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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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INTRODUCTION

In high temperature engineering applications, commercially available silicon nitride non-oxide ceramics have retained special attention because of their superior thermal, mechanical, and chemical properties. These properties mainly include a high fracture strength and toughness, a low coefficient of thermal expansion relative to other ceramics, good thermal shock resistance, and good chemical stability. With silicon carbide, silicon nitride was the second material selected for heat exchangers in the High Temperature Advanced Furnace being developed under the DOE Combustion 2000 program. Their potential use in heat exchangers is, however, limited in time since both materials corrode severely in high temperature coal combustion atmospheres containing alkali compounds.¹ Thus, this research will first focus on enhancing the performance of Si_3N_4 ceramics by coating them with alkali corrosion resistant materials such as CMZP and Mg-doped Al_2TiO_5 oxide ceramics.^{2,3}

EXPERIMENTAL PROCEDURE:

I. Surface Preparation:

In order to enhance adhesion of the film to the substrate, Si_3N_4 samples were pretreated to form a silicon oxide layer or OH group on the surface of the substrate.

For CMZP coating, Si_3N_4 was soaked in an ultrasonic cleaner containing acetone for 1 hour, dried at 110°C for 2 hours and then immersed for 10 minutes in a solution containing 20% HF. Next, samples were washed with deionized water, dried at 110°C for 2 hours and calcined in air at 1200°C for 6 hours. Finally, the specimens were soaked in a 10% HCl solution for 10 minutes, then rinsed with deionized water and dried at 110°C for 2 hours.

For Mg-doped Al_2TiO_5 coating, Si_3N_4 samples were first soaked in an ultrasonic cleaner containing deionized water for 30 minutes and then immersed in a 1:1 HNO_3 solution for 6 hours. They were then washed with deionized water and dried at 110°C for 2 hours. Next, samples were calcined at 1200°C for 6 hours and soaked in a 10% HCl solution for 10 minutes. Finally, the specimens were rinsed with deionized water and dried at 110°C for 2 hours.

II. Preparation of sol-gel solutions:

a) CMZP sol-gel:

The precursors selected for the sol-gel are calcium chloride (CaCl_2), magnesium perchlorate hexahydrate ($\text{Mg}(\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$), zirconium propoxide ($\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$), and triethyl phosphate ($(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$). The stoichiometric weight amounts calculated for the precursors are $\text{Ca} : \text{Mg} : \text{Zr} : \text{P} = 1 : 1.3926 : 28.106 : 16.413$. First, CaCl_2 and $\text{Mg}(\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ were mixed in ethyl alcohol and HCl was added drop by drop until a pH between 2.2 and 4 was reached. Then $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ were added dropwise. The solution obtained was clear with a slight yellow color.

b) Mg-doped Al_2TiO_5 sol-gel:

The alkoxides selected for the sol-gel solution are magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, aluminum tri-sec butoxide, $\text{Al}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{O}]_3$ and titanium butoxide, $\text{Ti}[\text{CH}_3(\text{CH}_2)_3\text{O}]_4$. The stoichiometric weight amounts calculated for the precursors are Al : Ti : Mg - 1 : 0.852 : 0.056. First, the three were mixed and then a solution of ethyl alcohol and nitric acid with resultant pH between 1 and 4.5 was added dropwise to the precursor mixture. The solution obtained was clear with a slight yellow color.

III. Coating techniques:

A) CMZP coating:

CMZP coating was performed on Si_3N_4 samples by dipping them in the sol-gel solution for 10 minutes and removing them at a lifting rate of 4 cm/min. The coated specimens were then hydrolyzed at RT and 40-80% RH for 72 hours. Condensation was achieved by drying the samples at RT for an additional 72 hours and at 40-60°C for 48 hours. To remove all solvents and organic components and to achieve crystallization of the amorphous gel, the specimens were fired in air at 1200°C for 24 hours. To reduce the formation of cracks the coated samples were first brought to 400°C at a heating rate of 1°C/min and held at 400°C for 6 hours. Next they were rapidly heated to 1200°C at a rate of 5°C/min. Upon crystallization, samples were cooled to RT at a rate of 5°C/min.

b) Mg-doped Al_2TiO_5 coating:

To obtain Mg-doped Al_2TiO_5 coatings, Si_3N_4 specimens were immersed in the sol-gel solution for 30 minutes and then removed at a lifting rate of 4 cm/min. Hydrolysis was achieved by keeping the samples in a container with 40-80% RH at RT for 72 hours. The gel was then condensed in air at RT for 24 hours and at 65°C for an additional 24 hours. Removal of all solvents and crystallization were then achieved by firing the specimens at 1300°C for 10 hours. In order to alleviate the formation of cracks, coated samples were first brought to 400°C at a rate of 1°C/min and held at 400°C for 6 hours. Then, to prevent the crystallization of Al_2O_3 and TiO_2 , they were rapidly heated to 1300°C at a rate of 5°C/min. Upon crystallization, specimens were cooled to RT at a rate of 5°C/min.

RESULTS AND DISCUSSION:

I. Surface Pretreatments:

Contact angle tests were conducted to assess the effectiveness of the surface preparation. Five measurements were performed on each sample and the results are given in Table 1 for Si_3N_4 as received, Si_3N_4 surface treated for CMZP and Mg-doped Al_2TiO_5 , respectively. The great difference in contact angle before and after the surface treatment indicates that good wetting and spreading were achieved, therefore, enhancing the adhesion.

	Si ₃ N ₄ As received	Si ₃ N ₄ surface treated for CMZP	Si ₃ N ₄ surfaced treated for Mg-doped Al ₂ TiO ₅
Contact angle (°)	70.7	< 5	< 5

Table 1. Contact angle values for as-received Si₃N₄ samples and Si₃N₄ surface treated samples for CMZP and Mg-doped Al₂TiO₅.

