

Influence of Precursor Densification on Strength Retention of Zirconia-Coated Nextel[™] 610 Fibers

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Strength degradation of Nextel[™] 610 fibers by continuous liquid phase coating was investigated for four different zirconia precursors. The precursors differed regarding their chemical composition (with or without yttrium), phase composition (amorphous or crystalline), and decomposition behavior. Phase transformation and densification of the films were characterized and found to depend on the kind of precursor. Single fiber Weibull's strength was measured for calcination temperatures between 250° and 1150°C for all precursors. Each precursor had an individual degradation behavior. For an annealing temperature of 1150°C highly damaged (~1600 MPa) and undamaged (>3300 MPa) fibers were obtained depending on the kind of precursor. Fiber degradation could be correlated to mechanical stresses. Stress concentration due to inhomogeneous film thickness distribution is proposed as the cause of fiber strength degradation. Full strength could be retained for porous coatings or coatings where stresses were reduced by phase transformation.

I. Introduction

Interphase materials between fiber and matrix are utilized to control the mechanical behavior of ceramic matrix composites.^{1,2} An economic process to apply this interphase is dip coating with a precursor liquid (e.g., a sol) and subsequent calcination. For such liquid-phase-coated fibers strength degradation has been reported by several authors and for several coating-fiber systems.^{3–6} Also nondegrading coatings were presented by Cinibulk *et al.*⁷ and Boakye *et al.*⁸ Most studies were done with either Nextel[™] 720 (composed of corundum and mullite) or Nextel[™] 610 (composed of corundum) fibers. Several correlations were investigated and different reasons were proposed to explain the degradation phenomenon. These correlations and other important findings shall be briefly itemized.

Extensive studies with different monazite (LaPO₄) precursors coated on Nextel[™] 720 fibers^{9–11} showed a dependence on individual precursor chemistry. It was concluded that surface-active decomposition products are the cause of the following degradation mechanism: Intergranular surface flaws of the fiber are attacked by surface-active decomposition products of the coating. Growth of the flaws is driven by the stress from the thermal expansion difference between alumina and mullite grains within the fiber. A nitrogen-containing species (released from the nitrate-based precursor) was speculated to act as the surfaceactive gas species, yet could not be unambiguously identified. A correlation was seen between fiber strength and weight loss of the monazite precursor at the particular temperature.⁸ A low coating permeability was considered to promote stress corrosion by trapping decomposition products at high partial pressure at the fiber-coating interface whereas high a coating porosity allows decomposition products to escape rather than attack the fiber.4,9-11 Fiber strength could be retained for more porous

monazite coatings obtained with particulate precursors. These rabdophane precursors contained no carbon compounds and were deliberated from nitrate by a washing procedure.⁸ Similar results were obtained for CePO₄ coatings.¹²

Further, it was observed that oxide coatings with a fugitive carbon phase⁷ did not affect fiber strength as long as carbon remained in the coating (calcination in inert gas). Degradation occurred when carbon was removed by an additional thermal oxidation.

A thermo-mechanical cause for the degradation of fibers was pointed out by Parthasarathy *et al.*^{2,13}: Stresses in the coating that derive from a larger CTE in the coating, which is strongly bonded to the fiber surface, can degrade the fiber.

The role of a solid-state interaction between the fiber and ions from the coating was assessed by several authors. Cinibulk¹⁵ investigated the solid-state reactivity by dip coating and calcination of NextelTM 610 fibers with the respective nitrate salt solutions. He reported that Ca²⁺ or Sr²⁺ degraded the fiber at 1000°C (10 h) while La³⁺ ions did not. Davis *et al.*¹⁴ found that NextelTM 610 fibers were degraded after coating with LaPO₄ from different salt solutions. This degradation could be suppressed by the addition of alumina powder that presumably acts as a buffer and even slightly enhanced fiber bundle strength. Boakye and colleagues^{10,11} disproved a degrading solid-state reaction of lanthanum or phosphate ions with the fiber: Stoichiometric, lanthanum-rich or phosphate-rich monazite coatings did not result in a significant difference of the fiber strength. Hence, something other than AlPO₄ or magnetoplumbite (LaAl₁₁O₁₈) formation was charged to degrade the fiber.¹¹

Finally it should be mentioned that coating thickness and the number of coatings were found to have no influence.^{10,12}

In general, it must be stated that the degrading mechanisms are not completely understood and individual coating processes/ systems are different.² As far as known to the authors, direct evidence of the degradation mechanism has not yet been found.

