

Microstructural characterization of the oxide scale on nitride bonded SiC-ceramics

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Abstract

The microstructure of the oxide scale formed at 1510 °C by oxidation of silicon nitride-bonded SiC-ceramics was studied by scanning electron microscopy (SEM). Etching by diluted HF etchants was used to help microstructural observation. This method revealed individual cristobalite crystallites as well as interfaces or interlayers between silica and non-silica phases. The ceramics–scale interface was covered by cristobalite crystallites showing that the devitrification of oxide scale begins here. Crystallites grown on SiC were smaller than those grown on binding phase. A thin HF-soluble interlayer was observed between SiC grains and cristobalite. No interlayer was found between cristobalite and oxynitride-type binding phases. The applied etching procedure gave supplementary information on the cracking, too. Partial etching by diluted HF delineated cracks in the scale. These cracks originate in the cristobalite and extend nearly perpendicularly to the substrate through the whole glassy part of the scale.

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1. Introduction

Silicon nitride-bonded silicon-carbide ceramic materials (NBSC) [1–3] are very promising for the use as structural components in high-temperature gas heated furnaces for long-term applications in which thermal cycling occurs.

The manufacturing process of this type of ceramics [4] generally involves a finishing oxidation step with the aim to produce a dense adherent oxide scale which constitutes a barrier to further oxidation [5]. For the understanding of the scale properties numerous oxidation and silica devitrification studies, SEM and TEM investigations have been performed using various silica formers: polycrystalline, monocrystalline bulk, CVD (chemical vapor deposition) and commercial SiC and Si₃N₄ materials (see Refs. [6–11] and references in the above mentioned papers). The properties reported for various

materials are widely divergent. It is generally agreed, that the oxidation kinetics and scale properties depend on the intrinsic oxidation properties of pure SiC and pure Si₃N₄ on one hand and on the influence of additives in the ceramics, water vapor and contaminants in the ambient on the other hand [12].

The comparison of the oxidation resistance of pure SiC and Si₃N₄ materials has been extensively studied by Ogbuji and Opila [13]. It was concluded, that the oxidation rate versus temperature curves for Si₃N₄ and for SiC are different, because rate controlling chemical processes are different. Therefore, it is difficult to predict the oxidation properties of silicon nitride-bonded silicon-carbide-based composite. Furthermore, the additives used for the development of liquid silicates at the oxidation temperatures [14] have to be taken into consideration. At room temperature amorphous and crystalline phases are present in the oxide scale. Fox⁶ has identified the major crystalline phase as α-cristobalite. Kingetsu et al. [15] studied kinetics of cristobalite growth on polycrystalline SiC film using high-temperature in situ X-ray diffractometry. Little is known on the growth process and distribution of cristobalite with the

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coexistence of amorphous silica in the scale covering nitride-bonded SiC-ceramics; however, scale properties, resistance to spalling failure, and oxide cracks that form on cooling could be a concern in applications in which thermal cycling occurs [16].

The aim of the present work was to study and characterize the complicated microstructure of the oxide scales produced by stabilizing oxidation of NBSC ceramic samples. Partial HF etching of the scale was employed to help microstructural observation by SEM.

2. Experimental

2.1. Test samples

Test samples with plane surfaces (A samples) and fractured surfaces (B samples) cut (and broken) from slip cast and nitridized NBSC (temperature of nitridation: 1520 °C) bodies have been used in this work. The samples were exposed to various duration and temperature heat treatments in air: oxidation at 1000 °C, for 36 h; oxidation at 1510 °C, for 8 h; oxidation in two steps, at 1000 °C, for 36 h + 1510 °C, for 8 h. Fragments of an oxidized NBSC plate (C_{fr}) after about 50 cycles from room temperature to 1400 °C in combustion heated furnace were also investigated.

2.2. Characterization

X-ray diffraction was used for phase analysis. Phase analysis was carried out on “as received” plane samples and after fractional grinding deep enough to outcrop the bulk of the ceramic body. X-ray powder diffraction scans were taken on a Philips PW 1050 Bragg Brentano goniometer with Cu K α radiation. The scans were evaluated for quantitative phase composition using a full profile fit. Etching experiments have been carried out in diluted hydrofluoric acid at room temperature. Scanning electron microscopy (SEM) was used to investigate morphology. Typical working parameters of the LEO 1540XB field emission SEM were 10 keV beam energy and 2000–50,000 $\times$ magnification range in secondary electron imaging mode. Sample preparation for SEM: the fragments are positioned by a carbon rib onto a silicon sample holder. The fracture surface at the thin edge of fragments is generally flat and appropriate to high magnification SEM investigations without polishing.

