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

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Si_3N_4 heat exchangers used in industrial systems are usually operating in harsh environments. Not only is this structural material experiencing high temperatures, but it is also subjected to corrosive gases and condensed phases. Past studies have demonstrated that condensed phases severely attack Si_3N_4 and as a consequence, dramatically reduce its lifetime in industrial operating systems.[1,2] Previous research conducted at Virginia Tech on low thermal expansion coefficient oxide ceramics,[3,4,5] $(Ca_{1-X},Mg_X)Zr_4(PO_4)_6$ (CMZP), and Mg-doped Al_2TiO_5, for structural application have shown that these two materials exhibited better resistance to alkaline corrosion than Si_3N_4. Thus, they were envisioned as good candidates for a protective coating on Si_3N_4 heat exchangers. As a result, the goal of the present work is to develop CMZP and Mg-doped Al_2TiO_5 protective thin films using the sol-gel process and the dip coating technique and to test their effectiveness in an alkali-containing atmosphere.

EXPERIMENTAL PROCEDURE

The most appropriate corrosion test for simulating coal slag conditions in real industrial systems is the laboratory film test. The specimen to study is coated with a film of the corrosive salt and placed in a furnace with a well-defined gas environment.[6] 5 x 5 x 3 mm Si_3N_4 coupons coated with CMZP and Mg-doped Al_2TiO_5 were first brought to 200°C and dip coated in a $NaNO_3$ saturated aqueous solution and then tested in an atmosphere containing a constant 8 vol.% $NaNO_3$ concentration at 1000°C for 48 h. A scheme of the apparatus used for the alkali corrosion experiment is given in Figure 1. Although Na_2SO_4 is the most common melt encountered in industrial systems, $NaNO_3$ (Aldrich, ACS Reagent) was preferred for the alkali source because of its high vapor pressure in the 700-800°C temperature range as compared to $NaCO_3$ or Na_2SO_4.[7] As shown in Figure 1, the apparatus consists of two separate heating zones. On the gas inlet side an alumina boat filled with $NaNO_3$ was heated to 720°C ± 10 using high temperature heating tapes coupled with a potentiometer and a K-type thermocouple gauge. A flow rate of compressed air fixed at 86 cm^3/min was used to carry the alkali containing species in the second heating zone, the reaction zone, where the temperature was maintained at 1000°C. Prior entering the alumina tube, the compressed air was filtered to remove moisture and CO_2. This was achieved by using a four compartment plastic tube filled with silica gel, drierite, activated alumina and silica gel, respectively.

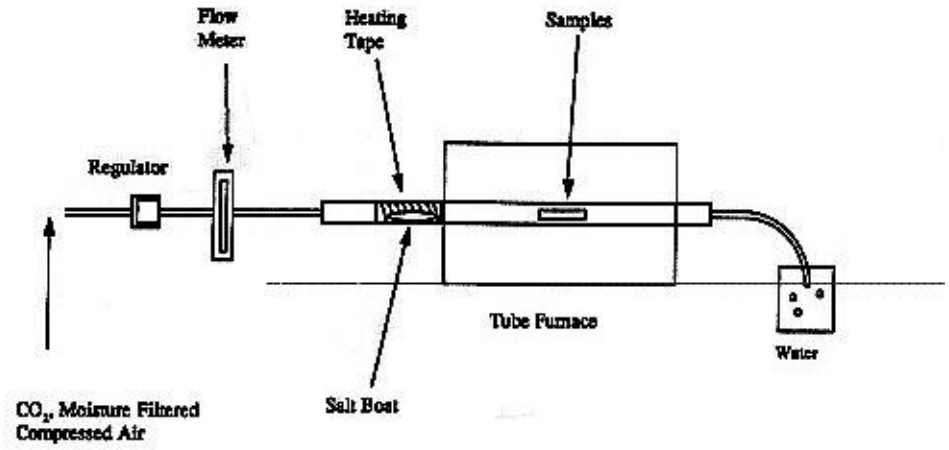
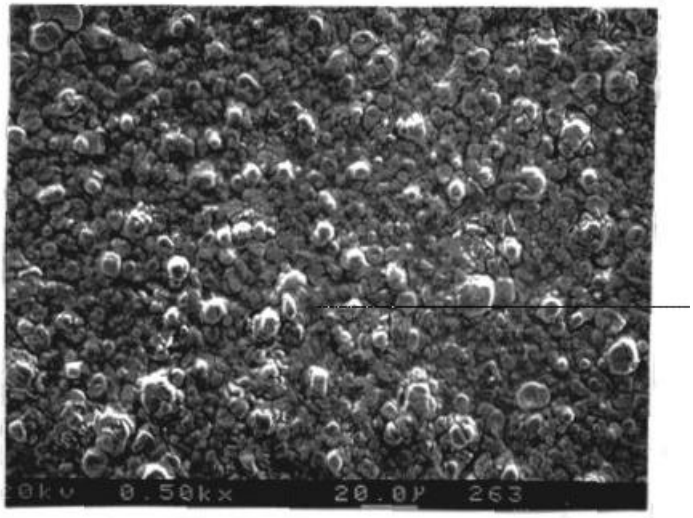


Figure 1 : Scheme of the apparatus used for the corrosion test.

