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Corrosion of silicon nitride materials in gas turbine environment

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Abstract

In the present study the corrosion behavior of various silicon nitride materials will be presented. Hot gas tests were conducted in an atmosphere similar to that in a gas turbine (high temperature, pressure and flow rate and the water vapor pressure as the corrosive component). While some materials displayed a high degree of microstructural stability, all materials suffered surface degradation during the rig test. The oxidation surface layer of mainly SiO_2, which is essential for the oxidation protection of nonoxide materials because it induces a passive, diffusion-controlled oxidation mechanism, was found to be degraded by evaporation processes involving volatile silicon hydroxides. As the mechanism of these processes a combination of linear oxidation and corrosion was proposed. The stabilization of the protective oxidation layer of silica should be considered as the main factor in stabilizing these materials in hot gas environments. This can be achieved by environmental barrier coatings (EBC), however their long-term stability was found to be still insufficient. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Diffusion; Engine components; Mechanical properties; Si_3N_4

1. Introduction

For various industrial and military applications, there is an increasing need for structural materials that are able to withstand temperatures of 1400 °C and more. For example, for the strategically important field of energy production, an increase in the efficiency with a simultaneous decrease in emissions (CO_2, NO_x) requires high-temperature materials that can operate at temperatures considerably higher than those attainable with the superalloys currently in use. In principle, two requirements must be fulfilled for the development of these kinds of high-temperature materials:

1. Depending on the application desired, the materials have to be featured by a combination of mechanical [e.g. reliable strength level, k_{Ic}, subcritical crack growth (SCG), creep], chemical (e.g. oxidation and corrosion resistance) and thermo-physicalical properties (e.g. thermoshock resistance) required during service at elevated temperatures at a sufficiently high level.
2. Most of the applications at elevated temperatures are long-term applications. For that reason the materials must exhibit superior long-term stability; i.e. the high level of properties required must be maintained as much as possible throughout the entire duration of operation.

Promising candidates for use as structural components in these kinds of high temperature applications include nonoxide silicon-based ceramics such as silicon nitride (Si_3N_4) or silicon carbide (SiC). Recently developed Si_3N_4 materials exhibit a remarkably high level of mechanical properties at elevated temperatures.[1–4] Additionally, significant progress has been achieved in improving the long-term stability of these materials at temperatures up to 1500 °C for application-relevant times of more than 10 000 h under laboratory conditions.[5,6] The main feature of these materials, and the key factor in stabilizing the mechanical properties, is their microstructural stability by minimization of oxidation enhanced diffusion processes in the bulk of the material during long-term service at elevated temperatures.

Nevertheless, employment of the results of these laboratory tests for gas turbine applications, for example, is of limited use due to the severe environmental conditions in a gas turbine combustor. The high pressure and flow rate and the corrosive component (H_2O) of the hot gas were found to have a great influence on the oxidation and corrosion behavior of the ceramic materials.[7–10]

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Table 1
Mechanical and oxidation properties of the materials; σ_{RT} and σ_{14}: four-point bending strength at room temperature and 1400 °C; K_{Ic}: SENB $t = 0.15$ mm, ε: 200 MPa, 1400 °C; oxidation 1500 °C, 1000 h

	ρ (g/cm^3)	σ_{RT} (MPa)	σ_{1400} (MPa)	K_{Ic} (MPa$\sqrt{m}$)	$\dot{\varepsilon}$ (1/h)	Δm_{ox} (mg/cm^2)	Ox-rate (mm^2/h)
SN 282	3.39	660	610	7.2	2×10^{-6}	0.7	0.1
AS 800	3.30	720	360	8.0	1×10^{-5}	>20	10
SNMo-Y	4.47	780	710	8.2	9×10^{-6}	1.3	0.3
SNMo-Yb	3.60	830	720	8.4	2×10^{-5}	1.8	0.4

The main problem of the application of silicon based non-oxide ceramic materials in such environments was found to be the formation and evaporation of silicon hydroxides [Si(OH)$_4$] as described by Opila and coworkers investigating the corrosion behavior of CVD SiC in humid environments. These processes were observed to be enhanced in burner rig tests with severe environmental conditions as like higher gas and water vapor pressure and flow rate.[11–14]

In the present study nonoxide ceramic materials based on Si_3N_4 were tested in a real hot gas environment. Finally some ideas about the surface stabilization of silicon based ceramic materials in hot gas environments will be introduced.