3. Results

After oxidation (at 1510 °C/8 h) a glassy surface layer was obtained both on the plane and the fracture surfaces. XRD patterns on standard plane (A) samples (Fig. 1) show that amorphous silica and cristobalite are the main components of the surface scale. Note that SiC and Si₂ON₂ phases are also present just under the scale, while Si₃N₄ is absent. XRD patterns from the bulk of the ceramic (measured after deep grinding) show SiC, Si₂ON₂ and Si₃N₄ phases. Fig. 2 shows the fracture surface of an NBSC B specimen and the glassy surface of its counterpart. The surface scale smoothes out the

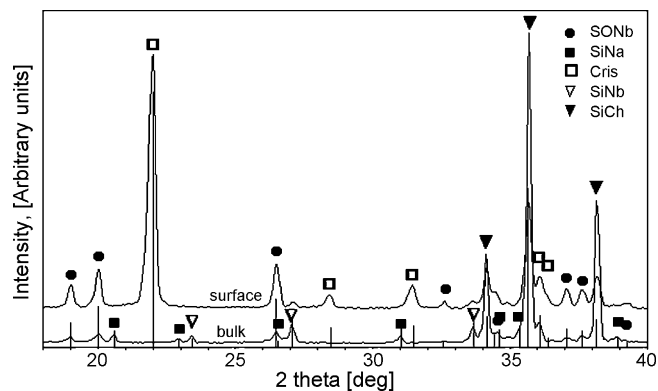


Fig. 1. XRD patterns of a typical NBSC ceramic body, Group A, covered by glassy surface layer (surface) and taken on the bulk of the same specimen (bulk). SONb: 33-1162 Si₂ON₂, o-phase, $z = 0$; rev; Si₂ON₂. SiNa: 41-0360 silicon nitride, alpha; 28H; Si₃N₄. Cris: 39-1425 cristobalite, syn; SiO₂. SiNb: 33-1160 silicon nitride, beta; Si₃N₄. SiCh: private, silicon-carbide, alpha, 12H; SiC.

