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Task 6.3 - Engineering Performance of Advanced Structural Materials

Semi-Annual Report
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

TASK 6.3 – 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. Work for this year includes testing the corrosion resistance of advanced alloys proposed for the construction of secondary superheaters in ultrasupercritical (USC) boilers and testing new methods of joining silicon carbide and silicon nitride.

2.0 OBJECTIVE

The objective of this work by the Energy & Environmental Research Center (EERC) is to assist in the development of new materials that can be used for the construction of high-temperature components in advanced energy systems. This work will include the development of data on corrosion resistance of selected high-temperature alloys and the development of a patentable technique for joining large silicon-based advanced ceramics in the field. The key to developing a successful joining 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 EERC Foundation.

3.0 ACCOMPLISHMENTS

3.1 Silicon Carbide and Silicon Nitride Joining

Advanced ceramics, such as silicon carbide (SiC) or silicon nitride (Si_3N_4), 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. One change made in the work for this year, however, was to move the silicon nitride joining work to Task 6.6, SiAlON Coatings for Alkali-Resistant Silicon Nitride.

3.1.1 Preparation of SiC 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.

Currently, to examine the formation of silicon carbide during joule heating, pellets are being made with only silicon and graphite powder. These powders are being combined in varying molar ratios. To date, molar ratios of 1.2 and 0.84 have been used and examined in Joule heating tests. Once the proper molar ratio is found that does not leave excessive amounts of silicon upon joining, varying amounts of silicon carbide powder will be added and tested to produce the final pellet formulation.

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. To increase our present abilities, an attrition grinder was constructed and utilized based on designs and techniques developed by the U.S. Bureau of Mines (1, 2). Results of a preliminary grinding test are shown in Figure 1. Particle sizing was performed by computer-controlled scanning electron microscopy (CCSEM).

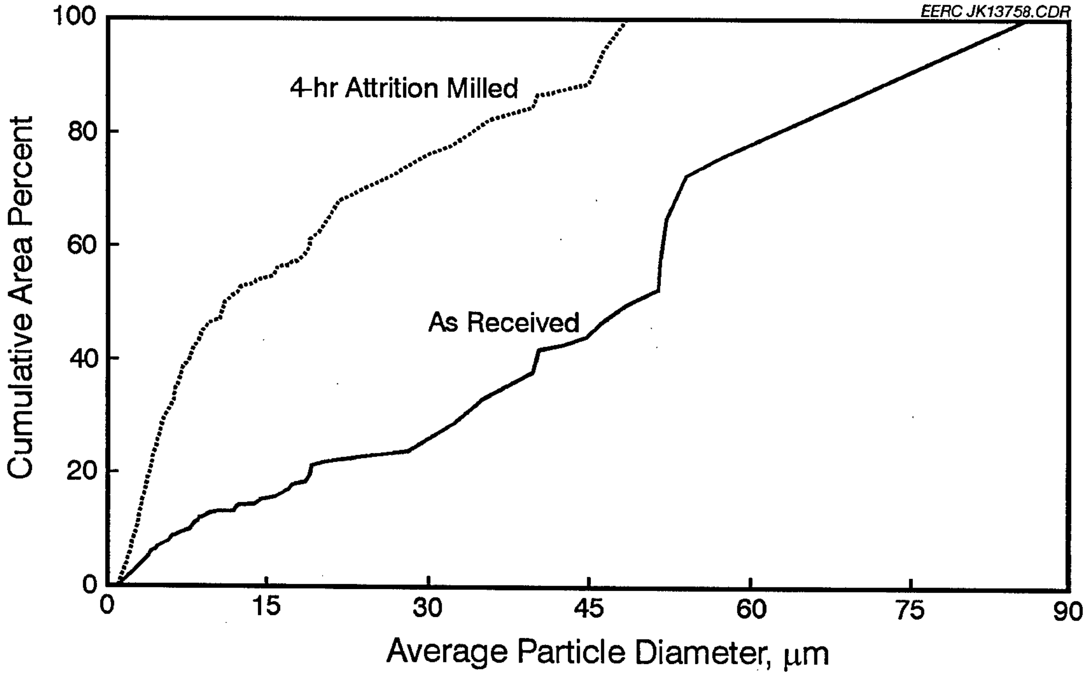

Figure 1. Graph showing the results of the attrition grinding of silicon powder for 4 hours as compared to the stock powder.

