensity, usually on logarithmic co-ordinates, while the second is the stress intensity at which fast fracture occurs. Table 6 shows the number of papers having data of this kind:

Table 6. Number of Papers in which High Temperature Fracture Mechanics Measurements have been Reported:

<u>Material</u>	<u>V-K</u>	<u>K_{IC}</u>
HPSN	6	13
RBSN	-	4
HPSC	4	4
SSC	3*	6
Sialons	2	2

*Three attempts, no SCG observed.

The preponderance of data has been obtained from HS-130, which is a hot-pressed silicon nitride containing about 5% MgO. No V-K plots for RBSN were found. Since the strength of this material is insensitive to temperature, it may be relatively immune to subcritical crack-growth. The same appears to be true of sintered silicon carbide, in which several attempts were made but no SCG was found.

The effects of environment on SCG were reported only in one study on two grades of silicon carbide, HPSC and DBSC. Subcritical crack-growth was observed on the hot-pressed material at temperatures below 1000°C. It was not observed in the direct-bonded material. The effects of environment on SCG appear to have been neglected and may provide useful information about the fracture mechanisms. The fact that the creep-rate in silicon

nitride is faster in air than in inert environments, and that creep may be no more than generalized cracking, suggests a process of environment-assisted crack-growth.

One of the objectives of this survey was to identify the data suitable for the construction of fracture mechanism maps. Although Table 6 suggests that a substantial amount of data is available, it is obtained from a large number of different materials, including numerous examples of HPSN. The data are generally adequate only for very rudimentary maps. The real test of what is available and what is needed will have to await the mapping process itself.

5.3. Mechanisms of Subcritical Crack-Growth.

The phenomenon of grain boundary separation by cavity formation was recognized about twenty years ago. It occurs in many materials, metals and ceramics. Several contributing phenomena are believed to be involved. One is simply the ability of grain boundaries to attract second phases, and another is the related ability of boundaries to act as paths for rapid diffusion.

The presence of second phases on grain boundaries, when the second phase is weak or undeformable, gives rise to two phenomena, cracking and void formation. If the second phase is weak or has a weak interface with the matrix, cracks may form even though the matrix is quite ductile. If the second phase is simply undeformable,

the plastic deformation in the surrounding grains may result in microvoid formation around the second phase particles.

The most persistent and invidious effect of grain boundary phases in ceramics is that they tend to soften at a lower temperature than the grains. This permits shear stresses between grains to cause sliding (relative displacement of neighboring grains), and tensile stresses to cause cavitation in the boundary phase. Grain boundary sliding can only be accommodated if the grains themselves deform, and in the silicon-based ceramics this is very difficult. In fact, the grains remain essentially rigid and wedge each other apart at the corners, producing cavities.

Even when grain boundary phases are absent, when the grains are directly bonded to each other, a sort of sliding is possible. The boundary material itself, constituting only of only a few unit cells on each side of the interface, is less resistant to shear stresses at high temperatures than are the grain interiors. Thus, even the elimination of second phases on grain boundaries does not remove the possibility of sliding and cavitation. This has led to heroic measures to control microstructure in refractory metals. These include directional solidification, to avoid having any grain boundaries normal to the maximum tensile stress, and single crystal structures, to avoid having grain boundaries at all. The silicon ceramics do not appear to be amenable to these measures as yet, although the possibility of fabricating oriented components

by vapour deposition should probably receive more attention.

The objective of theoretical treatments of the deformation of ceramics at high temperatures is to develop constitutive equations, i.e. equations that describe internal phenomena, such as strain and strain rate, in terms of external conditions such as stress and temperature. Success in this endeavour has two benefits. The first is that it gives the theoretician satisfaction in knowing that he has probably modelled the system correctly. The second and more practical benefit is that it gives working relationships that can be used to predict behaviour under varied conditions.

Two types of models are used to account for the growth of cavities on grain boundaries in materials. One relies on the flow of matter away from the cavity by diffusion, and the other relies on the viscous flow of a semi-liquid grain boundary phase. The diffusive growth of cavities and cracks has been studied for the longest time. Early attempts to understand this phenomenon were based on simple one-cavity models, and these have been steadily elaborated through the years. They now incorporate the concepts of fracture mechanics to model the stress field and the effects of interactions between cavities. In a recent statistical model (Evans and Rana), an attempt has been made to include the probability of occurrence of boundary cavities and a mechanism for linking them to form cracks.

