Microstructure characteristics related to the high temperature fracture resistance of the ESIS Silicon Nitride Reference Material

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ABSTRACT: *To better understand the high temperature properties of the ESIS Silicon Nitride Reference Material, the secondary phases it contains are investigated using X-ray diffraction, Differential Scanning Calorimetry and optical microscopy image analysis. The Impulse Excitation Technique was used to determine the elastic and damping properties, both at room and elevated temperature.*

Tests revealed the presence of a substantial amount of amorphous intergranular phase, which passes a glass transition around 950°C. This observation is used to interpret the high temperature fracture strength of the silicon nitride, as determined by other partners in the Reference Material Testing Program. It is also shown that the amorphous intergranular phase has limited or no tendency to crystallise, which will facilitate interpretation of time- and loading-rate-dependent and long term behaviour at elevated temperature.

Differences between surface and core of the sintered plates are observed. The content of a crystalline iron phase and the lattice parameters of the β-Si_3N_4 are larger in the core than in a surface region of about 1mm thickness. Concurrently the near surface samples show a higher Young's modulus. These observations will be taken into account when further assessing the structural integrity of the ESIS Silicon Nitride Reference Material.

INTRODUCTION

A joint European research program has been established by the Technical Committee 6 of the European Structural Integrity Society (ESIS) to create a set of material properties indispensable for design with a ceramic material [1]. This set will comprise strength, crack extension parameters and cyclic fatigue data at ambient, but also at elevated temperatures. The effect of temperature on the properties of silicon nitrides is known to be severely sensitive to subtle differences in the composition and amount of secondary, intergranular phases.

This report summarises the results of Impulse Excitation tests, Differential Scanning Calorimetry (DSC), Light-optical Microscopy Image Analysis (LOM) and X-ray diffraction (XRD), providing information on the secondary phases and their effect on the macroscopic elevated temperature properties of the ESIS silicon nitride reference material.

EXPERIMENTAL PROCEDURES

Material's Processing

The ESIS Silicon Nitride Reference Material is produced by CeramTec (Plochingen, Germany) under the name SL200 B. The microstructure of this gas-pressure sintered material, containing 3% Al_2O_3 and 3% Y_2O_3-additives, is described by Lube et al. [2].

Impulse Excitation Technique (IET)

Young's modulus, shear modulus, and Poisson's ratio were obtained on un-chamfered beam-like samples (nominal size of 47 x 8 x 2 mm³) following IET-procedures described in ENV 843-2. The length/width ratio of these samples is smaller than the value required by ENV 843-2. FE-calculations showed that for these particular samples the resulting systematic overestimation of the stiffness is about 0.1%.

The impulse excited resonant vibration signals were analysed with a RFDA apparatus (IMCE, Diepenbeek, Belgium), as described in [3]. The RFDA fits a sum of damped sinusoidal vibrations to the experimental signal. The result is a set of resonance frequencies, required to calculate the stiffness values, and the corresponding loss factors. The accuracy of these values depends on the assumption of amplitude-independent behaviour, which is generally observed for dense ceramics at low strain amplitude [4]. The internal friction is calculated as $Q^{-1} = k/(\pi f_b)$, with k the loss factor of the flexural vibration component of frequency f_b.

Elevated temperature IET tests in the flexural mode were performed according to the final draft of a new European Standard prENV 820-5. Bars were suspended in an IET-furnace (HTVP-1750-C, IMCE, Diepenbeek, Belgium) filled with dry N_2 (with 10 ppm H_2O). The sample is heated to and cooled down from 1400°C at a rate of 2°C/min. The sample is excited periodically by the impact of a small projectile [3]. The effect of thermal expansion on the sample dimensions was accounted for using the correction formula proposed in ASTM 1876 – 99, assuming a thermal expansion coefficient of 3.4 10^{-6}/K for Si_3N_4.

