HIGH TEMPERATURE APPLICATIONS OF STRUCTURAL CERAMICS

QUARTERLY PROGRESS REPORT

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INTRODUCTION

The achievement of higher efficiency thermochemical engines and heat recovery systems requires the availability of high temperature, high performance structural materials. Structural ceramics such as SiC, Si_3N_4 and certain Al_2O_3-Si_3N_4 combinations have received particular attention for these applications due to their basic characteristics of good strengths coupled with good corrosion and thermal shock resistances. Even with these positive attributes, improved reliabilities and extended lifetimes under service conditions are necessary for structural ceramics to gain industrial acceptance and use. The problems are mechanical and/or chemical in nature and are enhanced by the fact that these materials are subjected to high temperatures, reactive environments and extreme thermal gradients.

With an objective of improved performance for heat engine/heat recovery applications the NBS program on structural ceramics addresses these problems through the determination of the critical factors which influence mechanical and microstructural behavior. The activities of the program are grouped under four major subtasks with each designed to develop key data, associated test methods and companion predictive models. The status of the subtasks are detailed in the following sections.

NBS 5.2.10(A) - HIGH TEMPERATURE FRACTURE OF STRUCTURAL CERAMICS

RESULTS FROM PRIOR QUARTERS

Four-point bend tests on notched bars of Si_5AlON_7 were completed and the results compared with previous work on a yttria-doped SiC (NCX34) and with literature values for Si_3N_4. Reduced scale testing rigs using

SiC were manufactured to test small billets of experimental materials. Fifteen different compositions of Si_3N_4 + Y.A.G. materials obtained from Professor Tien of University of Michigan using these rigs were tested at 1300 °C in order to avoid oxidation. Further studies of Tien's Si_3N_4 were conducted to ascertain critical stress intensity factors and to clarify some inconsistencies in earlier results. A literature survey of available data on fracture toughness, crack growth behavior and creep properties of SiC, Si_3N_4 and sialon was completed. Four-point bending tests under constant displacement rate were performed on several SiC and sialon specimens. For α-SiC tested in air, the results showed little oxidation and high resistance to slow crack growth up to 1000 °C. For sialon specimens ($Si_{6-z}Al_zO_zN_{8-z}$), it was found that as z increases, the susceptibility to crack growth and oxidation decreases. The asymptotic behavior of the stress intensity factor as a function of crack length for 4-point bending at small and large crack lengths was investigated in more detail. This work is useful for future numerical solution schemes.

DISCUSSION OF CURRENT ACTIVITIES

Experimental Work

High temperature four-point bending tests under constant displacement rate condition have been performed on <u>notched</u> SiC specimens. Several ways of initiating cracks failed due to the high degree of hardness before a special chevron notch was successfully introduced into the beam specimens. This produces a short, stable crack growth period. However, the crack branches shortly into two subcracks which we speculate may be due to shearing effects. Techniques to avoid this problem are currently under investigation.

A paper entitled "Effects of Composition on the Fracture Toughness and Slow Crack Growth of Sialon" is being prepared and will be presented at the International Symposium on Fracture Mechanics of Ceramics, University Park, Pennsylvania July 17, 1981.

Theoretical Work

The P-Δ charts generated from the Instron testing machine have been digitized and thus can be input directly to the Cromenco computer. A computer program has been developed which converts the P-Δ curves into V-K crack growth law. Conversely, given the V-K relationship, say $V = AK^n$, it is possible to predict the P-Δ curve. Regarding a and c as the dependent variables and Δ as independent variable, we obtain a system of first order nonlinear ordinary differential equations for the unknowns c and a as follows:

$$\frac{dc}{d\Delta} = \frac{2AB}{E\dot{\Delta}} Y(a)^{n+2} \frac{\Delta^2}{c^n}$$

$$\frac{da}{d\Delta} = \left(\frac{A}{\dot{\Delta}}\right)\frac{\Delta^n}{c^n} Y(a)^n$$

With the initial conditions: $C = C_o$, $a = a_o$, when $\Delta = 0$, a computer program for solving this system of coupled equations has been developed which successfully predicts P-Δ curve for any given A and n. A paper addressing this problem will be prepared shortly.

NBS 5.2.10(B) - CRACK GROWTH MECHANISM MAPS

RESULTS FROM PRIOR QUARTERS

Preliminary maps for Si_3N_4 have been drawn. A computer program for automatically drawing maps from K-V data has been written. Data for SiC has been collected with the aim of constructing a crack growth mechanism map. An evaluation of K_{IC} was made because its definition by ASTM E-399 conflicts with common usage in the ceramic community. A preliminary crack growth mechanism map for a commercial hot pressed SiC was constructed from published information. The literature survey of fracture and crack growth mechanisms was completed for SiC, Si_3N_4 and sialon.