In this paper we present a study on the strength of NextelTM 610 fibers coated with stabilized and unstabilized zirconia derived from different precursors. Zirconia coatings on oxide¹⁶ and SiC fibers^{17,18} have previously been reported. In nonoxide composites these coatings can weaken the fiber–matrix interface especially when zirconia is not stabilized in its cubic polymorph. For oxide fibers and composites, zirconia coatings are of little technical importance and our interest is to understand fundamental aspects of the coating process and its effect on the fiber properties. From the phase diagram of the ternary system Al_2O_3 – ZrO_2 – Y_2O_3 (ACerS-NIST Phase Equilibria Diagram No. 06825) it can be seen that an alumina fiber cannot form mixed oxides with neither ZrO₂ nor 8 mol% yttria-stabilized zirconia (8YSZ).

The aim of the study was to investigate which process variables affect the strength of zirconia coated fibers. Furthermore, it was intended to assess if one of the above stated degradation mechanisms applies to our fiber coatings.

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II. Experimental Procedure

(1) Precursor Synthesis

Two amorphous precursor powders were synthesized for zirconia as follows: Zirconium iso-propylate was reacted with

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acetylacetone and afterwards hydrolyzed with water. Then, all volatile components were removed by rotational evaporation at reduced pressure and an amorphous precursor powder was obtained (designated "A_ZrO₂"). For the yttria-stabilized precursor ("A_8YSZ") 8 mol% yttrium acetate was added after hydrolysis. Further synthesis details are given in the literature.^{19–21}

Coating sols with an oxide yield of 8 wt% respective to ZrO_2 or 8YSZ were prepared by dissolution of the amorphous precursor powder in water. After stirring over night they were filtered through a 0.45 µm membrane.^{20,22} The cationic surfactant hexadecyltrimethylammoniumbromide was added below the critical micelle concentration (0.1 wt% respect to water content) in order to improve the fiber wetting.

The two crystalline precursor sols—unstabilized ZrO_2 (C_ZrO₂) and 8YSZ (C_8YSZ)—were obtained from the Chair for Chemical Technology of Materials Synthesis, University of Würzburg, Germany in an oxide concentration of 8 mass% and were used without any further purification. Synthesis of the crystalline precursors occurred in an aqueous medium under hydrothermal conditions. Preparation route was identical for C_ZrO₂ and C_8YSZ except for the addition of Yttrium acetate.

(2) Precursor Characterization

Small-angle X-ray scattering-measurements (SAXS) were done for evaluating the particle size in the sols. A Kratky compact camera (Anton Paar GmbH, A-8054 Graz, Austria) was used to observe the scattering of X-rays obtained from a 2 kW X-ray generator (Philips PW1731, Eindhoven, the Netherlands).

Thin films were applied on glass plates by multiple dip coating (approximately 30 times with 50 cm/min and a drying time of 10 min after each coating step). Then, the dried coating material was scraped off by a razor blade. As described by Bockmeyer *et al.*²³ this scraped-off material behaves more similar to a real coating on a substrate than the bulky precursor and was used for the thermal analysis of the precursors. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA; Setaram TAG24, Caluire, France) of the scraped-off coating materials were done at a heating rate of 10 K/min in dry air atmosphere (>99.999% N₂/O₂ = 79/21).

Thin film grazing incidence X-ray diffractometry (XRD; Siemens D-5005, Bruker AXS GmbH, Karlsruhe, Germany) was performed at an angle of incidence γ of 0.35°. Macroscopic film density was measured by X-ray reflectometry (XRR) using a Siemens D-5005 diffractometer (Bruker AXS GmbH) equipped with a reflectometry sample stage. The sample height was adjusted by the edge slit. Thin film density was evaluated by fitting the measured XRR data with the software DIFFRAC^{plus} REFSIM 2.0 (Bruker AXS GmbH).²⁴ Fitting of the reflection curves was done based of on a single layer model on a pure Si substrate. The film compositions were taken as pure 8YSZ and ZrO₂, respectively.

