HIGH TEMPERATURE ALKALI CORROSION OF DENSE SiC AND Si_3N_4
COATED WITH CMZP AND MgDOPED Al_2TiO_5 IN COAL GAS

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INTRODUCTION:

Si_3N_4 ceramics possess properties that are attractive for high temperature heat exchanger applications. These properties include high strength, good thermal conductivity and excellent resistance to thermal shock and oxidation. However when subjected to alkaline containing environments, Si_3N_4 is prone to corrode and eventually loses its properties.' Because it was found that oxide ceramics corrode substantially less 2, they can be used as a coating to protect Si_3N_4 . Therefore the first objective of this work is to develop thin film of CMZP and Mg-doped Al_2TiO_5 since both of them are good candidate coating materials of primary interest for the protection of Si_3N_4 against alkaline corrosion.

EXPERIMENTAL PROCEDURE:

I. Surface treatment:

In order to enhance the adhesion of the film to the substrate, Si_3N_4 samples were pretreated to form a silicon oxide layer or OH groups 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 an additional 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 an additional 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 Ca: Mg: Zr: 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. Water was added last and the pH readjusted. The solution obtained was clear with a slight yellow color.

b) Mg-doped Al₂TiO₅ sol-gel:

The alkoxides selected for the sol-gel solution are magnesium nitrate hexahydrate (Mg(NO₃)_{2.6}H₂O), aluminum tri-sec butoxide (Al[C₂H₅CH(CH₃)O]₃) and titanium butoxide (Ti[CH₃(CH₂)₃O]₄). The stoichiometric weight amounts calculated for the precursors are Al: Ti: Mg = 1: 0.852: 0.056. First, the three precursors 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. Water was finally added and the pH readjusted. The solution obtained was clear with a slight yellow color.

III. Coating techniques:

a) CMZP coatings:

CMZP single coating was performed on Si₃N₄ samples by dip-coating. 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 48 hours and at 50°C for 24 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 successively brought to 200°C, 300°C, 400°C and 500°C at a heating rate of 0.5°C/min and remained at each step for 2 hours. Next, they were brought at a heating rate of 5°C/min to 1000°C where they stayed 4 hours and then at 1200°C.

For the double coating the samples were dried at RT and 40-80% RH for 72 hours. Air dried at RT for an additional 48 hours and at 50°C for 24 hours. Next, they were brought to 400°C where they remained for 6 hours. The rate of increasing and decreasing temperature was 0.5°C/min and 5°C/min~ respectively. The second coating was applied and underwent the same procedure as the single coating.

b) Mg-doped Al₂TiO₅ coatings:

Mg-doped Al₂TiO₅ single coatings were obtained using the dip-coating method. 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 an additional 48 hours and at 65°C for 24 hours. Removal of all solvents and crystallization were achieved by firing the coated specimens at 1300°C for 10 hours. In order to alleviate the formation of cracks the samples were successively brought to 100°C, 200°C, 300°C and 400°C at a heating rate of 1°C/min and remained at each step for 1.5 hours. Then, to prevent the crystallization of Al₂O₃ and TiO₂³, they were rapidly heated to 1300°C at a rate of 10°C/min. Upon crystallization the specimens were cooled to RT at a rate of 5°C/min.

For the double coating the samples were dried at RT and 40-80% RH for 72 hours. Air dried at RT for an additional 48 hours and at 65°C for 24 hours. Next, they were brought to 400°C where they remained for 6 hours. The rate of increasing and decreasing temperature was 1°C/min and 5°C /min, respectively. The second coating was applied and underwent the same procedure as the single coating.

RESULTS AND DISCUSSIONS:

In this second report a new set of Si_3N_4 samples that exhibit better stability after the surface treatment (i.e. no swelling, no formation of glassy white SiO_2 spots) were studied. Figure 1a and 2a show the morphology of the surface treated samples for CMZP and Mg-doped Al_2TiO_5 coating, respectively. It will be noticed that the features evidenced are totally different from those presented in the first report. In addition no trace of Zr or P was detected as indicated by Energy Dispersive X-ray elemental mappings in Figure 1b and 2b and X-ray Diffraction analysis in Figure 1a. Concerning the XRD pattern the peaks labeled Si_3N_4 perfectly match with those of JCPDS Si_3N_4 reference card.

