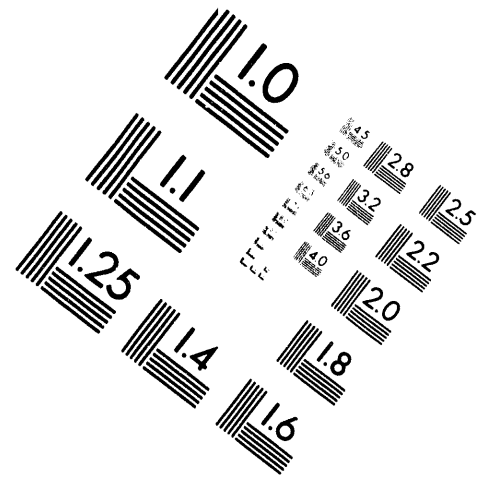


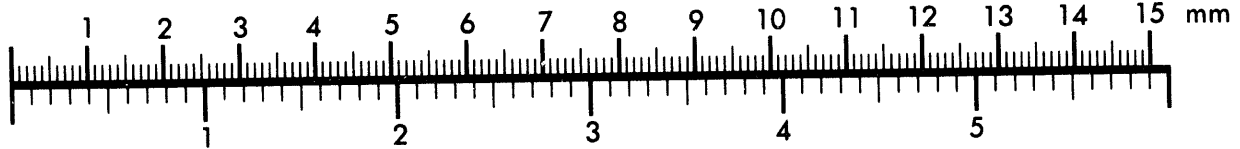
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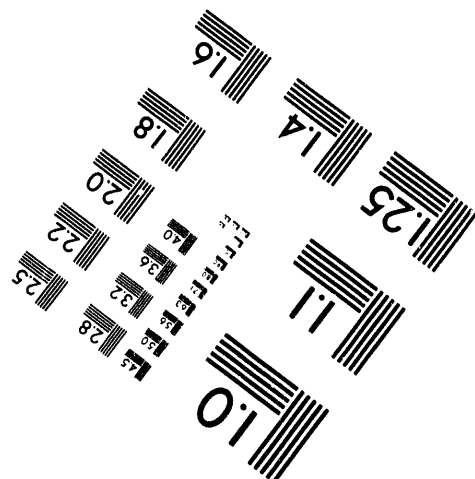
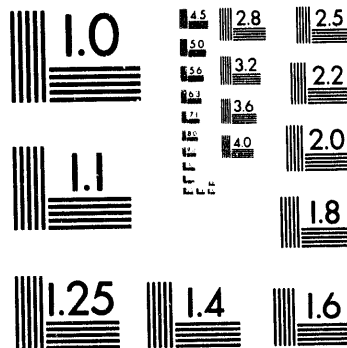
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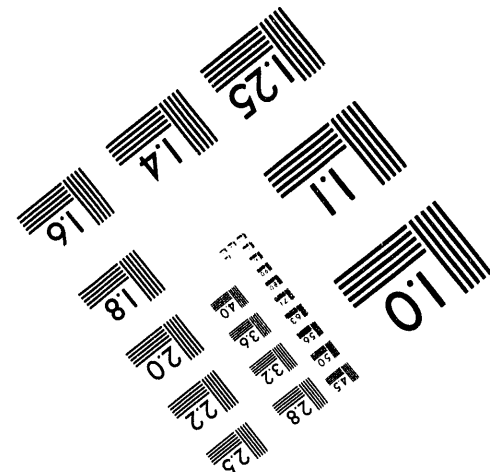
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## COMPARISON OF THE DYNAMIC FATIGUE BEHAVIOR OF TWO MONOLITHIC SiC AND AN Al<sub>2</sub>O<sub>3</sub>/SiC COMPOSITE.

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### ABSTRACT

Two monolithic silicon carbides, NT230 siliconized SiC from Norton Saint Gobain and sintered  $\beta$ -SiC from Coors, and a silicon carbide particulate reinforced alumina ceramic composite from Lanxide, which all are candidate materials for pressurized head exchangers in coal-fired power plants have been evaluated. The fast fracture flexure strength was measured as a function of temperature. All candidate materials retained a sufficient strength level up to 1400°C. The susceptibility to slow crack growth (SCG) was evaluated by the dynamic fatigue method at 1100°C and 1400°C. None of the materials exhibited SCG at 1100°C. At 1400°C the siliconized SiC ceramic showed limited SCG and the composite ceramic exhibited creep damage when stressed to 50% of fast fracture strength at the intermediate and slow stressing rates. This prevented the evaluation of the SCG properties of this material at 1400°C. Fractography supported the mechanical observations and with the exception of the specimens which exhibited creep damage, only the siliconized SiC showed a small SCG damage zone at long times at 1400°C.

