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

Quarterly Progress Report #12
for the Period
April 1, 1997 to July 1, 1997

Prepared by

Nguyen Thierry 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

July 1, 1997

U.S. DOE Patent Clearance is not required prior to

the publication of this document.

Hot pressed Si_3N_4 has been extensively studied in the past years mainly because it is a potential candidate for high temperature structural applications. If its behavior in alkaline environments has been widely investigated and is now well understood, only a few authors have conducted research on thin film to enhance Si_3N_4 lifetime in harsh environments^{4,5}. Thus, it is the first objective of this work to develop thin film of CMZP and Mg doped AlTiO_5 using the sol-gel process and the dip coating technique.

In the previous report relatively good coverage of the substrate surface was achieved with low concentration solutions and double coatings. However, the aggregation of the sol-gel at the bottom of some samples suggested that more viscous sol-gels, i.e. higher concentrations, could alleviate this phenomenon. This report will therefore present the results obtained with more concentrated solutions and also those obtained with two other CMZP solutions utilizing different precursors.

I. Sol-gel preparation:

In this work three different CMZP solutions, A, B, and C were synthesized. The precursors for CMZP solutions A are : calcium chloride $[\text{CaCl}_2]$, magnesium perchlorate hexahydrate $[\text{Mg}(\text{ClO}_4)_6\text{H}_2\text{O}]$, 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 $\text{Mg}(\text{ClO}_4)_6\text{H}_2\text{O}$ were mixed in ethyl alcohol and the pH was adjusted between 2 and 4 with HCl. 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 was clear with a yellow color.

CMZP solution B utilizes calcium acetate hydrate $[\text{Ca}(\text{CH}_3\text{CO}_2)\text{H}_2\text{O}]$, magnesium ethoxide $[\text{Mg}(\text{C}_2\text{H}_5\text{O})_2]$, zirconium ethoxide $[\text{Zr}(\text{C}_2\text{H}_5\text{O})_4]$, and triethyl phosphate $[(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})]$. The stoichiometric weight amounts for the precursors are: $\text{Ca}:\text{Mg}:\text{Zr}:\text{P} = 1:0.437:10.418:10.336$. First, $\text{Ca}(\text{CH}_3\text{CO}_2)\text{H}_2\text{O}$, $\text{Mg}(\text{C}_2\text{H}_5\text{O})_2$, and $\text{Zr}(\text{C}_2\text{H}_5\text{O})_4$ powders were mixed in ethyl alcohol and HCl was added until a pH value between 2 and 4 was reached. Then, $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ was incorporated. Water was added last and the pH readjusted. The solution obtained was slightly dim with a yellow color.

CMZP solution C uses calcium nitrate $[\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}]$, magnesium nitrite hexahydrate $[\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$, zirconium dinitrate oxide $[\text{ZrO}(\text{NO}_3)_x\text{H}_2\text{O}]$, and triethyl phosphate $[(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})]$. The stoichiometric weight amounts for the precursors are: $\text{Ca}:\text{Mg}:\text{Zr}:\text{P} = 1:0.724:7.678:7.711$. First, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and $\text{ZrO}(\text{NO}_3)_x\text{H}_2\text{O}$ were mixed in ethyl alcohol and nitric acid was added if needed to adjust the pH between 2 and 4. Then, $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ was included and water added last. A clear solution was obtained.

The X-ray diffraction patterns for the three powders are shown in Figure 1. Using X-ray data given for $(\text{ZrO})_2\text{P}_2\text{O}_7$ (ZP), $\text{CaZr}_4(\text{PO}_4)_6$ (CZP), $\text{MgZr}_4(\text{PO}_4)_6$ (MZP), and $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ (CMZP) powders,^{6,7} it was possible to identify the phases present

in the synthesized sol-gels. For the three powders CMZP was found to be the main phase. X-ray diffraction pattern for the powder derived from solution C indicated a nearly pure CMZP phase with a minor CZP peak. As for the powders obtained with solutions A and B, X-ray diffraction patterns clearly evidenced traces of CZP, ZP and MZP. Their occurrence may be attributed to an excess of calcium, zirconium and magnesium precursors.^{7,8}

Figure 1 : X-ray diffraction patterns of powders derived from CMZP solution A, B, and C, respectively.

II. Multiple coatings

Scanning electron microscope was used to investigate the quality of the films as a function of the number of coatings. To obtain a good coating Si_3N_4 specimens had to be coated up to three times using the procedure described in report # 11. The results for CMZP solution A, B, and C are reported in table 1. For the three sol-gels poor coverage of the surface was achieved when samples were dip coated one or two times. With three coatings only CMZP solution A and B gave good results as depicted in Figure 2. Two different morphologies were evidenced for sol-gel A. Indeed some coatings exhibited surface with well defined grains whereas others yielded non granular structures, probably due to the melting of the grains.

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Solution A (0.2 mol/l) Solution B (0.02 mol/l) Solution C (0.05 mol/l)			
Number of coatings	Coverage	Coverage	Coverage
1 coating	poor	poor	poor
2 coatings	better	better	poor
3 coatings	good	good	poor

Table 1 : Quality of the film as a function of the number of coatings.