2. Experimental

The studies were conducted using both commercial available Si_3N_4 materials (SN 282, Kyocera; SN 800, Honeywell) and several Si_3N_4/$MoSi_2$ composite materials under development, which are hot pressed and gas pressure sintered materials with Y_2O_3 or Yb_2O_3 as sintering additives. All these materials have been developed for application at elevated temperatures. Bending bars with 3×4×50 mm were used for all tests performed. Table 1 summarizes some mechanical and oxidation properties of the materials investigated in this study.

The EBC's were fabricated using different material systems (ZrO_2, HfO_2, TaO_2, Rare Earth and Rare Earth disilicates) at the surface of as finished and preoxidized bending bars using various preparation methods (electron beam deposition, laser PVD, dip-coating). General experiences obtained in these studies will be described on the hand of a Yb_2O_3-EBC produced by electron beam deposition.

The corrosion resistance of the materials was investigated on bending bars in burner rig tests in a real hot gas environment. Details about the test facility were described in a former report.[12] The conditions established in the test section were:

temperature: 1400 °C,
total pressure: 5 bar,
fuel natural gas,
ratio air/fuel 2.0
air mass flow: 90 g/s,
flow speed: 50 m/s,
partial steam pressure: 900 bar and
test time: 100 h.

After the tests, the weight loss of each bending bar was determined. Changes in the phase composition at the surface and the bulk region below the oxidation layer were investigated by XRD. Information about the microstructural alterations was obtained through observation of the microstructures (polished and CF_4 plasma-etched cross sections) and the surfaces after corrosion in the SEM.

3. Results

3.1. Unprotected Si_3N_4 materials

Several hot gas tests under the above mentioned conditions were performed during these studies. All unprotected Si_3N_4 materials suffered surface degradation in a range of 8–20 wt.% which corresponds to a regression constant between 0.24 and 0.6 mg/cm^2 h. The results of the hot gas tests are summarized in Table 2. In principle the Si_3N_4 materials behave alike. The surface layer, consisting of silica and the disilicates usually formed during oxidation from the sintering additives of Si_3N_4 materials [Fig. 1(A)], was found to be degraded by the corrosive environment in the burner rig. The measured weight loss was due to the evaporation of silicon hydroxides, mainly Si(OH)$_4$, and the $R_2Si_2O_7$ (R = Yb or Lu) formed during oxidation of the Si_3N_4 materials. As a consequence of the formation and evaporation of Si(OH)$_4$, the protective SiO_2 layer was destroyed during

Table 2
Results of corrosion tests in a high pressure burner rig of various Si_3N_4 materials

	Δm (wt%)	$\sigma_{HG\text{-}Test}$ (MPa)	σ_{HGT}/σ_o (%)	Corrosion rate (mg/cm^2 h)
SN 282	8.2	320	48	0.24
AS 800	19	207	29	0.57
SNMo-Y	8.2	600	77	0.24
SNMo-Yb	8.4	660	80	0.25

the test, leaving a very rough layer consisting of only disilicate grains [Fig. 1(B)] which were partially spalled off due to their low stability, as shown in Fig. 2. Despite its insufficient mechanical stability, the disilicate layer was found to have a higher chemical stability in this environment and may have a stabilizing effect on the evaporation of SiO_2.