1 (a)

1 (b)

Figure 1: a) SEM photomicrograph featuring the surface of Si_3N_4 after the surface treatment for CMZP coating. b) EDX elemental mappings for Si_3N_4 surface treated.

2 (a)

2 (b)

Figure 2: a) SEM photomicrograph featuring the surface of Si_3N_4 after the surface treatment for CMZP coating. b) EDX elemental mappings for Si_3N_4 surface treated.

I. Influence of the lifting rate for CMZP and Mg-doped Al₂TiO₅ coatings:

The influence of the lifting rate was investigated for a CMZP concentration of 0.05 mol/l and a Mg-doped Al₂TiO₅ viscosity of 6 cp. Visual inspection of the bottom of the coated samples was conducted after the drying step in order to disclose the presence of cracking. The observations are reported in table 1. It was found that when the samples were removed at a lifting rate exceeding 6.5 cm/min, a droplet tended to stick at the bottom of the Si₃N₄ bar. When the solvents were removed upon the drying a thick film was formed leading to aggregation and cracking.

Lifting Rate (cm/min)	Presence of cracks	
	CMZP	Mg-doped Al ₂ TiO ₅
4.2	no	no
6.5	no	no
8.5	yes	yes
12	yes	yes

Table 1: Influence of the lifting rate on the quality of the coating assessed for a CMZP concentration of 0.05 mol/l and a Mg-doped Al₂TiO₅ viscosity of 6 cp.

II. Influence of the concentration for CMZP coatings:

Previous research has demonstrated the importance of the sol-gel concentration on the quality of the thin films.³ The influence of this parameter was studied with respect to the thickness of the coatings. For Si₃N₄ specimens coated in this work it was found that the coverage of the surface was only partially achieved. Thus optical inspection was preferred to assess the quality of the coatings as a function of the sol-gel concentrations. The results obtained with a lifting rate of 6.5 cm/min are presented in Table 2. They indicate that aggregation of CMZP gel occurs near the bottom of the bar for concentrations higher than 0.05 mol/l.

CMZP Concentration (mol/l)	Presence of Aggregates	Coverage of the Surface
0.1	yes	very poor
0.05	a few	very poor
0.02	no	poor
0.01	no	poor

Table 2: Quality of the CMZP coating as a function of sol-gel concentration.

Figure 3: Photomicrograph of an aggregated area for a CMZP concentration of 0.1 mol/l.

Figure 3 illustrates the phenomenon of aggregation for a solution with concentration 0.1 mol/l. Indeed solutions with concentration 0.05 and 0.1 mol/l lead to relatively thick coatings which are more readily displaced at the bottom of the bar by gravity. It is believed that the displacement of the sol-gel takes place because the solution is not viscous enough. For lower concentrations the films formed are too thin and thus the sol-gel is less subjected to the effect of gravity. The coverage of the surface is however very poor as shown in Table 2. Therefore in order to improve the quality of the coatings, solutions with more consistency i.e. higher concentration should be tried.

III. Influence of the viscosity for Mg doped Al_2TiO_5 coatings:

In Mg-doped Al_2TiO_5 coating process the viscosity has been reported to have a critical influence on the quality of the film.^{4,5} In this work optical microscope was used to examine the quality of the thin films as a function of viscosity. Qualitative results obtained with a lifting rate of 6.5 cm/min are presented in Table 3. As indicated the lower the viscosity, the more aggregates are formed near the bottom of the sample.

Viscosity (cp)	Presence of Aggregates	Coverage of the Surface
4.5	yes	poor
6	yes	good
7.5	fewer	good
10	fewer	good

Table 3: Quality of the Mg doped Al_2TiO_5 coatings as a function of viscosity.

Figure 4 depicts an aggregated area for a specimen coated with a sol-gel viscosity of 6 cp. The discrepancy with the observations made by some authors^{4,5} is due to the fact that Si_3N_4 samples are not porous. Thus the above findings suggest that to achieve better quality thin films and avoid aggregation, viscosities higher than 10 cp are required.

Figure 4: Photomicrograph of an aggregated area for a Mg-doped Al_2O_3 sol-gel with viscosity 6 cp.