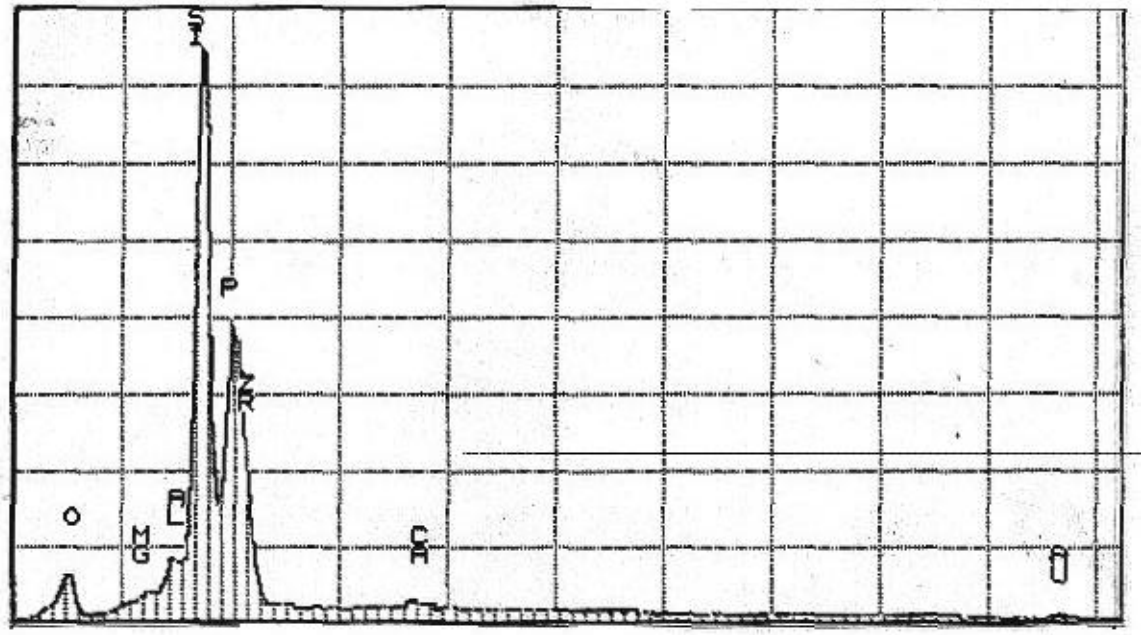
RESULTS AND DISCUSSION

CMZP coated samples :

Si_3N_4 samples coated three times with CMZP sol-gel using calcium chloride ($CaCl_2$), magnesium perchlorate hexahydrate ($Mg(ClO_4).6H_2O$), zirconium propoxide ($Zr(C_3H_7O)_4$) and triethyl phosphate ($(C_2H_5O)_3P(O)$) precursors were tested in an $NaNO_3$ atmosphere at 1000°C for 48 h. The microstructural changes of the coated samples were studied with scanning electron microscopy, SEM, X-ray energy dispersive spectrometry, EDX, and X-ray diffraction, XRD. The examination of the specimens' surface after corrosion reveals some very important microstructural effects. Figures 2 and 3 show the micrographs and associated EDX spectra of the surface of the material before and after corrosion. The appearance of a strong Na peak in the EDX spectrum of the corroded coupon indicates that some chemical reactions must have taken place during the 48 hour test. The surface morphology yielded after corrosion clearly suggests that the CMZP coating has been dissolved by the $NaNO_3$ melt. As can be observed, the corrosion product layer features nodular and needle like particles along with some coarse and smooth areas. Elemental EDX mappings made it possible to identify the different elements present on the surface and to determine their distribution as shown in Figure 2a. Based on these data, an attempt was made to label the different peaks yielded by XRD. An XRD pattern of the corrosion layer for the coated and uncoated sample is provided in Figure 4. The X-ray diffraction pattern obtained for the uncoated Si_3N_4 specimen seems to indicate that the corrosion product layer primarily consists of sodium silicate phase, $Na_2O.xSiO_2$. For specimens coated with CMZP, XRD patterns still confirm that sodium silicate is the main phase, but it also evidences other silicate phases. They are reported in Table 1.



a)

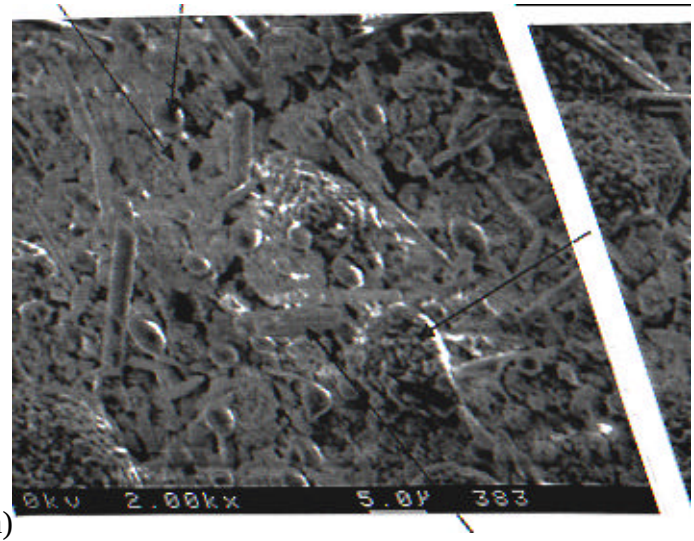


b)

