INTRODUCTION

The purpose of this project is to compare a limited number of candidate ceramics proposed for use in the air heater of a coal fired high temperature advanced furnace (HITAF) for power generation. This work will provide necessary initial structural ceramic parameters for design of a prototype system. Phase 1 of the work consisted of evaluation of the mechanical properties of three structural ceramics at high temperatures in air and a preliminary evaluation of mechanical properties of these structural ceramics after exposure to coal ash. This work was described in a final report,\(^1\) and the results will serve as baseline data for further work. An initial screening of candidate structural ceramics with respect to their creep properties in air at selected temperatures will be performed as Phase 2, and temperatures above which creep may become a design problem will be identified. Tubes and tube sections of the candidate ceramics will then be exposed to a combination of mechanical loads, coal ash exposure and high temperature, and corrosion behavior, mechanisms and post exposure mechanical properties will be evaluated.

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DISCUSSION OF CURRENT ACTIVITIES

Materials

Two of the materials studied in Phase I of this project exhibited creep at the highest test temperature, and these were therefore subjected to flexural creep measurements. These were NT230 siliconized silicon carbide from Saint Gobain Norton company and SiCp/Al₂O₃ from DuPont Lanxide Composites Inc. The third material tested in Phase 1 was β-SiC from Coors Ceramic Co., and this did not exhibit creep deformation at any of the test temperatures. NT230 SiC is siliconized silicon carbide and contains free silicon metal (8 vol%) and some residual porosity. The SiCp/Al₂O₃, which is manufactured by the Lanxide Directed Metal Oxidation process (DIMOX), contains 48 vol% SiCp, 38 vol% Al₂O₃ 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 coal ash exposure experiments in Phase 2 will be performed on tubes and C-ring specimens. They are NT230 Si-SiC from Saint Gobain Norton and Lanxide DIMOX SiCp/Al₂O₃ from DuPont Lanxide Composites Inc. as described above, β-SiC from Coors Ceramics Co., and Hexoloy sintered α-SiC from Carborundum Co. The tubes are nominally 50 mm (2") OD and 38 mm (1.5") ID and are 305 mm (12") long. A thorough description of the materials has been given previously.¹

Creep experiments

Flexure creep tests were carried out in four-point bending, with 40 mm outer and 20 mm inner spans and specimen dimensions 4 mm by 3 mm by 50 mm. The fixtures were sintered SiC with pins that were free to rotate. The experiments were carried out in the flexure test system (FTS), which is a hydraulic system with SiC push rods in load control. The fixtures and part of the push rods were entirely contained in the furnace which was heated by molybdenum disilicide elements and could be kept at temperatures up to 1600°C for more than 1000 hours. Two types of tests have been done: static tests at a fixed load for 300 hours and stepped loads of 100 h duration each. The static tests were performed at 1400°C, i.e. the temperature at which creep was observed in the dynamic fatigue experiments, and the loads were chosen such as to correspond to 25% and 70% of the fast fracture strength at that particular temperature. The stepped tests were carried out at 1200, 1300 and 1400°C at loads corresponding to stress levels of 50 MPa, 100 MPa, 150 MPa and so on up to 250 MPa (i.e. 500 h) or to failure.

An automatic data acquisition system records the time, temperature, load and deflection at specified intervals. The deflection is measured by the use of a linear variable differential transducer (LVDT), and the movement of the loading pins is measured. For these tests two of the three stations were loaded with fixtures and specimens while the third station was loaded with a dummy fixture only. The dummy fixture is used to subtract the deflection of the fixture and push rods from the data, and also to monitor any
irregular movements due to temperature changes or other effects. The resulting raw data are files consisting of load, LVDT reading and temperature versus time. As a first approximation, and for comparison between the materials and with previous experiments (Lin and Becher Al₂O₃/SiC whisker)²,³ the analysis by Hollenberg et al.⁴ was used. In this analysis the stress exponent, n, is obtained from the measured deflection rate and the resulting stress - strain rate relationship.