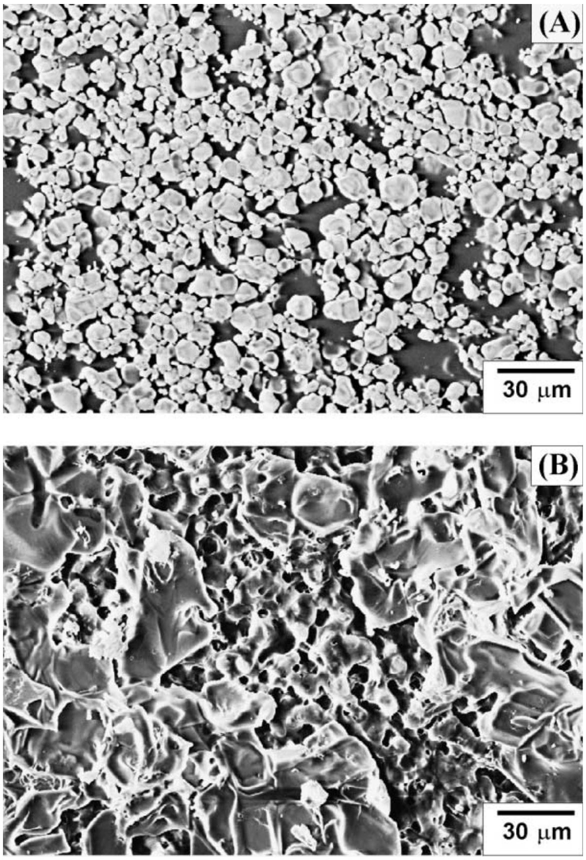

Fig. 1. Comparison of the surface layer of a Si_3N_4–$MoSi_2$ material after oxidation (A) and hot gas test (B), (1400 °C, 100 h).

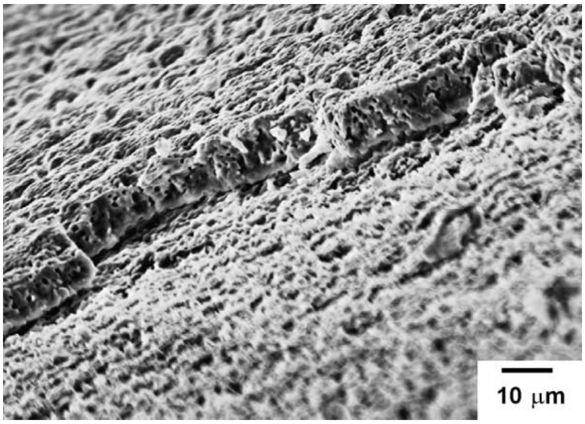

Fig. 2. Typical corrosion surface after hot-gas test (100 h, 1400 °C) of Si_3N_4–$MoSi_2$ composite with Yb_2O_3 as sintering aid, $Yb_2Si_2O_7$ partially spalled off.

The main factor influencing the evaporation processes was found to be the partial water vapor pressure as described in a former report.[13] This was similar to the results of Opila and Robinson found for the corrosion of CVD SiC in spite of the different burner rig set-ups and test conditions.[9,10]

General differences in the corrosion behavior between the Si_3N_4 materials investigated were obtained dependent on the high temperature resistance especially the oxidation behavior of the materials. A typical example for this behavior can be given by comparison of the commercial Si_3N_4 materials SN 282 and AS 800. As shown in Table 2 a quite higher weight loss of about 19 wt% was measured for the AS 800 in comparison to the SN 282 with 8 wt.% after the hot gas test. The reason of these results can be found in the different oxidation behavior of the materials. Caused by the use of only Lu_2O_3 as sintering additive a quite effective oxidation protection layer consisting on glassy SiO_2 and crystalline $Lu_2Si_2O_7$ was formed during oxidation of the SN 282 material. Only a few impurities of Lu-ions were observed by EDX-measurement in the amorphous SiO_2 oxidation layer which led consequently to a minimal oxygen diffusion into the material and a superior oxidation resistance with a parabolic growth rate of the oxidation layer of about 0.004 $\mu m^2/h$ for oxidation at 1400 °C. In the case of the AS 800 a mixture of Y_2O_3, La_2O_3 and SrO was used as sintering additive. The oxidation surface layer formed during oxidation of this material contained several impurities of Y-, La- and Sr-ions in the SiO_2 glass. For that reason a significantly higher oxygen diffusion into the material was observed. This was the consequence of lower softening point and viscosity of the SiO_2 glass. The oxidation resistance was found considerably lower with a growth rate of the oxidation layer of about 0.4 $\mu m^2/h$, 100 times higher in comparison to the SN 282 material. The lower oxidation resistance of the AS 800 with the consequence of the formation of a higher amount of SiO_2 should be the reason of the higher weight loss observed after the hot gas test of this material in comparison to the SN282.