(3) Coating Procedures

Planar coatings on Si wafers were prepared at a drawing speed of 50 cm/min calcinated at different temperatures in a preheated furnace (dwell time 10 min).

NextelTM 610 fibers were continuously desized, coated, and calcined at a speed of 50 cm/min. The hot zone of the calcination furnace is approximately 30 cm long resulting in a dwell time of 0.6 min at the indicated temperature. The coating procedure and apparatus is described in more detail by Krüger *et al.*²⁰

For tensile testing at room temperature single fibers were extracted from the coated tows and fixed in the rubber clamps of a test machine (Model Zwicki 1120, Zwick GmbH & Co., Ulm, Germany) with a cross-head speed of 1.45 mm/min and a gauge length of 20 mm. Alignment of the fiber with the direction of the load was carefully regarded. From the force–displacement curves Young's modulus and tensile strength were determined. For calculation of the stress a fiber diameter of 11.7 μ m was

assumed. This value was the average fiber diameter of the lot determined before by secondary electron microscopy (SEM; Model S-800, Hitachi Ltd., Tokyo, Japan) analysis of 20 fibers. Weibull's reference strengths were calculated from at least 30 tested fibers by the software ExcelToWeibull (Ceramic Materials and Components, Department of Production Engineering University of Bremen, Germany).

For SEM analysis original fracture surfaces of tested fibers were used. Here for secondary fractures caused by the release of the fracture energy were suppressed.

In tensile tests of single ceramic fibers usually the release of fracture energy at the rupture event leads to secondary fractures. In order to observe where the failure of the tested fiber originated, the primary fracture surface has to be obtained. For this purpose secondary fractures were suppressed by the application of grease as a damping medium onto the fiber. Before SEM investigation the grease was removed by acetone.

III. Results and Discussion

(1) Characterization of Precursors

Two of the four investigated zirconia precursors contained 8 mol% yttria as dopant (8YSZ) and two were without dopant (ZrO₂). One of the 8YSZ precursors and one of the ZrO₂ precursors contained amorphous colloidal particles (designation A) and the other contained crystalline particles (designation C). XRD measurements of coatings prepared from the sols containing crystalline particles and dried at room temperature revealed that the phase composition with yttria as a dopant is pure cubic zirconia and without a dopant it is a mixture of monoclinic and amorphous phase (Table I).

The precursor sols with the amorphous particles A_8YSZ and A_ZrO₂ have an appearance of clear orange–brown, while the precursors with crystalline particles (C_8YSZ and C_ZrO₂) show Tyndall's effect. This indication of larger particles was proven through particle size measurements by SAXS (Table I). The particles found in the two precursors are approximately four times larger in size than the precursors with the amorphous particles (Table I).

Thermal analysis of the precursor material scraped off coated glass plates (without calcination) is presented in Figs. 1 and 2. All coating materials show their major mass loss at temperatures <450°C (Fig. 1) which can be directly referred to the endothermic evaporation of water (20° – 200° C) and the exothermic decomposition reactions of organic residues (Fig. 2).^{20,23} Coating materials obtained from amorphous particles (A_8YSZ, A_ZrO₂) additionally show a second mass loss at around 800°C, which can be explained by an exothermic decomposition reaction of residual carbon.²¹

Generally, the amorphous coating materials (A_8YSZ and A_ZrO₂) show a larger mass loss (~50 mass%) than the crystalline coating materials C_8YSZ and C_ZrO₂ (~12 mass%). This points to the fact that the amorphous particles contain a larger amount of organic residues, like alkoxide and acetylacetonate groups. For coating materials obtained from amorphous particles it has been previously reported that the temperature region where the major part of the mass loss occurs is also accompanied by a high increase in skeletal densities.^{20,23} So, the densification behavior of thin films prepared from sols

 Table I.
 Phase Composition and Particle Size of Zirconia

 Precursors Used for Fiber Coating Experiments

Precursor	Phase composition (XRD)	Particle size (nm) (SAXS)			
A ZrO ₂	Amorphous	2.6			
$\overline{C}ZrO_2$	Monoclinic+amorphous	12.8			
A_8YSZ	Amorphous	2.1			
C_8YSZ	Cubic	9.5			

XRD, X-ray diffractometry; SAXS, small-angle X-ray scattering.