The stepped load deflection data look typically as shown in Fig. 1, where the load point deflection data corrected for the deflection in the dummy fixture are shown as a function of time for Lanxide DIMOX at 1400°C. As can be seen, the creep does not reach a constant creep rate during the 100 hours, and as can be seen from Fig. 2 a steady state creep rate is not achieved even after 300 h at a constant stress. The deflection rates at the various stress levels were therefore obtained as the slope of the deflection curve towards the end of the 100 h test interval.

Figure 3 shows the strain rate vs. stress for Lanxide DIMOX measured at 1200°C. The figure contains data obtained by both methods described above. Also shown, for comparison, are the strain rates for alumina and a SiC whisker reinforced alumina from ref. 3. The creep exponent, n, is found as the slope of the curves. The magnitude of the creep exponent is an indication of the active creep mechanisms and it can be seen that there is a difference in the n-value for Lanxide DIMOX and the two alumina materials. Figure 4 shows the strain rate as a function of stress for Lanxide DIMOX and NT230 measured at 1400°C. An increase in the strain rates for Lanxide DIMOX can be seen, and also the creep exponent, n, has increased dramatically, indicating that there is a change in creep mechanism from 1200°C to 1400°C. The creep rate for NT230 at 1400°C is comparable to the creep rate for Lanxide DIMOX at 1200°C. Creep experiments were carried out for NT230 at the lower temperatures as well. However, the creep rates were so low that the measured deflections lay within the accuracy of the experimental set-up.

The present results have implications for the proposed application, i.e. high temperature heat exchangers. The strain rates for Lanxide DIMOX at 1400°C are quite high, and in a design where even moderate localized stresses will occur, the components may be out of tolerance in an unacceptably short time. However, at 1200°C both the magnitude of the strain rates and the creep exponent are considerably lower, and this temperature may constitute a possible design temperature for this material. However, in order to ensure a reliable estimation of the life-time of components at this temperature, further measurements will be needed. Creep in tension should be performed, as well as time to failure experiments in tension. It is further necessary to investigate the creep and long time failure mechanisms for the temperatures under consideration. The NT230 Si-SiC exhibited improved creep properties compared to similar siliconized silicon carbides.⁵,⁶ Especially at 1200°C and 1300°C, the material exhibited very little creep. At 1400°C some creep was measured, and further measurements in tension might be warranted also for this material. It is, however, important to keep in mind that the NT230 exhibited slow crack growth at 1400°C,¹ and the result may be an unacceptably short lifetime at 1400°C because of this.
Figure 1. Load point deflection for a Lanxide DIMOX flexure bar stressed for 100 h each in increments of 50 MPa at 1400°C. The flattening out of the curve after approximately 220 h indicates that the specimen reached the bottom of the fixture.

Figure 2. Load point deflection for a Lanxide DIMOX flexure bar stressed at 50 MPa for 300 h at 1400°C.
Figure 3. Strain rate vs. stress for Lanxide DIMOX, alumina and SiC whisker reinforced alumina at 1200°C.

Figure 4. Strain rate vs. stress for Lanxide DIMOX and NT230 Siliconized SiC at 1400°C.
Description of coals

As stated above, the mechanical properties of the candidate ceramics measured at elevated temperature in air will serve as baseline data for extensive measurements of mechanical properties during and after exposure to coal ash. It is expected that the coal ash present in the proposed systems will degrade the materials, their mechanical properties and structural integrity. The severity of the degradation will be dependent on the ceramic, the coal, and the temperature. An extensive test matrix has been designed to address some of these issues.

Three types of coal ash have been obtained from the University of North Dakota Energy and Environmental Research Center (UNDEERC) for these measurements. These have been received by the UNDEERC from three different power plants, and chemical analysis and viscosity versus temperature data have been measured by UNDEERC. A description of the three coal ashes follow.