These approaches to the problem of cavity growth by diffusive flow appear to be based on sound principles and to be evolving toward a widely acceptable theory. They do, however, appear to suffer from a scarcity of model experiments against which to test their constitutive relations. There appears to be ground here for fruitful interaction between experimenters and theoreticians.

The growth of cavities and cracks by viscous flow appears to be even more difficult to model than the diffusive-flow case. However, attempts have been made to calculate the constitutive relations (Evans and Rana, Evans), and to do model experiments (Raj and Dang). The calculations are difficult to verify, because much of the needed experimental information, such as viscosity and its temperature dependence, and the distribution of void nuclei, are simply lacking. Even the distribution of the viscous phase is known only in a few cases, and these are the poorest materials, in which the viscous phase is relatively thick. Thus, a great need in this area is a more detailed knowledge of the physical and chemical properties of grain boundary phases. A further need is for model experiments in which fracture mechanisms are carefully examined.

6. Summary of the Survey:

6.1 Eighty-eight papers having information relevant to this survey were partially or completely copied. There were three times as many papers on Si_3N_4 as on SiC and only three papers on Sialons. Theoretical studies on fracture mechanisms may be the most active area of current research.

6.2 The following appear to be areas where research would be particularly fruitful:

- A. Effect of atmosphere on creep rate.
- B. Creep mechanisms in silicon carbide and RBSN.
- C. High temperature V-K plots: the effects of temperature, atmosphere and structure in all three materials.
- D. Model experiments on cavitation crack growth in grain boundaries.
- E. Direct measurement of the physical and chemical properties of grain boundary phases.

Appendix:

A list of titles of items relevant to this report. A set of partial or complete copies is supplied with the report.

Silicon Nitride

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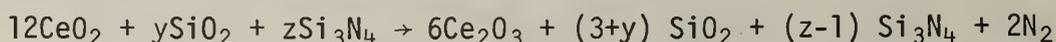
3. Thermochemical Data (R. S. Roth, J. L. Waring, H. S. Parker, and T. Negas)

Progress: Work was continued with Si_3N_4 related compositions in accordance with subtasks 3A, 3B. As mentioned previously, to minimize volatility and to maintain chemical composition, a radio frequency heated apparatus was constructed to heat specimens at pressures up to 300 psi. A Mo crucible and cover with an appropriate size hole for pyrometer measurements served as the susceptor. This apparatus was calibrated against the melting point of platinum (1773 °C). A small piece of high purity platinum was placed on single crystal sapphire and the fusion characteristics were observed. An appropriate temperature correction was applied for the system. Since Si_3N_4 is known to be volatile at high temperatures, a series of experiments were to be conducted to determine the weight loss at various pressures of gas (95% N_2 :5% H_2). A commercially prepared crucible of Si_3N_4 was placed in the Mo susceptor. The susceptor was covered with a Mo lid. The test sample pellet of Si_3N_4 was placed on another pellet of the same composition in the Si_3N_4 crucible. The apparatus was heated to 1784 °C for 1 hour at 15 psig of 95% N_2 :5% H_2 . In this experiment the bottom surface of the Si_3N_4 crucible was in contact with the Mo susceptor and apparently reacted catastrophically.

It is possible that the 15 psig pressure was not sufficient to inhibit the Si_3N_4 decomposition to $\text{Si} + \text{N}_2$ and the Si reacted with the Mo susceptor. It is more likely, however, that Si_3N_4 and Mo do not form an equilibrium join in the ternary system Si-Mo- N_2 . Instead, MoSi_2 , Mo_3Si_5 , etc. are in equilibrium with N_2 and modest over-pressure of gas would merely enhance the equilibrium reaction between Si_3N_4 and Mo. It is desirable, therefore, to reduce the amount of contact between the Si_3N_4 specimens and the Mo crucible.

