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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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Prepared by

J. J. Brown

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

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

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Abstract

The second phase, coating of Si_3N_4 by oxides, was started during this reporting period. Si_3N_4 samples were coated by CMZP and Mg-doped Al_2TiO_5 by a double-dip procedure.

Executive Summary

High temperature alkali corrosion has caused premature failure of SiC and Si₃N₄ components used in advanced high temperature coal combustion systems. The objective of this research is to develop and characterize CMZP and Mg-doped Al₂TiO₅ coatings on SiC and Si₃N₄ heat exchanger materials and 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. The portion of this study dealing with SiC has been completed; the remainder of the project will focus on coating Si₃N₄.

Results and Discussion

A. Preparation of Substrate Materials

The Si₃N₄ samples to be coated with CMZP were first washed with deionized water for 30 minutes in a solid state/ultrasonic container, then soaked in acetone for 1 h, and dried at 110°C for 2 h. Next, the samples were washed with 10% HF solution, rinsed with deionized water, dried at 110°C for 2 h, and calcined at 1200°C for 6 h. Finally, the calcined samples were washed in 10% HCl solution, rinsed with deionized water, and dried at 110°C for 2 h.

The samples to be coated with Mg-doped Al₂TiO₅ were first washed with deionized water for 30 minutes in a solid state/ultrasonic container, then soaked in 1:1 HNO₃ for 6 h, washed with deionized water, dried at 110°C for 2 h, and calcined at 1200°C for 6 h. Finally, the calcined samples were washed in 10% HCl solution, rinsed with deionized water, and dried at 110°C for 2 h.

B. Preparation of CMZP Solution

The precursors for CMZP solution are calcium chloride (CaCl₂), magnesium

perchlorate hexahydrate ($\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), zirconium propoxide ($\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$), triethyl phosphate ($((\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O}))$), hydrochloric acid, ethyl alcohol and deionized water. The stoichiometric amounts of calcium chloride and magnesium perchlorate hexahydrate were mixed in ethyl alcohol. The mixture was constantly stirred while hydrochloric acid was added drop by drop until a pH of between 2.0 and 4.0 was reached, then zirconium propoxide and triethyl phosphate were added drop by drop. The concentration of the CMZP solution was 0.2 mol/L.

C. Preparation of Mg-doped Al_2TiO_5 Solution

The precursors for Mg-doped Al_2TiO_5 solution are magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum tri-sec butoxide ($\text{Al}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{O}]_3$), titanium butoxide ($\text{Ti}[\text{CH}_3(\text{CH}_2)_3\text{O}]_4$), ethyl alcohol, nitric acid, and deionized water. The stoichiometric amounts of magnesium nitrate hexahydrate, aluminum tri-sec butoxide and titanium butoxide were first weighted and homogenized by stirring. A solution of ethyl alcohol and nitric acid with resultant pH between 1.0 and 4.5 was added drop by drop to the mixture of the magnesium, aluminum and titanium under constant stirring conditions. Deionized water required for the hydrolysis reaction of the alkoxides was added last while constantly stirring and solution pH was maintained between 1.0 and 4.5. The concentration of the $\text{Mg}_{0.1}\text{Al}_{1.8}\text{Ti}_{1.1}\text{O}_5$ solution was 2.5 mol/L. The solution was clear with slight green coloration.

D. Viscosity Measurement

Viscosity measurements for the Mg-doped Al_2TiO_5 solution are conducted following the preparation of the solution. The viscosity of the solution was measured according to standard procedures ASTM D445 and D446 prior to dip coating. The viscosity of the solution was controlled between 1.0 and 6.2 centipoises (cP) by varying the H_2O /alkoxide molar ratio or aging of the solutions.

E. Coating Techniques

1) **CMZP Coatings:** The pre-treated samples were soaked in the boiling CMZP solution for 30 minutes and remained in the solution while being cooled slowly to room temperature. The samples were withdrawn at a rate of 4-12 cm/min at room temperature. The coated samples were cured at room temperature for 72 h at a relative humidity of 40-80%, then air-dried at room temperature for an additional 72 h and dried at 40-60°C for 48 h, then finally heat treated following the schedule presented in Figure 1.

2) **Mg-Doped Al_2TiO_5 Coatings:** The pre-treated samples were immersed in the solution and vibrated for 30 minutes. The dip coating withdrawal rate was less than 8.00 cm/min, preferably between 2.2 and 4.1 cm/min. The coated samples were cured in a covered container for 72 h, then heat treated following the schedule in Figure 2.

Conclusions

Si_3N_4 seems to be very similar to SiC in its ability to be coated by oxides like CMZP and Mg-doped Al_2TiO_5 . Efforts to develop thicker coatings are needed.

Room temperature

↓ 0.5°C/min

500°C for 10 h

↓ 0.5°C/min

1000°C for 4 h

↓ 0.5°C/min

1200°C for 24 h

↓ 0.5°C/min

Room temperature

**Figure 1 Heat treatment schedule
for CMZP coating dense Si_3N_4**

Room Temperature

↓ 1°C/min

65°C for 1.5 h

↓ 1°C/min

100°C for 1.5 h

↓ 1°C/min

150°C for 1.5 h

↓ 1°C/min

250°C for 1.5 h

↓ 1°C/min

350°C for 1.5 h

↓ 1°C/min

450°C for 1.5 h

↓ 1°C/min

1300°C for 10 h

↓ 5°C/min

Room temperature

**Figure 2 Heat treatment
schedule for Mg-doped Al_2TiO_5
coating dense Si_3N_4**