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**OAK RIDGE
NATIONAL
LABORATORY**

Materials Support for HITAF
Final Report for Phase I

K. Breder
V. J. Tennery

MARTIN MARIETTA

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**MATERIALS SUPPORT FOR HITAF
FINAL REPORT FOR PHASE I**

K. Breder
V. J. Tennery

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MATERIALS SUPPORT FOR HITAF FINAL REPORT FOR PHASE I*

K. Breder and V. J. Tennery

INTRODUCTION

In order for the United States to be able to continue to use coal as a major energy source in electricity production, future improved coal-fired systems must have a minimal environmental impact and operate at much higher thermal efficiencies than the present systems. These systems must have low emissions of NO_x and SO_x and particulates and will have lower CO_2 emissions due to a higher thermal efficiency of the overall power generation cycle. Significant improvements in efficiencies compared to current systems will require a change to gas turbines (Brayton Cycle) instead of exclusive reliance on steam turbines (Rankine Cycle). In order to maximize efficiency, the working fluid at the turbine inlet must be at the highest possible temperature relative to ambient. Further, to minimize corrosion and erosion of the stators and rotors in the turbine, it is preferable that air rather than combustion products be used for the working fluid. This can be achieved through the use of ceramic heat exchangers which can operate at temperatures up to 1600°C (refs. 1-4).

The concept of ceramic heat exchangers for use in externally fired combined cycles (EFCCs) for power generation has been evaluated over several years. Much work was done in the late 1970s and early 1980s to conceptualize the design, test materials, and build prototypes.^{5,6} The leading candidate ceramic materials were identified as sintered or siliconized SiC. Several materials were tested in combustion environments, and in some environments, SiC survived quite well.⁷⁻¹⁴ Despite the considerable efforts put forward in these programs, a technology assessment performed in 1989 by Electric Power Research Institute¹⁵ on advanced fossil power systems concluded that in order to commercialize the use of pressurized ceramic heat exchangers in EFCCs, further research and development on both the materials and the engineering systems needed to be done.

Some of this work is presently under way and is funded by the Department of Energy (DOE). The present work is part of a larger development program (Combustion 2000), and the goal is to develop long-term mechanical properties data for the leading candidate materials in an air environment. These data are needed to aid in the design of the systems and to serve

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as baseline data for future required design data for conditions where the materials will be exposed to coal slags and ashes at elevated temperatures. Some of the work on coal slag exposure is under way in a parallel effort.^{16,17}

BACKGROUND

The leading candidate materials for high-temperature pressurized heat exchanger application are still SiC-based ceramics, due to their relatively low cost and demonstrated fabrication technology relative to alternate refractory materials. Much improvement in the properties of these materials has been achieved to the point that these are reaching a maturity as engineering materials. Some high-temperature mechanical properties data for clean environments are available; however, the amount of long-time data for creep and slow-crack growth (SCG) is limited. In addition to the sintered and siliconized SiC materials, other newer materials have been proposed. A relatively new SiC particulate-reinforced Al_2O_3 ceramic has emerged as another candidate for this application,¹⁸ but except for some tensile creep results, there are very few long-term data available.¹⁹ This particulate-reinforced material is produced by direct oxidation of molten metal containing the reinforcing phase, and the resulting composite contains some residual metal and porosity. The phase composition can be tailored to specific mechanical requirements. The thermal shock properties, as well as the thermal conductivity, are good for this type of material. Initial results further indicate that the composite has good corrosion resistance both in a coal slag environment and in sodium silicates.¹⁶⁻¹⁸

The high-temperature mechanical properties of sintered and siliconized SiC have been reported by many authors. However, these materials have been under continuous development, and several of the earlier reports describe materials with properties inferior to today's materials having essentially the same names. Work by Trantina and Johnson²⁰ and Evans and Lange²¹ on sintered SiC with boron as the sintering aid showed promising mechanical properties up to 1400°C. It was found that sintered SiC had essentially no SCG in air measured by double torsion (DT) or dynamic fatigue at 1550°C. The siliconized and hot-pressed SiC exhibited some SCG with crack velocity exponents, n , ranging from 20 to 50. Quinn and Katz²² performed stepped-temperature stress-rupture tests of sintered α -SiC at 1000 to 1400°C. At 1200°C, they reported a time-dependent failure which would be typical of SCG behavior with $n = 40$. However, there was no fractographic evidence of SCG, and the observed strength degradation was attributed to oxidation of surface connected porosity. They also indicate that this behavior would not be observed in specimens with artificially induced flaws (indentation or DT) because these specimen types fail at stress levels

which are not high enough to cause the stress corrosion to happen. The specimens stepped up to 1400°C showed fractographic evidence of SCG. McHenry and Tressler tested hot-pressed SiC and sintered α -SiC.^{23,24} They found no SCG for α -SiC at low oxygen partial pressures, but after oxidizing the specimens in air at 1200°C for 15 h, SCG was observed in both materials. Easler, Bradt, and Tressler²⁵ evaluated the room-temperature fast-fracture strength after oxidizing α -SiC and hot-pressed SiC (NC203) with and without mechanical stress. More severe oxidation and subsequent weakening were reported in the specimens exposed under applied stress. Later work also demonstrated that SCG was observed in the hot-pressed material after oxidation under stress.²⁶⁻²⁹ Depending on the type of test and the temperature, crack blunting or crack growth will occur in this material. The amount of SCG will depend on the level of oxidation, which again will depend on flaw shape and size, such that blunting would be preferred over growth for some material-test-temperature combinations. Some creep studies of sintered α -SiC have been performed,^{29,30} and a creep exponent of one was found in bending. A considerable amount of creep studies has been performed on various types of siliconized SiC, and it was reported that there is competition between creep and SCG as described above.³¹⁻³⁵ The creep mechanism is characterized mostly by the formation of cavities at the silicon-silicon carbide interface with the aid of high localized stresses and impurities in the silicon phase. The creep properties of Si/SiC are strongly dependent on the amount of Si and its distribution in the microstructure.

EXPERIMENTAL PROCEDURE

MATERIALS AND PROCEDURES

The mechanical properties of three materials are compared in this work. These are NT230 Si/SiC from Saint Gobain Norton, β -SiC from Coors Ceramics Co., and Lanxide DIMOX SiCp/Al₂O₃ from Du Pont Lanxide Composites Inc. The manufacturers' data on material properties are summarized in Table 1. NT230 SiC is siliconized silicon carbide and contains free silicon metal (8 vol %). This material has some residual porosity which is evident from the microstructure shown in Fig. 1. β -SiC is sintered silicon carbide with a fine grain structure and high density; see Fig. 2. The SiCp/Al₂O₃, which is manufactured by the Lanxide Direct Oxidation Process, contains 48 vol % SiCp, 38 vol % Al₂O₃, and 13 vol % Al-alloy. Some residual porosity is also present in the material; see Fig. 3. The SiC ceramics were tested as machined while the Lanxide DIMOX was reoxidized by the manufacturer after machining. The three materials were tested in 4-point flexure at room temperature, 1100 and 1400°C in a hydraulic flexure testing system in load control. Fast-fracture tests were carried