From the above, it was decided to forego the lower pressure experiment and redo the experiment at a higher pressure of 200 psi. For this experiment a Si_3N_4 test pellet was weighed and placed on a similar Si_3N_4 pellet was served as a setter. The setter in turn was placed on a Mo ring in the crucible. The material was heated to about 1800 °C/200 psi of gas (95% N_2 :5% H_2) for one hour and the weight loss was found to be about 1.92%. On the basis of these results it was concluded that this is a feasible testing technique, since volatility and container reaction problems were minimized. Si_3N_4 mixed with other materials can now be heated with some hope of successfully understanding the thermochemical reactions occurring in the specimens.

Most sintering aids and inherent impurities lead to poor mechanical/thermal properties of finished Si_3N_4 as secondary phases are formed during processing. Although contributing to densification these cause mechanical problems when the ceramic undergoes in-service oxidation as such reactions produce phase changes and large positive molar volume changes. Cerium oxide is an excellent densification aid. However, complex Ce^{3+} silicates develop during fabrication via the reduction process:



During service, reduced cerium silicates oxidize to $CeO_2 + SiO_2$. Associated volume changes contribute to loss of mechanical integrity, therefore, at least for this example, it would be desirable to maintain the Ce^{3+} state within an oxidizing environment. This can be accomplished by the addition of Ta_2O_5 which fixes or locks in Ce^{3+} . Additionally, pure Ta_2O_5 does not reduce under fabrication conditions and, therefore, might be expected to interact only with cerium oxide and not the Si_3N_4 .

Two compositions, $6Si_3N_4:CeO_2:Ta_2O_5$ and $3Si_3N_4:CeTa_3O_9$, were weighed, mixed, and pellets were calcined at $1350^\circ C$ for 20 hours in $95\%N_2:5\%H_2$. These pellets were buried in powder of the same composition. The composition $6Si_3N_4:CeO_2:Ta_2O_5$ previously calcined at $1350^\circ C$ (see Table 1 for x-ray diffraction data) was pressed into pellets for high temperature heat treatments. The experimental procedure used was the same as outlined previously. In this experiment both the test pellet and the setter melted and reacted with the Mo setter when heated to $1800^\circ C$ in 200 psi of $95\%N_2:5\%H_2$ for one hour. The process was repeated at about $1725^\circ C$ for one hour at 200 psi $95\%N_2:5\%H_2$. The resulting test pellet probably had undergone a small amount of melting as it was distorted and adhered to the setter. Although the distorted pellet was only 1 mm thick it was extremely hard and resistant to fracture.

Another pellet of the $1350^\circ C$ calcine mixture was heated similarly to about $1650^\circ C$ for one hour in $95\%N_2:5\%H_2$. The reaction product was a reasonably dense, well formed pellet which did not appear to be affected by the Mo environment. The x-ray pattern of this material (Table 1) showed a new phase + $\beta-Si_3N_4$.

A test pellet and setter of $3Si_3N_4:CeTa_2O_9$ previously calcined at $1350^\circ C$ were heated similarly to about $1700^\circ C$ for one hour at 200 psi $95\%N_2:5\%H_2$. The material when examined was found to be melted. A small portion of this $1350^\circ C$ calcine material was reheated in a small Mo tube to about $1550^\circ C$ for an hour in 200 psi $95\%N_2:5\%H_2$. The x-ray diffraction powder pattern appeared to be essentially single phase. This unknown phase appears to be the same as that found to occur in the $6Si_3N_4:CeO_2:Ta_2O_5$ specimen heated to $1650^\circ C$. The major d-spacings of this phase apparently can be indexed on a hexagonal unit cell related to TaN. From these results it would appear that the Si_3N_4 reacted with the Mo tube and that the remaining $CeTa_3O_9$ perovskite was chemically reacted with N_2 to form a (Ce,Ta)N solid solution.

Two compositions, $75Si_3N_4:12.5Y_2O_3:12.5Cr_2O_3$ and $75Si_3N_4:12.25La_2O_3:12.5Cr_2O_3$ were weighed, mixed, and calcined at $1350^\circ C$ - 16 hours in 1 atm of $95\%N_2:5\%H_2$. The x-ray diffraction data for these compositions is given in Table 1.

Table 1. Experimental Data for the System $\text{Si}_3\text{N}_4\text{-CeO}_2\text{-Ta}_2\text{O}_5$.

