DOE/PC/94224--74

HIGH TEMPERATURE ALKALI CORROSION OF DENSE SiC AND Si₃N₄ COATED
WITH CMZP AND Mg-DOPED Al₂TiO₅ IN COAL GAS

Quarterly Progress Report #4
for the Period
April 1 -- June 30, 1995

Prepared by

Shaokai Yang and J. J. Brown

Department of Materials Science and Engineering
Virginia Polytechnic Institute
and State University
Blacksburg, Virginia 24061

Prepared for

Grant # DE-FG22-94PC94224

Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pennsylvania 15236

June 30, 1995

U.S. DOE Patent Clearance is not required prior to
the publication of this document.

RECEIVED
USDOE/PETC
95 JUL 20 AM 11:11
ACQUISITION & ASSISTANCE DIV.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DUC

Objective/Scope

High temperature alkali corrosion has been known to cause premature failure of ceramic components used in advanced high temperature coal combustion systems such as coal gasification and clean-up, coal fired gas turbines, and high efficiency heat engines. Non-oxide ceramics, such as SiC and Si₃N₄, are applied in HITAF systems for their well-known and desirable high temperature thermal and mechanical properties. However, these materials are prone to rapid corrosion under some types of high temperature coal combustion conditions.

The objective of this research is to apply CMZP and Mg-stabilized Al₂TiO₅ as coatings to SiC and Si₃N₄ to improve the corrosion resistance under coal combustion atmospheres as well as to improve high temperature mechanical properties. The research will not only develop and characterize CMZP and Mg-Al₂TiO₅ coatings but will also strive to expand the existing knowledge of the mechanism of coal combustion corrosion of SiC and Si₃N₄ in the temperature range of 1000-1400°C.

Technical Progress

I. 100 hr Slagging Combustion Test

The following samples were prepared and submitted for inclusion in the 100 hr slagging combustion test which is part of the United Technologies Research Center Combustion 2000 effort. Also included were a set of uncoated samples.

1. Samples Coated with CMZP

SiC samples of size 6" x 1" x 0.5" were coated with CMZP as described previously. In order to obtain the pure phases, the samples were fired in large covered crucibles fully lined with CMZP powder according to the procedure presented in the Quarterly Progress Report #3. Double coating was applied to improve the quality of the samples.

2. Samples Coated with $\text{Mg-Al}_2\text{TiO}_5$

SiC samples of 6" x 1" x 0.5" were coated with $\text{Mg-Al}_2\text{TiO}_5$ as described previously. Unhydrolyzed $\text{Mg-Al}_2\text{TiO}_5$ solution was utilized instead of hydrolyzed solution to decrease viscosity, making the coatings more homogeneous, and the procedure was presented in the Quarterly Progress Report #3. To improve the quality of the samples, double coating was applied. This test will be completed shortly and the results presented in the next progress report.

II. Preparation and Characterization of Coatings on SiC

CMZP Coatings

In order to obtain dense, homogeneous and crack-free CMZP coatings, the influence of the solution concentration and the lift rate of the substrate were investigated. It was found that the quality of the CMZP coatings is strongly dependent on the solution concentration and lift rate. High concentrations and fast lift rates resulted in cracking of the coating during subsequent heat treatment. For forming crack-free coatings, the concentration of the CMZP solutions needs to be kept between 0.05 and 0.2 mol/L, while the lift rate stays between 4.3 and 8.1 cm/min. It was found that the high solution concentration made the coatings thick and inhomogeneous with holes and cracks, while low solution concentration made the coatings too thin, especially in the upper part of the samples for the influence of gravity.

Figure 1 shows the SEM micrographs of the as-received SiC sample: (a) the grains and holes on the sample surface, (b) the interior surface of a hole. Clearly, the good coatings must not only cover the surface of grains but also cover the interior surface of the holes. Figure 2 shows the SEM micrographs of CMZP coatings under the high solution concentration of 0.2 mol/L and a lift rate of 6.5 cm/min. Figure 3 shows the SEM micrographs of CMZP coatings under low solution concentration of 0.05 mol/L and lift rate of 6.5 cm/min. Figure 4 shows SEM micrographs of CMZP

coatings under the medium solution concentration of 0.1 mol/L and the lift rate of 6.5 cm/min. Table 1 shows the comparison of different coatings under different solution concentrations and lift rates.

Table 1. Comparison of different coatings under different solution concentrations and lift rates.

Solution Concentration (mol/L)	Lift Rate (cm/min)	Grain Surface	Interior Surface
0.02	4 - 8	thin	thin
0.05	4 - 8	thin	thin
0.10	4 - 8	good	good
0.15	4 - 8	better	better
0.20	4 - 8	thicker, little cracks	cracks
0.25	4 - 8	thick, cracks	many cracks

It was found that double coating improves the quality of the coatings and especially decreases the cracks. Comparison of the results of single and double coatings shows that double coatings are homogeneous and have fewer cracks. It was found that the different thickness of first coating and second coating also influences the quality of the coatings. Figure 5 shows SEM micrographs of double CMZP coatings of different first and second coatings: (a) the thicknesses of first and second coatings are 6 μm and 2 μm , respectively; (b) the thicknesses of first and second coatings are 4 μm ; (c) the thicknesses of first and second coatings are 2 μm and 6 μm , respectively.