Future work will include further reduction in particle size by attrition grinding. Changes in the molar ratio of silicon to graphite to achieve optimum strength will be conducted. 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 joints 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 further. The inverse relationship between temperature and resistivity leads to extremely rapid temperature escalations (approximately 300° to 500°C/sec), causing thermal shock and breakage of the bars. Therefore, a current-limiting circuit was constructed.

Over ten 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 × 8 × 25 mm and a joining pellet of approximately 6 × 8 × 0.5 mm. 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 ensured good electrical conduction between the electrode and the sample. The carbon paint initially conducted the electricity and heated the sample to 300° to 400°C. At these temperatures, the silicon carbide itself was sufficiently conductive to carry the current. The experiments were carried out in air and used an S-type (Pt-Rh) thermocouple for control. To improve the ability to make a straight joint, the test joint was placed in an additional bracket made from mullite plate and metal plates and bolts. This bracket kept the test bars from moving during the heating test which reduced the chance of producing a bent joint.

The latest tests have been using joining material composed of different molar ratios of silicon and graphite powders. All joints have been heated to 1425°C and held at temperature for 70 minutes. In all cases, the resulting joint was not breakable by hand. Flexure tests to compute joint strength were conducted using a 3-point flexure apparatus. The results of these early strength tests are shown in Figure 2.

All attempts at achieving a sample preparation technique to analyze the sample for excess carbon have proved inadequate. For precise analysis of the joints using SEM, the sample cannot be mounted in epoxy, sectioned, and polished. A technique needs to be developed to polish the sample without epoxy mounting which requires a carbon or metal coating to be applied to reduce charging in the SEM. This coating is believed to be the cause of the problems we are experiencing with the analysis.

Preliminary analysis of the joints formed with a silicon-to-carbon molar ratio of 1.2 revealed an excess of silicon of over 20%. No excess carbon could be detected. Within the silicon carbide formed, no continuous silicon channels were detected. The excess silicon was found to have formed a ring around the outer surface of the joint extending approximately 1 mm into the joint. The same ring was found during visual inspection of the joints formed with a silicon-to-carbon molar ratio of 0.84. It is currently believed that the ring is formed because of heating the joint in air. Varying amounts of oxygen were detected in the silicon ring.

Future work will include an improved preparation technique to determine the amount of excess silicon and silicon carbide formation in the joints. Further joining tests will be conducted with different silicon-to-carbon molar ratios to increase the strength of the joints. Improvements in the joining technique with the power supply will be sought to make the technique reproducible in the field.