Starting Material	Temp. °C	Time hr	Environment	X-ray Diffraction Results
$3\text{Si}_3\text{N}_4:\text{CeTa}_3\text{O}_9$	1350	20	95% N_2 :5% H_2 (1 atm)	perovskite + (Ce,Ta)N solid solution + $\alpha\text{-Si}_3\text{N}_4$
	1350 1550	20 1	95% N_2 :5% H_2 (13.6 atm)	(Ce,Ta)N solid solution
$6\text{Si}_3\text{N}_4:\text{CeO}_2:\text{Ta}_2\text{O}_5$	1350	20	95% N_2 :5% H_2 (1 atm)	$\alpha\text{-Si}_3\text{N}_4$ + (Ce,Ta)N solid solution
	1350 1650	20 1	95% N_2 :5% H_2 (13.6 atm)	(Ce,Ta)N solid solution + $\beta\text{-Si}_3\text{N}_4$
	1350 1725	20 1	95% N_2 :5% H_2 (13.6 atm)	$\beta\text{-Si}_3\text{N}_4$ + (Ce,Ta)N solid solution
$75\text{Si}_3\text{N}_4:12.5\text{Y}_2\text{O}_3:$ $12.5\text{Cr}_2\text{O}_3$	1350	20	95% N_2 :5% H_2 (1 atm)	α + perovskite
$75\text{Si}_3\text{N}_4:12.5\text{La}_2\text{O}_3:$ $12.5\text{Cr}_2\text{O}_3$	1350	20	95% N_2 :5% H_2 (1 atm)	α + perovskite

From the results of the current quarter it is apparent that it is very necessary to first understand the more simple two, three, and four component systems involved before expecting to obtain useful thermochemical data from specimens in the complex five and six-component systems. Therefore it will be necessary to first examine such systems as Si-Mo-N₂, Ce-Ta-N₂, Si-Ta-N₂, Si-Ce-N₂, Si-Ce-Ta-N₂ as well as the corresponding metal plus O₂ systems before studying the metal-N₂-O₂ systems.

Two commercially available forms of Si₃N₄ were obtained for these studies. The first was found to be a mixture of α-Si₃N₄ and β-Si₃N₄. The second was amorphous by x-ray diffraction. In an attempt to determine the polytype(s) which form when this material crystallizes, amorphous Si₃N₄ samples were heated to various temperatures. Some of the samples contained impurities to serve as "mineralizers" to enhance crystallization. The results of these studies are given in Table 2. From these results it can be seen that additional work will be necessary to properly characterize this amorphous material.

Plans: (1) Study thermochemical reactions in the systems Si-Mo-N₂ and Ce-Ta-N₂ to obtain knowledge of thermochemical relations between test specimens, container, and atmosphere. (2) Study high temperature thermochemical reactions in the calcined Si₃N₄-La₂O₃-Cr₂O₃ and Si₃N₄-Y₂O₃-Cr₂O₃ specimens. (3) Continue study of formation of crystalline Si₃N₄ in molten Si and silicon alloys to determine the thermochemistry of the α and β phases.

Table 2. Experimental data for amorphous Si_3N_4 .

Starting Material	Temp. °C	Time hr	Environment	X-ray Diffraction Results
Amorphous Si_3N_4 + 5 wt % $\text{LiOH}\cdot\text{H}_2\text{O}$	700	16	N_2	amorphous
	700	143	air	SiO_2 + $\text{Li}_2\text{Si}_2\text{O}_5$ + Li_2SiO_3 + unknown
Amorphous Si_3N_4	1375	1	sealed Mo tube	α - Si_3N_4 + Mo (silicides)
	500	20	95% N_2 :5% H_2	amorphous
	600	19	" "	"
	700	20	" "	"
	800	20	" "	"
	900	69	" "	"
	1000	21	" "	"
	1375	64	" "	crystalite

Task 4. Kinetics of Oxidation (T. Hahn)

Progress:

X-ray analysis has been completed on 17 β - Si_3N_4 plus garnet samples prepared by R. Muller of Professor Tien's group at the University of Michigan. The analyses of the "as-received" samples were made on a portion of the sample that was cut off the original billet obtained in preparing the high temperature test specimens. After the samples were fracture tested at 1300 °C in air (total exposure at temperature approximately one hour), they were re-analyzed to determine what new phases formed due to the extra heat treatment. This analysis was limited to the surface of the samples in order to preserve the samples for future SEM analysis. Thus the results reported are for the surface film which may not be characteristic of the bulk sample. The change of the β - Si_3N_4 peak intensities as compared to the as-received samples is a rough indication of the film thickness. Grading of the film thickness is as follows:

Thickest	V13
	V2, V5, V11, V22, V23
	V6, V14, -V17, V20
	V3, V8, V9
	V16
Thinnest	V1, V4, V10

From Table 4.1, which list the composition, presintering heat treatment, hot pressing temperature, and post sintering heat treatment for each of the samples, there was no obvious correlation between the past history of the samples and the film thickness.