Fig. 1. Thermogravimetric analysis of dried film powders scraped off glass substrates without calcination. The four different coating sols contained amorphous particles (designation A) or crystalline particles (designation C). Two precursors were stabilized by yttria (8YSZ) and two were undoped (ZrO_2).

containing amorphous and crystalline particles is expected to differ considerably. The synthesis procedure of the variants 8YSZ and ZrO_2 are very similar for the amorphous and crystalline precursors, respectively. Particle sizes hardly differ from each other (Table I). Their thermal analysis results are also very likewise (Fig. 2). Thus, for the amorphous and the crystalline precursors, decompositional release of gaseous species from the 8YSZ variant can be expected to resemble that of the ZrO_2 variant.

(2) Crystallization and Densification of Zirconia Coatings

Film porosity analysis from transmission electron microscope images is mostly vague and insufficient for quantitative determination of the densification behavior. By XRR reliable quantification of film densities is possible, provided the composition is known.²⁵ Unfortunately, due to the curved surface of coated fibers, it is neither possible to measure the macroscopic density by XRR, nor can phase composition be determined in good quality with grazing incidence X-ray diffraction (GIXRD). Hence, in order to obtain information about macroscopic density and phase development of zirconia films, XRR and GIXRD measurements were carried out with coatings that were prepared on Si wafers under comparable conditions. The influence of the type of substrate (Si wafer of Al_2O_3 fiber) on the thin film densification and phase transformation was assessed to be minor compared with the influence of precursor chemistry and calcination temperature.

The results of the GIXRD measurements of coatings calcined at temperatures of 400° – 1150° C are presented in Figs. 3 and 4. Coatings prepared from sols containing amorphous particles show reflections for crystalline phases starting at temperatures of 400°C. However, as expected, coatings prepared from sols C_ZrO₂ and C_8YSZ were already crystalline at room temperature.

Coatings that were prepared from yttria-doped precursor sols (A_8YSZ and C_8YSZ) resulted in the cubic phase at all investigated temperatures (Fig. 3). The increase of the full width at half-maximum of X-ray reflections qualitatively indicates an increase in the crystallite size as it has been shown in detail previously.^{20,21}

However, when thin films were prepared with nonstabilized zirconia-coating sols (A_ZrO₂ and C_ZrO₂), a more detailed distinction has to be made between the two precursors types (Fig. 4). At a calcination temperature of 400° and 700° C coatings prepared with the sol consisting of amorphous particles (A_ZrO₂) present only reflections of the tetragonal-zirconia phase (Fig. 4 (left)). After the 1000°C calcination step, a mixture of the monoclinic and the tetragonal polymorphs is observed. For the calcination temperature of 1150°C there are only reflections for monoclinic phase.

Thin sol-gel films that are exposed to low calcination temperatures develop a crystallite size in the nanometer (nm) range. Owing to the enhanced contribution of surface energy to the total free energy, phase stability regions of such small-grained microstructures can be shifted. Instead of the monoclinic phase, which is the common low-temperature polymorph of undoped zirconia,²⁶ tetragonal zirconia can become thermodynamically stable.^{27,28} By raising the temperature, grain growth in the zirconia films leads to an increasing formation of the monoclinic phase.

A different phase formation was observed in the case of the coatings synthesized with the sol C_ZrO_2 , which contains a mixture of mainly monoclinic and only a minor fraction of amorphous particles (Table I). Over the whole temperature range the monoclinic modification of zirconia was identified (Fig. 4, right). However, at relatively low temperatures like 700°C the observed phase composition additionally consists of a minor portion of tetragonal crystallites.

This tetragonal phase presumably evolves from the amorphous particles contained in the sol. Analogous to the phase



Fig. 2. Differential thermal analysis of dried film powders scraped off glass substrates without calcination. The four different coating sols contained amorphous particles (designation A) or crystalline particles (designation C). Two precursors were stabilized by yttria (8YSZ) and two were undoped (ZrO₂).



Fig. 3. Grazing incidence X-ray diffraction pattern of 8YSZ coatings prepared on Si-wafer using a coating sol either consisting of amorphous particles (A_8YSZ) (left) or crystalline particles (C_8YSZ) (right).

evolution of the coating sol A_ZrO₂, these amorphous particles tend to form tetragonal zirconia at low temperatures due to their very small grain size. At higher temperatures, transformation to monoclinic zirconia is induced by crystallite coarsening.