Table 1. Manufacturer's data for the candidate materials

<u>NT230 SiC - Siliconized SiC - Saint-Gobain/Norton</u>	
90 vol % SiC	Density, 3.1 g/cm ³
8 vol % Si-metal	Thermal conductivity, 120 W/mK
2 vol % Pores	Thermal expansion coeff., $4.4 \times 10^{-6}/^{\circ}\text{C}$
	Fracture toughness, 3.0 MPam ^{1/2}
<u>Coors β-SiC Sintered Silicon Carbide (SiC), Coors Ceramics Co.</u>	
99.9 % SiC	Density, 3.1, g/cm ³
	Thermal conductivity, 110 W/mK
	Thermal expansion coeff., $4.4 \times 10^{-6}/^{\circ}\text{C}$
	Fracture toughness, 3.0 MPam ^{1/2}
<u>Lanxide DIMOX - Al₂O₃ / SiCp - DuPont Lanxide Composites Inc.</u>	
48 vol % SiC	Density, 3.4 g/cm ³
38 vol % Al ₂ O ₃	Thermal conductivity, 60 W/mK
13 vol % Al-alloy	Thermal expansion coeff., $6.8 \times 10^{-6}/^{\circ}\text{C}$
1 vol % Pores	Surface re-oxidized
	Fracture toughness, 4.5 MPam ^{1/2}
<u>Lanxide DIMOX - Al₂O₃ / SiCp - DuPont Lanxide Composites Inc.</u>	
49 vol % SiC	Density, 3.4 g/cm ³
40 vol % Al ₂ O ₃	Thermal conductivity, 60 W/mK
10 vol % Al-alloy	Thermal expansion coeff., $6.8 \times 10^{-6}/^{\circ}\text{C}$
1 vol % Pores	Surface not re-oxidized
<u>Hexoloy SA - Sintered α-SiC - Carborundum Co.</u>	
99.9 % SiC	Density, 3.1 g/cm ³
	Thermal conductivity, 110 W/mK
	Thermal expansion coeff., $4.5 \times 10^{-6}/^{\circ}\text{C}$

Fig. 1. Polished section of the NT230 showing areas of SiC, Si-alloy, and porosity.

HIF-2

Fig. 2. Polished section of the Coors B-SiC showing areas of SiC and porosity.

HIF-3

Fig. 3. Polished section of the Lanxide DIMOX showing areas of SiC, Al-alloy, Al_2O_3 , and porosity.

out at a loading rate of 45 N/s, resulting in a stressing rate of 37 MPa/s at all three temperatures (30 specimens at each temperature); specimen size was $3 \times 4 \times 50$ mm and inner and outer spans were 20 and 40 mm, respectively. The Lanxide DIMOX material was tested at fast fracture at additional temperatures down to 600°C (six specimens at each temperature). Dynamic fatigue experiments were performed at 1100 and 1400°C in air at loading rates from 1.2 N/s to 1.2×10^{-4} N/s, resulting in stressing rates of 1.0, 0.01, 0.001, and 0.0001 MPa/s (ten specimens at each condition). The purpose of the dynamic fatigue experiments was to determine if SCG existed in these materials. These experimental data were obtained to serve as baseline data for later studies of these materials in environments expected in advanced coal-burning combined-cycle systems.

DYNAMIC FATIGUE

The conventional approach for comparing SCG of various materials is to determine and compare the slow crack growth parameter, n ,^{36,37} as determined by the fracture mechanics model. In this model, the subcritical crack velocity is commonly expressed empirically as a power function of the applied stress intensity factor, K_a , at the crack tip:

$$v = v_0 \left(\frac{K_a}{K_{IC}} \right)^n, \quad (1)$$

where v_0 and n are environmentally dependent constants, K_a is the applied stress-intensity factor, and K_{IC} is the critical stress-intensity factor. In a flexure experiment, the applied stress intensity is given by:

$$K_a = Y \sigma_a \sqrt{c} \quad (2)$$

where Y is a geometric constant whose value is a function of specimen dimensions and the loading geometry; σ_a is the applied stress; and c is the crack length, typically the depth of the crack in the case of flexure stress. Substituting Eq. (2) into Eq. (1) and solving the resulting differential equation for the dynamic fatigue test, in which the stressing rate, $\dot{\sigma}_a$, is constant, results in the dynamic fatigue equation:

$$\sigma_f^{n+1} = B (n + 1) \sigma_i^{n-2} \dot{\sigma}_a, \quad (3)$$

where σ_f is the fracture strength at the given stressing rate, σ_i is the inert (fast-fracture) strength, and

$$B = \frac{2K_{IC}^2}{(n-2) v_0 Y^2} . \quad (4)$$

As seen from Eq. (3), the crack velocity exponent n (fatigue parameter) and B can be determined by evaluating fracture strength as a function of stressing rate. The time to failure for the dynamic fatigue case can be expressed as:

$$t_f = B (n+1) \sigma_i^{n-2} \sigma_f^{-n} . \quad (5)$$

WEIBULL ANALYSIS

Weibull analysis is the statistical tool most commonly used to analyze fracture data for structural ceramics.³⁸ The Weibull probability density function describes the fast-fracture strength of many structural ceramics when the number of specimens in a given set is sufficiently large. For a reasonable confidence level, the specimen set size must be of the order of 30 or greater. Due to the brittle nature of ceramic materials, the fracture strength of a set of specimens may vary as much as 100% from its arithmetic mean strength, necessitating the incorporation of statistical analysis of the data into the final design parameters. The Weibull model for describing strength variability is a weakest-link theory stating that a given volume of a ceramic material under uniform stress will fail from the most severe or "largest" flaw. The probability of failure is given by:

$$P_f = 1 - \exp \left[- \int_V \left(\frac{\sigma_f}{\sigma_0} \right)^m dV \right] , \quad (6)$$

where P_f is the failure probability, V is the specimen volume, σ_f is the fracture strength, m is the Weibull modulus, and σ_0 is the Weibull material scaling factor. The failure probability for a given specimen volume is given by:

$$P_f = 1 - \exp \left[- \left(\frac{\sigma_f}{\sigma_0} \right)^m \right] , \quad (7)$$

where σ_0 is the Weibull characteristic strength for the given specimen volume. The Weibull modulus, m , describes the width of the fracture strength distribution and for various reasons is the most difficult to obtain experimentally; m is also the most important parameter in determining ceramic component lifetimes. The Weibull scaling parameter, σ_0 , is related to the arithmetic mean strength of the sample. It is desirable from an engineering application view that a structural ceramic have a high m and a high σ_0 or σ_0 . The Weibull parameters are directly obtained from strength data by several methods. The maximum likelihood method is now the preferred method and American Society for Testing and Materials (ASTM) standard C 1239 specifies that this procedure be used to obtain m and σ_0 from experimental strength data:

$$\frac{\sum[\ln\sigma(\sigma)^m]}{\sum(\sigma^m)} - \frac{1}{m} = \frac{\sum(\ln\sigma)}{N} \quad (8)$$

and

$$\sigma_0 = \left[\frac{\sum(\sigma^m)}{N} \right]^{1/m} , \quad (9)$$

where σ is the fracture strength of each specimen, N is the number of specimens, and m and σ_0 are the Weibull parameters as described above. By combining Eqs. (6) and (7), σ_0 can be obtained as described in ASTM C 1239.