The stability of the microstructure in the bulk of the material was found to be a second effect of the different oxidation resistance of the materials. During the rig test the microstructure changed due to oxidation processes that were dependent on the diffusion of oxygen into the upper region of the bulk and reaction of the oxygen in the grain boundary phase. These effects have been described in several former studies dealing with the oxidation behavior of Si_3N_4 materials with sintering additives.[5,6] The results of the oxidation processes in the bulk microstructure of the materials as the consequence of the amount of diffusion oxygen are shown by the comparison of the microstructures of AS 800 and SN 282 after 100 h hot gas test at 1400 °C in Fig. 3. The microstructure of the AS 800 showed the typical oxidation damage, i.e., surface and

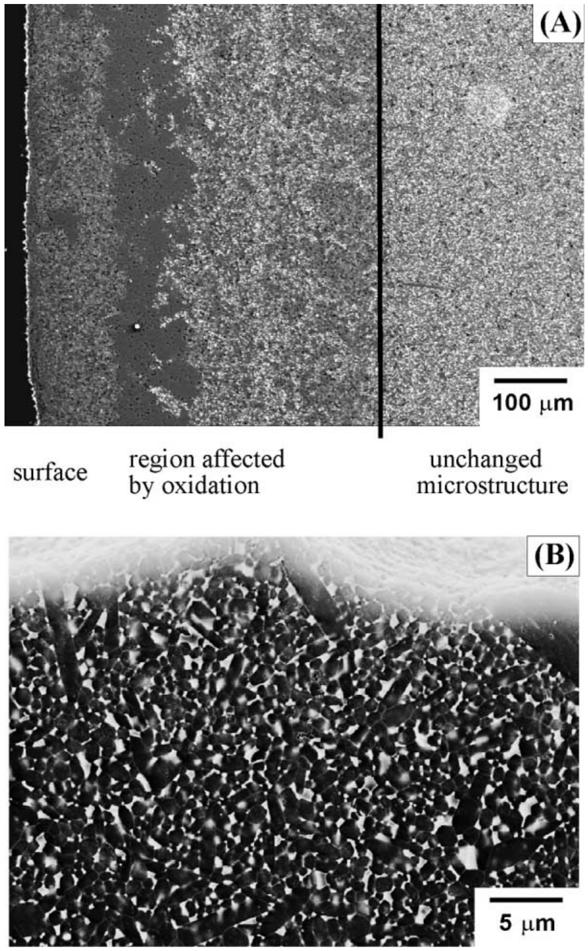

Fig. 3. Comparison of the microstructure after the hot gas test, (A) AS 800 (grain boundary inhomogenities as the consequence of oxidation processes in the bulk material), (B) SN282.

grain boundary phase inhomogenities and pores up to the middle of the materials [Fig. 3(A)]. These behavior wasn't found in the SN 282 material after 100 hot gas test at 1400 °C, which should be the consequence of the considerable smaller amount of diffusion oxygen reaching the bulk material in comparison of the AS 800 material with a high oxygen diffusion (Fig. 3(B)).

Typical for all materials tested in hot gas atmosphere was the absence of any oxidation layer of SiO_2. As shown in Fig. 3(B) the microstructure of the Si_3N_4 material reached directly up to the corrosion surface of the material. A comparison of the two processes, oxidation and corrosion, occurred during the hot gas test at 1400 °C, 100 h, showed an about 60 times higher corrosion rate (about 70 µm material loss in linear corrosion law) in comparison to the oxidation rate (about 1 µm formation of SiO_2 oxidation layer by parabolic mechanism). In hot gas conditions, however, the oxidation cannot be interpreated by a pure parabolic mechanism. All the silica formed during the test reacted immediately with the water vapor in the hot gas. As the consequence of the absence of the protective SiO_2 layer the oxidation should be described as a more "active" oxidation process with a linear oxidation law. An accelerated oxidation was observed by More and Torterelli due to the high pressure especially the high water vapor pressure.[15] As an explanation of these effects a direct oxidation of the Si_3N_4 by water was proposed. However, additionally studies are necessary for full understanding these processes under hot-gas conditions.

From an application point of view, the materials' surface degradation is quite high. A weight loss after 100 h hot gas test at 1400 °C of about 8% observed for the SN 282 Si_3N_4 material led to a material loss of about 70 µm in 100 h under these conditions. After a time of about 10 000 h or higher (relevant times for application in energy production) an unacceptably high material loss of about 7 mm would be observed.

