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**Task 6.3/6.7.4 - Engineering Performance of Advanced
Structural Materials**

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**By:
John P. Kay
John P. Hurley**

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U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Energy & Environmental Research Center
University of North Dakota
P. O. Box 9018
Grand Forks, North Dakota 58202-9018

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TABLE OF CONTENTS

LIST OF FIGURES	i
1.0 INTRODUCTION	1
2.0 OBJECTIVE	1
3.0 ACCOMPLISHMENTS/SILICON CARBIDE JOINING	1
3.1. Preparation of Joining Material	1
3.2 Joule Heating Tests	2
4.0 REFERENCES	6

LIST OF FIGURES

1	Graph showing the results of the attrition grinding of silicon powder for 4 and 8 hours as compared to the stock powder	3
2	Graph showing the results of the attrition grinding of silicon powder for 8 hours as compared to the stock powder sieved to -10 micron and sieved powder ground for 8 hours	3
3	Graph showing the results of 3-point flexural strength test for three powder formulations	5
4	Graph showing the results of 4-point flexural strength tests for four powder formulations	6

TASK 6.3/6.7.4 - ENGINEERING PERFORMANCE OF ADVANCED STRUCTURAL MATERIALS

1.0 INTRODUCTION

Future energy systems will be required to fire low-grade fuels and meet higher energy conversion efficiencies than today's systems. The steam cycle used at present is limited to a maximum temperature of 550°C, because above that the stainless steel tubes deform and corrode excessively. However, to boost efficiency significantly, much higher working fluid temperatures are required. Although high-temperature alloys will suffice for the construction of these components in the near term, the greatest efficiency increases can only be reached with the use of advanced structural ceramics.

2.0 OBJECTIVE

The objective of this work is to assist in the development of new materials that can be used for the construction of high-temperature components in advanced energy systems. The work will include the development of a patentable technique for joining large silicon-based advanced ceramics in the field. The key to developing a successful technique will be the use of reactive joining compounds to lower the joining temperature without leaving continuous channels of unreacted compounds that can weaken the joint at temperatures over 1250°C or serve as conduits for transport of corrodents. Special efforts will be made in this project to transfer the developed technologies to the materials industry via licensing agreements through the EERC Foundation.

3.0 ACCOMPLISHMENTS/SILICON CARBIDE JOINING

Advanced ceramics, such as silicon carbide (SiC), are resistant to corrosion and are very strong at much higher temperatures than today's metals. For example, SiC does not melt at temperatures as high as 2000°C. This makes SiC difficult to use in the fabrication of large structures, because pieces made from SiC cannot be joined together in the same way that metals can be welded. Therefore, the size of the monolithic ceramic structures that can be manufactured are limited by the size of the sintering furnaces (approximately 10 feet for sintered alpha silicon carbide). In order to make larger objects, such as heat exchangers, many small ceramic pieces must be fused or joined. In addition, repair of the objects will require the use of field-joining techniques. At present, no joining techniques for high-temperature structural ceramics are routinely available.

3.1 Preparation of Joining Material

Previous pellet materials were prepared by combining silicon carbide, graphite, and silicon powders with a solvent, binder, and plasticizer. Two size ranges of SiC were used to increase the packing efficiency of the material. The materials were mixed in a mortar with a pestle for 15 minutes and allowed to dry. After drying, the mixture was broken up into a uniform powder and pressed into pellets. However, the pellets had a relatively low green strength, and the joints were

weak, possibly because of insufficient mixing of the silicon and graphite and poor packing, leading to low levels of silicon carbide formation during the joining process.

Currently, to examine the formation of silicon carbide during Joule heating, pellets are being made which only contain silicon and graphite powder. These powders are being combined in varying molar ratios of silicon to graphite to approach an optimum, high strength joining material which contains no residual elements. The molar ratios being examined are 0.60, 0.80, 0.84, 0.90, and 1.2.

Homogeneous mixing and intimate contact of the powders are essential for the formation of silicon carbide. Intimate contact can be increased by reducing the particle size of the powder. Stock powders with average particle sizes of a few microns can contain particles larger than 40 microns. To create more uniform powders, an attrition grinder was constructed based on designs and techniques developed by the U.S. Bureau of Mines (1, 2). Results of grinding tests with stock silicon powder (average particle size of 1 to 5 microns) are shown in Figures 1 and 2. Particle sizing was performed by computer-controlled scanning electron microscopy (CCSEM).

Grinding the stock powder for 8 hours significantly reduced the particle sizes detected by CCSEM. The greatest reduction over the stock powder was achieved by first sieving the powder to -10 micron and attrition grinding for 8 hours, although some elongated particles over 10 microns along one axis were detected. The result is that a much more uniform particle size can easily be attained using attrition grinding methods.

The joining material is now made from silicon powder which has been attrition ground and graphite powder. These powders are then mixed in the attrition grinder, without grinding media, in the presence of alcohol. After grinding, the powder is then pressed into pellets without the use of a binder or plasticizer. This produces a pellet approximately 0.5 mm thick which can be cut to the proper dimensions with a scalpel.

Testing of the joints have revealed high porosity in the reacted joint material. Therefore, a new die assembly made from silicon carbide was designed that would allow a much higher pressing force to be used. It is hoped that such pressures may be attained so as to force the silicon powder to flow, thereby drastically reducing porosity.

Future work will focus on this and other methods to reduce porosity. Comparison of the effects of changes in the molar ratio of silicon to graphite will continue. Investigation of using sub-micron particle-sized powders will be conducted. Techniques utilizing solgels will be investigated which could possibly replace pellets.