X-ray diffraction

X-ray Diffraction (XRD) was performed on a θ-θ diffractometer (3003-TT, Seifert, Ahrensburg, Germany) using Cu-Kα radiation (40 kV, 30 mA), with a parabolic multilayer mirror and a long 0.4° collimator in front of the detector for increased angular resolution. XRD data were submitted to a Rietveld method refinement using DBWS software [5], to estimate the cell parameters of β-Si_3N_4 and the phase composition of the ceramic.

Differential Scanning Calorimetry

Tests were performed in a Netzsch DSC 404 apparatus on three specimens of nominally 100 mg, each from the core material of sintered blocks. The specimens are placed in an Al_2O_3 crucible. Tests were run from room temperature up to 1400°C and back to room temperature again. The test atmosphere was N_2. Tests were performed at different imposed heating rates (2, 8 and 20°C/min). The crucible for the reference material was left empty.

Light optical microscopy image analysis

Mirror-polished sections of the core and skin material were prepared from 4 different plates. On each section 10 to 23 images were acquired at a 50× magnification using a digital camera on a light optical microscope. The total investigated area was 1.73 mm^2 for the core materials and 1.42 mm^2 for the skin material respectively. On the polished sections a highly reflective second phase can be clearly distiguished from the silicon nitride material. The area fraction of this second phase was determined using the AnalySIS® image analysis software (Soft Imaging Systems, Münster, Germany) on each image by thresholding the corresponding grey values.

EXPERIMENTAL RESULTS

Impulse Excitation Tests

The obtained room temperature elastic properties are reported in Table 1.

TABLE 1: Average Young's modulus, shear modulus and Poisson's ratio (between brackets: sample-to-sample variability).

Material	*Young's modulus (GPa)*	*Shear modulus (GPa)*	*Poisson's ratio*
Core (7 samples)	302.8 (1.3)	119.9 (0.4)	0.262 (0.002)
Skin (8 samples)	307.0 (2.0)	121.2 (0.7)	0.266 (0.002)

A distinction is made between samples originating from the surface of the sintered plates, and samples originating from the core of the plates. A slightly but significantly higher stiffness is measured in the surface samples.

The results of a high temperature IET-test, shown in Figure 1, indicate a slow decrease of stiffness with increasing temperature up to 900°C. At this temperature the loss of stiffness accelerates and the internal friction starts increasing. A peak internal friction value is reached near 1150°C. When cooling down again, between 1150°C and room temperature, stiffness and internal friction cannot be distinguished from the values obtained during heating.

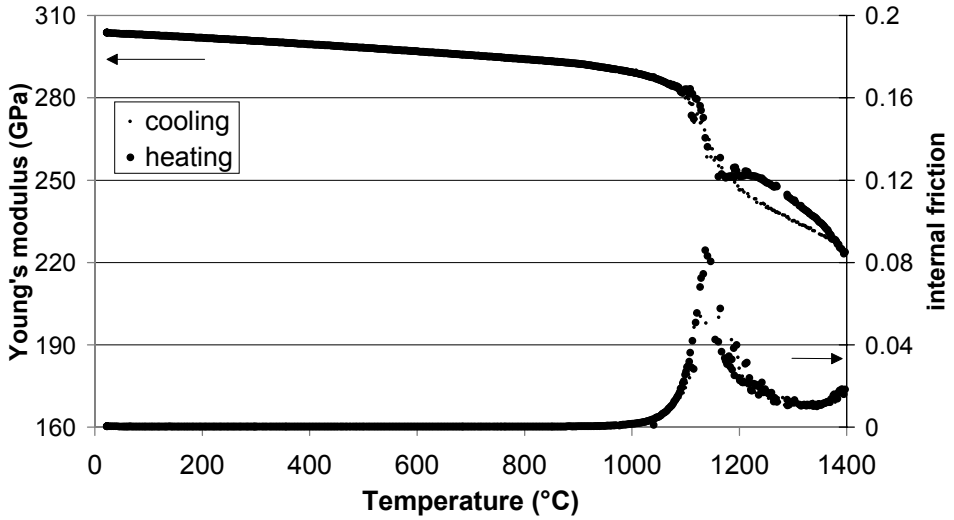

Figure 1: Young's modulus and internal friction during a thermal cycle between room temperature and 1400°C (nominal f_b = 8.5 kHz at 50°C).