**ILLINOIS No. 6 - Coffeen**

This coal ash came from coal burned at the Central Illinois Public Service Coffeen Plant. The coal was produced from a low sulfur spur of the main seam called the East Hornsby seam. The coal is low in sulfur because it contains less pyrite (FeS$_2$) than normal, and the resulting reduced iron (Fe) level leads to a high viscosity for the slag. Therefore, 1.5% limestone was added by the power plant to lower the viscosity. The resulting slag is a low Fe, high Ca Illinois No. 6 with the same viscosity as a "normal" Illinois No. 6 without limestone addition.

**Powder River Basin, Rochelle**

This coal came from coal burned at the Northern States Power Riverside Plant, and was produced from the Rochelle mine, Wyoming. Approximately 3% petroleum coke was added at the power plant which resulted in a high vanadium content. Since it contains burned coke (C), bubbling may occur during the test causing problems with slag everywhere in the furnace. The slag will therefore be heated to 800°C for 0.5 h, stirred, and heated for another 0.5 h in order to burn off the coke before the exposure experiments. The heat treatment may result in agglomeration of the ash, but it will be used without sieving out the agglomerates.

**ILLINOIS No. 6 - Baldwin**

This slag came from coal burned at the Illinois Power Company, Baldwin Plant. It is a mixture of Illinois No. 6 and Illinois No. 5 from the Peabody Coal Company Marissa Mine and from the Arch Mineral Company Captain Mine. Some minerals, especially FeS$_2$ were removed before shipping from the mine, something that is standard practice, and it contains no additives. The resulting slag is a typical Illinois No. 6 with less Ca and more Fe than the batch from the Coffeen Plant.
All the slag samples received at ORNL were split from the main barrel into smaller samples according to ASTM D.2013 "Standard Method of Preparing Coal Samples for Analysis".

The coal ash exposure tests will be carried out at 1090°C (2000°F), 1260°C (2300°F) and 1430°C (2600°F) in air. Two sets of experiments will be performed. For one set, sections of about 150 mm will be covered with the coal ash and exposed in a furnace for up to 500 h. Additional ash will be introduced during the test such that a minimum of 5 mm coal slag layer will be achieved. After exposure, the tubes will be examined, cut into 10 mm wide C-rings, and the remaining strength will be measured by performing a fracture test at the same temperature as the exposure temperature. After strength measurements fracture surfaces will be examined and the slag/ceramic interfaces will be evaluated using a scanning electron microscope (SEM) and a scanning electron microprobe. The second set of tests will be carried out in a modified version of the flexure test system. C-rings will be loaded to a given stress level, heated to the test temperature, and the coal slag will be introduced into the furnace in such a manner that the tensile surfaces (outer) of the C-rings will be exposed to the coal slag. Slag will be reintroduced at given intervals throughout the test to ensure that the corrosive species will be in contact with the specimens for the entire test time.

The University of North Dakota Energy and Environmental Research Center is a member of the United Technologies team in the development of a Combustion 2000 HiPPS concept. As part of that effort, a 100 hour pilot-scale slagging combustion test of some metal alloy heat exchanger materials and some extremely corrosion resistant refractories will be performed. The test will be performed in the UNDEERC 750,000 Btu/hr combustor while firing the same Illinois No. 6 coal that was burned at the Illinois Power Baldwin plant to produce the slag which will be used in part of the laboratory experiments. United Technologies will be evaluating a number of ceramics in the UNDEERC facility to compare their corrosion resistance, and tubes of the four ceramics described above will be included in the test. The samples will be uncooled and will be placed in a position in the furnace where it is believed that the gas temperature will approximate the skin temperature of the component that will be constructed of the material. Because the same fuel is being used as produced the slag, this will be an excellent chance to compare the high temperature slag corrosion laboratory experiments to specimens exposed in a real system.
REFERENCES