3.2 Joule Heating Tests

No matter what compounds are used in joining SiC, heat must be applied to the joint. Most often the heat comes from an external source, such as a furnace. Sometimes inductive heating or microwave heating is used, but in each of these cases, the object needs to be surrounded by the heater. This is not a problem for objects that are small in at least two dimensions, such as a pipe. For objects that are large in two dimensions, such as heat exchanger panels, these heating methods

Figure 1. Graph showing the results of the attrition grinding of silicon powder for 4 and 8 hours as compared to the stock powder.

Figure 2. Graph showing the results of the attrition grinding of silicon powder for 8 hours as compared to the stock powder sieved to -10 micron and sieved powder ground for 8 hours.

are not applicable. Instead, we are attempting to connect electrodes to either side of a SiC joint and pass an electric current through the material to cause resistive or Joule heating. With proper attachment of the electrodes, combined with the high thermal conductivity of SiC, heating of the joint can be made very uniform, and very large structures could be heated. This method has an additional advantage because the joint is placed in an electrical field known to reduce the temperature necessary for reaction between ceramic precursors—a technique known as combustion synthesis. This is an especially valuable attribute in cases where the joining is accomplished by reaction sintering.

Preliminary work showed that it was possible to heat SiC by passing an electric current through it. However, when using a constant-voltage power source such as a Variac for control, current runaway occurred as the SiC was heated. This happened because when using a fixed voltage, the resistance drops as the temperature is raised; this causes the current to increase, further heating the sample and dropping the resistance. The inverse relationship between temperature and resistivity leads to extremely rapid temperature escalations at constant voltage (approximately 300° to 500°C/sec), causing thermal shock and breakage of the bars. Therefore, a current-limiting circuit was constructed which can be used to closely control the joint temperature.

Test samples were made up of Hexoloy SA sintered alpha silicon carbide flexure test bars of $6 \times 8 \times 25$ mm and a joining pellet of approximately $7 \times 9 \times 0.5$ mm. The pellets used were slightly larger to ensure contact with the full cross-sectional area of the bar. Test preparation included etching the bars in hydrofluoric acid to remove any silicon oxide surface layer. The samples were held in a jig between graphite electrodes. The samples were painted with carbon conducting paint, and the connections between the electrode and test bar were also coated with silver conducting paint. The silver paint helps ensure good electrical conduction between the electrode and the sample. The carbon paint initially conducts the electricity and heats the sample to 300° to 400°C. At these temperatures, the silicon carbide itself is sufficiently conductive to carry the current. The experiments were carried out in two atmospheres: air and nitrogen/2% hydrogen. An S-type (Pt-Rh) thermocouple was used for temperature control.

In order to quantify the quantities of silicon, carbon, silicon carbide, and porosity, the joints were cross-sectioned and analyzed in a scanning electron microscope (SEM). However, problems arose in the analysis when epoxy was used to fill the pores to give the flat surface necessary for proper quantification. Epoxy mounting requires a carbon or metal coating to be applied to reduce charging in the SEM, but this coating made differentiating between epoxy-filled pores and excess carbon difficult. Therefore, a new method has been developed which enables analysis of the joints for porosity and allows for the detection of excess carbon. The method involves the use of indium foil which is rubbed into the cross-sectioned sample to fill the pore spaces. The sample is polished and examined without a carbon or metal coating. Indium appears very bright during SEM analysis which provides excellent contrast when making porosity calculations from grey-level histograms.

Preliminary analysis of the joints formed in air revealed an excess of silicon of over 20%. No excess carbon could be detected. The excess silicon was found to have formed a ring around the outer surface of the joint extending approximately one millimeter into the joint. The ring was independent of the molar ratio of the pellet used. It is believed that the ring formed because the carbon burned off, leaving excess silicon behind. Varying amounts of oxygen were detected in the silicon ring. Using a nitrogen/hydrogen gas mix prevented the carbon from burning off and thus

prevented the silicon ring from forming. Preliminary analysis of the joints formed in nitrogen revealed no excess silicon or carbon in any of the molar mixtures. However, porosities of over 40% were evident, most of which was due to the molar volume reduction that occurred when the silicon and carbon reacted to form the silicon carbide. It is believed that by mixing in a large fraction of preformed silicon carbide powder into the joining material and pressing the pellets at higher pressures with the silicon carbide die to cause silicon flow and increase carbon/silicon contact, we will be able to reduce this residual porosity.

Flexure tests were conducted on the joints prepared in both air and nitrogen/2% hydrogen. Early tests were conducted using a 3-point flexure apparatus. Initial silicon carbide bars were too short to conduct 4-point flexure tests. Later joint and flexure tests were conducted with bars of sufficient length to allow 4-point flexure testing. Results of the flexure tests are shown in Figures 3 and 4. An increase in strength will be observed once the porosity is successfully reduced.

Corrosion tests have begun on the joints. The test entails exposing the joint to Illinois No. 6 slag at a temperature of 1300°C for 100 hours and examining slag penetration of the joint. The joint lies horizontally in the furnace, and slag is introduced by placing 3 to 4 grams of powdered slag, pressed into a pellet, on top of the joint. The slag melts, runs down the joint, and is collected in an alumina crucible. The pellets are replaced as needed for the duration of the test.

Figure 3. Graph showing the results of 3-point flexural strength tests for three powder formulations.

Figure 4. Graph showing the results of 4-point flexural strength tests for four powder formulations.

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