LIFETIME PREDICTION

The dynamic fatigue results must be combined with the Weibull analysis in order to obtain a time-to-failure prediction at a given level of probability. Applying Weibull statistics to the fast-fracture (inert) strength data described above, we have:

$$\ln\sigma_i = \frac{1}{m} \ln\ln\left(\frac{1}{1 - P_f}\right) + \ln\sigma_0 , \quad (10)$$

where P_f is the cumulative failure probability, and m and σ_0 are the Weibull parameters. Taking natural logarithms of Eq. (5) and substituting into Eq. (10), we get:

$$\ln t_f = \ln B + \frac{n-2}{m} \ln\ln\left(\frac{1}{1 - P_f}\right) + (n-2) \ln\sigma_0 - n \ln\sigma_f . \quad (11)$$

Equation (11) shows that the time to failure depends on the failure stress, the resistance to SCG, the failure probability, and the Weibull parameters of the inert test.

STATIC FATIGUE

Some additional tests were performed as interrupted static fatigue tests in order to compare the creep properties of the materials. In these tests, the 4-point bend specimens were loaded to 25 and 70% of fast-fracture load for 300 h, while the displacement was monitored. After 300 h, the specimens were fractured at temperature so that the retained strength could be compared to the initial strength. If the retained strength was significantly less than the initial strength, this change would suggest the presence of SCG. The measured displacement after 300 h was correlated with the residual curvature of the fractured specimens after the test, and the materials were compared with respect to creep loads, amount of permanent deflection, and temperatures. A measure of creep exponents and creep rates was not intended as the 4-point flexure configuration is not suited for that purpose.

FRACTOGRAPHIC INVESTIGATION

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. When a sample of test specimens yields two or more distinct flaw distributions, the sample is said to contain censored data, and the associated method for censored data analysis must be employed. These methods are statistically more efficient than simply separating the two populations into two separate sets. Further, fractography is a necessary tool in assessing SCG behavior. If strength degradation as a function of time is observed, the microscopy can aid in determining the mechanisms for the degradation, i.e., whether SCG or other strength-degrading mechanisms are operative. The fractography was performed by light optical and scanning electron microscopy (SEM) methods. The importance of performing fractography in experiments like these cannot be overestimated, as it is important to determine whether the fracture mode changes with time, temperature, environment, and crack velocities.^{22,39}

COAL ASH EXPOSURE

Four ceramics were evaluated in a coal ash exposure experiment performed in collaboration with University of North Dakota Energy and Environmental Research Center. They were NT230 Si/SiC manufactured by Saint-Gobain Norton as described above; sintered

α -SiC (Hexoloy SA) manufactured by Carborundum Co.; and two grades of SiC particulate-reinforced Al_2O_3 from DuPont Lanxide Composites Inc., the standard-grade DIMOX (described above) and an experimental-grade DIMOX with a different composition of the parent Al-alloy. A summary of the manufacturers' data on the materials is given in Table 1. Note that the standard-grade Lanxide DIMOX was reoxidized after machining into test coupons while the experimental grade was not.

Four coupons of each material were machined to $50 \times 44 \times 3$ mm, and each was embedded in a castable refractory tray (Carborundum 11L1 SiC). The refractory trays were cured for 24 h, prefired to the test temperature, and returned to room temperature. The coal ash was then packed onto the surface of the coupons, and the samples were brought up to the appropriate test temperature at $120^\circ\text{C}/\text{h}$, held at temperature for 300 h, and returned to room temperature at $120^\circ\text{C}/\text{h}$. After cooling, the coupons were examined in an optical microscope for cracks, etc. The coupons then were machined into flexure bars of $4 \times 3 \times 50$ mm size and tested in 4-point flexure at room temperature such that the corroded surfaces were in tension. After fracture, the fracture surfaces were examined by optical microscopy and SEM and the fracture origins determined.

Two coal ash types at two exposure temperatures were employed in the experiments. The two ashes were derived from a high-iron Illinois #6 coal and a high-calcium Powder River basin coal, Wyodak, representing typical eastern and western coals, respectively. The two selected temperatures, 1093 and 1260°C , are expected in advanced gas turbine-based, coal-burning cogeneration systems. In many of these designs, a ceramic heat exchanger is a critical component. These temperatures were chosen so as to represent areas in the heat exchanger that are relatively distant from or closer to the burner, respectively. The viscosity of the coal slag varies with temperature and coal type, and at 1260°C , both the selected ashes formed liquid slags. In a coal-burning system, the mechanisms by which ash and slag are deposited on the downstream equipment vary with the surface temperature of the component and with the distance from the burner. At the hotter areas close to the burner, the deposit consists of larger particles which are SiO_2 rich, and at the lower temperatures, the deposited particles are smaller and rich in CaO. The ashes used in the current experiments were therefore sized using <3 - and <6 - μm particle size ash for the 1093°C experiments and unsized ash for the 1260°C experiments. At 1093°C , 1.3 g of ash was packed onto the surface, and at 1260°C , 6.0 g were used. The ash compositions are given in Table 2.

Table 2. X-ray analysis of the starting compositions for the ashes used in the corrosion

Oxide	1093°C Test		1260°C Test	
	Wyodak ($<3\ \mu\text{m}$) wt %	Illinois #6 ($<6\ \mu\text{m}$) wt %	Wyodak (unsized) wt %	Illinois #6 (unsized) wt %
Na ₂ O	1.0	0.8	1.0	0.4
MgO	10.3	1.4	7.7	0.9
Al ₂ O ₃	21.6	22.8	18.6	20.0
SiO ₂	26.3	48.3	38.7	51.2
P ₂ O ₅	2.3	0.3	1.2	0.0
SO ₃	0.8	3.7	0.3	0.9
K ₂ O	0.3	2.1	0.2	1.9
CaO	29.7	5.2	25.2	5.5
TiO ₂	1.4	1.4	1.3	0.9
Fe ₂ O ₃	6.4	14.1	5.8	18.4

RESULTS AND DISCUSSION

RESULTS FROM STRENGTH MEASUREMENTS, FRACTOGRAPHY, AND WEIBULL ANALYSIS OF NT230

Fast-fracture strength measured as a function of temperature is shown in Fig. 4; the data points represent 30 specimens each. The error bars shown represent $\pm$ one standard deviation. The same data are shown as Weibull graphs in Fig. 5. The strength as a function of stressing rate measured at 1100 and 1400°C is shown in Fig. 6.

The fast-fracture strengths compare well with those reported by the manufacturer for this material, except that a strength reduction at 1400°C is observed. McEntire et al.⁴⁰ report a room-temperature strength of 410 MPa with an increase of 30% at 1260°C and a strength at 1370°C still 20% above that for room temperature. In the present case, a strength increase of 10% is seen from room temperature to 1100°C and then a strength decrease of 20% at 1400°C. The average strength at 1400°C is 308 MPa, but the measured strengths have a

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Fig. 4. Fast-fracture flexure strength as a function of temperature for NT230. Data points are the average of 30 specimens, and error bars are +/- one standard deviation.

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Fig. 5. Weibull analysis of NT230 fast-fracture data.

Fig. 6. Fracture strength as a function of stressing rate for NT230 at 1100 and 1400°C.

wide scatter as can be seen from the Weibull analysis in Fig. 5. The individual strength values essentially fall into two groups. The higher-strength group has an arithmetic mean strength of 396 MPa with a standard deviation of 74 MPa, i.e., slightly higher than the room-temperature strength, while the lower-strength group has an average strength of 176 MPa with a standard deviation of 35 MPa. The existence of these two strength groups will be discussed in detail below.