Figure 5 shows the evolution of the macroscopic density in dependence of the calcination temperatures of the coatings. Measurement of macroscopic density by XRR usually requires an exact knowledge of the elementary composition of the coatings as otherwise the error of measurement is significantly large.

Thus, due to the high organic content, no measurements were done for coatings prepared with amorphous coating sols for calcination temperatures below 400°C. The given densities represent the overall density of the film.

Densification of this kind of the amorphous precursors leads to a dense surface layer and closed porosity underneath as soon as organic is degassed $\geq 300^{\circ}C$.^{23,29} Elimination of the closed pores occurs with higher calcination temperatures. To control XRR densities of films, SEM investigations were done for fiber coatings calcinated at 700°C (Fig. 6). Coatings showed an open porous microstructure for the film derived from the crystalline precursors and dense coating surfaces for films from amorphous precursors. This is in good correlation with the densification behavior of coatings on Si wafers observed by XRR.

As already described in Section III (1), the observed densification behavior of coatings prepared from sols containing either amorphous particles or already crystalline particles is considerably different. The retarded densification of the crystalline precursors can be explained from the larger size and crystalline nature of the particles. The evolution of density is only slightly influenced no matter whether yttria-doped or undoped zirconia coating sols were used.

The density of a green film prepared from amorphous zirconia precursors is about $1.6 \text{ g/cm}^{3.21}$ Upon annealing, organic

residues decompose and the material crystallizes which leads to a substantial densification and shrinkage process in the same temperature regime. Considering this circumstance the amorphous films annealed at 550°C have already gone through considerable densification. Additional heating up to 1150°C causes skeletal densification and sintering, which lead to a further increase of the macroscopic film density close to the theoretical density of zirconia.²¹

The densification behavior of coatings prepared with crystalline particles is in contrast to that of coatings prepared with sols containing amorphous particles. The macroscopic density of the former coatings starts at a very low level and stays nearly unchanged until a first significant rise in density is observed at calcination temperatures $\geq 1000^{\circ}$ C. From 1000° C up to 1150° C, the largest increase of density close to the theoretical density of zirconia occurs.

When already crystalline particles with a low content of organic residues and a high skeletal density are used, during the dip coating and pyrolysis ($<700^{\circ}$ C) procedure, no major additional network densification can occur. The film density is mostly defined through the packing and aggregation of the particle during the dip coating procedure. Further increase in thin film density can then only be achieved by sintering at the corresponding temperatures ($>700^{\circ}$ C).

(3) Strength of Coated Fibers

The tensile strengths were measured for single fibers extracted from the bundles after coating with one of the four precursors and for different calcination temperatures. In Fig. 7 the Weibull reference strengths are displayed as a function of the calcination temperature. Table II additionally lists strength data and Weibull's moduli. Strength of uncoated fibers that passed through the coating apparatus (without a precursor bath) at 1150°C is



Fig. 4. Grazing incidence X-ray diffraction pattern of ZrO_2 coatings prepared on Si-wafer using a coating sol consisting either of amorphous particles (A_ZrO₂) (left) or crystalline particles (C_ZrO₂) (right).





Fig.5. Macroscopic density of thin films on Si-wafer determined by X-ray reflectometry as function of annealing temperature. Films were prepared by using four different coating sols consisting of amorphous particles (designation A) or crystalline particles (designation C). Two precursor were containing yttria as dopant (8YSZ) and two were undoped (ZrO₂).

also indicated (dashed line). The strength of these fibers is virtually equal to that of as-received fibers. This proves that fibers are neither mechanically damaged by the transport system nor from exposure to the calcination temperature. Hence, fibers with decreased strength are degraded through the coating.

First the strength of fibers coated with yttria-stabilized precursors is treated (Fig. 7, left). For the amorphous precursor (A_8YSZ), fiber strength drops off from the value of the uncoated fibers at $\geq 550^{\circ}$ C and remains at a low level (~1600 MPa) for all higher calcination temperatures. For C_8YSZ, fiber strength degradation starts at 1000° C and becomes more severe at 1150° C.