A crack growth model based on diffusion mechanisms was developed. The model entails a grain-boundary crack growing in steady state due to applied stress by stress assisted surface and grain-boundary diffusion. By further assuming the grain on either side of the crack behaves elastically, the model predicts a unique K-V relationship and a threshold K below which no crack growth will take place. A comparison of this prediction to a set of creep crack growth data on sialon at 1400 °C showed good agreement.

DISCUSSION OF CURRENT ACTIVITIES

The paper entitled "A diffusive crack growth model for creep fracture" (NBSIR 81-2255) was submitted to J. Am. Ceram. Soc. on 4/10/81 for publication.

An investigation into the energy release rate on this crack growth model was also included in the report. The results show that J is the total amount of energy consumption rate which consists of a portion consumed in the creation of new crack surfaces and the remaining portion dissipated in the matter transport processes.

The theoretical prediction of V-K functional relationship based on diffusion-controlled crack growth is being converted into K-T space in order for the future data to fit in the diffusive crack growth area of the mechanism maps.

NBS-5.2.10(C) - MICROSTRUCTURE AND PHASE ALTERATION

RESULTS FROM PRIOR QUARTERS

X-ray analysis of sialon samples having the formula

$$Si_{6-z}Al_zO_zN_{8-z} \quad (z = 1 \text{ to } 3)$$

showed that the lattice parameters varied linearly with z. Surface analysis of β-Si_3N_4 and garnet samples indicated the presence of β-Si_3N_4, β-cristobalite, β-$Y_2Si_2O_7$ and mullite.

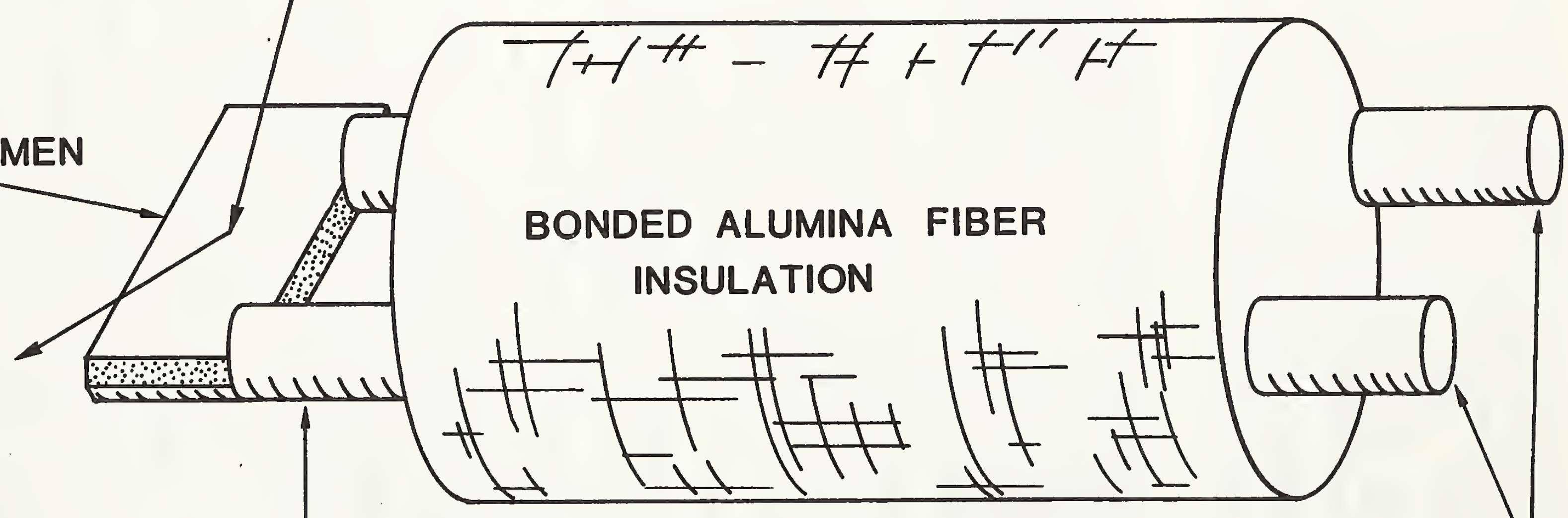
X-ray analysis were performed on various "as-received" commercial silicon carbide ceramics. Carborundum's α-SiC was shown to be composed of both 6H and 4H polytypes; Norton's recrystallized SiC, to be composed exclusively of the 6H polytype; Norton's NC203, to contain the 6H polytype, WC, a trace of Al_2O_3 and a trace of an unidentified phase; and Norton's NC403, to have the 6H polytype, free Si and a well-developed, but unidentified phase.