The dynamic fatigue graphs in Fig. 6 show clearly that there is no strength reduction as a function of stressing rate at 1100°C, i.e., no SCG exists. The strengths measured at the slowest stressing rate are consistently found to lie around 400 MPa, and at a stressing rate of 0.0001 MPa/s, that resulted in a total time to failure of about 1100 h. In order to check if the specimens had undergone creep in that time, the load deflection curves were monitored as well as the specimens inspected for permanent deflection after the measurement. Creep was not found to be present in the specimens to any significant degree in the experiment. At 1400°C, a significant strength reduction was seen as a function of stressing rate. Also, more scatter was seen in the strength data at the various stressing rates. The total time to failure at the slowest stressing rate at 1400°C was approximately 400 h, and these specimens showed

essentially no permanent deflection; the strength calculations (elastic beam) were assumed to be valid. The SCG parameter, n , was calculated according to Eq. (3) and found to be 15.5. This value is of the same order of magnitude as reported for hot-pressed SiC (refs. 23-27) and lower than for sintered SiC (refs. 23, 29). It is important to notice that this is a value of the SCG parameter, which indicates that there will be a significant strength reduction over time, and this must be taken into account in the design of components of this material if used at this temperature.

The fractography provided further insight into the fast-fracture and SCG results. At room temperature and at 1100°C at all stressing rates, the fracture surfaces have all the characteristics of fast fracture. The fracture-initiating flaws are predominantly pores located near the tensile surface. Two examples are shown in Fig. 7. Figure 7(a) shows a specimen tested at room temperature at fast fracture, and Fig. 7(b) shows a specimen tested at 1100°C at 0.0001 MPa/s. At 1400°C, the fractography showed that the low-strength specimen group failed predominantly from Si-rich areas [see Fig. 8(a)], and the high-strength group failed from pores as shown in Fig. 8(b). Another distinct difference in the appearance between the two groups was that the low-strength group had significant amounts of metal beads on the fracture surface and on the sides of the specimens; see Fig. 8(c). This was seen only occasionally and only to a very little degree in the high-strength group. At 1400°C at the two slowest stressing rates (0.0001 MPa/s and 0.001 MPa/s), strength degradation was observed and the fracture surfaces showed evidence of damage zones. These damage zones seemed to be created from areas which were rich in Si-alloy; see Fig. 9 for a typical example.

The depth of the damage zone in Fig. 9 is approximately 200 μm , and fracture mechanics calculations [see Eq. (2)] give a fracture stress of 190 MPa, close to the measured strength of 208 MPa for this specimen. The specimens tested at 1400°C at this very slow stressing rate exhibit essentially no creep, evidenced by the lack of a residual permanent curvature in the tested specimen.

Analysis of all the strength results at 1400°C fast fracture resulted in an extremely low Weibull modulus when they were considered to be from one population. However, the fractography showed that the two groups had different flaw populations. These observations therefore necessitated a reevaluation of the Weibull analysis. Flaw populations existing in a set of strength specimens may be either exclusive, concurrent, or partially concurrent.⁴¹ Exclusive means that the specimens which contain a flaw of one type will not contain flaws of the other type and vice versa. This is the simplest of situations. Concurrent means that the flaw types are present concurrently in every specimen and that the specimen may fail from either one, and partially concurrent means that some specimens may contain all types of flaws while some specimens only contain one set of flaws.

ET00677

ET00502

Fig. 7(a) . A pore acting as fracture-initiating flaw in a specimen tested in fast fracture at room temperature (batch B).

(b)

Fig. 7(b) A pore acting as fracture-initiating flaw in a specimen tested at 0.0001 MPa/s at 1100°C (batch O).

ET00436

Fig. 8(a) . An Si-rich area acting as fracture-initiating flaw in a specimen tested in fast fracture at 1400°C (batch O).

(b)

ET00438

Fig. 8(b) . A pore acting as fracture-initiating flaw in a specimen tested in fast fracture at 1400°C (batch B).

ET00231

Fig. 9. Slow-crack growth zone in a specimen tested at 0.0001 MPa/s at 1400°C.

HIF-4

(c) Fig. 8(c) . Fracture surface from a specimen of batch O tested at 1400°C showing beads of Si-alloy on the surface.

The distinction between these cases can be determined by thorough fractography and by analyzing the shape of the Weibull graphs presented earlier. In the present case, the form and behavior of the Weibull graph of the 1400°C data in Fig. 5 indicate the existence of two exclusive flaw populations, one population consisting of Si-rich areas and one population consisting of pores, both being volume distributed. The material was supplied from the manufacturer in two batches, the first batch consisting of material from four different production series and the second batch containing material from the same processing batch (labeled batch B). The first batch was not marked so that the four groups could be distinguished, so all of these were treated as one batch (batch O). During the present experimental work, specimens from the two batches were tested in a random fashion, such that the two batches are randomly distributed in terms of when they were measured, and both batches exist in the entire test matrix.

The Weibull analyses of the results from all five stressing rates at 1400°C are shown in Fig. 10. It can be seen that specimens from batch B are consistently in the high end of their respective distributions, and at the stressing rate of 37 MPa/s, the effect becomes most visible. The specimens have higher strength all come from batch B, and the specimens having lower strength all come from batch O. The 1-MPa/s data also fall into two groups;

Fig. 10. Weibull analysis of the 1400°C dynamic fatigue data. The specimens from batch B are filled symbols; batch O are open symbols.

however, all specimens at this stressing rate came from Batch B. The sample sizes of the dynamic fatigue test series are not large enough so that it is meaningful to perform a Weibull analysis, but it is clear that both batches exhibits SGC and that the SCG mechanisms seem to be similar for the two batches with fracture initiating from damage zones like the one shown in Fig. 9 (a specimen from batch B). A summary of the strength and Weibull parameters for NT230 at 1400°C is given in Table 3. The strength drop from the fastest to slowest stressing rate is approximately the same for both batches, i.e., they have an SCG parameter n of the same order of magnitude. Also given in Table 3 are the unbiased Weibull moduli and confidence bounds for m as calculated according to ASTM 1239. It can be seen that the confidence bounds for all stressing rates overlap, so that Weibull modulus for the dynamic fatigue series is somewhere between 1.6 and 10.5 i.e., the m cannot be determined very accurately with this number of specimens.

However, in order to perform a prediction of time to failure according to Eq. (10), the Weibull parameters of the fast-fracture (inert) test series are needed, and then it becomes necessary to distinguish between the two batches. The fractographic evidence, the existence of different material batches, and the Weibull graph in Fig. 5 indicate that two (or more) exclusive flaw populations exist. For an exclusive mixture of flaws, the Weibull distribution is given by:⁴¹

$$P_f = 1 - \pi_O \exp \left[- \left(\frac{\sigma}{\sigma_{O\theta}} \right)^{m_O} \right] - (1 - \pi_O) \exp \left[- \left(\frac{\sigma}{\sigma_{B\theta}} \right)^{m_B} \right] , \quad (11)$$

where π_O is the fraction of specimens containing only flaws from the O population, and $\sigma_{O\theta}$, m_O and $\sigma_{B\theta}$, m_B are the Weibull parameters for distributions O and B, respectively. The Weibull parameters for the two populations can be obtained by identifying each specimen as belonging to batch O or B and treating the two groups as separate Weibull distributions, or the entire data set can be fitted to Eq. (11) by a numerical procedure. In the present case, there were 12 specimens from batch O and 18 from batch B, and the two procedures yielded very similar Weibull parameters; see Table 3.

