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Oxidation behaviour of Si_3N_4–TiN ceramics under dry and humid air at high temperature

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Abstract

The oxidation in air of Si_3N_4-based ceramics containing 35 vol.% of TiN secondary phase and different amounts of sintering additives has been studied at different temperatures up to 1400 °C in dry or humid environment. The oxidation starts by crystal growth of TiO_2 at the surface, then a multilayered scale develops under the rutile layer from 1000 °C. This subscale is composed of silicon nitride in which TiN particles are oxidized to agglomerates of rutile, glass and pores. The oxidation process is controlled by the matter transports, which take place in the intergranular phase. These transport phenomena are affected by the changes in distribution and composition of the glassy phase and by humidity which modifies the glass network structure and thus the in-diffusion rate. From 1200 °C, Si_3N_4 grains are also oxidized, the additional glass formed closes the residual porosities yielding scales more compact and developing an autoprotective behavior. At 1400 °C, glass phase crystallizes into cristobalite and the rutile top layer becomes discontinuous. Only composites with low amounts of sinter additives keep an autoprotective oxidation mode.

Keywords: Composites; Electron microscopy; Oxidation; Diffusion; Si_3N_4

1. Introduction

Compared to silicon nitride materials, silicon nitride–titanium nitride composites have improved mechanical properties, higher fracture toughness and stiffness, and are machinable by electric discharge providing thereby the realization of ceramic parts with very complicated shape. These properties make the composite a suitable high temperature structural material, however, its corrosion resistance at temperatures above 1000 °C is reported to be poor compared to pure silicon nitride ceramics. For silicon nitride ceramics, the oxidation resistance depends strongly of quality and quantity of the sinter additives and can be tremendously improved by carefully designing the microstructure. Since silicon nitride–titanium nitride composites are also processed with sinter additives, optimization of their chemistry and distribution may also lead to an important improvement of their corrosion resistance. Therefore, for high-temperature applications, a precise knowledge of the oxidation behavior in the working environment is needed. In the past, several studies showed that the oxidation mechanism is complex and multilayered oxidation scales form on Si_3N_4–TiN composites.[1–5] Oxidation of the composites starts at 600 °C; only TiN particles at the surface suffer oxidation and form islands of TiO_2 nanocrystals.[5] At around 1000 °C, these nanocrystals start to grow laterally. In parallel, oxidation progresses in subscales. Mechanism and kinetics in this temperature range are of particular importance for the high temperature performance of this class of materials and are needed for lifetime prediction possibilities of materials improvement.

In the present work, we studied the microstructural evolution of TiN particulate reinforced silicon nitride composites in dry and humid air in the range 1000–1400 °C. Special attention is attributed to the role of the intergranular glass phase

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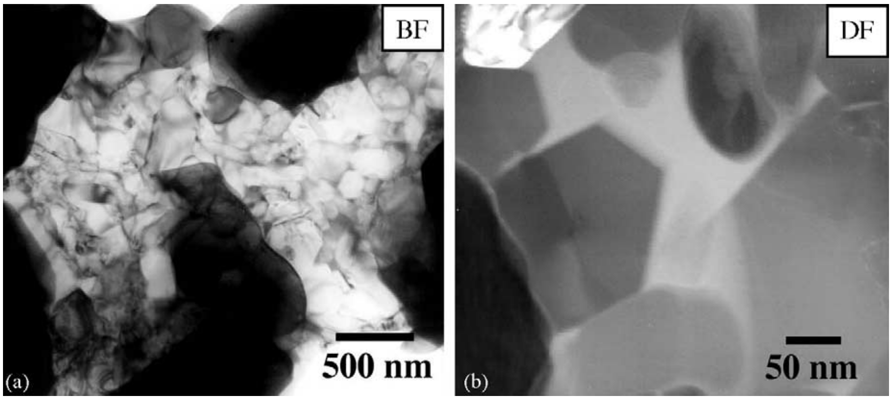

Fig. 1. As-sintered composite A: (a) bright-field image showing micrometer-sized TiN grains embedded in a fine-crystalline silicon nitride matrix, (b) dark-field image showing the distribution of the intergranular phase by the bright contrasts.

during oxidation, its distribution and changes in chemical composition.