IV. QUALITY OF THE COATINGS:

In this section morphological features of the coatings were examined with SEM and information regarding the composition of the coatings were investigated using XRD and EDX.

a) Single CMZP coatings:

Si_3N_4 specimens coated with a single layer of CMZP at a lifting rate of 6.5 cm/min were first analyzed by XRD. No CMZP peaks were yielded as revealed in Figure 10b. The presence of a coating was only suggested by a slight decrease in SiO_2 and Si_3N_4 peak intensities compared to the peak intensities of the surface treated sample (see Figure 10a). Photomicrographs of the coated samples obtained with SEM evidence a surface partly covered with white nodular particles as can be seen in Figure 5. Further investigation conducted with EDX clearly indicate that the white nodular particles contain P, Zr, Ca and very small traces of Mg. EDX elemental mappings are given in Figure 6. For the different concentrations the coverage of the surface was poor as previously mentioned and could obviously be improved by double coating.

Figure 5: SEM photomicrograph of a single CMZP coating obtained with sol-gel concentration of 0.05 mol/l and a lifting rate of 6.5 cm/min.

b) CMZP double coatings:

In order to alleviate aggregation and improve the quality of the thin film, double coating was performed on Si_3N_4 samples. Observations made with SEM prove the results to be positive as depicted in Figure 7. The photomicrograph features a good coverage of the surface by bigger CMZP grains. Table 4 gives an overview of the characteristics of other double coated specimens. In order to avoid aggregation and thus have a relatively uniform coating the sol-gel concentration needs to be kept below 0.05 mol/l. Higher concentrations result in the formation of a non uniform coating as illustrated in Figure 8 where two different morphologies were yielded for a same double coated specimen with concentration 0.05 and 0.1 mol/l for the first and second coatings, respectively. The best coating found requires a first thin film of concentration lower than 0.02 mol/l and a second coating of concentration 0.02 mol/l preferentially.

6 (a)

6 (b)

Figure 6: a) High magnification SEM photomicrograph of a single CMZP coating obtained with a sol-gel concentration of 0.05mol/l and a lifting rate of 6.5 cm/min b) corresponding EDX elemental mappings.

Concentration of first coating (mol/l) Concentration of second coating	Coverage of the surface	Presence of aggregates
0.01	poor	no aggregate
0.01		
0.01	good	no aggregate
0.02		
0.01	good	a few aggregates
0.05		
0.01	good	a lot of aggregates
0.1		
0.02	good	no aggregate
0.02		
0.02	good	a few aggregates
0.05		
0.02	good	a lot of aggregates
0.1		
0.05	good	a few aggregates
0.05		
0.05	good	a lot of aggregates
0.1		
0.1	good	a lot of aggregates
0.1		

Table 4: Quality of CMZP double coatings obtained with a lifting rate of 6.5 cm/mint

Figure 7: Double CMZP coating obtained with sol-gel concentration of 0.01 and 0.02 mol/l, respectively and a lifting rate of 6.5 cm/min.

Figure 8 SEM photomicrographs showing two different features for a CMZP double coated sample obtained with asol-gel concentration of 0.05 and 0.1 mol/l for first and second coating, respectively and a lifting rate of 6.5 cm/mint

The quality of the coating regarding its composition was assessed by EDX and XRD. Figure 9 shows an energy dispersive spectrum of a Si_3N_4 specimen double coated with a CMZP concentration of 0.01 and 0.02 mol/l, respectively. Only a sharp peak corresponding to Si was evidenced. Peaks of Au comes from the coating of the sample prior analysis. This finding suggests that a thin film of SiO_2 seems to develop on top of the coating during the heat treatment. This hypothesis was confirmed when analyzing XRD pattern: only small peaks of SiO_2 and Si_3N_4 were yielded as shown in Figure 10c.

Figure 9 a) : Energy Dispersive X-ray spectrum of a) a CMZP double coated sample with sol-gel concentration of 0.01 and 0.02 mol/l, respectively and a lifting rate of 6.5 cm/min.

Figure 9 b): Energy Dispersive X-ray spectrum of a Mg-doped AlTiO_5 single-coated sample with sol-gel viscosity of 6cp and a lifting rate of 6.5 cm/min.