Following the results on the thermal decomposition and densification, the two major differences between the two precursors are obvious: the amounts of organic decomposition products and the temperature intervals where densification of the films occur.

In the case of the A_8YSZ precursor the major part of decomposition reactions and film shrinkage both coincide with the degradation of the fiber strength.

For the C_8YSZ, decomposition reactions are completed around $500^{\circ}\overline{C}$ (Fig. 2, left) yet strength degradation starts at temperatures above $700^{\circ}C$ simultaneously with the film densification. Note that the film densification coincides with the strength degradation for both precursors.

For unstabilized ZrO_2 precursors, up to 700°C the same strength behavior as for the 8YSZ precursors is observed, the amorphous precursor degrades the fiber from 550°C on, while the crystalline precursor does not affect the fiber strength (Fig. 7 (right)).

Above 700°C however, the ZrO_2 precursors show a different behavior compared with the 8YSZ precursors. For the crystalline precursor C_ZrO₂, no fiber strength degradation is observed up to 1150°C. The strength of fibers coated with the amorphous precursor A_ZrO₂ is unaffected (1000°C) or only slightly reduced (1150°C).

Precursor decomposition (Fig. 2) and film densification (Fig. 5) are analogous to the 8YSZ precursors. Up to 700° C for the amorphous precursor, decomposition reactions and film densification coincide with fiber strength degradation. For the crystalline ZrO₂ precursor, the observed decomposition reactions do not result in a loss of fiber strength. Only minor film densification has occurred up to 700° C.

Interestingly for high calcination temperatures ($\geq 1000^{\circ}$ C), where decomposition of organics is already finished, doped and



Fig. 6. Secondary electron microscope images of zirconia films on Nextel^M 610 fibers after calcination at 700°C (top view, unsputtered). Films were prepared by using the four different sols consisting of amorphous particles or crystalline particles. Two precursors were containing yttria as dopant (8YSZ) and two were undoped (ZrO₂).





Fig. 7. Single fiber Weibull's strengths as function of annealing temperature of NextelTM 610 fiber coated with different zirconia precursors. Strength depends on the particular precursor and temperature. Amorphous (designation A) and crystalline (designation C) precursors exhibit different degradation behavior for yttria doped (left) and undoped (right) zirconia. The strength of an uncoated fiber that passed at 1150°C through the coating apparatus is given as reference (dashed line).

undoped precursors show different degradation behavior although their densification is nearly equal (depending on the precursor type). The only difference between the respective precursors is the observed phase evolution (Figs. 3 and 4). The stabilized precursors exhibit no phase transformation (Fig. 3) whereas in the undoped precursors the tetragonal crystallites transform to the monoclinic phase between 700° and 1000°C (Fig. 4). This phase transformation, which is associated with a volume expansion, occurs in the same temperature regime where the doped precursors degrade the fiber strength.

In the following, the observed fiber degradation behavior shall be discussed with regard to the degradation mechanisms described in 'Introduction'.

Comparing the strength for 8YSZ- and ZrO_2 -coated fibers, it may be assumed that Y^{3+} ions undergo a degrading solid-state reaction with the fiber as found for Ca^{2+} or Sr^{2+} ions by Cinibulk¹⁵ Therefore additional coating experiments with an 8 wt% yttrium acetate solution were performed. Up to calcination temperatures of 1150°C the strength of these fibers was unaffected (3405 MPa at 1150°C). Thus fiber degradation by Y^{3+} ions can be ruled out.

Strength reduction of the fibers by stress corrosion from surface-active species which are released during precursor decomposition, has been mentioned.^{6,8} For our results no consistent correlation between decomposition of organics and fiber strength can be seen. For instance, precursors with nearly identical composition and decomposition reactions (e.g., A_8YSZ and A_ZrO₂) lead to very different fiber strengths at high temperatures. Therefore this point was excluded.