Figure 2 : a) SEM photomicrograph of CMZP coating before corrosion b) associated EDX spectrum.

smooth area (Ca, Zr, P, Si, O

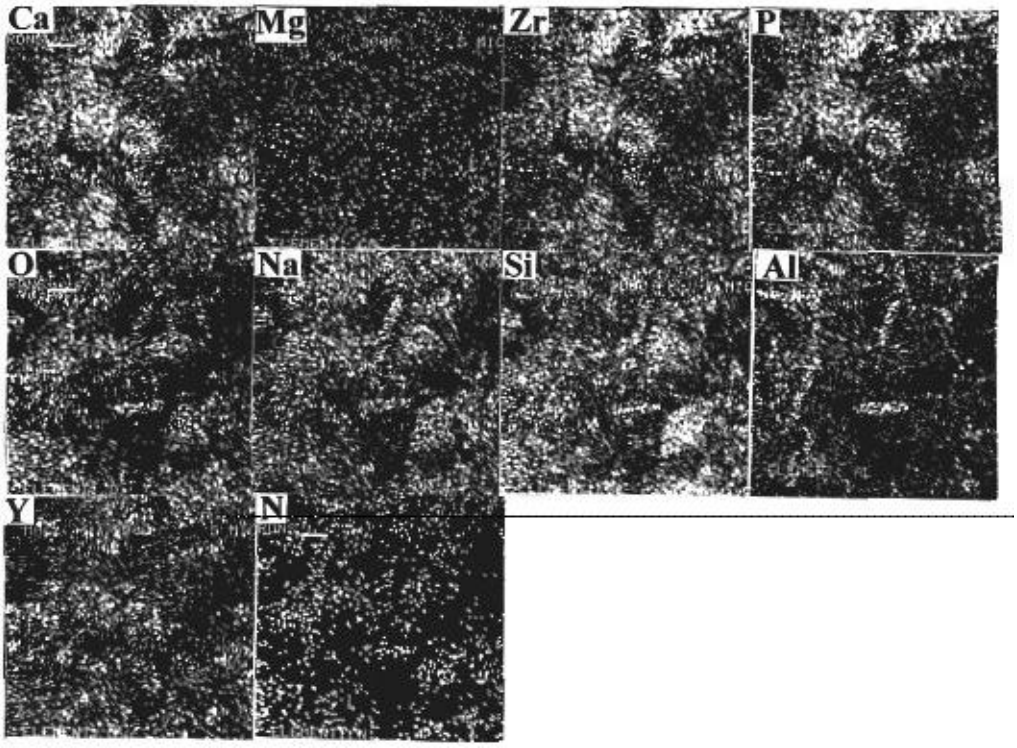
nodular particle (Y, Si)



coarse area (Si, Na, O)

a)

needle like particle (Al, Si, O, Na)



b)

c)