Table 2. Comparison of one coating and double coatings of CMZP.

	Total Thickness (μm)	Thickness of first coating (μm)	Thickness of second coating (μm)	Quality of Coating
one coating	8			worse
double coating	8	6	2	better
double coating	8	4	4	better
double coating	8	2	6	good

Mg-Al₂TiO₅ Coatings

It was found that the quality of the Mg-Al₂TiO₅ coatings is strongly dependent on the solution concentration and lift rate. Similarly to CMZP, high concentration and fast lift rate resulted in cracking of the coatings during subsequent heat treatment. The solution concentration needs to be kept between 0.3 and 2.5 mol/L while the lift rates are kept between 4 and 8 cm/min. It was found that coatings formed using a high solution concentration were thick and had holes and cracks, while low solution concentration coatings were too thin, especially in the upper end of samples, for the influence of gravity.

Figure 6 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min. Figure 7 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the low concentration of 0.3 mol/L and lift rate of 6.5 cm/min. Figure 8 shows the SEM micrographs of Mg-Al₂TiO₅ coatings under the medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min. Table 3 shows the comparison of different coatings under different solution concentrations and lift rates.

Table 3. Comparison of different coatings under different solution concentrations and lift rates.

Solution Concentration (mol/L)	Lift Rate (cm/min)	Grain Surface	Interior Surface
0.3	6.5	too thin	too thin
0.6	6.5	thin	thin
0.9	6.5	better	better
1.2	6.5	good	good
1.5	6.5	better	better
1.8	6.5	thick	thick
2.1	6.5	too thick	too thick
2.5	6.5	too thick	too thick

It was found that double coatings can improve the quality of the coatings. Comparison of the results of single and double coatings shows that double coatings are homogenous and have fewer cracks. It was found that the quality of double coatings was influenced by different thicknesses of first and second coatings. Figure 9 shows SEM micrographs of double $\text{Mg-Al}_2\text{TiO}_5$ coatings of different first and second coatings: (a) the thickness of first and second coatings is $6\text{ }\mu\text{m}$ and $2\text{ }\mu\text{m}$, respectively; (b) the thickness of first and second coatings is $4\text{ }\mu\text{m}$; (c) the thickness of first and second coatings is $2\text{ }\mu\text{m}$ and $6\text{ }\mu\text{m}$, respectively. The results indicate (c) is better. The most likely reason for this is that, similar to CMZP coatings, $\text{Mg-Al}_2\text{TiO}_5$ adheres more readily to the layer of $\text{Mg-Al}_2\text{TiO}_5$ than to the surface of SiC. Table 4 shows the comparison of one coating and different double coatings.

Table 4. Comparison of one coating and different double coatings.

	Total thickness (μm)	Thickness of first coating (μm)	Thickness of second coating (μm)	Quality of coating
One coating	8			Worse
Double coating	8	6	2	Better
Double coating	8	4	4	Better
Double coating	8	2	6	Good

(a)

(b)

Figure 1. SEM micrographs of the as-received SiC Samples:
 (a) grains on the sample surface (300 x)
 (b) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 2. SEM micrographs of CMZP coatings under the high solution concentration of 0.2 mol/L and lift rate of 6.5 cm/min:

- (a) grains on the sample surface (300 x)
- (b) surface of a grain (1000 x)
- (b) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 3. SEM micrographs of CMZP coatings under the low solution concentration of 0.05 mol/L and lift rate of 6.5 cm/min:

- (a) grains on the sample surface (300 x)
- (b) surface of a grain (1000 x)
- (c) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 4. SEM micrographs of CMZP coatings under the medium solution concentration of 0.1 mol/L and lift rate of 6.5 cm/min:

- (a) grains on the sample surface (300 x)
- (b) surface of a grain (1000 x)
- (c) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 5. SEM micrographs of CMZP coatings of different first and second coatings:

- (a) thickness of first and second coatings are 6 μm and 2 μm respectively (3000 x)
- (b) thickness of first and second coatings are 4 μm (3000 x)
- (c) thickness of first and second coatings are 6 μm and 2 μm respectively (3000 x)

(a)

(b)

(c)

Figure 6. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the high solution concentration of 2.5 mol/L and lift rate of 6.5 cm/min:

- (a) grains on the sample surface (300 x)
- (b) surface of a grain (1000 x)
- (c) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 7. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the low solution concentration of 0.3 mol/L and lift rate of 6.5 cm/min:

- (a) grains on the sample surface (300 x)
- (b) surface of a grain (1000 x)
- (c) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 8. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings under the medium solution concentration of 1.2 mol/L and lift rate of 6.5 cm/min:
 (a) grains on the sample surface (300 x)
 (b) surface of a grain (1000 x)
 (c) interior surface of a hole (3000 x)

(a)

(b)

(c)

Figure 9. SEM micrographs of $\text{Mg-Al}_2\text{TiO}_5$ coatings of different first and second coatings:

- (a) thickness of first and second coatings are 6 μm and 2 μm respectively (3000 x)
- (b) thickness of first and second coatings are 4 μm (3000 x)
- (c) thickness of first and second coatings are 2 μm and 6 μm respectively (3000 x)