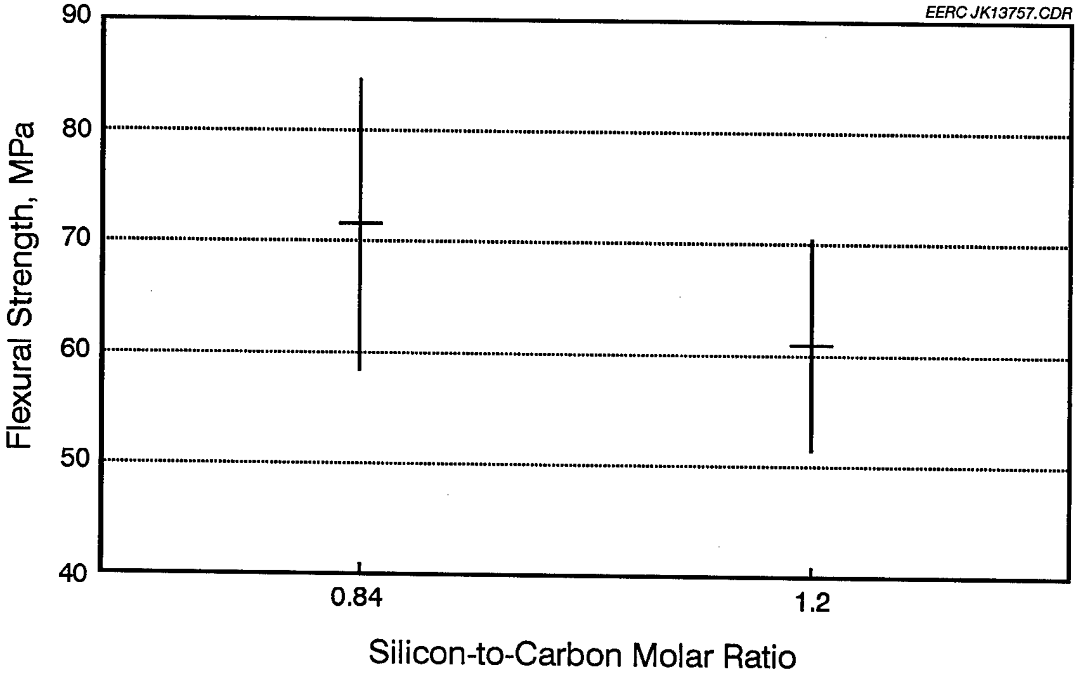

Figure 2. Graph showing the results of the preliminary flexural strength tests for the two powder formulations.

3.2 High-Temperature Alloy Corrosion Testing

The object of this task is to evaluate the corrosion resistance of new high-alloy and austenitic steam tube materials in the presence of high-alkali ash from low-rank coal. Many studies have been completed in which alloys were subjected to the temperatures and pressures seen in modern and future combustion systems, but very few included the high-alkali ash required to simulate ash corrosion in a coal-fired boiler.

The task manager attended a conference on Hot-Gas Filtration in Karlsruhe, Germany, the week of September 15, 1996. The travel to the conference was funded from another project. However, while in Europe, the task manager was to travel Denmark for discussions on corrosion of alloys to be used in the construction of secondary superheaters in an USC coal-fired power system and a tour of the plant site. The side trip to Denmark was to be funded from this project, but the trip fell through because of scheduling difficulties. If possible, the trip will be rescheduled for the summer of 1997.

Four alloys to be tested in the high-temperature alloy corrosion objective have been selected. The materials to be tested were selected by reviewing articles which have been published on USC systems being built and also specific studies of alloys. The next step will be to acquire samples of these four materials. Calls have been made to the developers of these new alloys, and we are now awaiting responses.

Table 1 contains candidate materials for superheater tubes at 325 bar/620°–630°C. Many of these were considered for use in the ELSAM system in western Denmark (3).

TABLE 1

Candidate Materials for Superheater Tubes, wt%

Material	Cr	Ni	Mo	W	Nb	Ti	Other
TP347HFG	18	10	–	–	1.0	–	–
St3Cu	18	9	–	–	0.4	–	Cu, N
NF709	20	25	1.5	–	0.25	0.05	N
SUPER 304	18	9	–	–	0.45	–	Cu, N
800 HT	21	32.5	–	–	–	0.38	Si, Cu, Al, Al+Ti
HR3C	25	20	–	–	0.4	–	N
HR6W	23	43	1	6	0.2	0.1	–
HCM9M	9	–	–	–	–	–	–
HCM12	12	–	0–3.0	0–3.0	0–0.4	–	V, N

The ELSAM USC units under construction will implement the following:

Fuel: Natural gas and coal

Size: 2 × 400 MW

Steam Data: 290 bar/580°C

Boiler: C-steel, 1Cr1/2Mo, 2-1/4Cr1Mo, P91, AISI 347HFG

Steam Lines: P91

Turbine: 10% Cr, Mo, V, Nb, N

The alloys to be evaluated are HCM12, HR3C, HR6W, and NF709. Both the HR3C and HR6W alloys were developed to withstand the harsh environment of USC boilers and have corrosion resistance which is superior to that of 18-8 stainless steels. There are also alloys such as SUPER 304 and TP347HFG which are being considered for the superheater tubes. These were not included in our test matrix because the Cr-content of 18 wt% may only be sufficient for steam temperatures of 615°-620°C (3).

Three of the alloys selected, HR3C, HR6W, and NF709, are highly alloyed steels with improved high-temperature corrosion resistance and creep strength. These alloys were developed by Sumitomo Metals Industries, Ltd., and Mitsubishi Heavy Industries, Ltd., and are expected to allow steam temperatures of up to 630°C. For each of these steels there is limited knowledge of their long-term high temperature corrosion behavior in coal-fired systems. By evaluating these materials in a simulated coal-fired boiler environment, the desired hot corrosion information will be acquired.

The final alloy, HCM12, was also developed by Sumitomo Metals Industries, Ltd., and Mitsubishi Heavy Industries, Ltd., to be used in superheater and reheater tubing. HCM12 is expected to allow steam temperatures up to 650°C with a live steam pressure of 325 bar. Confirmation was also made that the HCM12 austenitic steel had superior steam oxidation resistance to the fine-grained TP347HFG (4). Another use being considered for this material is in water panels of USC systems.