X-ray diffraction

The XRD-spectrum of a sample from the core of the sintered plates (Figure 2) reveals two crystalline phases: β-Si_3N_4 and α-Fe. Rietveld analysis on data obtained from both core and near surface samples, provides estimates of the lattice parameters of the β-Si_3N_4 phase and of the weight fraction of α-Fe, as shown in Table 2. XRD on a tested IET-sample (heated @2°C/min to 1400°C) does not indicate the occurrence of newly formed crystalline intergranular phases.

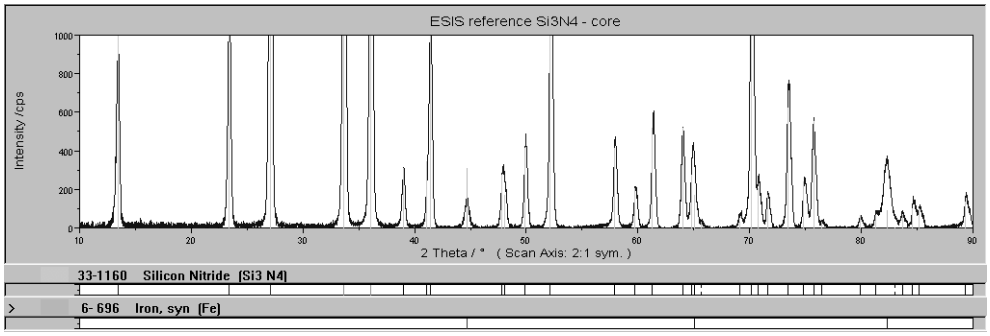

Figure 2: XRD-spectrum of a sample from the core of a sintered plate, with the two identified phases (β-Si_3N_4 and α-Fe).

TABLE 2: β-Si_3N_4 lattice parameter and weight fraction of α-Fe

Material	*β-Si_3N_4 lattice parameters (nm)*		*weight fraction of α-Fe*
	a	*c*	
Core	0.7628	0.29189	0.16 %
Surface	0.7626	0.29175	0.10 %

Differential Scanning Calorimetry

DSC-test results are shown in Figure 3. Depending on the heating rate, a more or less pronounced shoulder is observed between 900°C and 1000°C.

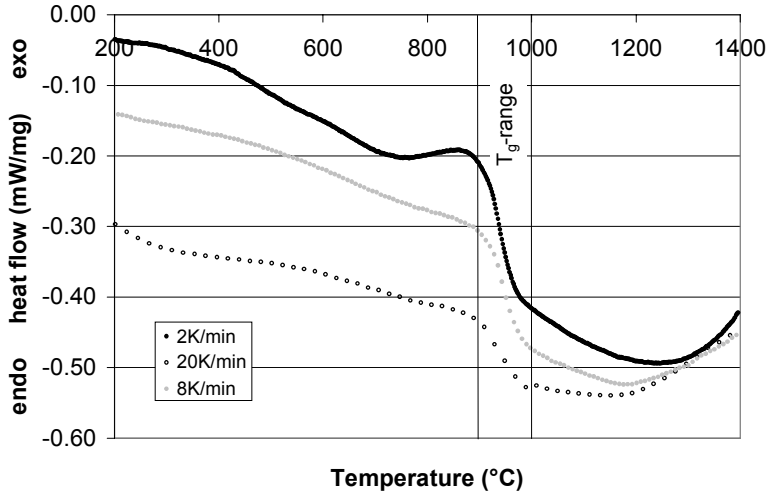

Figure 3: DSC-trajectories at different heating rates.