The numerical fit and the separate fits are shown in Fig. 11. It is seen that the combined distribution has the separate distributions as asymptotes and it is further striking how well the exclusive distribution fits the data. It is important to note that the Weibull moduli, m , for the two populations are very similar; i.e., the slopes are similar and at a higher value than the one obtained without separating the data. Most striking, however, is the large difference in the Weibull scaling parameter and the average strengths for the two groups.

Table 3. Weibull parameters for the NT230 dynamic fatigue data at 1400°C

Stressing rate MPa/s	Spec. No*	Weibull modulus, m	Weibull modulus, m, unbiased	Weibull modulus, m, lower limit 90% level	Weibull modulus, m, upper limit at 90% level	Weibull char. strength [MPa] σ_0	Weibull material scaling parameter [MPa] σ_0	Average strength [MPa]
1	9	3.1	2.6	1.6	4.3	301	954	269
0.01	9	4.3	3.7	2.3	6.0	210	448	191
0.001	9	7.7	6.5	4.0	10.5	171	245	160
0.0001	9	4.0	3.3	2.1	5.4	167	390	150
37	30	2.8	2.7	2.1	3.4	348	1289	308
37								
B type only	18	7.3	6.8	4.9	9.3	425	620	396
37								
B type exclusive fit	18	6.0	5.5	4.0	7.6	432	712	396
37								
O type only	12	6.5	5.4	3.8	8.6	190	298	176
37								
O type exclusive fit	12	5.8	4.8	3.4	7.7	192	323	176

*Nine specimens at each stressing rate were compared because not all rates had 10 complete runs.

Fig. 11. Weibull analysis of the 1400°C fast-fracture data assuming two exclusive flaw populations.

The Weibull analysis and the SCG parameters were combined to estimate time to failure according to Eq. (10). It is clear that the estimated lifetime using the entire data set is both shorter and has larger variability than that obtained for the high-strength data using the separate Weibull distribution for this set; see Fig. 12. It is further obvious that if this material is to be used for structural applications at temperatures around the melting point of the Si-alloy, i.e., 1400°C, it is important to control the processing parameters tightly in order to maintain the alloy melting point at a well-defined temperature above 1400°C.

The results indicate that the batch-to-batch variations are related to either the amount or the composition of the Si-alloy or both. Batch O had more Si beads at the surface after testing at 1400°C, indicating that there either was more Si-alloy in this batch or that it had a slightly lower melting point than that in batch B, i.e., a slightly different alloy composition. The amount of Si-alloy was compared by using quantitative metallography on polished sections of one specimen from each batch, and no significant differences could be found. The composition of the alloy has not yet been compared.

Fig. 12. Prediction of time to failure for NT230 at 1400°C assuming unimodal and bimodal flaw populations.

The static loading at 70 and 25% of fast-fracture load at 1100 and 1400°C resulted in no strength degradation at any condition. On the contrary, some strengthening was seen, probably due to blunting of flaws. Only a small amount of creep evidenced by permanent curvature of post-test specimens was observed at 1400°C.

RESULTS FROM STRENGTH MEASUREMENTS, FRACTOGRAPHY, AND WEIBULL ANALYSIS OF COORS β -SiC

The fast fracture strength of Coors β -SiC as a function of temperature is shown in Fig. 13; the data points represent 30 specimens each. The error bars shown represent $\pm$ one standard deviation. The same data are shown as Weibull graphs in Fig. 14. The strength as a function of stressing rate measured at 1100 and 1400°C is shown in Fig. 15. All these results show that the strength of Coors β -SiC is remarkably unaffected by

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Fig. 13. Fast-fracture flexure strength as a function of temperature for Coors β -SiC. Data points are the average of 30 specimens, and error bars are $\pm$ one standard deviation.

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Fig. 14. Weibull analysis of Coors β -SiC fast-fracture data.

Fig. 15. Fracture strength as a function of stressing rate for Coors β -SiC at 1100 and 1400°C.

temperature and stressing rate. The average strength is 374 MPa at room temperature, 373 MPa at 1100°C, and 397 MPa at 1400°C with Weibull moduli being 12.0, 12.3, and 9.5, respectively. A slight strength reduction as a function of time is seen at 1100°C, but the 8% drop in strength at a time to failure of more than 1000 h (stressing rate of 10^{-4} MPa/s) will result in an n value of 250, not enough to classify as a significant amount of SCG. At 1400°C, the strength level remains almost unchanged at all stressing rates. The Weibull parameters remain quite unchanged with temperature; a slight drop in the m value was seen at 1400°C. The fractography of the β -SiC showed that the failure mode remained unchanged with temperature and stressing rate as well. The majority of specimens at all conditions failed from pores of the type shown in Fig. 16 (a) and (b). Also, during static loading, no significant changes in strength were observed, and essentially no permanent deflection was observed at any of the test temperatures.

ET00656

(a)

Fig. 16(a) . Fracture origin of Coors β -SiC fractured in fast fracture at room temperature.

(b)

Fig. 16(b). Fracture origin for Coors β -SiC in fast fracture at 1400°C.

RESULTS FROM STRENGTH MEASUREMENTS, FRACTOGRAPHY, AND WEIBULL ANALYSIS OF LANXIDE DIMOX

Fast fracture as a function of temperature for Lanxide DIMOX is shown in Fig. 17; the data points at room temperature, 1100 and 1400°C represent 30 specimens each, and the data points at 600, 800, and 1000°C represent 6 specimens each. The error bars shown represent $\pm$ one standard deviation. Note that the strength for this material was measured at temperatures down to 600°C in order to investigate the strength-temperature relationship. As can be seen in Fig. 17, a reduction in strength was found at about 600°C, which is close to the melting temperature for the aluminum alloy, and it is reasonable to assume that the strength reduction is due to softening and melting of the alloy. The Weibull graphs for room temperature, 1100 and 1400°C are given in Fig. 18. The Weibull modulus was 9.6 at room temperature, 8.9 at 1100°C, and 13.2 at 1400°C; it is believed that the increased modulus at 1400°C stems from the fact that at this temperature the fast-fracture specimens failed consistently from soft, metal-rich areas. The strength as a function of stressing rate is shown in Fig. 19 for both temperatures. It is evident that no significant strength reduction was observed as a function of applied stressing rate for any of the temperatures. However, it is important to notice that the Lanxide DIMOX could only be tested up to stressing rates of 0.01 MPa/s at 1400°C. At the slower stressing rates, creep became so pronounced that the four-point flexure fixtures no longer could accommodate the specimens, and, of course, the elastic beam assumption was violated. Also, at the 0.01-MPa/s stressing rate, the creep was measurable; see Fig. 20 for a comparison of load deflection curves between the three ceramics. The strength values calculated according to beam theory are therefore overestimating the strength of Lanxide DIMOX at this condition.

The fractography for Lanxide DIMOX showed that the majority of the specimen failed from metal inclusions of the type shown in Fig. 21. At 1400°C, the inclusions tended to be larger, and the slower stressing rates, the specimens failed from creep damage as shown in Fig. 22 (a) and (b). The creep damage differs from SCG zones in the existence of an area with a rough surface and multiple cracks and ridges, and it seems to be a more generalized phenomenon in the tensile zone.