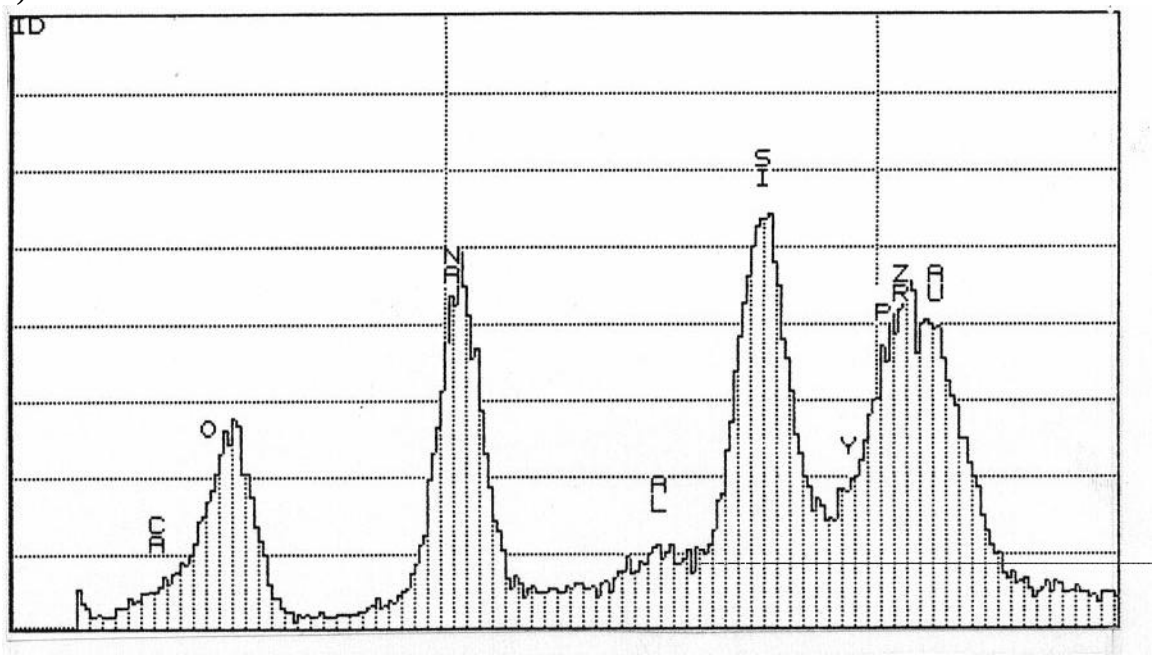


Figure 3 : a) SEM photomicrograph of CMZP coating after corrosion b) corresponding EDX elemental mapping c) associated EDX spectrum.

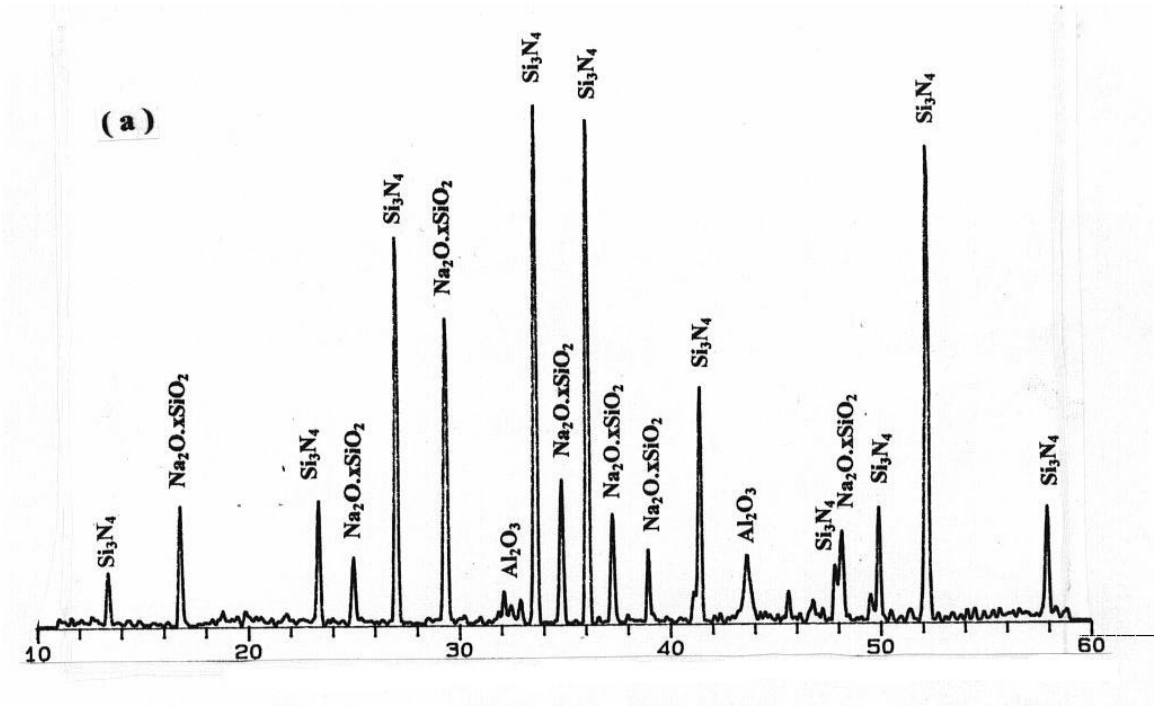


Figure 4: XRD pattern of the corrosion product layer for a) uncoated Si_3N_4. b) Si_3N_4 coated with CMZP.

particle or area	element detected with EDX	possible phase identification
needle like particle	Al, Si, O, Na	$NaAlSiO_4$ (sodium aluminum silicate)
nodular particle	Y, Si	Y_2SiO_5 (yttrium silicate)
coarse area	Si, Na, O	$Na_2O.xSiO_2$ (sodium silicate)
smooth region	Ca, Zr, P, Si, O	SiZr (zirconium silicate) $CaZr(PO_4)_2$ (calcium zirconium phosphate) $CaZrSi_2O_7$ (calcium zirconium silicate) Ca_2SiO_7 (calcium silicate)

Table 1 : Possible phases present in the corrosion product layer.

To examine the microstructure of the coated ceramic without the interference of the corrosion products, a cross-section was first prepared by mounting the specimen in epoxy and polishing it with grinding paper to a 6 µm finish. High purity kerosene was used as a lubricant to preserve any water soluble phases present in the corrosion product layer.[1] Figure 5 shows an EDX mapping of a polished cross-section. The elemental maps indicate that the corrosion product layer is primarily composed of Si, Al, O, N, and Na. The element distribution is in relatively good agreement with the previous findings and doesn't conflict with the idea that the corrosion product layer probably contains several different silicate phases. Note also that traces of Zr and P were located in the silicon nitride part and not in the corrosion product layer. This observation, which seems to conflict with EDX mappings of the as corroded surface presented in Figure 3, may come from the fact that calcium, zirconium or phosphor containing phases were removed during the polishing This would account for the presence of Zr and P in the Si_3N_4 part.

