DOE/PC/94224--T6

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

Quarterly Progress Report #6
for the Period
October 1, 1995 - December 31, 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

December 31, 1995

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *α*

RECEIVED
USDOE/PETC
95 JAN 17 AM 10:18
ACQUISITION & ASSISTANCE DIV.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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-Al₂TiO₅ as coatings to SiC to improve 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 in the temperature range of 1000-1400°C.

Technical Progress

I. Thermal Shock Resistance Test

1. CMZP Coated SiC Samples

The thermal shock resistance of CMZP coated SiC samples was investigated. The samples were heated to 300, 500, 750, and 1000°C, respectively, and then quenched in water at room temperature (25°C). The results are shown in Table 1. Surface microstructure of coatings and adhesions between the coatings and substrates were examined by SEM. The surface microstructure of the samples after a thermal shock of 1000°C exhibited cracks and small spalling (Figure 1); after a 750°C thermal shock, cracks appeared but no spalling (Figure 2); and after a 500°C thermal shock, no cracks were present (Figure 3).

Table 1. The thermal shock resistance of CMZP coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Group 1 (4 samples)	No cracks			
Group 2 (4 samples)		Small cracks		
Group 3 (4 samples)			Cracks	
Group 4 (4 samples)				Cracks and small spalling

2. Mg-Al₂TiO₅ Coated Samples

The thermal shock resistance of Mg-Al₂TiO₅ coated SiC samples was also examined. The samples were heated to 300, 500, 750, and 1000°C, respectively, and then quenched in water at room temperature (25°C). The results are shown in Table 2. Surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. The surface microstructure of the samples after a thermal shock of 1000°C exhibited cracks and small spalling (Figure 4); after a 750°C thermal shock, cracks appeared (Figure 5); and after a 500°C thermal shock, no cracks were present (Figure 6).

II. Alkali Corrosion Resistance Test

1. CMZP Coated SiC Samples

The alkali corrosion resistance of both CMZP coated and uncoated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to an atmosphere containing sodium. The weighed samples were heated in the sodium atmosphere at 900, 1000, and 1100°C, respectively, for 48 hours. The coated and uncoated samples as

Table 2. Thermal shock resistance of Mg-Al₂TiO₅ coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Group 1 (4 samples)	No cracks			
Group 2 (4 samples)		Small cracks		
Group 3 (4 samples)			Cracks	
Group 4 (4 samples)				Cracks and small spalling

well as the crucible containing sodium carbonate were placed in a tube furnace in which alkali vapors were generated during the alkali corrosion test. The crucible was weighed before and after each run to determine the amount of weight loss of the sodium carbonate during the corrosion time interval.

Assuming the vapors behave as ideal gasses and using the data from the weight loss and volume of the furnace tube, the alkali vapor concentration was calculated to be approximately 5 vol%. To determine the weight loss after the exposure, the samples were rinsed in acetone and washed in distilled water at 100°C to remove any physically absorbed salt and sodium silicates. The glass formed on the surface of the samples was then dissolved in dilute hydrofluoric acid. The etching was repeated until no noticeable difference in weight change with time was detected.

Table 3 shows the weight loss and Table 4 shows the room temperature flexural strength of both as-received and corroded SiC samples determined by 4-point bending using an ATS Test System. To decrease the random errors the average strengths of every group were selected. The microstructure and fracture surfaces of the sample surfaces before and after corrosion were identified using XRD.

Table 3. The weight loss of CMZP coated and uncoated SiC samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained value	2.8	3.7	2.1	3.6	2.3	3.7
	2.4	3.6	2.0	3.5	2.7	3.4
	2.1	3.3	2.7	3.2	1.9	3.3
	2.2	2.6	2.6	2.5	2.1	2.4
Average value						
	2.4	3.3	2.4	3.2	2.3	3.2

The sodium corrosion resistance of CMZP coated SiC samples is improved over that of uncoated samples as indicated in Figures 7 and 8. Compared to CMZP coated SiC samples, uncoated samples exhibited a greater weight loss and reduction in strength. The SEM micrographs of uncoated SiC after corrosion show the formation of holes on the surface and considerable penetration of alkali (Figure 9).

Table 4. Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained value	468	424	417	432	432	414	449	426
	455	468	469	407	411	432	438	397
	432	465	438	402	448	412	436	411
	444	447	425	410	436	398	443	408
Average value	450	450	437	413	432	414	442	411

SiC is thermodynamically unstable in air and relies on a thin film of SiO₂ for oxidation protection. The SiO₂ film on SiC, although very thin, is normally protective in an oxidizing atmosphere at high temperatures. The

presence of sodium with SiC dissolves the SiO₂ protective film and enhances oxidation. It is believed that the following reactions occur:

The protective SiO₂ film is dissolved to form Na₂SiO₃. Accelerated scale growth occurs because the silicate is liquid at 1000°C. The CMZP reacts with the SiO₂ film on the surface of the SiC substrates and sodium to produce a more refractory layer, which assists in maintaining a continuous reaction layer and minimizes corrosion. SEM micrographs showed that a dense protective layer on the surface of CMZP coated SiC samples was formed after sodium corrosion (Figure 10). The distribution of Ca, P, Si, and Zr on the sample surface, obtained by EDX, proves that the protective layer came from CMZP coating (Figure 11).