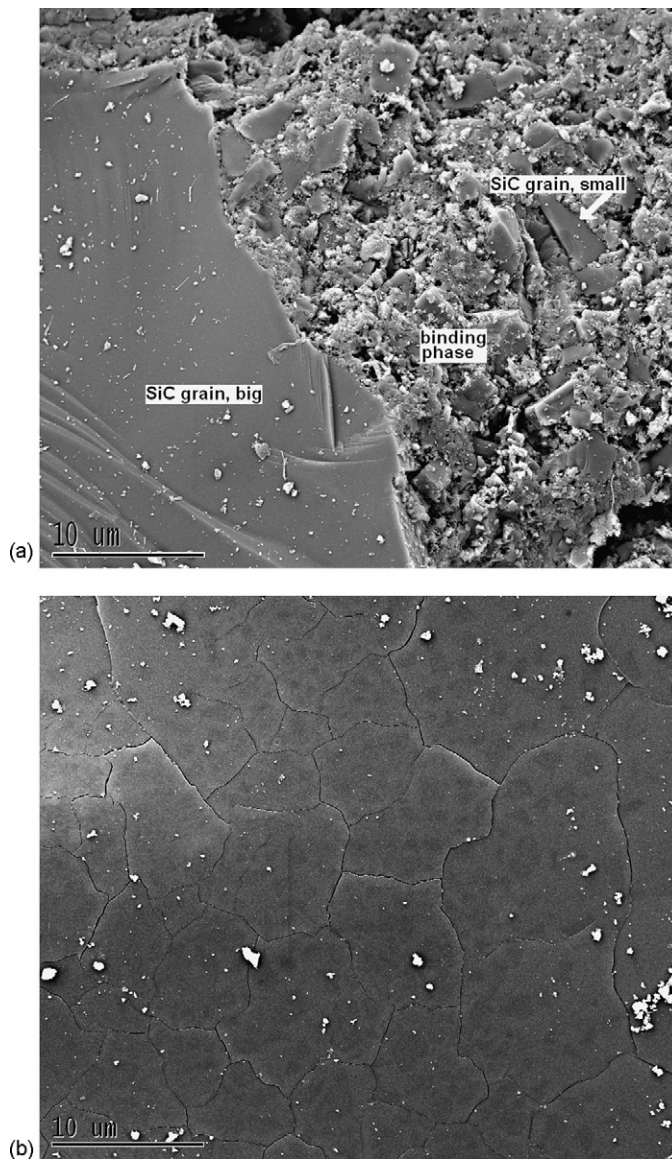


Fig. 2. SEM micrographs of material B. (a) Fracture surface of slip cast nitride-bonded silicon-carbide composite, broken, non-oxidized, Sample B_n . (b) Fracture surface after oxidation at 1510 °C in air for 8 h, Sample B_{ox} .

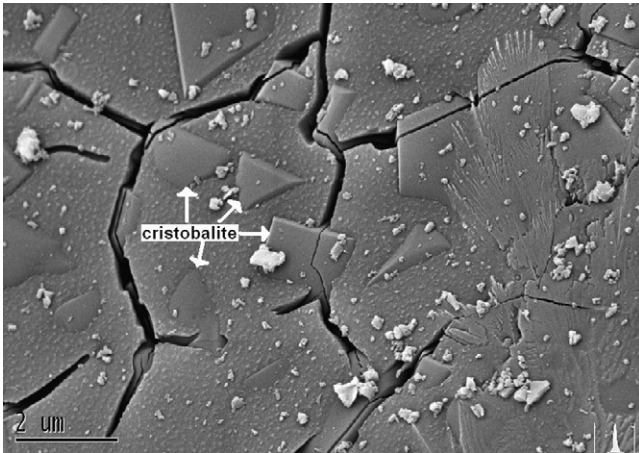


Fig. 3. SEM micrograph of oxide scale after HF etching. Sample etched for 60 s in 2% HF.

morphological features characteristic of the fractured ceramics with big SiC grains and much smaller grains of the nitride binding phase. Network of surface cracks, a mudflat pattern similar to those reported in papers of Wagner et al. [1], Lopez and Phoomiphakdephan [2], and Opila et al. [9] can be observed on the glassy surface even without any chemical etching. The effect of short-time etching with 2% HF solution is shown in Fig. 3. Short-time etching causes widening of the crack spacing in the oxide scale while thinning of the glassy layer takes place. Well-defined crystallites of cristobalite are made visible under the glassy amorphous layer of the surface scale. Sixty seconds of RT etching by 2% HF solution etched off $\sim 0.2 \mu\text{m}$ thickness of the amorphous silica. The cristobalite grains revealed by 60 s/2% HF etching are cracked too. Another feature revealed by the short-time etching is that the glassy part of the scale is not homogeneous. A fractal-like etching pattern (typical for “preferential etching” is shown on the top of the scale (upper right part on the micrograph). Under

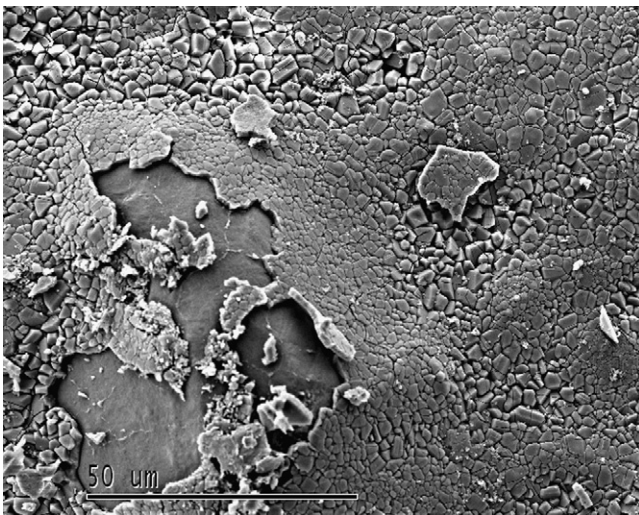


Fig. 4. SEM micrograph on under etching and lifting off layers of cristobalite from SiC substrate grains after long-time etching (30 min, RT, 2% HF, Sample B_{ox}). Note the differences in cristobalite morphology on SiC and binding phase grains.

this very thin layer the etching seems to be isotropic in the amorphous layer.