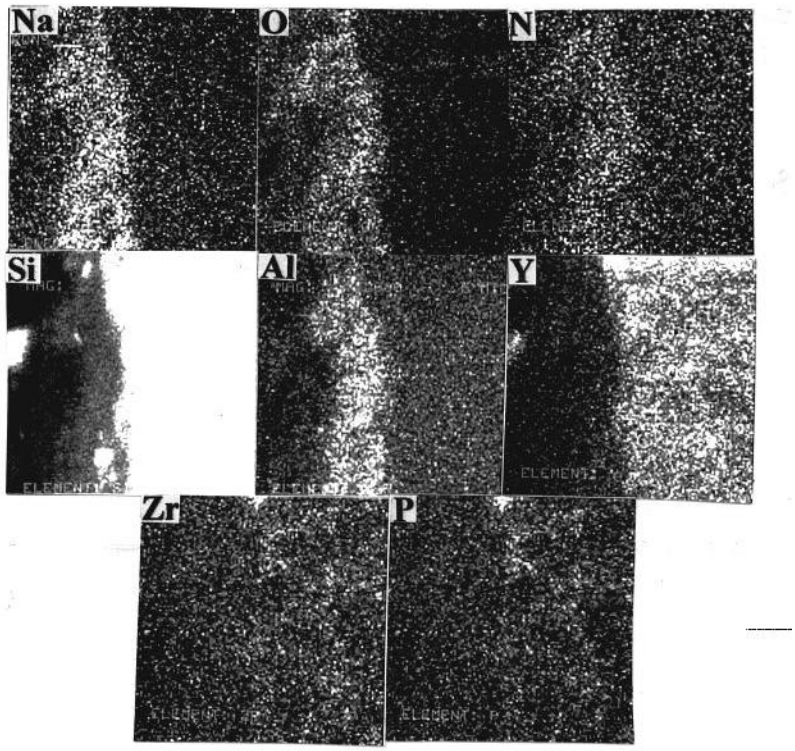
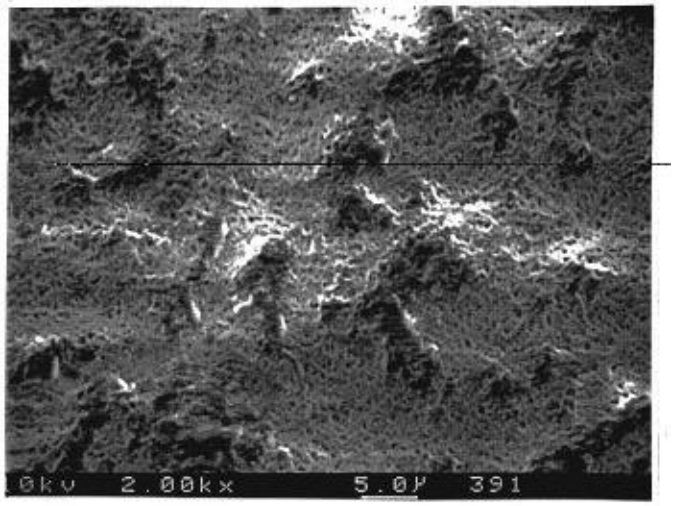
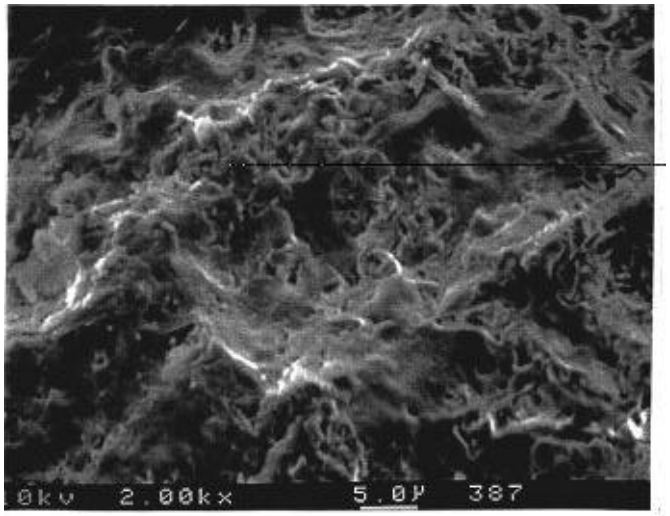


Figure 5 : EDX elemental maps of the crossection of a Si_3N_4 coupon coated with CMZP.

To study the attacked microstructure of the ceramic, the corrosion products were first removed during a two-hour treatment in H_2O. After the water leach, the corrosion scale was identified as an aluminum yttrium silicate phase for both coated and uncoated samples. Figure 6 features the morphology of the corrosion scale for Si_3N_4 uncoated and coated specimens. As can be seen, the two photomicrographs yield interesting differences. For the uncoated sample, pores or pittings are observed in the silicate layer, whereas a relatively unattacked corrosion scale is depicted for the coated specimen.