The HCM12 has been exposed in a boiler for approximately 60,000 hr. The operating conditions of the field test boiler were as follows:

- Boiler: No. 3 Boiler of Wakayama Kyodo Power Co., Ltd. (156 MW)
- Type: Forced circulation type
- Maximum pressure: 195 kgf/cm^2 G (for superheater) 43 kgf/cm^2 G (for reheater)
- Steam temperature: 571°C (for superheater) 543°C (for reheater)
- Feed water temperature: 267°C (economizer inlet)
- Main steam flow: 510,000 kgf/hr
- Reheater steam flow: 427,770 kgf/hr
- Fuel: Mixture of blast furnace gas and oil

The steel for the superheater and reheater tubes were service-exposed in a boiler for over 6 years. There was no significant property degradation and deterioration after 1-, 3-, and 5-year exposure. The HCM12 was confirmed to have stable creep rupture strength and superior steam oxidation resistance by this long-term exposure (4).

The information gained by placing the HCM12 steel in a boiler burning blast gas and oil is very important, but what also must be considered is the effect of ash on the hot corrosion resistance of the material. By exposing the steel to an environment simulating coal-fired boiler conditions, this hot corrosion information can be obtained.

As stated earlier, the next step will be to obtain samples of the selected materials from Sumitomo Metal Industries and begin exposure and evaluation. There may be opportunities in the future to evaluate the materials not included in this test matrix.

An AGFA digital scanner and 35-mm macro lens were purchased. These will allow corrosion photographs to be placed into reports more efficiently and the photographs to be stored on disk for future use. A 35-mm microscope adapter, to allow photographs to be taken at higher magnitudes, will also be purchased.

4.0 REFERENCES

1. Stanczyk, Martin H.; Feld, I.L. "Comminution by the Attrition Grinding Process," United States Bureau of Mines Bulletin 670, **1981.**

2. Hoyer, Jesse L. "Turbomilling: A Processing Technique for Advanced Ceramics," *Materials and Manufacturing Processes* **1994,** *9,* 623–636.

3. Blum, R. "Materials Development for Power Plants with Advanced Steam Parameters - Utility Point of View," *In* Proceedings of the COST 5th Conference: Materials for Advanced Power Engineering; Liege, Belgium, Oct. 1994, 21.

4. Iseda, A.; Sawaragi, Y.; Teranishi, H.; Kubota, M.; Hayase, Y. "Development of New 12%Cr Steel Tubing (HCM12) for Boiler Application," the Sumitomo Search No. 40, Nov. 1989.

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FORM EIA-459E
(10/88)

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-93MC30097	**2. Program/Project Title** TASK 6.0 HIGH-TEMPERATURE MATERIALS	**3. Reporting Period** 10-1-96 through 12-31-96
4. Name and Address	Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000	**5. Program Start Date** 01-12-93 **6. Completion Date** 12-31-97

7. FY 96/97	**8. Months or Quarters** Quarters	**b. Dollar Scale**	1st			2nd			3rd			4th			
			JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	

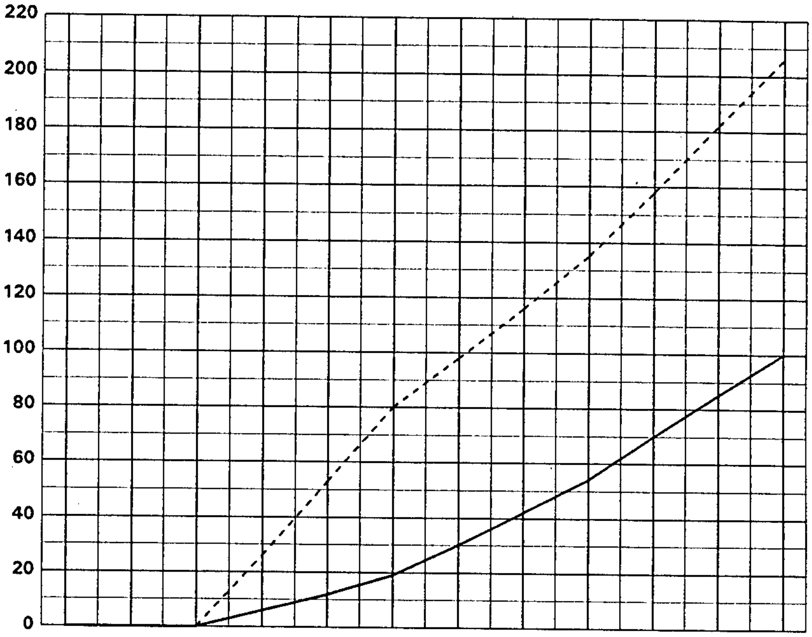
9. Cost Status **a. Dollars Expressed In Thousands**

