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

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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. Aging Process

An aging process was utilized to improve the quality of the CMZP and Mg-Al₂TiO₅ coated samples. The aging process is described below:

The CMZP coated samples were fired in large covered crucibles fully filled with CMZP powder at 1200°C for 100 hours. The cover was sealed with liquid K₂DiO₃. This technique results in an atmosphere which is nearly oxygen free.

The Mg-Al₂TiO₅ coated samples were fired in air at 1300°C for 100 hours.

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II. Thermal Shock Resistance Test

1. CMZP Coated SiC Samples

The thermal shock resistance of aged and unaged CMZP coated SiC samples was determined. 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. The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. The surface microstructure of the aged and unaged samples after a thermal shock of 1000°C and 750°C (Figures 1, 2, 3, and 4) shows that the aging process improved the quality of the CMZP coatings.

Table 1. Thermal shock resistance of aged and unaged CMZP coated SiC samples

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Aged (4 samples)	No cracks	No cracks	Small cracks	Cracks
Unaged (4 samples)	No cracks	Small cracks	Cracks	Cracks and small spalling

2. Mg-Al₂TiO₅ Coated SiC Samples

The thermal shock resistance of aged and unaged Mg-Al₂TiO₅ coated SiC samples was tested. 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. The surface microstructure of coatings and adhesion between the coatings and substrates were examined by SEM. The surface microstructure of the aged and unaged samples after a thermal shock of 1000°C and 750°C (Figures 5, 6, 7, and 8) shows that the aging process improves the quality of the Mg-Al₂TiO₅ coatings.

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

Sample	Heated Temperature and Results			
	300°C	500°C	750°C	1000°C
Aged (4 samples)	No cracks	No cracks	Small cracks	Cracks
Unaged (4 samples)	No cracks	Small cracks	Cracks	Cracks and small spalling

III. Alkali Corrosion Resistance Test

1. CMZP Coated SiC Samples

The alkali corrosion resistance of both aged and unaged CMZP coated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to a sodium containing atmosphere. The weighed samples were heated in sodium containing atmospheres at 900, 1000, and 1100°C, respectively, for 48 hours. The aged and unaged samples as 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 removed 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. The room temperature flexural strength of both aged and unaged SiC samples was determined by 4-point bending using an ATS

Test System. To decrease the random errors the average strengths of every group were selected. The distribution of Ca, Mg, Zr, P, and Si on sample surface both before and after corrosion were examined by EDX.

The sodium corrosion resistance of aged CMZP coated SiC samples is improved over that of unaged samples as indicated in Tables 3 and 4, and Figures 9 and 10. Compared to aged CMZP coated SiC samples, unaged samples exhibited a greater weight loss and reduction in strength.

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

	1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained value	2.5	2.8	2.2	2.1	2.2	2.3
	2.3	2.4	2.2	2.0	2.1	2.7
	2.1	2.1	2.4	2.7	2.1	1.9
	2.1	2.2	2.3	2.6	1.7	2.1
Average value						
	2.3	2.4	2.3	2.4	2.0	2.3

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

	Before Corrosion		1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained value	442	468	429	417	448	432	449	449
	453	455	467	469	424	411	436	338
	455	432	457	438	427	448	453	436
	450	444	411	425	436	436	442	443
Average value	450	450	441	436	434	432	445	442

Figures 11 and 12 and Table 5 show the distribution of Ca, Mg, Zr, P, and Si on the aged and unaged sample surfaces after the sodium corrosion at 1000°C as obtained by EDX. This proves that the aging process improves the quality of CMZP coatings.

Table 5. Distribution of Ca, Mg, Zr, P, and Si on the sample surfaces after the sodium corrosion at 1000°C (%)

Aged				Unaged			
Ca	Mg	Zr,P*	Si	Ca	Mg	Zr,P*	Si
3.97	2.09	14.83	77.36	2.13	0	11.23	85.43

*The peaks of Zr and P overlap

2. Mg-Al₂TiO₅ Coated SiC Samples

The alkali corrosion resistance of both aged and unaged Mg-Al₂TiO₅ coated SiC samples was examined by determining the weight loss and flexural strength degradation of samples exposed to sodium containing atmospheres. The weighed samples were heated in sodium containing atmospheres 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 to that of CMZP. 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 like the CMZP coated samples.

The sodium corrosion resistance of aged Mg-Al₂TiO₅ coated SiC samples is improved over that of unaged samples as indicated in Tables 6 and 7 and Figures 13 and 14. Compared to aged Mg-Al₂TiO₅ coated samples, unaged samples exhibited a great weight loss and reduction in strength.