### 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. The improved systems must have low emissions of NO<sub>x</sub> and SO<sub>x</sub> and particulates, and lower CO<sub>2</sub> emissions due to a higher thermal efficiency of the overall power generation cycle. Large improvements in efficiencies will require a change to gas turbines (Brayton Cycle) instead of exclusive reliance on steam turbines ((Rankine Cycle). In order to increase the efficiency of the gas turbine it is necessary that the working fluid (air) is at the highest possible temperature, and that it (due to the corrosion and erosion problems of the turbine)

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be clean air and not contain coal ash. This can be achieved through the use of ceramic heat exchangers to separate the coal combustion product stream from the turbine working fluid. For system efficiencies well above 50%, these heat exchangers must be able to operate at temperatures up to 1600°C.<sup>1,2</sup>

The concept of ceramic heat exchangers for the use in externally fired combined cycles (EFCC) for power generation has been evaluated over several years. Much work was done in the late seventies and early eighties to conceptualize the design, test materials, and build prototypes.<sup>3,4</sup> The leading candidate materials were identified as sintered SiC or siliconized SiC. Several materials were tested in combustion environments, and in some environments SiC survived quite well.<sup>5,6,7,8</sup> Despite the considerable efforts put forward in these programs, a technology assessment performed in 1989 by EPRI<sup>9</sup> on advanced fossil power systems, concluded that in order to commercialize the use of pressurized ceramic heat exchangers in externally fired combined cycles, further research and development on both the materials and the engineering systems needed to be done.

Some of this work is presently funded by the United States Department of Energy. The present work is part of a large development program (Combustion 2000) and the goal of the present task 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 as base line data for later experiments where the materials will be exposed to coal slags at elevated temperatures. Some of the work on coal slag exposure is underway in a parallel effort.<sup>10, 11</sup>

## EXPERIMENTAL PROCEDURE

Three materials have been compared. These are  $\beta$ -SiC from Coors Ceramics Company, NT230 siliconized SiC from Norton Saint Gobain and Lanxide Dimox SiC<sub>p</sub>/Al<sub>2</sub>O<sub>3</sub> from Lanxide Corporation. The manufacturers' data on material properties are summarized in Table 1.  $\beta$ -SiC is sintered silicon carbide with a fine grain structure and high density. NT230 SiC is siliconized silicon carbide and contains free silicon metal (8 Vol%) and some residual porosity. The SiC<sub>p</sub>/Al<sub>2</sub>O<sub>3</sub> which is manufactured by the Lanxide Direct Oxidation process (Dimox) contains 48 Vol% SiC<sub>p</sub>, 38 Vol% Al<sub>2</sub>O<sub>3</sub> and 13 Vol% Al-alloy, and some residual porosity. 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°C and 1400°C in a hydraulic flexure testing system. Fast fracture tests were carried out at a stressing rate of 40 MPa/s at all three temperatures, with a specimen size of 3 mm x 4 mm x 50 mm, and inner and outer spans of 20 mm and 40 mm respectively. The Lanxide Dimox material was tested under fast fracture conditions at additional temperatures down to 600°C.

Dynamic fatigue experiments were performed at 1100°C and 1400°C in air at stressing rates of 1 MPa/s, 0.01 MPa/s, 0.001 MPa/s and 0.0001 MPa/s, resulting in testing times from a few minutes up to about 1000 hours. The purpose of the

dynamic fatigue experiments were to determine the tendency for slow crack growth (SCG), and to establish baseline data for later experiments in different environments.