2. Experimental

The oxidation behavior of two distinct Si_3N_4–TiN composite ceramics was studied in the temperature range 25–1400 °C under humid and dry atmospheres. The composite materials were manufactured by hot-pressing (HP) and hot-isostatically-pressing (HIP).[2,6] They are made of Si_3N_4 matrices containing different amounts of Al_2O_3 and Y_2O_3 as sinter additives. The composites A prepared by HP contains a high amount of additives (2.5 wt.% Al_2O_3, 5 wt.%Y_2O_3) and the second type of composite (B) was prepared by HIP with a low amount of sinter additives (0.25 wt.% Al_2O_3, 0.5 wt.%Y_2O_3) corresponding to 10 times less than the composite A. The second phase in both composites consists of 35 vol.% of TiN.

Specimen were cut in the form of bars (10 mm × 4 mm × 2 mm). The bars were exposed in flowing air, and isothermal tests were carried out for 4 h, 24 h and 100 h at 1000 °C, 1200 °C and 1400 °C for each time. A heating rate of 50 °C min^{-1} was used to bring the specimens to temperature in order to minimize oxidation during the heating period. Dry air and air saturated with water vapor at 18 °C (vapor pressure 20 mbar) were used as oxidizing atmospheres.

The surface of oxidized composites was analyzed by X-ray diffraction (XRD) using Co Kα radiation on a Philips PW1830 diffractometer. Surfaces and cross-sections were sputter-coated with an Al–Pd alloy and examined in a field-emission scanning electron microscope (FEG-SEM) of the model Leo Gemini 1530. The latter was equipped with different electron detectors (SE, BSE) and with an energy-dispersive X-ray detector (EDXS). For transmission electron microscopy (TEM) obsevations, cross-sectional thin foils of the corrosion scales were prepared from oxidized samples by wedge-polishing slices of 500 μm on a tripode down to zero thickness at the thinner part of the wedge. The final thinning and cleaning step of the wedge-shaped sample was achieved by ion-milling with Ar^+ using a GATAN ion-miller.

TEM investigations by bright- and dark-field imaging (BF, DF) and selected area diffraction (SAD) were performed at 200 kV in a JEOL 2000EX. High-resolution electron microscopy (HREM) studies were conducted at 200 kV on a TOPCON 002B microscope that provides a point resolution of 0.18 nm.

3. Results

The TEM bright field image in Fig. 1a shows the microstructure of composite A consisting of Si_3N_4 grains (light grey contrast) with a much smaller size than TiN grains (dark contrast). The size of TiN grains ranges from 500 nm to several micrometers. The TEM image in Fig. 1b reveals in DF contrast a glassy intergranular phase between the faceted

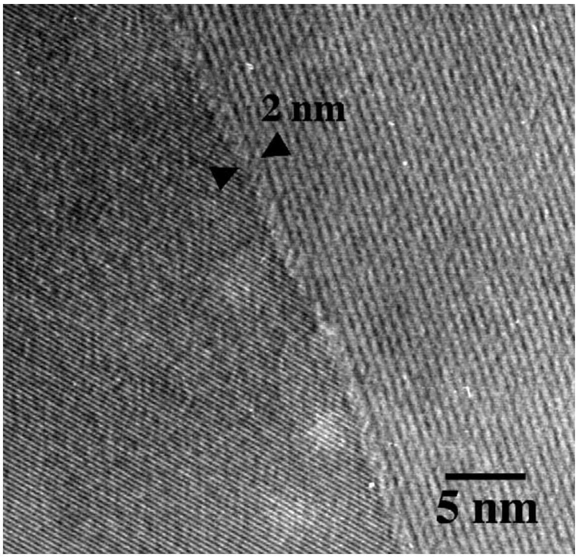

Fig. 2. HREM image of the as-sintered composite B showing amorphous phase between grains of silicon nitride.