Static loading at 1400°C at 70% of fast-fracture load resulted in extensive creep, and the specimens reached the bottom of the fixture early in the experiment. Figure 23 shows a crept specimen after the experiment. At 25% of fast-fracture load, creep was also significant. After 300 h, the remaining fracture load could be measured, but the elastic beam theory was no longer valid, and the resulting stress value was therefore uncertain. Further work in this area is clearly needed.

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Fig. 17. Fast-fracture flexure strength as a function of temperature for Lanxide DIMOX. Data points are the average of 30 specimens at room temperature 1100 and 1400°C, and 6 specimens at the intermediate temperatures. Error bars are +/- one standard deviation.

Fig. 18. Weibull analysis of Lanxide DIMOX fast-fracture data.

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Fig. 19. Fracture strength as a function of stressing rate for Lanxide DIMOX at 1100 and 1400°C.

ORNL-DWG 94-12491

Fig. 20. Comparison of time-deflection curves for the three ceramics at an intermediate stressing rate at 1400°C.

ET00667

Fig. 21. Fracture initiation for Lanxide DIMOX at room temperature was at metal inclusions.

ET00607

(a)

Fig. 22(a). High-temperature fractography for Lanxide DIMOX. Fast fracture at 1400°C with metal inclusion as fracture-initiation point.

ET00240

(b)

Fig. 22 (b). Creep failure in Lanxide DIMOX at 1400°C.

YP17757

Fig. 23. Permanent damage in a Lanxide DIMOX specimen measured at 1400°C at 0.001 MPa/s.

RESULTS FROM POST -EXPOSURE STRENGTH MEASUREMENTS

A summary of the remaining room-temperature strengths after exposure at the two temperatures to two coal ash types for four different ceramics is given in Table 4. Between five and seven specimens could successfully be machined from each coupon, with the exception of the experimental Lanxide material exposed at the higher temperature.

Table 4. Remaining room-temperature strength after exposure for 300 h at two temperatures and two coal ashes

NT230				
RT As-received	W/1093°C	I#6/1093°C	W/1260°C	I#6/1260°C
386 MPa	340 (3) ^a MPa	208 (27) MPa	175 (32) MPa	204 (80) MPa
N=30	N=7	N=5	N=6	N=5
Lanxide DIMOX				
RT As-received	W/1093°C	I#6/1093°C	W/1260°C	I#6/1260°C
414 MPa	365 (20) MPa	352 (22) MPa	364 (16) MPa	388 (29) MPa
N=30	N=6	N=6	N=5	N=6
Lanxide DIMOX Experimental Grade				
RT As-received	W/1093°C	I#6/1093°C		
414 MPa ^b	343 (39) MPa	287 (7) MPa		
	N=4	N=6		
Hexoloy SA				
RT As-received	W/1093°C		W/1260°C	I#6/1260°C
400 MPa	339 (36) MPa		321 (61) MPa	259 (11) MPa
(Hecht ref. 15)	N=7		N=6	N=6

LEGEND:

W = Wyodak coal ash

I#6 = Illinois No. 6 coal ash

N = number of specimens

^aNumbers in parenthesis are the standard deviation.

^bAssumed same as Lanxide DIMOX.

These coupons were cracked after cooling to room temperature and could therefore not be machined. Hexoloy SA was not exposed to Illinois #6 at 1093°C due to lack of coupons for this material. The same data are shown in Fig. 24, where the strengths after exposure are shown as a percentage of the initial strength. Unless otherwise noted, the initial strength was measured on specimens produced at the same time as the exposed material and is an average of 30 strength values. As is evident from Table 4 and Fig. 24, all the exposed materials exhibit some loss of strength after the exposure. However, for Lanxide DIMOX, the strength loss is only about 15% and stays unchanged for the two coal ashes and temperatures.

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Fig. 24. Retained fast-fracture flexure strength normalized to the as-received strength for specimens tested after exposure to coal ash.

The NT230 experienced a loss in strength for all the test conditions; up to 55% strength reduction was seen at 1260°C. Lanxide DIMOX experimental grade had a strength loss of up to 30%, and Hexoloy SA lost up to 35% of original strength. Each of the fractured specimens was reassembled, and the primary fracture surface was identified and examined in detail using SEM. The fracture-initiating flaws were identified in each case, and, hence, comparisons in fracture mechanisms could be made. Below is a summary of the different materials/coal ash/temperature combinations.

NT230 / Wyodak / 1093°C

Average strength was 340 MPa, a 12% reduction from initial strength. There was no slag layer remaining on the surface, but corrosion pits could be seen at the surface. These were rather shallow, but in every case, failure was initiated from one of these pits. A typical fracture origin is seen in Fig. 25.

ET00371

Fig. 25. Fracture-initiating flaw in NT230 exposed to Wyodak coal ash at 1093°C.

NT230 / Illinois #6 / 1093°C

Average strength was 208 MPa, a reduction of 46% from the initial strength. The slag layer was clearly visible and more or less continuous. Corrosion pits formed under the slag layer and in some cases became quite large. Fracture initiated from the corrosion pits as seen in Fig. 26. The corrosion product that is seen in the figure was rich in carbon and iron.

NT230 / Wyodak / 1260°C

Average strength was only 175 MPa, 55% lower than the initial strength. The slag layer appeared continuous and adhered well, and it contained large bubbles. In some instances, the areas where the slag layer was thin acted as fracture-initiation points, i.e., the bubbles or damaged regions in contact with the bubbles acted as flaws, and in other instances, the fracture origins were corrosion pits underneath the slag layer. Further, it was observed that the porosity of the ceramic had increased in a zone near the slag layer; see Fig. 27.

SEM039460

Fig. 26. Fracture-initiating flaw in NT230 exposed to Illinois #6 coal ash at 1093°C.

SEM039900

Fig. 27. Fracture surface of NT230 exposed to Wyodak coal ash at 1260°C.

NT230 / Illinois #6 / 1260°C

Only two of the five specimens failed in a manner that makes the flexure test valid; in some cases, the specimens failed outside the gage section, and in some cases, the specimens simply split lengthwise. The specimens had a continuous, thin slag layer and an enhanced porosity near the slag/ceramic interface. The fracture origins were generally an assembly of pores in this pore-rich region; see Fig. 28.

A microprobe analysis of an NT230 specimen exposed to Illinois #6 coal ash at 1260°C was performed. Figure 29(a) shows a backscattered image of the specimen with the remaining slag layer and Fig. 29(b) shows that the iron rich slag forms areas of high iron content at the slag specimen interface. These areas are also rich in Si and it is likely that iron silicides have formed.

SEM039910

Fig. 28. Fracture surface of NT230 exposed to Illinois #6 coal ash at 1260°C.

HIF-5

Fig. 29. Microprobe analysis of NT230 exposed to Illinois #6 coal ash at 1260°C. (a) Backscattered image. (b) Element map for Iron.

Lanxide DIMOX / Wyodak / 1093°C

Average strength was 365 MPa, 12% lower than the initial strength. Only small areas of ash were left on the specimens, and no corrosion attack was apparent. The fracture origins were volume-distributed, metal-rich areas similar to what has been observed in the as-received material. The metal inclusions seemed to be somewhat enlarged, in line with the observed 10% strength decrease. This enlargement of the metal phase regions along with a loss in strength has been observed in aging experiments of a similar material,¹⁹ where a strength reduction of about 10% was seen after aging for short and intermediate times, while longer aging brought the strength back to near the initial value. A typical fracture origin is seen in Fig. 30.