Table 1. Properties of the selected materials.

|  |   |
|--|---|
| <b>Coors <math>\beta</math>-SiC Sintered Silicon Carbide (SiC), Coors Ceramics Company</b> |   |
| 99.9% SiC  | Density 3.1 g/cm <sup>3</sup>               |
|  | Thermal Conductivity 110 W/mK               |
|  | Thermal Expansion 4.4 x10 <sup>-6</sup> /°C |
|  | Fracture Toughness 3.0 MPam <sup>1/2</sup>  |
| <b>NT 230 Siliconized Silicon Carbide (SiC), Norton Saint Gobain</b>                       |   |
| 8 Vol% Si - metal  | Density 3.1 g/cm <sup>3</sup>               |
| 90 Vol% SiC  | Thermal Conductivity 120 W/mK               |
| 2 Vol% Pores   | Thermal Expansion 4.4 x10 <sup>-6</sup> /°C |
|  | Fracture Toughness 3.0 MPam <sup>1/2</sup>  |
| <b>Lanxide Dimox Aluminum Oxide with Silicon Carbide Particles, Lanxide Corp</b>           |   |
| 48 Vol% SiC  | Density 3.4 g/cm <sup>3</sup>               |
| 38 Vol% Al <sub>2</sub> O <sub>3</sub>   | Thermal Conductivity 60 W/mK                |
| 13 Vol% Al - alloy   | Thermal Expansion 6.8x10 <sup>-6</sup> /°C  |
| 1 Vol% Pores   | Fracture Toughness 4.5 MPam <sup>1/2</sup>  |

A convenient parameter for comparing slow crack growth is to determine the crack velocity exponent  $n$ .<sup>12,13</sup> The subcritical crack velocity is commonly expressed empirically as a power function of the applied stress intensity factor  $K_a$ :

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

where  $v_0$  and  $n$  are environmentally dependent constants and  $K_{IC}$  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 geometrical constant,  $\sigma_a$  the applied stress and  $c$  the crack length. Substituting (2) into (1) and solving the resulting differential equation for the dynamic fatigue condition, 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  $\sigma_f$  is the fracture strength at the given stressing rate,  $\sigma_i$  is the inert (fast fracture) strength and

$$B = \frac{2K_{IC}^2}{(n-2)v_0Y^2} \quad (4)$$

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:

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

In the case of static loading the time to failure is given by:

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

so that in a graph of time dependent strength versus time to failure, the curves for the static case and the dynamic case should all be parallel and  $\log(n+1)$  apart. However if the mechanisms operating are not the same this may not be so.

Some additional measurements were performed as interrupted static fatigue tests in order to compare the creep properties of the materials. In these tests, the four point flexure specimens were loaded to 70% of the estimated fast fracture load for 300 hours, while the displacement was monitored. After 300 h the specimens were fractured at temperature so that the remaining strength could be compared to the as-received strength.

The fracture testing was accompanied by fractography 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 and crack velocities.<sup>14,15</sup>

## RESULTS AND DISCUSSION

Fast fracture strength as a function of temperature for the three materials is shown in Fig. 1. As is seen in Fig. 1 the as received room temperature strength for the three materials is very comparable, ranging from 373 MPa for the sintered SiC to 412 MPa for the composite ceramic. At 1100°C the strength of both the siliconized SiC and the sintered SiC has increased somewhat, while the strength of the SiC particulate reinforced Al<sub>2</sub>O<sub>3</sub> ceramic has dropped to 223 MPa. At 1400°C the strength of the siliconized SiC has decreased to 176 MPa, the strength of the SiC particulate reinforced Al<sub>2</sub>O<sub>3</sub> ceramic has only dropped slightly more to 206 MPa. The sintered SiC remains at a fairly high strength level of 330 MPa at 1400°C consistent with literature values for this type of material. The SiC

particulate reinforced  $\text{Al}_2\text{O}_3$  was tested at temperatures down to  $600^\circ\text{C}$  and it is seen that the lower strength level for this material is attained around the melting point of aluminum.<sup>16</sup> It is further clear that the dramatic drop in strength for the siliconized SiC is due to the presence of free Si-metal which melts slightly above  $1400^\circ\text{C}$ . The melted metal is apparent as small balls on the surface of the specimens after the flexure strength measurements. It is clear from these results that for the proposed application in heat exchanger tubes, the three materials will likely have the necessary strength in the lower temperature range, but that at high temperatures the strength of the two materials containing free metal may be in question.