Figure 2 : SEM photomicrographs of Sn_4 coated one and three times with a) CMZP solution A, b) CMZP solution B, and c) CMZP solution C.

III. Influence of CMZP sol-gel concentration

a) CMZP solution A

Silicon nitride specimens dip coated with sol-gel solutions of concentration 0.2 and 0.4 mol/l, respectively, were studied using a scanning electron microscope. The quality and morphology of the thin films are listed in Table 2. For both concentrations no good coating was achieved. Indeed, with a solution of concentration 0.2 mol/l the surface was poorly covered with grains of varied sizes and shapes as depicted in Figure 2. Higher concentrations resulted in a better coverage of the surface, but no grains were evidenced. The coating is thought to be too thick and is mainly formed of segregated pieces of CMZP as shown in Figure 3. When compared with previous findings (see report # 11), it was concluded that coatings obtained with lower concentrations yielded grains of more uniform size and shape and more evenly distributed. However, those results need to be checked again for a different grade of SiN_4 was used.

concentration	coverage of the surface	morphology of the coating
0.2	poor	needle like, round
0.4	good	pieces of aggregates

Table 2 : Influence of high concentration on the quality of the coating for CMZP solution A.

Figure 3 : SEM photomicrograph of one CMZP coating derived from sol-gel A with concentration 0.4 mol/l.

b) CMZP solution B

The quality of the coatings obtained with solution B was assessed for three different concentrations : 0.02, 0.05, and 0.2, respectively. First, it was found that the drying procedure didn't need to include a three day exposure in a 40-80 RH atmosphere. Indeed coated samples, which were not put in a dessicator at 40-80 RH, presented a better coating. SEM inspections clearly indicated that when the relative humidity exceeded 60 %, the sol-gel took up too much moisture and as a consequence was driven to the bottom of the specimen. Results regarding the influence of the concentration are displayed in table 3. As can be seen a good film was achieved for a minimum concentration of 0.05 mol/l. Figure 4 presents a photomicrograph of the thin film at magnification 2000. Grains of CMZP with size ranging from 1.3 to 3.5 μm appeared to be uniformly distributed. However, EDX energy dispersive spectrum and elemental mappings presented in figure 5 still evidenced the presence of Si, Al, and O on the surface. This may be attributed to the fact that the amorphous alumino silicate layer which forms during the surface treatment, can react with CMZP or develop on top of the coating during the firing.

concentration	coverage of the surface	morphology of the coating
0.02	poor	needle like, round
0.05	good	round
0.2	excellent	round

Table 3 : Influence of sol-gel concentration on the quality of the coating for CMZP solution B.

Figure 4 : SEM photomicrographs of one CMZP coating derived from sol-gel B with concentration 0.2mol/l.

Figure 5 : a) EDX energy dispersive spectrum for CMZP coating derived from solution B. b) corresponding EDX elemental mappings.

c) CMZP solution C

Coatings developed from sol-gel C with concentrations 0.05, 0.1, and 0.4 were studied by means of SEM. Like CMZP solution B, samples directly dry in air at a relative humidity lower to 60 % yielded the best results. The quality of the films are summarized in table 4. A good coverage was achieved when using solution with concentration higher

than 0.05, but the thin film appears to be formed of small pieces of aggregates as illustrated in figure 6.

concentration	coverage of the surface	morphology of the coating
0.05	poor	needle like, round
0.1	good	pieces of aggregates
0.4	good	pieces of aggregates

Table 4 : Influence of sol-gel concentration on the quality of the coating for CMZP solution C.

Figure 6 : SEM photomicrograph of one CMZP coating derived from sol-gel C with concentration 0.4 mol/l.

Conclusion

Concerning CMZP solution A investigated so far in the previous reports, it was found that higher sol-gel concentrations did not significantly improve the quality of the coatings. The aggregation phenomenon was indeed eradicated, but the quality of the coating assessed in terms of grain size, grain shape and grain distribution on the substrate surface was not as good as the one involving low concentration solutions. Besides, the work conducted over the past four months has also shown that among the three CMZP sol-gels synthesized, solution B using the precursors $\text{Ca}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{C}_2\text{H}_5\text{O})_2$, $\text{Zr}(\text{C}_2\text{H}_5\text{O})_4$, and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$ gave the best results in terms of thin films. To obtain a good coating it was necessary to coat Si_3N_4 samples up to three times. However, XRD diffraction patterns indicated that the powder was not single phase. Indeed in addition to

CMZP, which is the main phase, small peaks relative to $(\text{ZrO})_2\text{P}_2\text{O}_7$, $\text{CaZr}_4(\text{PO}_4)_6$, and $\text{MgZr}_4(\text{PO}_4)_6$ were yielded. The purest CMZP powder was achieved with CMZP solution C using the precursors $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_x \cdot \text{H}_2\text{O}$, and $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$, but the quality of the coating still need to be improved.

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