2. Mg-Al₂TiO₅ Coated SiC Samples

The alkali corrosion resistance of both Mg-Al₂TiO₅ coated and uncoated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to an atmosphere containing sodium. The weighed samples were heated in the sodium atmosphere at 900, 1000, and 1100°C, respectively, for 48 hours. The system from which alkali vapors were generated during the alkali corrosion test is the same as that used for the CMZP coating tests. The crucible was weighed before and after each run to determine the amount of weight loss of the sodium carbonate during the corrosion time interval. The alkali vapor concentration was calculated to be approximately 5 vol%. To determine the weight loss after exposure, the samples were treated similar to the CMZP

coated samples. The microstructure and fracture surfaces of the samples both before and after corrosion were examined by EDX. Also, the phases of sample surfaces before and after corrosion were identified using XRD.

The sodium resistance of $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples is improved over that of uncoated samples as indicated in Tables 5 and 6 and Figures 12 and 13. Compared to $\text{Mg-Al}_2\text{TiO}_5$ coated SiC samples, uncoated samples exhibited a greater weight loss.

Table 5. Weight loss of $\text{Mg-Al}_2\text{TiO}_5$ coated and uncoated SiC samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained value	3.1	2.9	2.4	4.1	3.2	3.2
	2.8	3.0	2.2	3.8	2.1	3.7
	2.4	3.5	2.6	3.6	2.5	4.0
	2.3	3.8	3.3	3.0	2.3	4.3
Average value						
	2.7	3.3	2.6	3.6	2.5	3.8

Table 6. Flexural strength of $\text{Mg-Al}_2\text{TiO}_5$ coated and uncoated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated
Obtained value	464	469	424	401	441	434	447	419
	432	423	462	404	419	409	436	437
	453	446	441	413	456	404	432	416
	447	463	414	431	442	413	443	403
Average value	449	450	435	412	439	415	440	419

The mechanism of improving corrosion resistance of Mg-Al₂TiO₅ coated SiC samples is similar to that of CMZP coated samples described above. SEM micrographs showed that a dense protective layer on the surface of Mg-Al₂TiO₅ coated SiC samples was formed after sodium corrosion (Figure 14). The distribution of Mg, Al, Ti, and Si on the sample surfaces, obtained by EDX, proves that the protective layer came from Mg-Al₂TiO₅ coating (Figure 15).

Figure 1. Surface microstructure of CMZP coated samples exhibited cracks and small spalling after a thermal shock of 1000°C.

Figure 2. Surface microstructure of CMZP coated samples exhibited cracks after a thermal shock of 750°C .

Figure 3. Surface microstructure of CMZP coated samples exhibited no cracks after a thermal shock of 500°C.

Figure 4. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited cracks and small spalling after a thermal shock of 1000°C.

Figure 5. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited cracks after a thermal shock of 750°C.

Figure 6. Surface microstructure of Mg-Al₂TiO₅ coated samples exhibited no cracks after a thermal shock of 500°C.

Figure 7. Weight loss of CMZP coated and uncoated SiC samples after sodium corrosion.

Figure 8. Flexural strength of CMZP coated and uncoated SiC samples before and after sodium corrosion.

Figure 9. Corrosion of uncoated SiC samples by sodium carbonate.

Figure 10. Dense protective layer on surface of CMZP coated SiC samples formed after sodium corrosion.

Spectrum: CMZP
Comments:

Figure 11. Distribution of Ca, P, Si, and Zr on sample surfaces, obtained by EDX, proves that the protective layer came from CMZP coating.

Figure 12. Weight loss of Mg-Al₂TiO₅ coated and uncoated SiC samples after sodium corrosion.

Figure 13. Flexural strength of Mg-Al₂TiO₅ coated and uncoated SiC samples before and after sodium corrosion.

Figure 14. Dense protective layer on surface of Mg-Al₂TiO₅ coated SiC samples formed after sodium corrosion.

Spectrum: MGAL2TIO
Comments:

Figure 15. Distribution of Al, Ti, Si, and Mg on the sample surfaces, obtained by EDX, proves that the protective layer came from $\text{Mg-Al}_2\text{TiO}_5$ coating.

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.