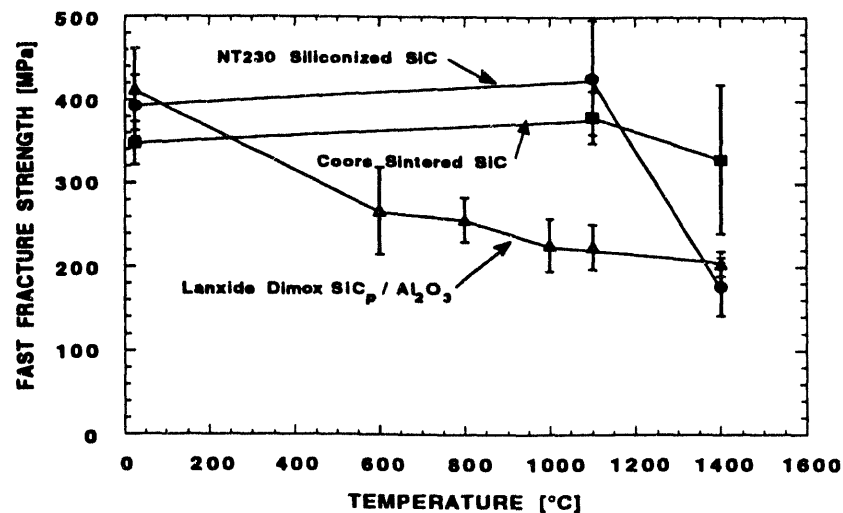


Figure 1. Fast fracture strength as a function of temperature for NT230 SiC, Coors sintered SiC and Lanxide Dimox SiC particulate reinforced  $\text{Al}_2\text{O}_3$ .

The dynamic fatigue data for the three materials are given in Figs. 2 and 3 for  $1100^\circ\text{C}$  and  $1400^\circ\text{C}$  respectively. There are several important observations to be made about the results of the dynamic fatigue experiments.

At  $1100^\circ\text{C}$  no SCG was observed in any of the materials. This is clearly evidenced by the slopes of the curves being essentially zero, i.e. there is no degradation in strength due to the long time exposure to ambient air. It is further seen that the ranking in strength between the three materials remain the same at all stressing rates as it was at the fast fracture tests shown in Fig. 1.

At  $1400^\circ\text{C}$  the NT230 data indicate that this material has a limited strength degradation with time, the resulting  $n$  value calculated by Eq. 5 is 82. The sintered SiC showed no SCG at  $1400^\circ\text{C}$ . Both these results are consistent with the literature although the  $n$ -value for this version of the siliconized SiC is higher than that of earlier versions.<sup>17,18</sup> Notice that the curve for Lanxide Dimox stops at a stressing

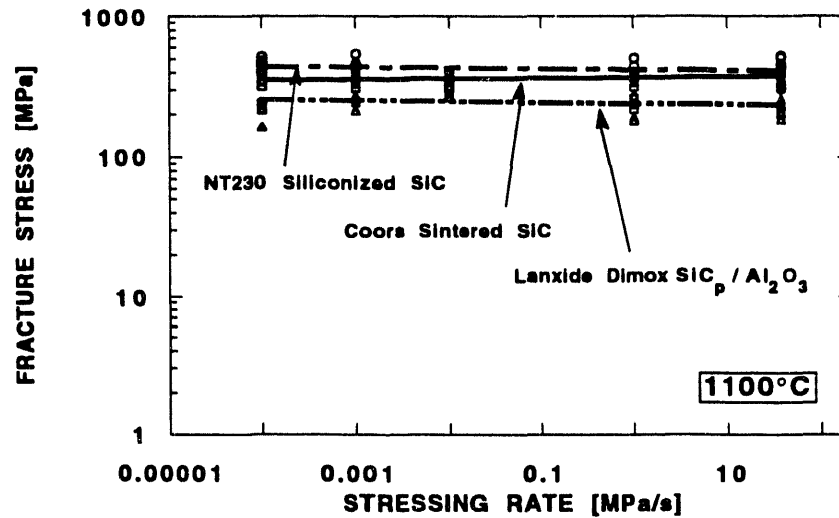


Figure 2. Fracture strength as a function of stressing rate for NT230 SiC, Coors sintered SiC and Lanxide Dimox SiC particulate reinforced Al<sub>2</sub>O<sub>3</sub> tested in four-point flexure at 1100°C. Open symbols are individual datapoints, closed symbols are average values.

