TASK 6.7.4 – SILICON CARBIDE JOINING

Final Topical Report

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1.0 INTRODUCTION

Future energy systems will be required to fire lower-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. 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 be reached only with the use of advanced structural ceramics such as silicon carbide (SiC). However, SiC does not melt, but instead sublimes at temperatures over 2000°C. Therefore, it is not possible to join pieces of it through welding, and most brazing compounds have much lower melting points, so the joints lose strength at temperatures much lower than the maximum use temperature of the SiC. Since larger objects such as heat exchangers cannot be easily created from smaller ceramic pieces, the size of the SiC structures that can presently be manufactured are limited by the size of the sintering furnaces (approximately 10 feet for sintered alpha SiC). In addition, repair of the objects will require the use of field-joining techniques. Some success has been had by causing silicon and carbon to react at 1400°–1500°C to form SiC in a joint (Rabin, 1995), but these joints contain continuous channels of unreacted silicon, which cause the joints to corrode and creep excessively at temperatures below 1260°C (Breder and Parten, 1996).

2.0 OBJECTIVE

The objective of this work conducted at the Energy & Environmental Research Center (EERC) is to develop a patentable technique for joining large SiC structures 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 below 1260°C or serve as conduits for transport of corrodents. In addition, the method of heating the joint to cause the reaction bonding must be applicable to structures that are large in two dimensions, which precludes the use of furnaces for heating the samples. 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 PREVIOUS WORK

In previous work, a method was developed for heating the joints through joule heating, which is applicable to large structures. In addition, previous pellet materials were prepared by combining SiC, graphite, and silicon powders with a solvent, binder, and plasticizer. Two size ranges of SiC (1200 and 9000 grit) 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 SiC formation during the joining process.

Pellets were made that contained only silicon and graphite powder in varying molar ratios of silicon to graphite. Joints created with pellets of this composition were very porous and therefore displayed low strength. Four-point flexural tests revealed strengths of 20 to 30 MPa (2900 to 4350 psi). Scanning electron microscopy (SEM) results for joints showed an overall average porosity of about 48%, with 11% excess silicon and 3% excess carbon. Porosity was not distributed uniformly throughout the joints, but rather the joints contained areas with porosity as high as 73% and as low as 15%. Sizes of some pore spaces were in the tens of microns. This leads to the conclusion that the material was not mixed well. No continuous channels of silicon could be detected. If strength is to be increased, porosity must be greatly reduced. To reduce porosity, more intimate contact must be made between the carbon source and the silicon metal, and another material must be added to the mix to aid in the reduction of the size of the voids.

SiC produced from the reaction of silicon and graphite has only 69% of the volume of the original materials. This volume reduction causes porosity to form in the joint. The carbon source was changed to polystyrene and carbon paste in an attempt to improve the silicon–carbon interaction within the joint. In one formulation, silicon metal powder was added to polystyrene in proper Si/C molar ratios, mixed in the presence of toluene, and allowed to dry. The resultant mix was then pyrolized, which produced carbon-coated silicon metal particles. However, much of the polystyrene depolymerized and vaporized, leaving too little carbon on the silicon. The second formulation involved mixing silicon metal powder with carbon paste. After drying, the mixture was added to SiC powder. Carbon paint was shown to be ineffective as a carbon source. During pressing, the carbon paint tended to flow and concentrate in zones.

4.0 ACCOMPLISHMENTS

Boron and titanium were examined as possible sintering aids to improve the SiC formation during heating. One percent titanium powder was added to a joint mixture, and a pressed pellet was sintered in the presence of nitrogen/1% hydrogen gas in a tube furnace at 1420°C. Examination of this mixture showed that the titanium did not mix well and stayed isolated in large concentrations. Boron was added in the form of boric acid. A boric acid solution containing 1% boron was added to silicon and carbon, mixed using a mortar and pestle, and allowed to dry. A pressed pellet was then sintered under the same conditions as the titanium pellet. Examination of this pellet revealed no increase in the density of the pellet. Further tests with boron and polystyrene will be conducted.

The use of other sintering aids is being investigated. In particular, materials that will form alloys with silicon with lower melting points than pure silicon are being tested to see if they will increase the interaction between the silicon and the carbon. In addition, any remaining unreacted material must have a higher melting point than silicon and have a very low potential for corrosion. These materials will be tested for melting point and reactivity with the carbon source first using heated-stage microscopy, then by forming actual joints. In addition, other carbon sources, primarily including resins which will produce a greater amount of fixed carbon, are being investigated. If necessary, the carbonized material will be reinfiltrated with resin or, possibly, a polysilane to increase the carbon density. We have purchased SiC powder with an average particle size of 1 micron to mix with the joining compound to try to reduce shrinkage upon reaction sintering. Finally, a larger hydraulic press has been located that can produce pressures twice as great as those produced by the press currently used. It will be used to press denser pellets.

5.0 REFERENCES

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