These processes must be avoided or minimized if non-oxide ceramic materials based on silicon should be applied in hot gas atmospheres. The critical factor observed after the hot gas test was the destruction of the oxidation protection layer of SiO_2. However, apart from the corrosion mechanisms during the tests in hot gas atmospheres at elevated temperatures, all non-oxide ceramic materials must be protected against oxidation. For that reason the stabilization of the oxidation protection layer of SiO_2 should be the final goal of the development of corrosion stable nonoxide ceramic materials.

3.2. Si_3N_4 materials with environmental barrier coating (EBC)

Any stabilization of SiO_2 by chemical modification of the SiO_2 glass seems to be less practicable. It is not expected that the water vapor resistance can be increased significantly by modification of the structure of the SiO_2 glass by doping of several ions. In addition, the doping of any ions would weaken the oxidation protection function of the SiO_2 layer.

For that reason a protection of the material can only be achieved by an additional surface layer preventing the corrosion attack of the water vapor in the hot gas atmosphere. In order to find a working system for such environmental barrier coating (EBC) several factors have to be considered:

1. Material selection
   The main requirement of the EBC material is a high stability in hot gas atmosphere. This includes a high stability against oxygen, water vapor and all compounds and impurities in the hot gas. Additionally a minimal evaporation pressure and a superior chemical compatibility with the base material is demanded.
2. Fabrication of EBC
   Besides a simple and coast efficient coating method various morphology factors of the EBC

like thickness, grain size distribution and porosity have to be considered.

3. Long term stability
   The main problem in developing EBC should be their long-term stability up to application relevant times (> 10 000 h). This includes both a superior thermal, mechanical and chemical stability (diffusion, particle impact, impurities) and problems as the consequence of thermal expansion mismatch and shock cooling. Additionally it should be considered, that any alternations in the upper region of the material as the consequence of oxidation cannot be avoided completely. As small the oxygen diffusion into the material can be optimized, there will be a growth of the SiO_2 layer between the EBC and the bulk material. For that reason the EBC have to be completely compatible to SiO_2, which is quite complicated. Actually the thermal expansion coefficient of SiO_2 is quite small in comparison to the other materials in this system, however during cooling crystalline SiO_2 crystobalite will be formed, connected by shrinkage cracking of the SiO_2 layer caused by the higher density of the crystobalite.

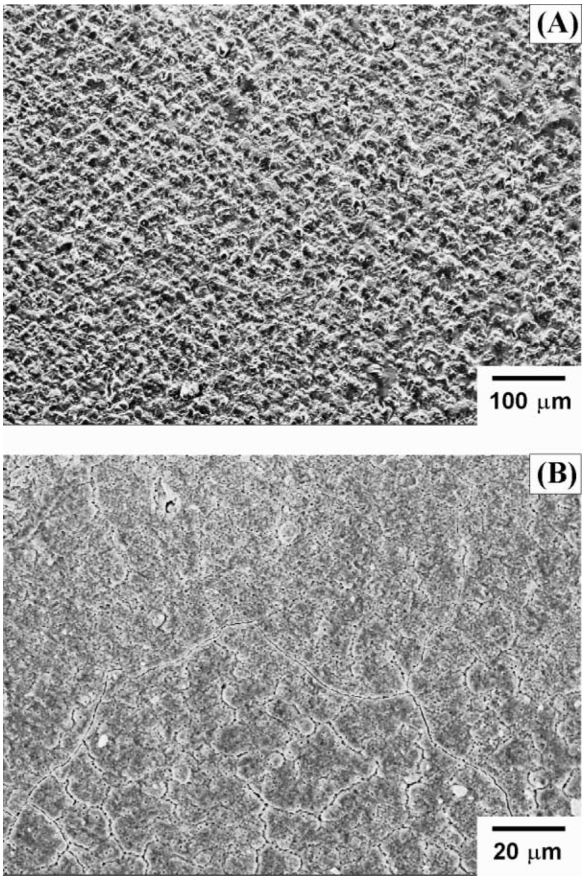

Fig. 4. Corrosion surface after 100 h hot gas test at 1400 °C of Si_3N_4 material with oxide EBC produced by electron beam deposition.