Fig. 30. Fracture surface of Lanxide DIMOX exposed to Wyodak coal ash at 1093°C.

Lanxide DIMOX / Illinois #6 / 1093°C

Average strength was 352 MPa, 15% lower than as-received strength. The coal ash layer was not visible on these specimens, and failure occurred from inclusions as described for Lanxide DIMOX exposed to the Wyodak ash. The protective oxide layer was clearly visible on these specimens, and this remained undamaged by the coal ash exposure.

Lanxide DIMOX / Wyodak / 1260°C

Average strength was 364 MPa, a reduction of 12% from as-received strength. The coal ash layer was not visible on these specimens, and they all failed from metal-rich inclusions as described above. Also, in these specimens, the protective oxide layer was clearly visible; see Fig. 31.

SEM039914

Fig. 31. Fracture surface of Lanxide DIMOX exposed to Wyodak coal ash at 1260°C.

Lanxide DIMOX / Illinois #6 / 1260°C

Average strength was 388 MPa, 6% lower than the as-received strength. The oxide layer was clearly present, and in some instances, an enhanced porosity was observed just below the interface between the composite and the original oxide layer. In some cases, these pores acted as fracture-initiation points (see Fig. 32) but no pitting related to the coal ash exposure was observed.

SEM040060

Fig. 32. Fracture-initiating flaw in Lanxide DIMOX exposed to Illinois #6 coal ash at 1260°C.

A microprobe analysis of a Lanxide DIMOX specimen exposed to Illinois #6 coal ash at 1260°C was performed. Figure 33(a) shows a backscattered image of the specimen, and Fig. 33(b) shows that iron from the slag reacts with the porous reoxidized alumina layer. The reaction depth does not go beyond the oxide layer, and no areas of high Si-content were found indicating that iron silicides were not present.

Lanxide Experimental Grade/ Wyodak / 1093°C

The average strength was 343 MPa, a reduction of 17% assuming the as-received strength is the same as for the standard DIMOX. The coal ash layer was visible but not very thick, and small corrosion pits were visible. The corrosion pits acted as fracture origins; a typical example is shown in Fig. 34. The experimental material from Lanxide was not re-oxidized after the coupons had been machined, and it is evident that the lack of protective oxide layer is detrimental to the material, leaving the ceramic surface open to corrosive attack. It can also be seen in Fig. 34 that the SiC is being preferentially attacked.

HIF-7

HIF-8

Fig. 33. Microprobe analysis of Lanxide DIMOX exposed to Illinois #6 coal ash at 1260°C. (a) Back-scattered image. (b) Element map for Iron.

SEM042848

Fig. 34. Fracture-initiating flaw in Lanxide experimental grade exposed to Wyodak coal ash at 1093°C.

Lanxide Experimental Grade / Illinois #6 / 1093°C

The average strength was 287 MPa, a reduction of 30%. The coal slag layer was very thin, and the corrosion pits were few and mainly associated with the SiC phase, but many were large enough to act as strength-controlling flaws.

Hexoloy SA / Wyodak / 1093°C

Average strength was 339 MPa, a reduction of 15% from an as-received strength of 400 MPa. The coal ash layer was not very thick and was discontinuous, and corrosion pits were evident as in Fig. 35. The pores near the surface seemed to be enlarged, and some acted as fracture-initiation points.

ET00368

Fig. 35. Fracture-initiating flaw in Hexoloy SA exposed to Wyodak coal ash at 1093°C.

Hexoloy SA / Wyodak / 1260°C

Average strength was 321 MPa, a reduction of 20% from the as-received strength. No residual coal ash layer was evident on these specimens, but the protective oxide layer could be seen, and it was evident that this was damaged in certain places. The fractures seemed to initiate where the oxide scale was damaged; see Fig. 36.

Hexoloy SA / Illinois #6 / 1260°C

Average strength was 259 MPa, a reduction of 35% from an as-received strength. A continuous coal ash layer was evident with several corrosion pits through and under the layer. These pits acted as strength-controlling flaws; see Fig. 37.

ET00339

Fig. 36. Fracture-initiating flaw in Hexoloy SA exposed to Wyodak coal ash at 1260°C.

ET00363

Fig. 37. Fracture-initiating flaw in Hexoloy SA exposed to Illinois #6 coal ash at 1260°C.

A microprobe analysis of a Hexoloy SA specimen exposed to Illinois #6 coal ash at 1260°C was performed. Figure 38(a) shows a backscattered image of the specimen, and Fig. 33(b) shows that iron from the slag is enriched in areas near the slag specimen interface. These areas coincide with areas with Si-content indicating the existence of iron silicides. As pointed out above, these corrosion products were strength determining in the subsequent strength test.

Fig. 38. Microprobe analysis of Hexoloy SA exposed to Illinois #6 coal ash at 1260°C. (a) Backscattered image. (b) Element map for Iron.

Table 5. Summary of fast fracture Weibull parameters for three ceramics

	No. of specimens	Weibull modulus, m	Weibull modulus, m, unbiased	Weibull modulus, m, lower limit 90% level	Weibull modulus, m, upper limit at 90% level	Weibull char. strength [MPa] σ_0	Weibull material scaling parameter [MPa] σ_0	Average strength [MPa]
NT230 RT ^a	30	10.8	10.2	8.1	13.1	404	505	386
NT230 1100°C	30	7.7	7.3	5.7	9.4	450	643	424
NT230 1400°C	30	2.8	2.7	2.1	3.4	348	1289	308
Coors β -SiC RT	30	12.0	11.5	9.0	14.7	390	472	374
Coors β -SiC 1100°C	30	12.3	11.8	9.2	15.0	388	466	374
Coors β -SiC 1400°C	29	9.5	9.0	7.1	11.6	397	518	376
Lanxide DIMOX RT	30	9.6	9.2	7.2	11.7	435	565	414
Lanxide DIMOX 1100°C	30	8.9	8.5	6.7	10.8	246	330	233
Lanxide DIMOX 1400°C	30	13.1	12.6	9.9	16.0	217	257	210

^aRT = room temperature.

CONCLUSIONS

COMPARISON OF THE CANDIDATE MATERIALS

The room-temperature strengths of the three ceramics studied in the strength and dynamic fatigue measurements are very comparable and lie around 400 MPa. This strength level is assumed to be sufficient for the present application, i.e., for transport and assembly. In place, it is not expected that heat exchanger tubes would experience stresses at such high levels. At 1100°C, the strengths of Coors β -SiC and NT230 are basically unchanged from room temperature, while at this temperature, Lanxide DIMOX has attained a lower strength level of about 200 MPa. At 1400°C, the strength of Coors β -SiC is still unchanged while the strength of NT230 dropped to about 300 MPa. The strength of Lanxide DIMOX remained at the 200-MPa level. It is important to notice that the variability of the fast-fracture strength of NT230 increased with temperature. At room temperature, the Weibull modulus was 10.8, and at 1400°C, it was as low as 2.8. It was seen that the reason for the high variability was a batch-to-batch variability in the NT230 which was delivered to Oak Ridge National Laboratory in two batches. The batch-to-batch variations probably were in the impurities in the Si-alloy, resulting in the melting point of the alloy varying over and under the test temperature of 1400°C. Dividing the 1400°C strength distribution into two exclusive flaw populations resulted in two populations both having a Weibull modulus of about six, see Table 3. The variability of the strength of Coors β -SiC was significantly less with a Weibull modulus ranging from 12.0 to 9.5 at room temperature and 1400°C, respectively. The Lanxide DIMOX experienced an increase in the Weibull modulus with temperature ranging from 9.6 to 13.1; see Table 5.