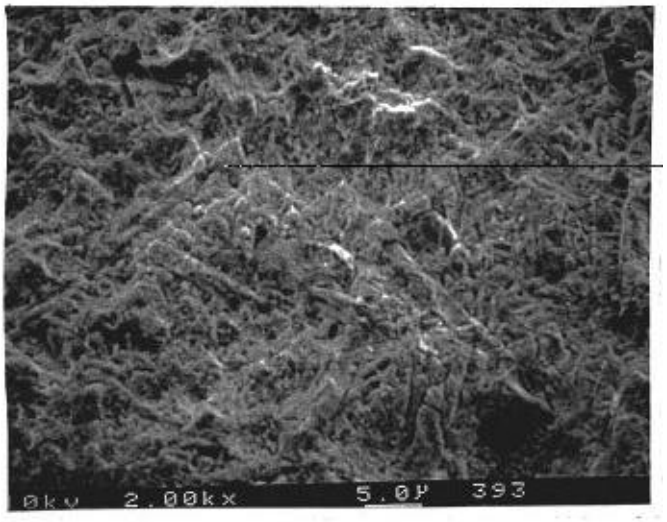
a)



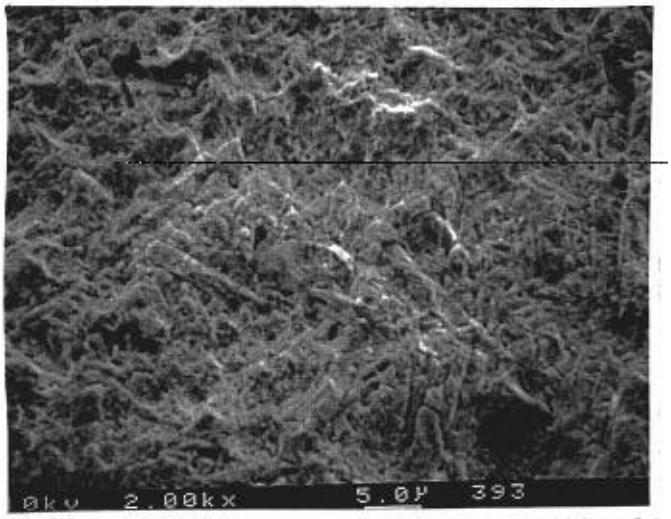
b)

Figure 6 : SEM photomicrographs of the corrosion scale obtained after water leach for a) uncoated Si_3N_4 ,and b) Si_3N_4 coated originally with CMZP.

Finally, the corrosion scale was removed using a mild HF treatment (15 min, 10%HF, 60°C).[7,8] Photomicrographs of the attacked morphology are depicted in Figure 7. As expected, two different features were evidenced. For the uncoated Si_3N_4 coupon, some silicon nitride grains can be observed, suggesting that attack at the grain boundary seems to have occurred. For the originally coated sample, it is believed that little or no attack has taken place.



a)



b)

Figure 7 : SEM photomicrographs of the attack morphology obtained after mild HF (15 min, 10% HF, 60°C) treatment for a) uncoated Si_3N_4 ,and b) Si_3N_4 coated originally with CMZP.

Mg-doped Al_2TiO_5 coated samples :

Si_3N_4 samples dip coated in the Mg-doped Al_2TiO_5 sol-gel did not give the expected coatings as shown in Figure 8. The coating clearly features the presence of needle like particles. These particles did appear to have a higher level of yttrium and phosphor than the surrounding matrix as revealed in the corresponding elemental maps. Similar needle like particles have also been observed by other investigators using yttria containing Si_3N_4.[9,10] Indeed it is very likely that yttria used as sintering aid diffuses outward from the grain boundary and reacts with phosphorous contamination present in the furnace to form these crystallites. As the XRD pattern yielded no peak corresponding to a phase containing both Y and P, it is believed that the needle like particles may be a mixture of yttrium silicate, Y_2SiO_5, and a phosphor-containing compound which could not be identified.

