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MATERIALS SUPPORT FOR HITAF

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OBJECTIVE

The primary objective of this work is to compare the mechanical performance of structural ceramic materials which are being proposed for use in the air heater of a coal fired high temperature advanced furnace (HITAF) for power generation. The effort is focused on providing preliminary evaluations of key mechanical properties required of ceramic materials for this application. The critical properties studied include fast fracture strength distribution at room temperature and two elevated temperatures, any trends in slow crack growth (SCG) susceptibility at elevated temperatures, and preliminary creep behavior. In addition residual fast fracture strength of a limited number of specimens corroded in a coal ash environment will be evaluated at a later stage in the project.

BACKGROUND

The present project is a small part of a large effort under the Combustion 2000 program designed to develop an advanced, high-efficiency coal fired power generation system. Two project teams, led by United Technologies Research Center (UTRC) and Foster Wheeler Development Corporation (FWD) respectively, are working in Phase I to design a system which will meet several specific requirements set by the Department of Energy (DOE) for a future commercial power plant.^{1,2} The commercial plant must meet the following criteria:

- Have a minimum conversion efficiency of 47%
- Emit NO_x less than 0.15 lb per million BTU of fuel input
- Emit SO_x less than 0.15 lb per million BTU of fuel input
- Emit particulates less than 0.0075 lb per million BTU of fuel input
- Produce only benign solid wastes
- Operate initially on coal and natural gas, with coal providing at least 65% of heat input, and ultimately coal must provide 95% of the heat input
- Be able to operate with a wide variety of American coals
- Generate electricity at a cost 10% lower than today's systems.

MASTER

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Both teams developing systems according to these guidelines have recognized that in order to achieve the goals it will be necessary to include a ceramic air heater in the design for two important reasons. First, because the air heater will be subjected to combustion gas inlet temperatures in excess of 1100°C, existing alloys cannot be used, whereas ceramic alternatives can be. Second, the coal burning atmosphere is very corrosive and few alloys perform well in this environment, even at temperatures much lower than 1100°C.

Therefore, this present task was established as a support effort to provide preliminary data for design of a ceramic air heater. Presently, the material database for structural ceramics being considered for this application is very limited, and in order to address the special design needs connected with ceramic materials, certain key mechanical properties must be determined. At low temperatures there is concern about the low toughness of ceramics and large variation in strength. At high temperatures there is concern about slow crack growth which will eventually lead to failure, and creep/creep-rupture which will also lead to failure or render the component out of specifications. Furthermore, at high temperatures and in a corrosive environment the materials will degrade due to the synergistic effects of stress and corrosion.

The ceramics community has developed the necessary tools to use in design with ceramics, which may be utilized as the materials databases are established. Most notable is the CARES-code developed by NASA, in which a Finite Element Method (FEM) for analyzing the stresses in a component is coupled with the necessary ceramic materials and probability data to provide a probability of survival (reliability) map for the component in question.

TECHNICAL APPROACH

The following key properties are being evaluated in the present task: fast fracture strength at room temperature, 1100°C and 1400°C; statistical analysis in the form of a Weibull analysis and necessary fractography; slow crack growth properties evaluated by the dynamic fatigue method; and creep/creep-rupture effects measured through interrupted static fatigue experiments. In addition the two Combustion 2000 teams are performing initial corrosion experiments, and ORNL will perform fast fracture measurements of corroded specimens for the UTRC team.

FAST FRACTURE

The fracture strength of ceramic materials is most commonly measured in four-point flexure.³ In this test a specimen of 4x3x50mm is subjected to bending in a fixture providing an inner span of 20mm and an outer span of 40mm. The specimen is loaded to fracture while load and deflection are monitored, and the flexure strength is calculated according to standard beam theory. The flexure method offers the possibility of testing a large number of samples quite inexpensively, the load train arrangement is simple, and several specimens may be tested simultaneously.

Alternatively fracture strength may be measured in a tensile test in which a cylindrical rod with a narrow gauge section is loaded in tension with the aid of a gripping system which imposes minimum bending. The bulk properties are directly measured, and creep deflection can be measured directly. The tensile method is better suited for

evaluating mechanical properties of ceramics; however, due to the high cost of both the gripping system and the tensile specimens themselves, tensile testing of structural ceramics is not widely performed.