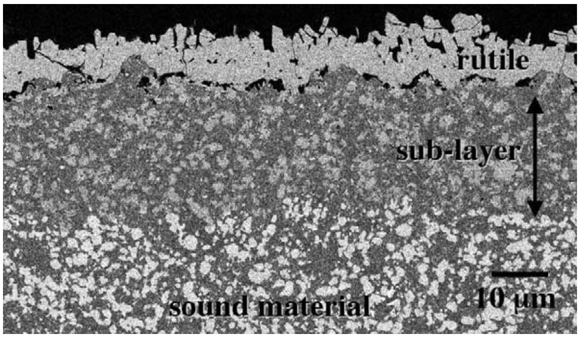

Fig. 3. Cross-section of the oxidation scale on composite A after oxidation in humid air for 24 h at 1000 °C.

Si_3N_4 grains that completely fills all triple pockets, even those of 50 nm or more in diameter. Thus locally, the width of the intergranular phase is larger than the diameter of the smallest matrix grains. The smallest width of the grain boundary films is about 5 nm. In composite B (with less sinter additives) the glass phase consists of a film between Si_3N_4 grains. The HREM image in Fig. 2 reveals the typical width of about 2 nm. In both composites the intergranular phase forms an continuous network between Si_3N_4 and TiN and plays the role of a matrix. It will be shown in this paper its crucial influence in the oxidation process.

After several hours of oxidation at 1000 °C, layered oxidation scales developed and completely covered all faces of the specimen. The typical microstructure of these scales is shown in Fig. 3. The surface oxidation layer is a relatively dense continuous scale of TiO_2 crystals (in rutile structure) which adopted different morphologies, varying with both, the additive content and atmosphere (dry or humid air). In the case of composite A, TiO_2 crystals at the surface display a needle-like morphology frequently observed for rutile (Fig. 4a). These grains are often heavily faulted and their fast growth direction revealed by electron diffraction is [1 0 0]. After the same thermal treatment the surface of composite B is more uniform and exhibits more equi-axe grains (Fig. 4b).

Under this coverage, a sub-scale is observed (Fig. 3), containing within the silicon nitride matrix mainly small rutile crystals and a high density of pores developed at the site of the former TiN particles. At this temperature silicon nitride remained almost unaffected by oxidation. The interface between the polycrystalline outer layer and the sub-scale layer shows remarkable roughness on the micrometer scale and it is marked by micrometer-sized pores. In this way we can consider two oxidation fronts: the Si_3N_4 phase one which corresponds to the boundary between the outer layer and the sub-layer and the TiN one, deeper, corresponding to the interface between the sub-layer and the sound material.

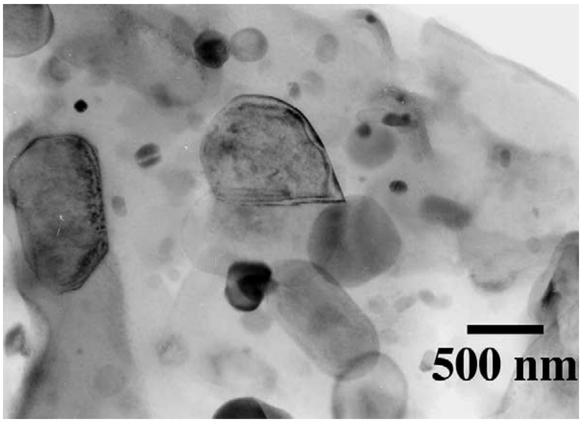

Fig. 5. Composite A—detail of a part of the subscale-layer after 24 h at 1000 °C in humid air (TEM image).

In humid atmosphere, after oxidation at 1000 °C for up to 2 h, we observed that kinetics of initial lateral growth of rutile on the surface were slowed down compared to oxidation under dry air. Moreover, a similar effect was revealed for subscales that were generally thinner in humid air than in dry air.