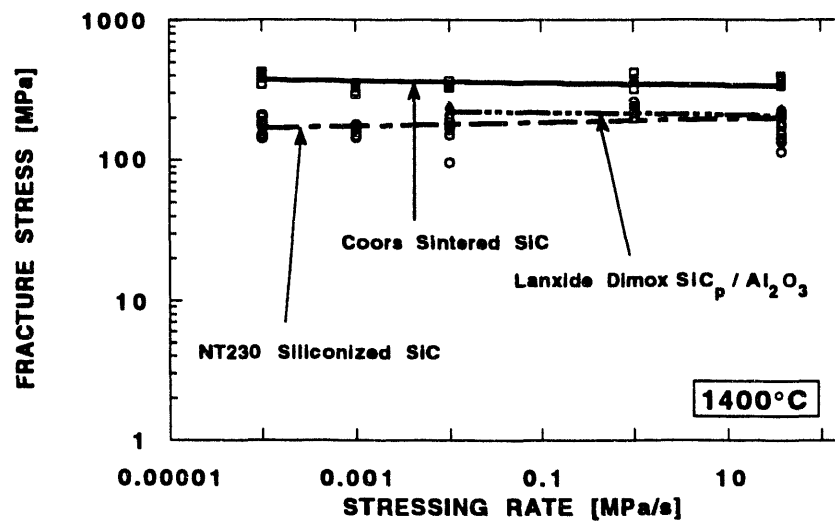


Figure 3. Fracture strength as a function of stressing rate for NT230 SiC, Coors sintered SiC and Lanxide Dimox SiC particulate reinforced Al<sub>2</sub>O<sub>3</sub> tested in four-point flexure at 1400°C. Open symbols are individual datapoints, closed symbols are average values.



rate of 0.01 MPa/s. Experiments at the slower stressing rate was attempted, but the specimens then spent so long a time at high stress that creep became dominant and it was impossible to fracture the specimens in a four-point flexure test. As a matter of fact, the creep in Lanxide Dimox at 1400°C became evident already at a stressing rate of 0.01 MPa/s so that the strength calculated at this rate is not accurate as the small scale deflection condition for the beam theory is violated at that point. The creep is evidenced by looking at the actual load deflection data as shown in Fig. 4 for the three materials at 1400°C and a stressing rate of 0.01 MPa/s. The two monolithic ceramics show only elastic deflection, while at a load of approximately 130 N (corresponding to about 50% of the fast fracture load) the Lanxide Dimox starts to creep excessively. It is seen from Fig. 5 that this is not a problem at 1100°C, neither is creep a problem for any of the other two materials which shows mainly elastic deflection curves at the two test temperatures. It is well known from the literature<sup>19</sup> that crack growth and crack blunting and other creep related phenomena are competing deformation mechanisms, and the temperatures and stress levels at which these transitions will occur will vary from material to material. It is clear that under the given conditions Lanxide Dimox will not exhibit SCG but undergo a transition from fast fracture to creep failure.

The limited number of interrupted static fatigue experiments completed to date support the results of the slow fracture tests. After 300 h at 70% of fast fracture stress at 1400°C NT230 and Coors  $\beta$ -SiC show very limited creep and no strength reduction while Lanxide Dimox crept to the bottom of the fixture and therefore the remaining strength could not be measured. Creep data measured by the material

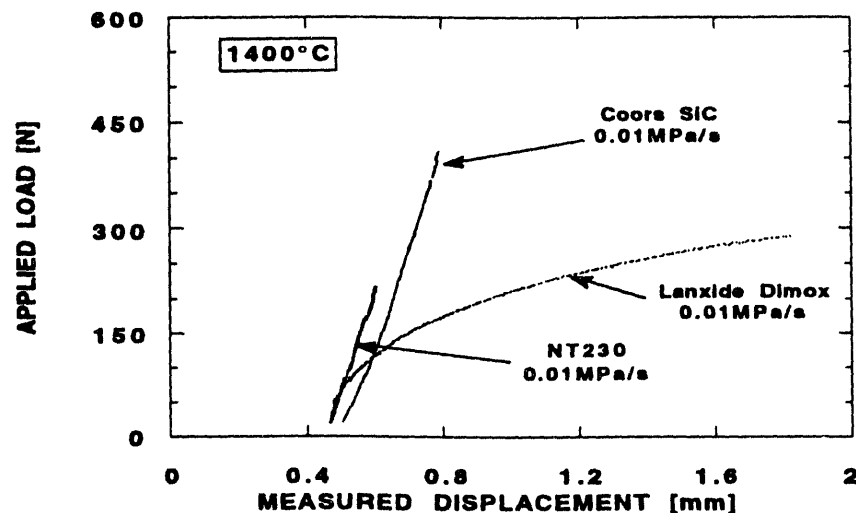


Figure 4. Typical load displacement curves for NT230 SiC, Coors sintered SiC and Lanxide Dimox SiC particulate reinforced  $\text{Al}_2\text{O}_3$  at 0.01 MPa/s and 1400°C.

