Task 6.3- Engineering Performance of Advanced Structural Materials

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TASK 6.3- ENGINEERING PERFORMANCE OF ADVANCED STRUCTURAL MATERIALS

1.0 INTRODUCTION

Future energy systems operating at higher temperatures and pressures than current coal-fired boilers require improved materials to achieve high performance and long life. These energy systems will be required to fire low-grade fuels and meet higher energy conversion efficiencies. 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.

Advanced ceramics, such as silicon carbide (SiC) or silicon nitride (Si₃N₄), 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.

2.0 OBJECTIVE

The objective of this work is to develop 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 1400°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 Energy & Environmental Research Center (EERC) Foundation.

3.0 ACCOMPLISHMENTS

3.1 Silicon Carbide Joining

3.1.1 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, leading to low levels of silicon carbide formation during the joining process. Corrosion testing of the joints has been postponed until stronger joints are formed.

In an attempt to increase the green strength, reduce thickness, and improve silicon carbide formation, pellets of joining compound have been made using polystyrene powder to replace the graphite, binder, and plasticizer in the formulation. Introducing toluene as a solvent allowed the polystyrene to coat the silicon carbide and silicon metal particles and act as a binder. The sample was pressed in a 31-mm-diameter, cylindrical uniaxial die in a manually operated 30-ton hydraulic press (Spex Industries, Edison, New Jersey) for 10 minutes at 220 MPa (32,000 psi). During sintering, only approximately 8% of the polystyrene should volatilize, leaving carbon to combine with the silicon metal. Pellets have been made of 50 % silicon carbide and 50% silicon and carbon, with a thickness of 0.23 mm, which have displayed better strength than previous pellets. To date, two polystyrene pellets have been sintered at 1450°C for 1 hour. These pellets have not yet been analyzed.

Future work will include further investigation into the benefits of polystyrene as a joint ingredient. Thinner pellets and an improved pressing technique will also be investigated. Techniques utilizing sol-gels will be investigated which could possibly replace pellets.

3.1.2 *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 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 could 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, in turn, causes the current to increase, further heating the sample and dropping the resistance. This leads to extremely rapid temperature escalations (approximately 300° to 500°C/see), causing thermal shock and breakage of the bars. Therefore, a current-limiting circuit was constructed.

To date, four tests have been completed with the power supply. The test sample was made up of Hexoloy SA sintered alpha silicon carbide flexure test bars of 6 x 8 x 25 mm and a joining pellet of approximately 6 x 8 x 0.5 mm. Test preparation included etching the bars in hydrofluoric acid to remove any silicon oxide surface layer. Molybdenum disilicide was then ground into the bar surface to increase the conductivity between the sample and electrodes. The ends of the bars which contact the joining pellet were not ground. The samples were held in a jig between graphite electrodes. A paste of vitreous carbon and water was painted on the entire sample surface and allowed to dry. For the latest test, the joint was covered with vitreous carbon rather than painted on in paste form. The vitreous carbon 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. To reduce the oxidation of the carbon paste and allow the use of C-type (W-Re) thermocouples, the experiments were carried out under a nitrogen purge.

The joining test used a pellet composed of 75 % silicon carbide and 25% silicon and carbon. This sample was able to maintain a temperature between 1350° and 1360°C for 17 minutes before losing conductivity, which was caused by a break in the electrical contact with the SiC. The second test also used the 75% :25 % pellet. This test achieved a temperature slightly above 1400°C for 38 minutes. The test could have continued, but the thermocouple failed, which would not allow temperature control. The third test used a pellet composed of 50 % silicon carbide and 50% silicon and carbon. This sample was held at a constant temperature of 1453°C for 67 minutes, at which time the test concluded under controlled conditions. The fourth joining test used the 50%: 50% pellet; a constant temperature of 1405°C was maintained for 45 minutes and concluded under controlled conditions.

In all four cases, the joint remained intact after cooling to room temperature. Although the joint could be broken with force applied by hand, the failure occurred in the center of the pellet. The Hexoloy SA bars from the third test showed significant loss caused by active oxidation, although the joining material was not affected. The fourth test showed no such loss. Investigation of the active oxidation of the Hexoloy bars will be examined as further tests continue.

Many of the preparation problems were solved prior to examination of the fourth test joint. Carbon could be distinguished from the epoxy by the addition of iodoform (15 wt %) to the resin. Improvements to the polishing technique yielded a flatter surface, with no detectable ridge at the bar-pellet interface.

Figure 1 is a SEM micrograph showing the bar-pellet interface from the fourth test. Necking of pellet material with the bar can be seen. Estimation of average porosity was performed using a grey-level histogram of six areas. Porosity was found to be less than 2%. Although the silicon and graphite are sintering into a cohesive matrix, no direct method has yet been developed to determine the amount of silicon carbide formation from this matrix in the pellet material. Figure 2 is a SEM micrograph showing the interface at a higher magnification. Silicon carbide particles in the pellet can be seen within the matrix of sintered silicon and carbon.

Figure 1. SEM micrograph of the fourth test sample showing the pellet-Hexaloy bar interface. The bar is on the far right of the image.

Figure 2. SEM micrograph of the fourth test sample showing silicon carbide particles within the silicon and carbon matrix.

Future work will include improved analysis techniques to determine the amount of silicon carbide formation in the joints. Further joining tests will be delayed until this problem is solved. Improvements in the joining technique with the power supply will be sought to make the technique reproducible in the field. The use of sonic probes to assist in joining will be examined as well.

3.2 High-Temperature Alloy Corrosion Testing

The task manager will be attending a conference on Hot-Gas Filtration in Karlsruhe, Germany, the week of September 15, 1996. The travel to the conference is funded from another project. However, while in Europe, the task manager will travel to Denmark for discussions on corrosion of alloys to be used in the construction of secondary superheaters in an ultrasupercritical coal-fired power system and a tour of the plant site. The side trip to Denmark will be funded from this project.