The shoulder is associated with the glass transition of an intergranular silicate phase. Contrary to some other Y- and Al-containing sintered silicon nitrides [6], no exothermic crystallisation-related peaks are observed at temperatures between the glass transition temperature range and 1400°C. Repeated DSC-tests up to 1400°C do not reveal any change of the microstructure as could be induced by the repeated heating.

Light optical microscopy image analysis

The second phase on the LOM-images was identified as Fe-inclusions by EDX-analysis. Assuming that the area fraction determined on a polished section equals the volume fraction of a phase [7], the volume fractions of Fe in the skin and core regions can be determined. With the densities of iron (7.87 g/cm^3) and silicon nitride (3.19 g/cm^3) the corresponding mass fractions can be calculated (Table 3).

TABLE 3: Volume and weight fraction of α-Fe

Material	*volume fraction of α-Fe*	*weight fraction of α-Fe*
Core	0.08 %	0.17 %
Surface	0.01 %	0.03 %

The result for the core material corresponds well with the value determined by Rietveld-analysis (Table 2), considering the large uncertainties inherent to both Rietveld analysis at <1 wt% fraction and the image analysis (on some images of the skin material only one or two particles were detected). A larger difference is observed for the values of the surface material, but the same trend is established: the core material contains more of the Fe-phase.

DISCUSSION

The intergranular amorphous phase and high temperature strength

The results presented above (a large internal friction peak, the lack of crystalline intergranular silicate or siliconoxynitride phases, the pronounced glass transition shoulder in DSC-curves) indicate the presence of a substantial amount of amorphous silicate phase. From DSC and IET-tests, the T_g of the intergranular phase of the ESIS reference material is estimated at 950°C.

The presence of an amorphous intergranular phase is known to affect the mechanical behaviour of the silicon nitride at temperatures above its glass transition range [8,9]. This is why flexural strength tests [1,10,11] reveal indeed a pronounced drop of the flexural strength from the room temperature value of 870 MPa, to an average of 750 MPa at 1000°C, to 520 MPa at 1200°C and 330 MPa at 1400°C.

The thermal stability of the intergranular glass phase

The amorphous phase is resistant to crystallisation, at least when heated to 1400°C at a heating rate of 2°C/min, in N_2. This observation is very relevant for the interpretation of the results of long term high temperature tests in later stages of the ESIS Reference Material Test Program. If conducted under a protective nitrogen atmosphere, the results of long term tests in the temperature range of the Reference Material Test Program (from room temperature to 1300°C) should not be affected by time-dependent changes in the microstructure. The oxidation resistance remains to be assessed.

The difference between core and surface

The skin of the sintered plates is affected by the sinter process. Slight discolouration is accompanied by an increased stiffness. The detailed microstructural cause remains to be identified. So far, XRD has revealed that the material near the surface is less rich in Fe-inclusions, as is confirmed with optical image analysis. XRD data also show that the lattice parameter of the silicon nitride phase is smaller near the surface, indicating a lower amount of Al-substitution. These observations indicate that metallic atoms preferentially disappear into the sintering atmosphere.

It is expected that these subtle differences affect the local crack initiation and propagation resistance. Therefore, precrack procedures will need to be followed so as to obtain crack tips in material from the core of the sintered plates.

CONCLUSIONS

The surface of the sintered plates is more Fe-rich, and has a higher stiffness. This difference will be taken into account when further assessing the structural integrity of the ESIS silicon nitride reference material.

The reference silicon nitride contains a large amount of amorphous intergranular phase, with a glass transition temperature near 950°C. The elevated temperature properties of the reference material are strongly

affected by this phase. This explains the sharp decrease of elevated temperature strength from 1000°C on, up to 1400°C, the maximum test temperature.

The amorphous phase is rather stable when tested up to 1400°C. This will facilitate the interpretation of long term high temperature tests later on in the reference material program.

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