Also, in Table 5, the confidence bounds for the Weibull moduli are given showing, with the exception of NT230 at 1400°C as discussed above, the Weibull moduli for all conditions are not significantly different.

The dynamic fatigue experiments showed that Coors β -SiC exhibited no SCG over the temperature and stressing rate regime used in these experiments. Earlier studies on sintered SiC had shown that some SCG may exist at higher temperatures, but the current material exhibited no such behavior. It is important to note that the present experiments also range over considerably longer testing times (slower stressing rates) than were employed in most of the results cited in the literature. It would therefore seem to be a sound conclusion that this type of SiC does not exhibit SCG up to 1400°C.

The NT230 does not exhibit SCG at 1100°C, but at 1400°C, a strength degradation as a function of stressing rate was observed. Employing all data (including both batches), the n value was found to be 15.5 for NT230 at 1400°C. This is a significantly low number so that strength degradation over time must be accounted for in design. As was seen in Fig. 10, the effect of the two different batches became less significant for the slower stressing rates, although specimens from one batch fell predominantly in the high-strength end of the population. There were not enough data points to separate the two batches for all stressing rates, but it is seen that both batches experienced a strength reduction as a function of time. So, although the strength levels might be different, the difference between fast fracture and the slowest stressing rate will be about the same, resulting in a similar n value. The consequences for lifetime prediction are evident from Fig. 12, where two sets of Weibull parameters are compared at two different levels of failure probability. It is clear that in order to achieve a time to failure of more than 2 years with an acceptable level of reliability, the applied stresses (thermal and mechanical) have to be low. It is further clear that if the NT230 is to be used at 1400°C or above, it becomes important to control the processing closely so that the properties of the components are the same as the test material and so that the batch-to-batch variability is minimized.

Lanxide DIMOX did not exhibit SCG at 1100 or 1400°C. However, at 1400°C, creep became the dominating failure mechanism at stressing rates of 0.01 MPa/s and less. At 0.001 MPa/s, the creep became so large that the specimens deformed and reached the bottom of the fixture before they fractured. At 0.01 MPa/s, the specimens were fractured at a load comparable to the fast-fracture load; however, the specimens had undergone considerable creep deformation, and the resulting strength calculated from elastic beam theory therefore overestimated the strength. Therefore, the Lanxide DIMOX experienced some strength reduction as a function of stressing rate, but this was primarily due to creep rather than SCG, as was confirmed by the fractographic investigation discussed below. At 1100°C, creep was much less important, although some permanent deflection was observed after long testing times at this temperature. In order to use this material in the proposed application, the creep properties need to be better established at the temperature under consideration. Creep will not be a significant problem at temperatures up to 1100°C, but the creep rates may be high enough to be taken into consideration.

The failure modes were investigated by optical microscopy and SEM. The observations on fracture-initiation points are consistent with the strength measurements. NT230 experienced failure from pores at room temperature. At elevated temperature, fast fracture failures were from pores or metal-rich areas, dependent on the batch of material. At 1100°C,

the failures at the various stressing rates were consistent with no strength loss, i.e., failures were initiated from pores or metal-rich areas as in the case of fast fracture. At 1400°C, the failure modes changed as a reduction in strength was observed. At stressing rates of 0.001 and 0.0001 MPa/s, SCG zones which had effused from metal-rich areas were observed. Coors β -SiC failed from pores at all temperatures and stressing rates, consistent with the very uniform strength values and Weibull moduli. Lanxide DIMOX failed from metal-rich areas at lower temperatures and faster stressing rates, but the fracture mode changed to creep failure for the slower stressing rates at 1400°C. The difference between the SCG zones observed in NT230 and creep failure observed in Lanxide DIMOX is that the SCG zone is localized and has clearly grown out from a specific flaw, while the fracture surface in the crept specimens shows a larger damage area spread out over the tensile zone and containing numerous small cracks. It is not clear whether the Lanxide DIMOX will exhibit SCG at certain stress and temperature combinations, or whether a direct transition from fast-fracture to creep mode occurs.

Four materials were exposed to two different coal ashes at two different temperatures. The Coors β -SiC was not exposed due to lack of available material at the time of the experiment, but a sintered α -SiC (Carborundum) was exposed instead, and an experimental grade of Lanxide DIMOX was also included. The only material whose strength was unaffected by the exposure to coal ash was the Lanxide DIMOX material. This material has a protective aluminum oxide coating produced by reoxidizing the specimens after they had been machined into coupons. The reoxidation procedure was performed in order to utilize the residual aluminum alloy exposed during the machining to form a protective aluminum oxide layer on the material. This alumina layer reacts further into mullite or anorthite depending on the chemistry of the coal ash. After the 300-h exposure, a slight drop in strength was observed for Lanxide DIMOX, similar for all temperature/coal ash combinations, and it was believed that this was a result of an aging effect similar to what has been observed during aging in air. For the three other ceramics, NT230 SiSiC, Hexoloy SA α -SiC, and the experimental-grade Lanxide, a significant strength reduction was observed as a result of the coal ash exposure. In general, the NT230 seemed to be most strongly affected, and a trend was seen toward more corrosive attack for Illinois #6 at the higher exposure temperature.

RECOMMENDATIONS FOR FURTHER WORK

In comparing the materials under consideration, Coors β -SiC stands out from a strength and reliability standpoint when exposed to air at elevated temperature. This material exhibited no strength loss as a function of temperature or stressing rate, and the material further exhibited Weibull parameters and failure modes which were essentially unchanged with time

and temperature. However a similar material, Hexoloy SA α -SiC, experienced corrosive attack and strength loss when exposed to coal ash at elevated temperature. Lanxide DIMOX experienced no SCG in air, but creep became the dominant failure mechanism at elevated temperature. However, Lanxide DIMOX withstood the coal ash exposure quite well and showed no corrosive attack or strength loss after exposure to two different coal ashes at two different temperatures. NT230 exhibited loss of strength due to SCG at 1400°C in air, and this material also showed a high variability in the properties at that temperature, making lifetime predictions rather uncertain. The coal ash exposure caused severe pitting on the surface of NT230, resulting in strength loss after 300-h exposure.

The present experiments were designed to produce baseline data for candidate materials for heat exchangers in advanced, gas turbine-containing coal-fired power plants. Further work for obtaining design parameters for these ceramics for this application is needed. Research should include work on determining strength as a function of stress and temperature during coal ash exposure as well as further exploration of corrosive attack and strength reduction mechanisms after long-time exposure to coal ash at elevated temperature. In order to obtain necessary design data for Lanxide DIMOX at elevated temperatures, the creep properties of this material need to be investigated in detail. In addition materials utilizing Al_2O_3 and mullite coatings should be explored to determine their resistance to coal ash. Silicon carbide based ceramics are a logical first choice as the substrate.

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