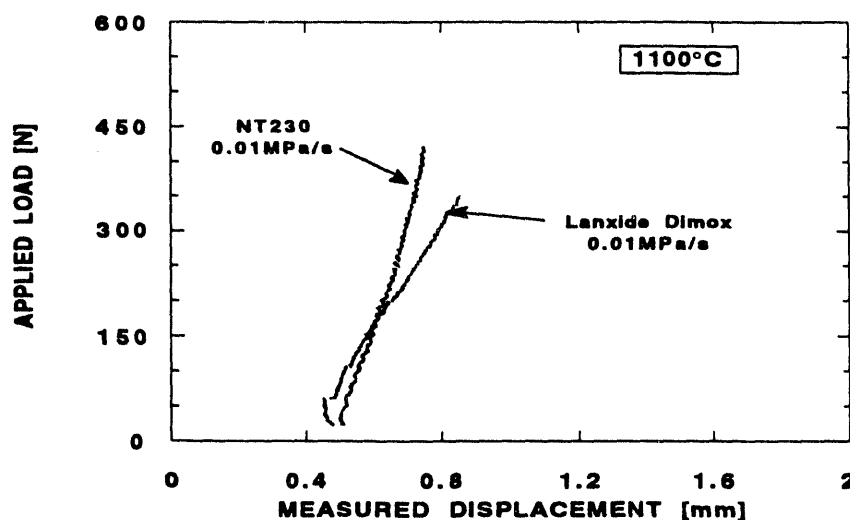


Figure 5. Typical load displacement curves for NT230 SiC and Lanxide Dimox SiC particulate reinforced  $\text{Al}_2\text{O}_3$  at 0.01 MPa/s and 1100°C.

supplier confirm a higher creep rate for this composite than for SiC, although the creep is improved over monolithic alumina.<sup>20</sup> The temperature and stress level for the onset of creep is under further investigation.

Fractography studies by stereo optical and scanning electron microscopy methods support the strength observations well. The sintered SiC fails predominantly from subsurface pores both at room temperature and at elevated temperatures. The fracture surfaces at the slower stressing rates at 1400°C have distinct fast fracture features and no damage zones can be seen. The siliconized SiC fails predominantly from Si-metal inclusion sites at room temperature and elevated temperatures. The fracture surfaces look like fast fracture, but at the longer testing times at 1400°C the fracture initiation sites are larger with the possible existence of a small damage zone. This will be investigated further in the continuation of this work. The Lanxide composite fails generally in a fast fracture mode from inclusion or pores. The longer times at 1400°C produces a surface with metal smeared over it, and also in some instances a small damage zone may be seen.

## CONCLUSIONS

Three ceramics are under evaluation as candidate materials for heat exchangers in fossil energy systems; NT230 siliconized SiC from Norton Saint Gobain, sintered  $\beta$ -SiC from Coors, and a silicon carbide particulate reinforced alumina ceramic composite from Lanxide. The materials were evaluated with respect to fast fracture strength at room temperature, 1100°C and 1400°C and for slow crack growth

properties at the elevated temperatures. The fast fracture strength of the materials ranges from 370 MPa to 410 MPa at room temperature and from 175 MPa to 320 MPa at 1400°C. The strength levels are consistent with literature values and will be used in the evaluation of the heat exchanger design. The failure origins are predominantly pores in the sintered  $\beta$ -SiC, and metal-rich inclusions in siliconized SiC and the ceramic composite.

Neither of the materials exhibited any SCG at 1100°C, as evidenced by the flat dynamic fatigue curves and by fractography. At 1400°C the sintered  $\beta$ -SiC showed no SCG while the siliconized SiC showed some SCG, with a crack velocity exponent  $n=82$ . This was supported by the existence of a very small damage zone in this material tested at very low stressing rates. The silicon carbide particulate reinforced alumina ceramic composite showed no SCG at 1400°C, but creep became the dominant mechanism for specimens tested at slow stressing rates. To the authors' knowledge, this is the first time this ceramic composite has been subjected to a dynamic fatigue study, and the results indicate that under the given conditions SCG will not occur and there will be a transition directly from a fast fracture mode to a creep failure mode for this material.

## ACKNOWLEDGMENTS

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