After 24 h at 1000 °C, a continuous film of several hundred nanometers (up to 3 μm) in thickness formed directly under the outer layer. It is composed of a SiO_2 glassy phase with numerous crystalline precipitates with a size ranging from 10 nm to 100 nm. The larger precipitates correspond to TiO_2 and the smaller ones are complex oxides (especially for composite A) containing cations from the sinter additives (yttrium and aluminium) (Fig. 5). This intermediate subscale developed more slowly in the case of composite B. It was not

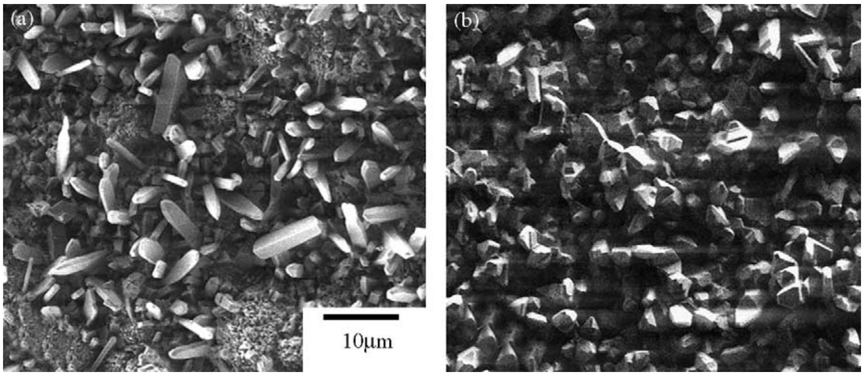

Fig. 4. Plane view of Si_3N_4–TiN composites after 4 h at 1000 °C in dry air: (a) composite A, (b) composite B.

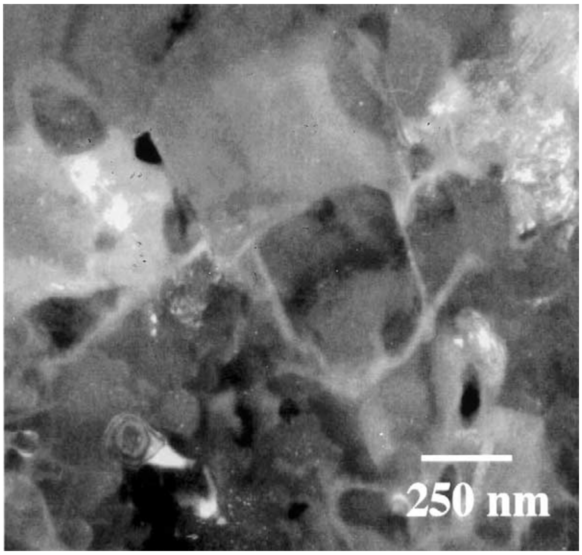

Fig. 6. TEM dark-field of oxidation scale formed on composite B after oxidation for 4 h at 1000 °C in dry air.

observed after a 4 h thermal treatment at 1000 °C, however an intergranular glass film wider than the as-sintered composite was revealed by TEM in the sub-layer (Fig. 6).

In order to study oxidation kinetics at 1000 °C, we have followed evolution of the oxidation scales thickness for both composites materials at 1000 °C. In Fig. 7, thickness of the surface scale (TiO_2), of sub-scale and the total scale thickness (sum of both) are presented as a function of the square root of time for experiments in dry air (hollow markers) and in humid air (full markers). Only the composite A, seems affected by a humid oxidizing atmosphere in the first hours of the thermal treatment. The thickness of every scale is lightly higher in humid air, and particularly for the sub-layer. After 100 h this effect has disappeared. These phenomena could be caused by the influence of water on the transport properties of the intergranular glass and will be discussed further in the text.