Table 6. Weight loss of aged and unaged Mg-Al₂TiO₅ coated SiC samples after sodium corrosion (%)

	1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained value	2.1	3.1	2.7	2.4	2.5	3.2
	2.1	2.8	2.4	2.2	2.0	2.1
	2.6	2.4	2.5	2.6	2.2	2.5
	2.4	2.3	2.3	3.3	2.4	2.3
Average value						
	2.3	2.7	2.5	2.6	2.3	2.5

Table 7. The flexural strength of aged and unaged Mg-Al₂TiO₅ coated SiC samples before and after sodium corrosion (MPa)

	Before Corrosion		1100°C		1000°C		900°C	
	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged
Obtained value	432	464	423	424	438	441	435	447
	458	432	450	462	431	419	451	436
	455	453	451	441	453	455	441	432
	452	447	426	414	452	442	449	443
Average value								
	449	449	438	435	444	439	444	440

Figures 13 and 14 and Table 8 show the distribution of Mg, Al, Ti, and Si on the aged and unaged sample surfaces after sodium corrosion at 1000°C, obtained by EDX, which proves that the aging process improves the quality of the Mg-Al₂TiO₅ coatings.

Table 8. Distribution of Mg, Al, Ti, and Si on the sample surfaces after sodium corrosion at 1000°C (%)

Aged				Unaged			
Mg	Al	Ti	Si	Mg	Al	Ti	Si
0.23	5.00	9.36	81.89	0.12	2.69	3.29	92.27

Figure 1. Surface microstructure of aged CMZP coated samples after a thermal shock of 1000°C.

Figure 2. Surface microstructure of unaged CMZP coated samples after a thermal shock of 1000°C .

Figure 3. Surface microstructure of aged CMZP coated samples after a thermal shock of 750°C.

Figure 4. Surface microstructure of unaged CZMP coated samples after a thermal shock of 750°C.

Figure 5. Surface microstructure of aged Mg-Al₂TiO₅ coated samples after a thermal shock of 1000°C.

Figure 6. Surface microstructure of unaged Mg-Al₂TiO₅ coated samples after a thermal shock of 1000°C.

Figure 7. Surface microstructure of aged Mg-Al₂TiO₅ coated samples after a thermal shock of 750°C.

Figure 8. Surface microstructure of unaged Al₂TiO₅ coated samples after a thermal shock of 750°C.

Figure 9. Weight loss of aged and unaged CMZP coated SiC samples after sodium corrosion.

Figure 10. Flexural strength of aged and unaged CMZP coated SiC samples before and after sodium corrosion.

Spectrum: CMZP-A-2

Comments:

Name: CMZP-A-2

Comments:

Centroid (KeV)	Gross Area	Normalized	Comments
1.260	3112.47	2.09	Mgk
1.743	115377.9	77.36	SiK
2.037	22125.63	14.83	ZrL
3.717	5922.33	3.97	CaK
6.447	2611.99	1.75	

Figure 11. Distribution of Ca, Mg, Zr, P, and Si on aged CMZP coated sample surfaces, obtained by EDX.

Spectrum: CMZP-A-3

Comments:

Name: CMZP-A-3

Comments:

Centroid (KeV)	Net Area	Normalized	Comments
1.743	75669.01	85.43	Si
2.058	9944.37	11.23	Zr
3.717	1885.15	2.13	Ca
4.032	500.36	0.56	
15.834	577.84	0.65	

Figure 12. Distribution of Ca, Mg, Zr, P, and Si on unaged CMZP coated sample surfaces, obtained by EDX.

Figure 13. Weight loss of aged and unaged Mg-Al₂TiO₅ coated SiC samples after sodium corrosion.

Figure 14. Flexural strength of aged and unaged Mg-Al₂TiO₅ coated SiC samples before and after sodium corrosion.

Spectrum: MGTIAL7E
Comments:

Name: MGTIAL7E
Comments:

Centroid (KeV)	Net Area	Normalized	Comments
1.050	362.63	0.16	
1.260	507.88	0.23	Mgk
1.491	11016.50	5.00	Alk
1.743	180379.6	81.89	Sik
4.536	20608.54	9.36	Tik
4.956	3440.68	1.56	
5.229	63.05	0.03	
5.586	456.20	0.21	
6.090	66.22	0.03	

Figure 15. Distribution of Mg, Al, Ti, and Si on aged Mg-Al₂TiO₅ coated sample surfaces, obtained by EDX.

Spectrum: MGTIAL5C
Comments:

Name: MGTIAL5C
Comments:

Centroid (KeV)	Net Area	Normalized	Comments
1.281	54.05	0.12	Mgk
1.491	1207.12	2.69	Alk
1.743	41385.61	92.27	Sik
2.772	101.15	0.23	
3.423	28.75	0.06	
4.515	1474.45	3.29	Tik
4.977	122.91	0.27	
5.670	41.89	0.09	

Figure 16. Distribution of Mg, Al, Ti, and Si on unaged Mg-Al₂TiO₅ coated sample surfaces, obtained by EDX.