In principle several oxide compounds are suitable to be used as EBC. Oxides like ZrO_2, HfO_2, Ta_2O_5 the Rare Earth or some silicates are featured by a low vapor pressure at application temperature. However, there exists a lack of experimental data of there chemical long-term stability especially about their behavior in atmospheres with high water vapor pressure.

The functionality of an EBC is demonstrated by the example of an electron beam produced EBC (Yb_2O_3) on a Si_3N_4-$MoSi_2$ composite with Yb_2O_3 as sintering aid. After fabrication the EBC was obtained homogeneous and without any cracking [Fig. 4(A)]. After the hot gas test the coating was found to be partially present. Their adhesion at the Si_3N_4 material was quite poor caused by the cracks formed during the test [Fig. 4(B)]. It is supposed that these cracks are the consequence of the shrinkage cracking during the crystallization of the SiO_2 formed during the oxidation just beneath the EBC. However, the function of the EBC during the 100 h endurance hot gas test could be demonstrated. A polished cross section of the materials with the different layers obtained after the hot gas test is shown in Fig. 5. Below the oxide EBC a stable oxidation layer of amorphous SiO_2, crystobalite and $Yb_2Si_2O_7$ was observed protecting the high temperature Si_3N_4 material against oxidation. The presence of this SiO_2 layer can be interpreted as a typical sign that the corrosion attack did not occur at this surface region since any SiO_2 was not

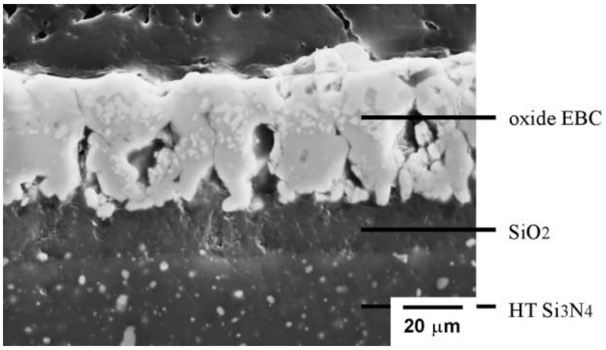

Fig. 5. Typical surface layer composition after hot gas test of Si_3N_4 material with oxide EBC fabricated by electron beam deposition.

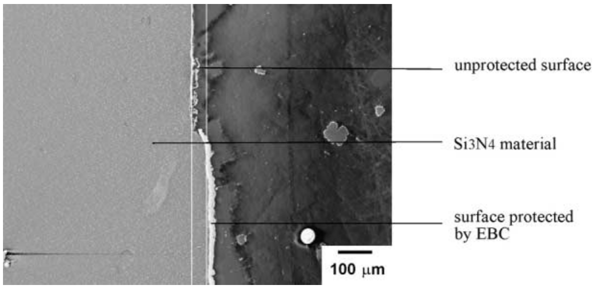

Fig. 6. Comparison of hot gas corrosion at material surface with and without EBC.

found in the uncoated surface of the testing bar. A comparison of the material surface with and without EBC in Fig. 6 shows this effect quite clear. A material loss by corrosion of about 50 μm was observed at the unprotected surface. Calculated to the whole bending bar this corrosion zone correspond to about 6 wt% weight loss. This weight loss was measured for the same material in uncoated condition. The corrosion processes did practically not occur at the surface protected with the EBC.

4. Conclusion

In the present study the results of hot gas tests of various silicon nitride materials were presented. Due to the severe environmental conditions in a gas turbine combustor (high temperature, pressure and flow rate and the water vapor pressure as the corrosive component) the silicon nitride materials suffer a surface degradation. This was the consequence of the formation and evaporation of silicon hydroxides, mainly $Si(OH)_4$ and spalling off of the disilicate of the sintering additive formed during the oxidation process at the surface of the material. As the mechanism a combination of linear oxidation and corrosion (evaporation of silicon hydroxides) was proposed. The corrosion can be minimized by environmental barrier coatings, however the thermal, mechanical and chemical stability of the system bulk material — oxidation protection layer — EBC was found to be insufficient.

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