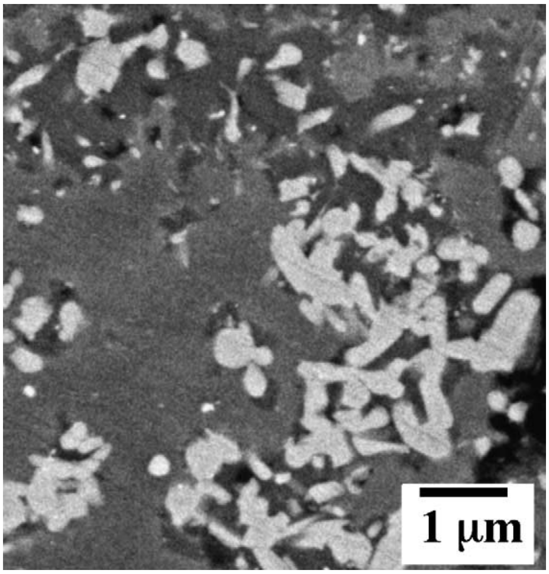

Fig. 8. Composite B—BSE image of oxidation scale under the cover layer after 100 h at 1000 °C in dry air (light grey: TiO_2, medium grey: Si_3N_4, dark grey: glass, dark: porosity).

In case of Composite A, kinetics of all subscales follow approximately a parabolic law for the entire investigated time scale suggesting reaction control by diffusion. For composite B, almost the same kinetics is observed for treatments up to 24 h. For longer time (100 h) the subsurface scale growth exhibits slower kinetics than expected from an extrapolation of the parabolic law. This result can be explained from SEM studies which show that composite B, after a 100 h oxidation, displays a stronger glass formation than composite A. Consequently, by filling the microporosity that had developed in the scale, glass closes the channels for fast in-diffusing oxygen via the gas phase and an autoprotective oxidation mode is reached (Fig. 8).

Oxidation scales formed at 1200 °C exhibited a similar sequence as those formed at 1000 °C. The subsurface scale

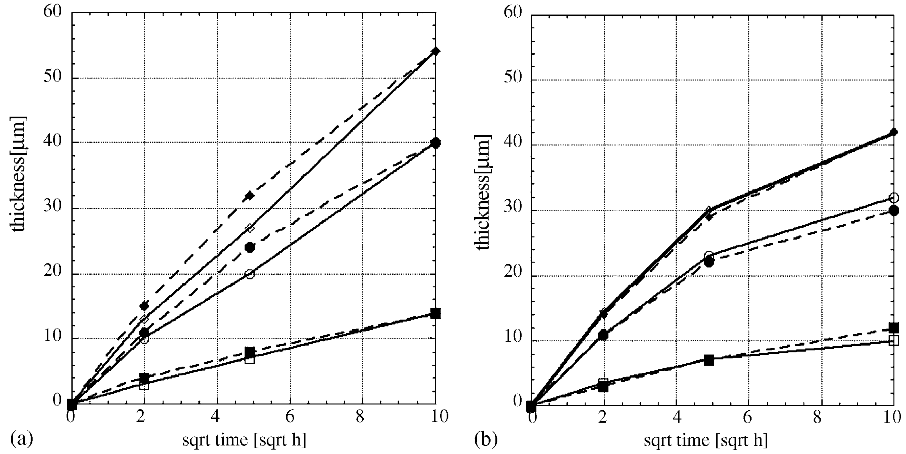

Fig. 7. Thickness of oxidation scales as a function of the sqare root of time: (a) composite A, (b) composite B (boxes: cover layer, circles: intermediate layer, diamonds: sum of both, empty markers: dry air, full markers: humid air).

is broader because upon 1100 °C oxidation of silicon nitride and associated glass formation are more important and it only consists of glass containing oxide precipitates (TiO_2 for both composites and $Y_2TI_2O_7$ in more in the case of composite A). Nevertheless, if we consider the microporosity observed at 1000 °C, the scales formed at 1200 °C, were much more compact and protective. After 24 h of oxidation scales were generally thinner at 1200 °C than at 1000 °C.

At this temperature humidity does not modify growth kinetic of the outer-layer and of the sub-layer for both composites. Results are similar to experiments in dry air.