The result of a longer etching (30 min, RT, 2% HF) can be seen in Fig. 4. The glassy silica layer is absent. The bulk of ceramics is covered by an incomplete layer of cristobalite crystallites. The crystallites are not uniform in size. Those grown over big SiC grains are smaller than the ones grown over the binding phase. The layer of cristobalite crystallites over big SiC grains has a tendency to be under-etched and lifted off in HF etchant indicating the presence of a HF-soluble interlayer between cristobalite and SiC. Oblique view SEM investigation of the interface between cristobalite grains and SiC and binding phase parts of the ceramic substrate has shown the differences between these cases. In Fig. 5a the interlayer between cristobalite grains and SiC substrate can be seen in a slightly under-etched and lifted off corner of the oxide scale. The

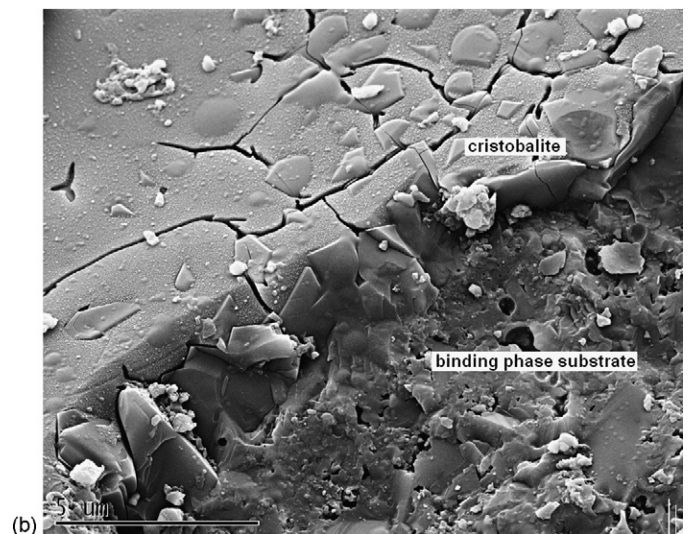
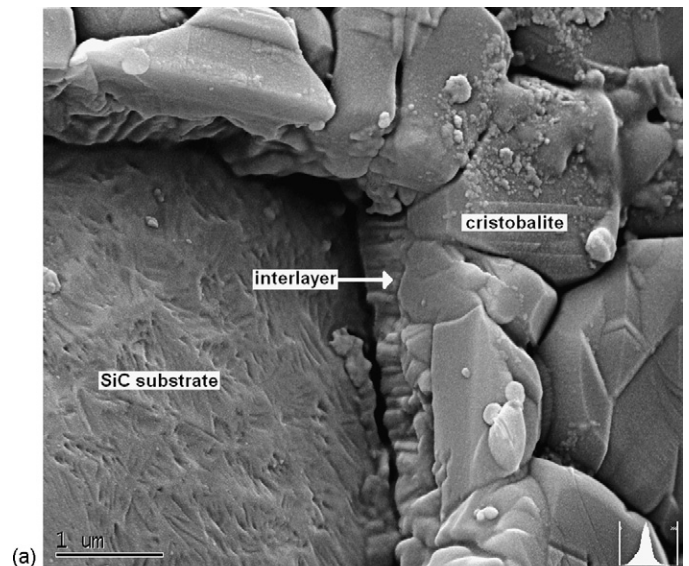


Fig. 5. Oblique view of Sample B_{ox} . (a) Interlayer between cristobalite and SiC substrate. Etched for 30 min, RT, in 2% HF. (b) The lack of interlayer: oxide scale (cristobalite crystallites in vitreous silicate) on binding phase substrate. Etched for 60 s, RT, in 2% HF.