However, after calcination at 1200°C for 6 hours, swells and white glassy spot products were observed on a great number of specimens. Thus, evidence of the growth of a silica layer on the substrate surface was investigated using SEM and EDX. Figure 1 shows an SEM photomicrograph of Si₃N₄ pretreated for CMZP and Mg-doped Al₂TiO₅ coatings. The topographical feature observed clearly indicates a non-homogeneous surface with relatively smooth areas and zones containing small grains. EDX elemental mappings of the two surface treatments are presented in Figure 2. These mainly evidence the presence of silica layers alongside the phosphor containing regions. Ca, Mg, As, and Zr elements were also detected but were not mapped. As the two above surface pretreatments have previously been successfully carried out,^{2,3} the features observed may be due to the fact that the as-received Si₃N₄ specimens were already pretreated or coated with CMZP.

Figure 1. SEM photomicrograph of Si₃N₄ samples pretreated for CMZP coating and Mg-doped Al₂TiO₅ coatings.

Figure 2. EDX elemental mappings of Si_3N_4 samples pretreated for a) CMZP coating, b) Mg-doped Al_2TiO_5 coating.

II. Coatings:

a) Influence of sol-gel concentration:

The influence of the solution concentration on the quality of the coating was investigated. Sol-gel solutions with controlled concentrations ranging from 0.02 to 0.8 mol.l⁻¹ and from 0.4 to 2.4 mol.l⁻¹ for CMZP and Mg-doped Al_2TiO_5 , respectively, were obtained by varying the alcohol/alkoxide ratio. Upon drying at RT, the crack-free quality of the coating was assessed by visual inspection. It was observed that cracks formed mainly at the bottom of the specimens. Results are given in Tables 2a and 2b. The coatings remained crack-free up to a concentration of 0.15 mol.l⁻¹ and 1.0 mol.l⁻¹ for CMZP and Mg-doped Al_2TiO_5 , respectively.

Due to prior treatments most of the samples underwent chemical reactions and weight losses after calcination at 1200°C, thus, it has not been possible to estimate the thickness of the coatings.

CMZP sol-gel concentration	Presence of cracks
0.02	no
0.05	no
0.1	no
0.15	no
0.2	yes
0.25	yes
0.3	yes
0.35	yes
0.4	yes
0.5	yes
0.6	yes
0.7	yes
0.8	yes

Table 2a. Influence of CMZP sol-gel concentration

Mg-doped Al_2TiO_5 sol-gel concentration	Presence of cracks
0.4	no
0.6	no
0.8	no
1.0	no
1.2	yes
1.4	yes
1.6	yes
1.8	yes
2.0	yes
2.2	yes
2.4	yes

Table 2b. Influence of Mg-doped Al_2TiO_5 sol-gel concentration

b) Characterization of sol-gel derived CMZP and Mg-doped Al_2TiO_5 coatings:

Information on the coatings was obtained using X-ray diffraction (XRD), X-ray energy dispersive analysis (EDX), and Scanning Electron Microscopy (SEM). Figures 3 and 4 present XRD patterns of calcined powders and coatings of CMZP and Mg-doped Al_2TiO_5 , respectively. XRD peaks of both sol-gel powders are the same as those previously reported.^{3,4} XRD patterns for CMZP coatings exhibit peaks identical to those of the calcined powder, suggesting that a CMZP film was successfully formed on the Si_3N_4 substrate. However, the presence of two peaks assigned to Si_3N_4 indicated that the CMZP phase was not totally pure. XRD patterns of the Mg-doped Al_2TiO_5 coatings yield very low intensity peaks and clearly indicate that only a partial Mg-doped Al_2TiO_5 phase was formed.

To reinforce these results, EDX mappings were conducted on coated Si_3N_4 samples and are presented in Figure 5. The elemental mappings depicted a good uniform distribution of Ca, Mg, Zr, and P for CMZP coatings and a very poor distribution of Mg, Al, Ti, and O for Mg-doped Al_2TiO_5 coatings. The microstructure of the coated specimens was also examined by SEM. Photomicrographs of CMZP and Mg-doped Al_2TiO_5 coated samples are shown in Figures 6 and 7. Comparison with features of uncoated samples given in Figure 1 indicates the presence of a thin film for both coatings. For CMZP coatings, however, small cracks were observed even for low concentrations.

Figure 3 : XRD patterns of a) CMZP calcined powder. b) CMZP coating.

Figure 4 : XRD patterns of a) Mg-doped Al_2TiO_5 powder. b) Mg-doped Al_2TiO_5 coating.

(a)

(b)

Figure 5 : EDX elemental mappings of a) CMZP and b) Mg-doped Al_2TiO_5 coatings.

Figure 6 : SEM photomicrograph of a CMZP coating.

CONCLUSIONS AND FUTURE WORK

In these first two months, CMZP and Mg-doped Al_2TiO_5 sol-gel solutions were successfully synthesized. In order to avoid the formation of cracks upon the drying at RT, the concentration of the sol-gel solution must not exceed 0.15 mol.l^{-1} and 1 mol.l^{-1} for CMZP and Mg-doped Al_2TiO_5 , respectively. Si_3N_4 was successfully coated with CMZP sol-gel, but the non pure phase suggests that calcination in air can not yield a totally pure phase. As for Mg-doped Al_2TiO_5 coatings, the poor quality of the film indicates that the influence of other factors such as viscosity and lifting rate should be investigated. To alleviate the occurrence of small cracks at low concentrations for CMZP coatings, the heatings and calcination schedule should be conducted more stepwise and double coating should also be examined in order to obtain thicker crack-free films.

Figure 7 : SEM photomicrograph of a Mg-doped Al_2TiO_5 coating.

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