After 24 h of oxidation at 1400 °C, a dense cristobalite (SiO_2) containing surface scales had developed. Its thickness was about 15 μm for composite B and 50 μm for composite A. Thus, an autoprotective oxidation mode was only conserved for the composites containing a low amount of sinter additives.

4. Discussion

These results show that, during oxidation, important transport processes take place in the intergranular phase. The temperature of 1000 °C corresponds to typical glass transition temperatures of the sintered system SiO_2–Al_2O_3–Y_2O_3.[7] Consequently, the constituents of the glass and the species dissolved in this glass display an enhanced mobility. Generally, silicate glasses represent good solvents and transport media for the cationic species present in our composites (Ti, Si, Y, Al) and also for oxygen and nitrogen.[8,9] In the course of oxidation, the intergranular glass is subjected to a gradient in oxygen chemical potential between the outer sample surface and the bulk. This oxygen potential gradient acts as a driving force for the in-diffusion of oxygen and the counter diffusion of nitrogen and cationic species through the glassy phase. Thus, oxygen diffuses into the composite and internally oxides all grains in contact with the glass film. In this temperature field (1000–1050 °C), the oxidation rate of titanium nitride is higher than that of silicon nitride. Thus, oxidation of Si_3N_4 only yields a thin glassy subscale and widened grain boundary glass films. Under the surface, titanium dioxide grown from TiN dissolves into the glass. According to studies on the oxidation of different silicon nitride ceramics, it occurs in the glass a demixtion in the above-mentioned oxygen chemical potential gradient. Consequently, cations in the glass counter-diffuse to the surface, which is strongly enriched with the faster diffusing species. For these composites, Ti ions diffuse faster than Si, Al or Y cations. At the surface, titanium cations are exsoluted from the oversaturated glass to form the rutile cover layer. Microstructural observations show the rounded surfaces of rutile crystals in the top layer that are in contact with the glass layer and confirm this dissolution–precipitation process. The growth rate of the surface scale of TiO_2 is determined by the latter multi-step process. The growth rate of the subsurface scale is tailored by the in-diffusion of oxygen. In addition to the diffusion in the glassy phase, gas phase transport in the porous surface scale contributes considerably to the oxygen transport.

Humidity seems to play distinct roles depending on the advance of the oxidation reaction. For very short times water slows down the oxidation rate at 1000 °C, then, for longer times it favors the formation of a more compact cover layer of rutile. In the initial steps of oxidation, the intergranular glass phase contains only sintering additives. Its composition is close to an yttrio-alumino-silicate with little or no titanium. Thus, its transport properties are mainly controlled by the trivalent yttrium and aluminium cations which are glass former and modifier. Presence of water in the glass involves formation Si–OH bonds in breaking Si–O–Si bonds and the network modifier cations will be more strongly bonded to –OH groups. Consequently they will be less mobile and should diffuse more slowly. At low concentrations, titanium ions are usually considered as network former. They are tetravalent and located in [TiO_4]tetraedra, and only a low amount of free Ti can diffuse. When the titanium concentration increases in the glass (solubility can reach 20%) Ti^{4+} ions are often reduced in Ti^{3+} and these trivalent ions are located in [$Ti^{III}O_6$] octaedra.[10] Titanium is less strongly bonded to –OH groups and therefore is more mobile than Y^{3+} and Al^{3+} ions. Consequently, water promotes the out-diffusion of titanium cations in the glass. At higher temperatures, oxidation of silicon nitride leads to a higher amount of glass and humidity at a low water vapor pressure has not a big influence. Experiments with higher water vapor pressures (air saturated by water at 40 °C and 60 °C) are presently on way for a better understanding of the role of humidity in oxidizing atmosphere.

These results have shown very important role of the glass in the oxidation mechanism from 1000 °C which corresponds to the glass transition temperatures for alumino-silicate glasses. It is involved in all steps of the progressive oxidation of the composites. They suggest that the oxidation behavior of such composites could be optimized and controlled by tailoring the intergranular phase (chemical composition and quantity).

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