10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	0	80	55	71	206	206
	A	0	19	35	46	100	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		0	80	55	71	206	206
Total A		0	19	35	46	100	
Variance		0	61	20	25	106	

P = Planned A = Actual

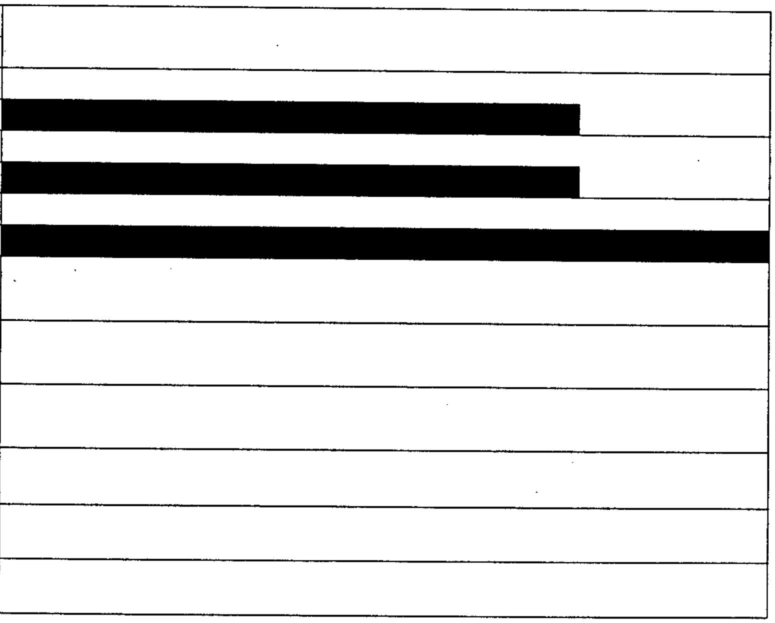
Total Planned Costs for Program/Project
$206



c. Cumulative Accrued Costs

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Planned			0			80			135			206
Actual			0			19			54			100
Variance			0			61			81			106

11. Major Milestone Status	Units Planned Units Complete
6.3 Engineering Performance of Advanced Materials	P
	C
6.5 Materials for Gas Separation	P
	C
6.6 SiAlON Coatings for Alkali-Resistant Silicon Nitride	P
	C
	P
	C
	P
	C
	P
	C
	P
	C
	P
	C
	P
	C



12. Remarks
The remainder of Year 3 , Task 6.3 -$16,000 was transferred to Year 4, Task 6.3.

13. Signature of Recipient and Date 2/3/97

14. Signature of DOE Reviewing Representative and Date

FORM EIA-459E
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U.S. DEPARTMENT OF ENERGY
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FORM APPROVED
OMB NO. 1900 0127
Page 2 of 2

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Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Subtask 6.3	Engineering Performance of Advanced Materials			All milestones should be moved back 3 months to reflect the late start of the work.
a	Complete joining tests of silicon carbide using Joule heating	9/96		
b	Complete joining tests of silicon nitride with SiAlON	9/96	9/96	*
c	Complete corrosion tests of ceramic joints	12/96		
d	Complete corrosion tests of high-temperature alloys	12/96		
Subtask 6.5	Materials for Gas Separation			
a	Complete preparation of substoichiometric aluminosilicate membranes with the electron-beam coater	9/96		
b	Complete testing of hydrogen and hydrogen disulfide permeability of the substoichiometric aluminosilicate membrane	12/96		
Subtask 6.6	SiAlON Coatings for Alkali Resistant Silicon Nitride			
a	Determine morphologic and mechanical properties of alkali vapor-corroded SiAlON	9/96	12/96	
b	Determine morphologic and mechanical properties of coal slag-corroded SiAlON	12/96	12/96	

* Moved to Subtask 6.6 for reporting

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