The various phases observed in each sample are also listed in Table 4.1. The major phase observed in the "as-received" samples was β - Si_3N_4 , as expected, while a distinct garnet phase was only observed in a few of the samples. A glassy phase was also optically observed on a few of the samples. A number of the samples contained some other phases; however, their x-ray pattern was not intense enough for positive identification.

After the 1300 °C fracture test in air a number of new phases were positively identified. These phases along with their relative amounts are listed in Table 4.1. These amounts were determined by the intensity of the x-ray pattern relative to the same phase in the other samples of this set. The phases that were positively identified include β - Si_3N_4 , β -cristobalite, β - $\text{Y}_2\text{Si}_2\text{O}_7$ (garnet), mullite, and a well developed but as yet unidentified phase. In general the samples with 20 wt. % garnet, as opposed to the samples with 10 wt. % garnet, contained more of the β - $\text{Y}_2\text{Si}_2\text{O}_7$ garnet phase, mullite, and the unknown phase. There was, however, no obvious correlation between the amounts of the different phases and the reported processing schedule supplied with the samples by R. Muller of the University of Michigan. After further analysis of these samples, the surface layer will be removed by polishing to better determine the bulk composition of these samples.

Plans:

Work will continue on the high temperature furnace for exposing the samples at elevated temperatures and the high temperature x-ray furnace.

Table 4.1. Phase composition of β - Si_3N_4 plus Garnet samples.

Sample Number	Sample Preparation		Heat Treatment	As Received β - Si_3N_4 plus			Phases Observed After High Temperature Strength Test				
	Composition β - Si_3N_4 Plus	Presintered		Hot Pressed	$\text{Y}_3\text{Al}_5\text{O}_{12}$	Glass	Other	Relative Amount to Other Samples Tested	Tested	Strength	
							β - Si_3N_4	β -Cristobalite	β - $\text{Y}_2\text{Si}_2\text{O}_7$	Mullite	Unknown
V1	10 wt% Garnet		30 min. at 1850 °C				D	A	B	B	A
V2	10 wt% Garnet		30 min. at 1750 °C			x	B	D	O	B	D
V3	10 wt% Garnet		(30 min. at 1750 °C)				C	C	B	A	B
V4	10 wt% Garnet + Pt	30 min. at 1700 °C in BN	(30 min. at 1750 °C)		x		D	C	B	B	B
V5	10 wt% Garnet		(30 min. at 1750 °C)		x		B	C	C	B	A
V6	10 wt% Garnet + Pt	30 min. at 1600 °C	(30 min. at 1750 °C)			x	B	B	A	A	B
V8	10 wt% Garnet + Pt	30 min. at 1750 °C	(1 hr. at 1750 °C)			x	C	C	B	C	B
V9	10 wt% Garnet + Pt		(1 hr. at 1750 °C)				C	C	A	B	B
V10	10 wt% Garnet + Pt		1 hr. at 1800 °C				D	B	A	B	A
V11	10 wt% Garnet + Pt		1 hr. at 1750 °C				B	B	A	A	B
V13	10 wt% Garnet + Pt		(1 hr. at 1800 °C)				A	B	O	B	C
V14	10 wt% Garnet As Crystal		(1 hr. at 1800 °C)				C	B	O	B	A
V16	10 wt% Garnet As Crystal		(1 hr. at 1800 °C)				D	D	A	C	C
V17	10 wt% Garnet + Pt		(1 hr. at 1800 °C)			x	B	A	O	B	A
V20	20% Garnet + Pt		(1 hr. at 1800 °C)			x	B	C	C	D	B
V 22	20% Garnet		(1 hr. at 1800 °C)				B	C	D	D	D
V 23	20% Garnet		(1 hr. at 1800 °C)			x	B	D	C	D	D