WEIBULL ANALYSIS

Weibull analysis is the statistical tool most commonly used to analyze fracture data for structural ceramics.⁴ Due to the brittle nature of ceramic materials, the fracture strength of a set of specimens may vary as much as 100% from its mean strength, necessitating a statistical analysis of the data. The Weibull analysis is a weakest link theory stating that a given volume of a ceramic material under uniform stress will fail from the most severe flaw. The probability of failure is given by:

$$P_f = 1 - \exp \left[- \int V \left(\frac{\sigma_f}{S_0} \right)^m dV \right] \quad (1)$$

Where P_f is the failure probability, V the specimen volume, σ_f the fracture strength, m the Weibull modulus and S_0 the Weibull scaling factor.

The Weibull modulus m is used as a design parameter for ceramics and describes the range of the strength data. The Weibull scaling parameter S_0 is related to the average strength of the sample. It is desirable that a structural ceramic have a high m and a high S_0 . The Weibull parameters are directly obtained from strength data by, for instance, the maximum likelihood method:⁵

$$\frac{\sum [\ln(\sigma)^m]}{\sum (\sigma^m)} - \frac{1}{m} = \frac{\sum (\ln \sigma)}{N} \quad (2)$$

$$S_0 = \left[\frac{\sum (\sigma^m)}{N} \right]^{1/m} \quad (3)$$

where,

σ is the fracture strength,

N is the number of specimens,

m and S_0 are the Weibull parameters as described above.

FRACTOGRAPHY

The Weibull theory assumes that all failures used to generate the Weibull parameters are similar in nature, i.e., stem from the same type of flaws. This may not always be the case, most notably there will be a difference in flaws stemming from the powder pressing and sintering process and flaws stemming from machining and handling of the components. The purpose of performing thorough fractography is to identify the different sources of failure origins, and take that information into account by appropriately censoring the Weibull distribution.

STATIC AND DYNAMIC FATIGUE

The term "fatigue" as used for structural ceramics is different from that commonly used for metals. For ceramics the term fatigue is used to describe the decrease in strength due to the combined action of *static* stress and degrading environment. The mechanism which causes this is known as Slow Crack Growth (SCG) and is the growth of small preexisting cracks or voids at stress levels less than those needed to cause catastrophic failure. This happens because the bond strength of individual atoms is decreased due to the specific environment. Eventually, a small crack has grown to a size large enough to cause catastrophic failure at the given stress level. In order to predict the lifetime for components in a given environment, the velocity at which cracks grow at a given stress must be known.⁶

A static fatigue experiment is performed by loading a specimen to a given stress in the given environment and recording the time to failure. This type of test can be extremely time consuming (> 1000 hours) and several specimens are needed at each condition in order to obtain the required statistics. A common way to accelerate the test is to perform a dynamic fatigue experiment in which the specimens are loaded to failure at several given stressing rates and the fracture strength is recorded as a function of applied stressing rate.⁷ If a material is susceptible to SCG, the fracture strength will decrease as a function of decreasing stressing rate, i.e., increasing time, and by applying the following fracture mechanics framework on the measured data, the SCG parameters may be determined. The crack velocity during slow crack growth is often described in a power law form:

$$v = A \left(\frac{K_{\text{appl}}}{K_{\text{IC}}} \right)^n \quad (4)$$

where,

K_{appl} is applied stress intensity,
 K_{IC} is the critical stress intensity,
 v is the crack growth velocity and
 A and n are materials constants.

Combining this with the Griffith criteria for fast fracture strength:

$$\sigma_f = Y K_{\text{IC}} c^{-1/2} \quad (5)$$

where,

σ_f is the fast fracture strength,
 c is the crack length, and
 Y a specimen geometry and crack shape parameter.

The time to failure under constant applied stress may be obtained:

$$t_f = B \sigma_i^{n-2} \sigma_f^{-n} \quad (6)$$

where,

$$B = \frac{2 K_{IC}^2}{(n-2)AY^2} \quad \text{is a material constant,}$$

and

t_f is time to failure, and
 σ_f is fatigue strength

In the case of the dynamic fatigue experiment, the equations combine to give

$$t_f = B (n+1) \sigma_i^{n-2} \sigma_f^{-n} \quad (7)$$

and

$$\sigma_{fatigue}^{n+1} = B (n+1) \sigma_i^{n-2} \dot{\sigma} \quad (8)$$

where

$\dot{\sigma}$ is applied stressing rate.

The fatigue parameter n is obtained by plotting $\log \sigma_{fatigue}$ vs $\log \dot{\sigma}$.

Interrupted static fatigue is a method to supplement the dynamic fatigue data. The specimens are held at a load known to be a certain percentage of the actual fast fracture load in the given environment, and after a given time the test is interrupted and the remaining strength is measured by loading the specimen to failure. In this manner limited information about the tendency for a material to creep is also obtained.