From our results we reflect that for all degraded fibers the coatings were nearly densified. For the undamaged fibers the coating was either still porous or had undergone a phase transformation. Hay *et al.*⁴ also reported a correlation of strength reduction of NextelTM 720 fibers and the densification and pore coarsening of the coating. He explained the benefit of permeable porosity by an easier release of gaseous decomposition products which prevents fiber degradation by surface-active species.^{4,8}

For the degradation mechanism two explanations are possible. First, thermal expansion mismatch between a strongly bonded coating and the fiber leads to mechanical stresses that cause defects in the fiber.^{2,13} The CTE of ZrO_2 or 8YSZ is higher than the one of Al₂O₃. When the coated fiber cools down, tensile stress arises in the coating. This thermal stress is highest for dense coatings which have a higher Young's modulus than porous coatings (as an example it is mentioned that the relative Young's Modulus of a silica gel with 40% porosity is only 1/5 of the fully dense material).³² Furthermore bond strength between coating and fiber surface is expected to be higher for the dense coatings.

Second, constrained shrinkage of the film can also result in tensile stress of the coating. Stresses in densifying zirconia coatings can be as high as 800 MPa³⁰ and abruptly rise during decomposition of organic compounds and densification.³¹ As a consequence of the strong dependency of elastic modulus on porosity, large stresses evolve from film densification only for quite dense coatings.

For unstabilized zirconia coatings the densification stresses can be relaxed and/or the interface bonding between the coating and the fiber can be weakened when tetragonal to monoclinic phase transformation occurs. This phase transformation in unstabilized zirconia leads to a volume expansion of 8 vol%.³³ Hence, *densified and transformed* ZrO₂ coatings (1000° and 1150°C for A_ZrO₂ and C_ZrO₂) do not degrade the fiber strength while *densified but untransformed* ZrO₂ coatings (A ZrO₂ 700°C) do.

Irrespective of its origin, the tensile stress of the coating is compensated by a compressive stress in the fiber. In case of an ideal homogenous film thickness the resulting homogenous stress distribution should not lead to strength degradation. However, real coatings from liquid precursors always have an inhomogeneous film thickness and there are coating bridges between neighboring fibers.²⁰ This results in an inhomogeneous stress distribution and stress concentration.

This stress concentration is assumed to be the cause of fiber strength degradation observed for our coatings. From our results it cannot be distinguished whether these stresses arise from

Table II. Weibull Strength and Weibull Modulus *m* of Zirconia-Coated Nextel[™] 610 Fibers

Temperature (°C)	C_ZrO ₂ strength (MPa)	т	C_8YSZ strength (MPa)	т	A_8YSZ strength (MPa)	т	A_ZrO ₂ strength (MPa)	т
250	3146	12.0	3330	19.1	3177	9.8	3088	14.5
400	3137	9.7	3353	10.0	3175	14.7	2948	15.6
550	3262	10.2	3318	10.1	1900	17.7	2012	13.9
700	3121	10.2	3053	12.1	1522	9.4	1849	14.1
1000	3427	13.7	3060	9.5	1769	9.2	3213	9.2
1150	3339	10.7	2022	5.7	1718	7.3	2887	10.6

Strength of fibers passing through the apparatus at 1150° C without coating is 3395 MPa (m = 7.8).



Fig.8. Secondary electron microscope images of a typical fracture surface of degraded coated Nextel[™] 610 fiber.

a thermal expansion mismatch, the constrained film shrinkage, or both.

For fractographic analysis original fracture surfaces of degraded coated fibers were studied with SEM. As a typical example a fracture surface of a fiber coated with C 8YSZ and calcination at 1150°C is given in Fig. 8. It can be clearly seen that the fracture starts from the surface at a position where film thickness is larger. This observation appears for all four coating precursors. This confirms the assumption that stress concentration due to inhomogeneous coating thickness is the cause of fiber degradation.

IV. Conclusion

Crystalline and amorphous ZrO2 and 8YSZ precursors showed different effects on the strength coated Nextel[™] 610 fibers. The precursors and resulting films differed in their decomposition, phase transformation and densification behavior.

It was found that stress corrosion by precursor decomposition products was not a sufficient explanation for the observed fiber degradation. Rather, the individual densification behavior of the coatings was in good correlation with fiber strength.

In densified coatings large tensile stresses are present by thermal expansion mismatch and the shrinking process constrained by the fiber. Stress concentration arising from inhomogeneous film thickness was identified as the cause of fiber degradation.

Degradation can be avoided for coatings that scarcely densify, have weak adhesion to the fiber or can relax stresses by e.g. phase transformation.

The generalization of the presented results to other coating materials and fiber types will be the aim of future investigations.

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