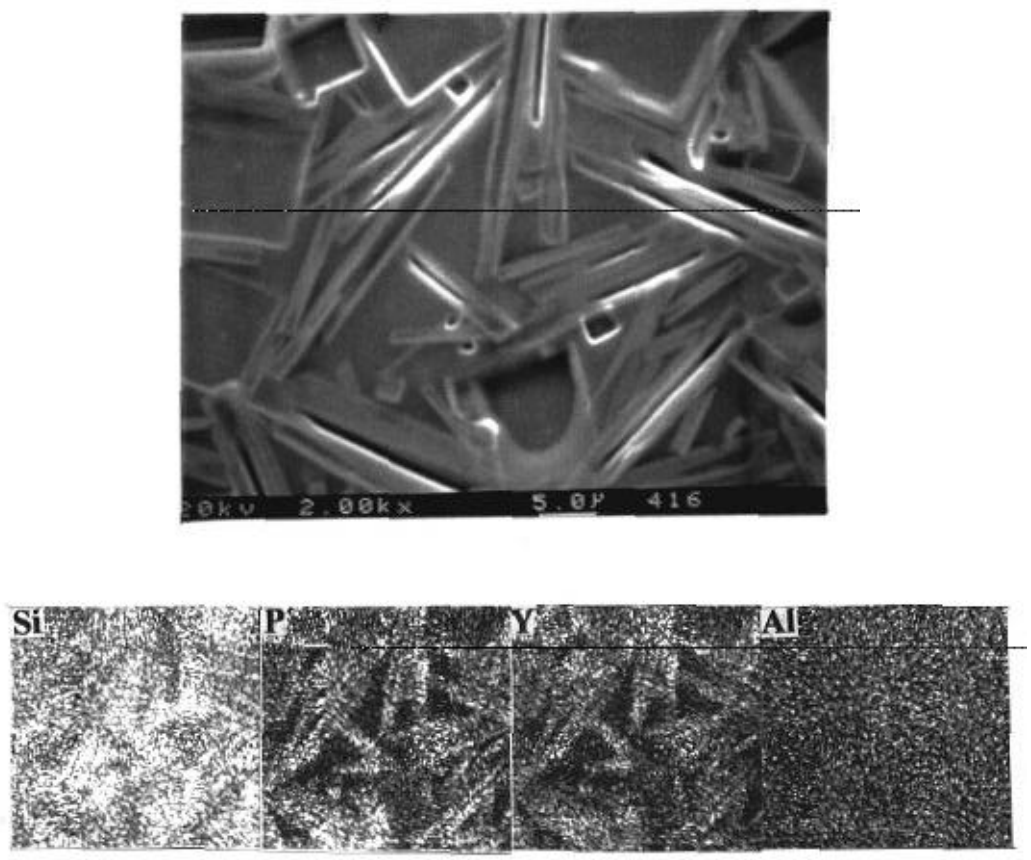


Figure 8 : SEM photomicrograph and corresponding elemental maps for Si_3N_4 originally dip coated in a Mg-doped Al_2TiO_5 sol gel.

SEM photomicrograph and corresponding elemental mappings obtained for the corroded specimen are shown in Figure 9 and indicate that the needle like particles are preferentially attacked by the $NaNO_3$ melt. To determine the nature of the corrosion product layer, a polished cross-section of the corroded samples was also mapped with EDX (see Figure 10). The even distribution of Si, Na, O, P, Al, and Y suggests that the corrosion product layer is probably composed of different silicate phases. The attacked morphology obtained after water leach and a mild HF treatment, presented in Figure 11, features some needle like particles, which tends to indicate that the coating has not been totally dissolved.