DISCUSSION OF CURRENT ACTIVITIES

Preliminary x-ray diffraction data for NC-203 silicon carbide fracture specimens were analyzed. These specimens had been oxidized at temperatures from 1200 to 1500 °C for 1 week. An unoxidized specimen showed predominantly alpha silicon carbide with a lesser amount of tungsten carbide. The development of a tridymite surface layer was evident on specimens oxidized at 1200, 1300 and 1400 °C. At 1500 °C, a glassy phase was observed to be present along with the tridymite in the surface layer.

A literature survey covering the period from 1977 to the present was begun to assemble high-temperature thermal and mechanical data for SiC and SiO_2 (tridymite). This data will be used to estimate internal stresses generated in the SiC substrate and in the oxide layer during high-temperature oxidation of SiC. In addition, the previous studies related to the oxidation kinetics of SiC are being surveyed.

A concept for a high-temperature x-ray furnace is illustrated by the schematic shown in the attached figure. By using the specimen as its own heating element, it is anticipated that the problems with heat loss and temperature uncertainty in the specimen will be reduced, if not eliminated. Electrical power will be coupled to the specimen through a pair of low-resistance, siliconized SiC rods. Temperature will be measured by locating a thermocouple junction (not shown) adjacent to, but not touching, the bottom of the specimen. In addition to the cylinder of bonded alumina fiber insulation separating the specimen and the power input ends of the SiC rods, a second hollow cylinder (not shown) of similar insulation will surround the specimen with the exception of a window for the x-ray beam. Finally, the furnace will be enclosed in a gas-tight, water-cooled metal chamber similar to a previous NBS design.


X-RAY BEAM
SiC SPECIMEN
BONDED ALUMINA FIBER
INSULATION
SILICONIZED SiC ROD
ELECTRICAL POWER
INPUT

RESULTS FROM PRIOR QUARTERS

Various alternate systems were considered for an apparatus in which to conduct high temperature mechanical tests under gaseous environments of fossil fuel combustion products. The following decisions have been made concerning the system and its operation:

1. Heating System - $MoSi_2$ element electric furnace has been chosen. A gas furnace was initially considered. Due to limitations on possible gaseous environments, this system was rejected. The electric furnace decided upon will allow a much wider range of gas compositions to be employed.
2. Gaseous Environment System - Provided by gas mixing from compressed tank supply. Steam will be obtained either from a steam generator or by bubbling gas composition through water at a specific temperature to give the desired vapor pressure.
3. Loading System - A choice will be made between either an existing Instron displacement rate controlled machine or a hydraulic ram coupled to a load cell and specially assembled for the present purpose.
4. Specimen Configuration - Single-edge notched bars will be tested in 3 or 4 point flexural loading. These specimens will be 25 to 50 mm long and will be used to determine K_{IC}. Double torsion specimen 15 x 20 x 2 up to 25 x 72 x 2 mm will be used for crack velocity measurements.

DISCUSSION OF CURRENT ACTIVITIES

Design of the apparatus for high-temperature mechanical testing in simulated fossil fuel environments was presented at the DoE program review on May 8, 1981. The apparatus consisted of a gas-tight, high-temperature (1600 °C) electrically heated furnace with attachment fixtures to allow application of a load with a universal testing machine. Simulated environments will be gaseous mixtures of steam and of up to four component gases (typically, N_2, O_2, CO_2, and SO_2). Procurement of the two major components of apparatus (the gas mixing system and the furnace with temperature controller) is in process.

Specimen configurations proposed last quarter for obtaining high-temperature crack growth and fracture data were the single edge notched bar (SENB) in bending and the double torsion (DT) configuration. Both specimens have their advantages and disadvantages, but their main disadvantages from a testing viewpoint are that the SENB specimen is difficult to precrack in a stable manner and the DT specimen has a highly curved crack front making the analysis somewhat questionable. Although we will utilize both of these specimens, an alternate testing configuration is being evaluated for possible usage to obtain high-temperature crack growth and fracture data. It is the double cleavage drilled-compression (DCDC) specimen used by Janssen to obtain crack growth data of glass at room temperature in various liquid environments. The specimen, a compression bar with a center drilled hole, precracks stably initiating two symmetric cleavage cracks. A stress-intensity-factor solution for this specimen has been given by Janssen using a finite element code for his specimen dimensions. We are currently examining stress-intensity-factor solutions for other specimen dimensions in an effort to determine if there is a regime of constant K behavior for this specimen.