EXPERIMENTAL RESULTS

To date, two materials have been selected by the UTRC team. The materials are NT230 which is a siliconized silicon carbide (SiC) produced by Saint-Gobain Norton Company and Lanxide Dimox, a silicon carbide particulate reinforced aluminum oxide produced by Lanxide. The manufacturers material data are presented in Table 1.

All specimens are four-point bend bars with dimensions 3x4x50mm with chamfered edges. All measurements are performed using a hydraulic flexure testing facility with silicon carbide bend fixtures with an outer span of 40mm and an inner span of 20mm. Fast fracture is measured at room temperature using a stressing rate of 37MPa/s and dynamic fatigue experiments are carried out at 1100°C and 1400°C using stressing rates of 1, 0.01, 0.001 and 0.0001MPa/s, resulting in times to failure of typically 3 min, 11h, 110h and 1100h, respectively. Figures 1 and 2 show the fast fracture strength as a function of temperature for NT230 and Lanxide Dimox, respectively. Figure 3 is a Weibull plot of the room temperature fracture strength of NT230. Note that this figure is meant as an illustration of the Weibull graph, as the nine data points obtained to date are too few to give a statistically valid determination of the Weibull parameters.

Figures 4, 5, 6 and 7 are the dynamic fatigue results of the two materials at 1100°C and 1400°C. A summary of the strength results is given in Table 2.

DISCUSSION AND SUMMARY

The fast fracture strength as a function of temperature is different for the two materials. NT230 keeps its strength level of approximately 400MPa up to 1100°C after which it drops off. Lanxide Dimox loses strength at a much lower temperature (approximately 800°C), but does maintain some residual strength up to 1400°C.

The four dynamic fatigue graphs in Figures 4 through 7 show that neither material exhibits any significant slow crack growth at the two temperatures in air. This is a very important result as several other ceramics will exhibit significant slow crack growth at these temperatures in air.⁸

However, not evidenced from the dynamic fatigue analysis are the creep tendencies, especially for Lanxide Dimox at 1400°C. The creep deformation at 1400°C for this material is large, and the dynamic fatigue experiments at the lowest stressing rates will not be carried out. At these times the creep will be excessive and it will no longer be meaningful to carry out a flexure test.

Microstructural observations show that there are significant amounts of free metal in both materials, Al in the Lanxide and Si in the NT230. At 1400°C the free metal starts to leak out, and even at fairly short exposure times (<10h) beads of free metal exist on the specimen surfaces.

In summary, the tests carried out in air so far indicate that both NT230 and Lanxide Dimox have acceptable properties at 1100°C but that serious problems, i.e., excessive creep of Lanxide Dimox and loss of strength for NT230, exist at temperatures around 1400°C.

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Table 1. Material Data.

NT 230 Siliconized Silicon Carbide (SiC), Saint-Gobain Norton	
8 Vol% Si - metal	
90 Vol% SiC	
2 Vol% Pores	
Lanxide Dimox Aluminum Oxide with Silicon Carbide Particles, Lanxide	
48 Vol% SiC	Density 3.4 g/cm ³
38 Vol% Al	Thermal Conductivity 60Wm/K
13 Vol% Al - alloy	Thermal Expansion 7x10 ⁻⁶ /°C
1 Vol% Pores	Fracture Toughness 7.0MPam ^{1/2}

Table 2. Summary of results from the dynamic fatigue experiments.

Stressing Rate [MPa/s]	Mean Strength NT230 [MPa]			Mean Strength Lanxide Dimox [MPa]		
	RT	1100°C	1400°C	RT	1100°C	1400°C
37	372.1	427.2	176.2	404.8	228.2	206.2
1.0		412.8	228.9		233.8	208.2
0.01		343.3	160.0		283.9	219.9
0.001		475.2	160.6		242.9	
0.0001		445.4	176.9		218.6

Figure 1. Fast fracture as a function of temperature for NT230.

Figure 2. Fast fracture as a function of temperature for Lanxide Dimox.

Figure 3. Weibull plot of fast fracture strength for NT230 at Room Temperature.

Figure 4. Fracture stress as a function of stressing rate for NT230 at 1100°C.

Figure 5. Fracture stress as a function of stressing rate for NT230 at 1400°C.

Figure 6. Fracture stress as a function of stressing rate for Lanxide Dimox at 1100°C.

Figure 7. Fracture stress as a function of stressing rate for Lanxide Dimox at 1400°C.

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