Figure 10: XRD pattern for a) SiN_4 surface treated. b) CMZP single coated SiN_4 sample. c) CMZP double coated SiN_4 sample.

c) Mg-doped Al_2TiO_5 single coatings:

Si_3N_4 samples coated with three different viscosities and at a lifting rate of 6.5 cm/min were first examined with XRD. The coatings exhibit the same XRD pattern as the one shown in Figure 13b. Comparison of the pattern yielded for Si_3N_4 surface treated and Si_3N_4 coated specimens depicted a clear decrease in SiO_2 and Si_3N_4 peak intensities and the appearance of Al_2O_3 , TiO_2 and Mg-doped Al_2TiO_5 peaks. The crystallization of Al_2O_3 and TiO_2 may result from the vaporization of Mg initially added to stabilize the Al_2TiO_5 structure and prevent its decomposition into Al_2O_3 and TiO_2 . The vaporization of Mg probably located in an interstitial position in the Al_2TiO_5 structure was confirmed by the absence of the Mg peak in the energy dispersive X-ray spectrum presented in Figure 9 b.

When studying the morphology of the coating with SEM two different kinds of features were evidenced. Figure 11a shows a photomicrograph of a sample coated with a sol-gel solution with viscosity 6 cp. As can be seen the coating is mainly composed of grains and needle particles. Identification of the previous particles was determined by EDX. Elemental mappings in Figure 11b depicts a non-uniform distribution of Al and Ti and reveal that the grains and the needles consist of Al and Ti, respectively. When crossing these results with those obtained by XRD, it was concluded that the needles are rutile particles and the grains are alumina particles.

The second feature evidenced is shown in Figure 12 and witnesses the formation of what seems to be a liquid phase of SiO_2 covering the Al_2O_3 and TiO_2 particles. This smooth layer is probably an aluminosilicate glass layer resulting from a metastable eutectic found around 1250°C by Aksay and Pask⁶ or from an immiscible aluminosilicate liquid as reported by Mac Dowel and Beals.

11 (a)

11 (b)

Figure 11: a) SEM photomicrograph of a Mg-doped Al_2TiO_5 single coated sample obtained with sol-gel viscosity of 6 cp and a lifting rate of 6.5 cm/min. b) Corresponding EDX elemental mapping.

12 (a)

12 (b)

Figure 12: a) SEM photomicrograph of a Mg-doped AlTiO_5 single coated sample obtained with sol-gel viscosity of 6cp and a lifting rate of 6.5 cm/min. b) Corresponding EDX elemental mapping.

d) Mg-doped Al_2TiO_5 double coatings:

Double coatings were performed on Si_3N_4 samples to obtain a better coverage of the surface, to avoid the formation of aggregates and to improve the quality of the coating with respect to the composition. SEM inspections revealed that double coating successfully led to a better coverage of the surface but failed to alleviate the formation of aggregates as summarized in Table 5.

Viscosity of first coating Viscosity of second coating (cp)	Coverage of the surface	Presence of aggregates
4.5	very good	yes
6		
4.5	very good	yes
7		
4.5	very good	less aggregates
10		
6	very good	yes
6		
6	very good	yes
7.5		
6	very good	less aggregates
10		
7.5	very good	yes
7.5		
7.5	very good	yes
10		

Table 5: Quality of Mg-doped Al_2TiO_5 double coatings obtained with a lifting rate of 6.5 cm/min.

Concerning the morphology of the coatings the two features encountered with the single coating were also yielded. XRD analysis demonstrate that the quality of the coating regarding its composition was improved especially with a sharp increased in the Mg-doped Al_2TiO_5 peak as evidenced in Figure 13c).

Figure 13: XRD pattern for a) Si_3N_4 surface treated. b) Mg-doped AlTiO_5 single coated Si_3N_4 sample. c) Mg-doped AlTiO_5 double coated Si_3N_4 sample.

CONCLUSION:

- The concentrations and viscosities achieved for CMZP and Mg-doped Al_2TiO_5 solution, respectively, lead to the formation of aggregates which are prejudicial to the homogeneity of the coatings. It is believed that higher solution concentrations can significantly reduce the formation of aggregates.
- A SiO_2 layer seems to develop on top of the CMZP and Mg-doped Al_2TiO_5 coatings. Although this phenomenon is not necessarily detrimental to the effectiveness of the coating, an attempt will be made to prevent its formation.
- Mg-doped Al_2TiO_5 coating witness the crystallization of Al_2O_3 and TiO_2 due probably to the vaporization of Mg. Future work should therefore focus on finding ways to retain Mg in the coatings.
- Double coating significantly improves the quality of the CMZP and Mg-doped Al_2TiO_5 coatings.

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