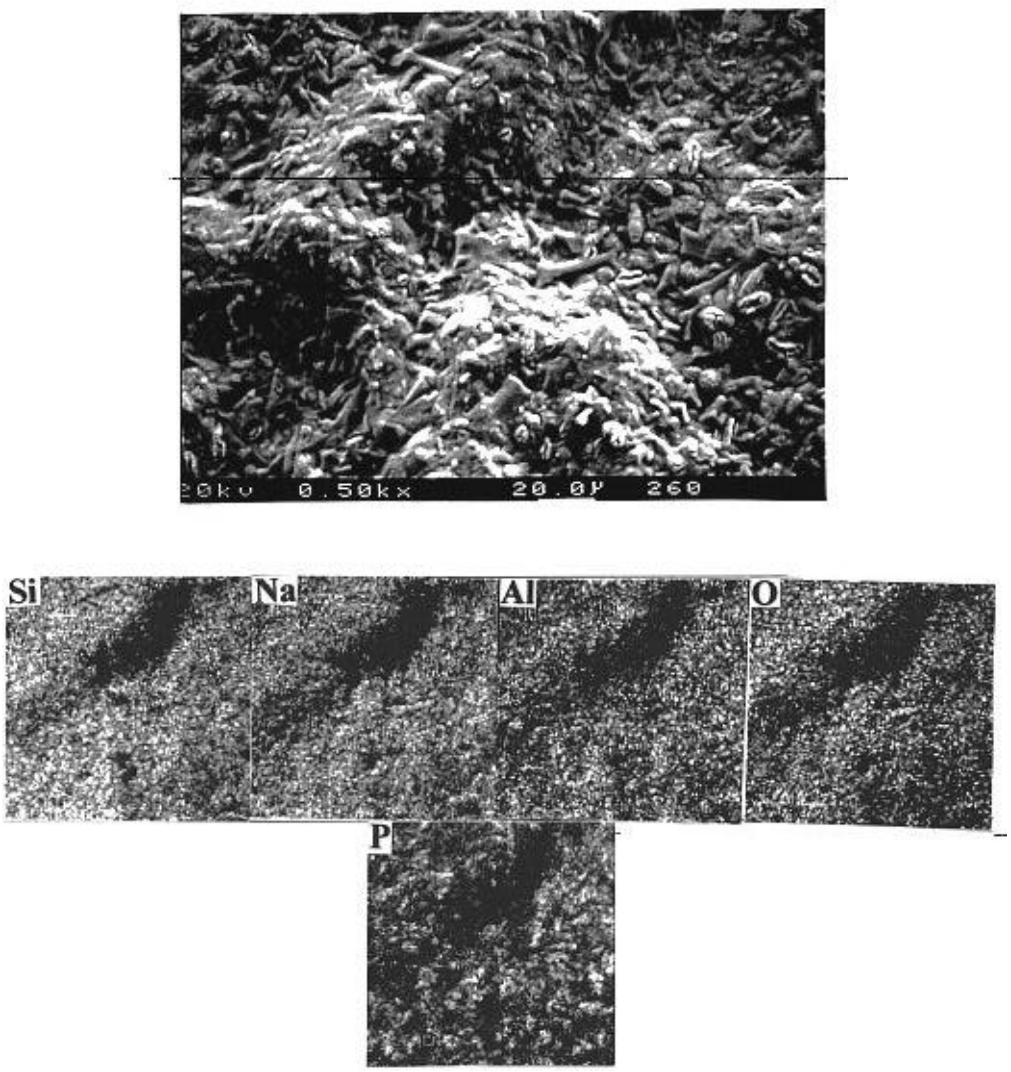


Figure 9 : SEM photomicrograph of the corrosion product layer and associated elemental maps for Si_3N_4 originally dip coated in a Mg-doped Al_2TiO_5 sol gel and corroded at 1000°C for 48 h in a $NaNO_3$ containing atmosphere.

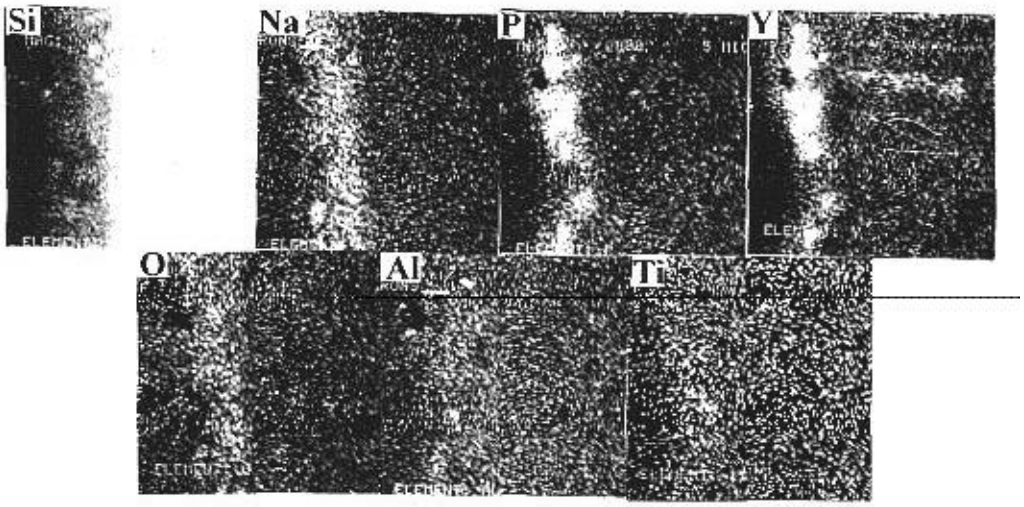


Figure 10 : EDX elemental maps of a polished crossection of Si_3N_4 originally dip coated in Mg-doped Al_2TiO_5 sol gel and corroded at 1000°C for 48 h in a $NaNO_3$ containing atmosphere.

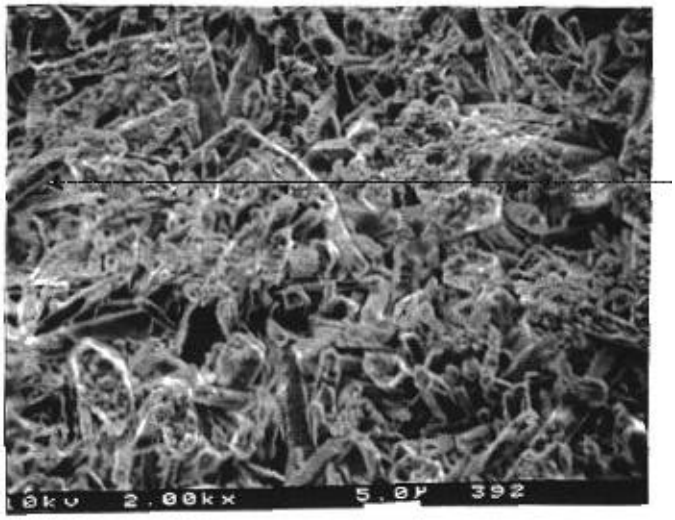


Figure 11 : SEM photomicrograph of the attacked microstructure obtained after water leach and mild HF treatment for Si_3N_4 originally dip coated in a Mg-doped Al_2TiO_5 sol gel and corroded at 1000°C for 48 h in a $NaNO_3$ containing atmosphere.

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