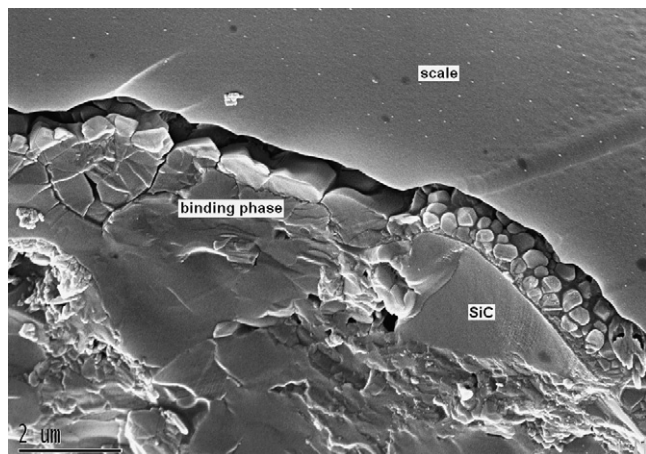


Fig. 6. Cross-section view SEM micrograph of NBSC ceramic, Sample C_{fr} with oxide scale showing difference in grain size of cristobalite grown on SiC or on oxynitride substrate grains.

interlayer with a thickness of 300–400 nm seems to consist of columnar particles. In Fig. 5b the interface between cristobalite and binding phase substrate grains is shown for comparison. Note the lack of any interlayer between binding phase and cristobalite.

Cross-section view SEM micrograph of a Sample C fragment after HF etching is shown in Fig. 6. The scale consists of a relatively thin layer of cristobalite crystallites and thick layer of featureless amorphous phase. A thin interlayer can be seen between cristobalite layer and SiC substrate. The cristobalite crystallites grown on SiC and on binding surface elements are different in size. The ones covering big SiC grains are smaller by a factor of two than the ones grown over the binding phase. Only a few of cristobalite crystallites are cracked; small connected cracks originating from cristobalite cause fragmentation in the ceramic matrix close to the surface (see the upper left side in Fig. 6).

4. Discussion

High-temperature oxidation of NBSC ceramics is generally associated with the onset of cristobalite phase in the scale. In this investigation devitrification has been found to start from the ceramics-glass interfaces, indicating heterogeneous nucleation of the cristobalite phase. A thin interlayer between cristobalite and SiC particles of the NBSC composite is found. The thickness of the interlayer is ~200–400 nm; it can be clearly distinguished from the neighboring phases under the scanning electron microscope and it can be selectively etched off by dilute HF etchants at conditions characteristic to the etching of the silica scale. This finding is consistent with the paper of Tortorelli and More [8] reporting on thin vitreous SiO_2 layers between cristobalite and homogenous SiC and Si substrates. The heterogeneous nucleation of cristobalite actually takes place on the surface of the interlayer and not directly on the SiC substrate. The crystallites grown over this interface are typically smaller in size than those grown on binding phase elements indicating a higher density of nuclei for crystallization.

The formation of an interlayer between the oxide scale and Si_3N_4 at oxidation of Si_3N_4 as well as the identification of the interlayer as Si_2ON_2 are extensively described in the literature [7,12,13,17,18]. In this work neither cross-section nor oblique view SEM investigation has shown any interlayer between cristobalite and the binding phase. However, this contradiction is only illusory. According to XRD results the binding phase of the investigated NBSC ceramics of this study consists of Si_3N_4 and Si_2ON_2 components (see the patterns taken from the “bulk” in Fig. 1). After completion of the oxidation process only Si_2ON_2 can be found at the surface (“surface” pattern in Fig. 1). It appears that “bulk” Si_3N_4 has totally transformed to Si_2ON_2 at the vicinity of the interphase either the plane surface (Sample A) or the fracture surface was oxidized (Sample A).

5. Conclusion

A simple HF etching combined with SEM was used to study the oxide scale on NBSC (nitride-bonded SiC) ceramics. It has been shown that

- Devitrification of the oxide scale begins in the vicinity of the ceramics-oxide scale interface.
- Cristobalite crystallites totally cover the interface and penetrate deeply into the open pores of the ceramics.
- If the oxide scale is cracked, cracks originate in the cristobalite and extend fully into the glassy part of the scale.
- Cristobalite crystallites covering SiC are significantly smaller than those grown on oxynitride-type binding phase grains.
- A thin HF-soluble interlayer exists between SiC grain substrate and covering cristobalite.

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