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Low-Temperature Aging of Zirconia Ferrules for Optical Connectors

Michael J. Lance,[*,†,‡] Eva M. Vogel,[*,§,¶] Leslie A. Reith,[§,¶] and W. Roger Cannon[*,‡]

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6068; Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey 08854-8065; and Bellcore, Morristown, New Jersey 07960

Zirconia ferrules for optical connectors were examined after aging at 85°C and 95% relative humidity. Two degradation mechanisms were the roughening and the deformation of the zirconia ferrule surface. Raman microscopy revealed that this relatively low-temperature degradation of zirconia ferrules is caused by the tetragonal to monoclinic transformation of zirconia, and is accelerated by stress relief during polishing. The surface upheavals associated with low-temperature aging may significantly degrade the performance of optical connectors over time.

I. Introduction

OPTICAL fiber connectors are devices used to transfer optical power between two optical fibers. The connectors are designed to be connected and disconnected repeatedly, in contrast to optical splices, which are used for the permanent connection of two or more optical fibers. Optical connectors are made with a variety of materials that have to be compatible in the service environment. These include silica glass fibers, metallic ferrules, sleeves, casings, and springs, ceramic ferrules and sleeves, and a variety of polymers that are used for the housing (PBT), the boot (PVC), and the fiber coating (acrylates). Connectors may vary in the type of latching mechanisms or housing, but they all have an optical fiber secured in a ferrule. The mating surfaces of the optical fiber and ferrule are machined and polished to produce a convex surface with the fiber at the apex. The contact area between two mated ferrules is concentric to the fiber and has a diameter slightly larger than the fiber.[1,2] In this work, we focus on the zirconia ferrule of single-fiber coupling (SC) optical fiber connectors, as shown in Fig. 1.

Several techniques are used to reduce light reflection at the fiber-end in optical connectors. One technique employs an angled fiber endface that prevents the reflected power from returning along the optical path.[3] Laser ablation of the fiber endface is often used when very low reflectance has to be achieved.[4] However, less-expensive flat endface connectors are predominantly used by today's telecommunication providers.[5] In this case, low reflectance is achieved by physical contact between the adjacent fiber cores. Physical contact is guaranteed by tightly controlled polishing techniques. Over the past several years, changes in the polishing process have produced vast improvements in connector back-reflection performance. These results were achieved by tighter control of the endface parameters, and by a polishing process that does not significantly change the optical properties of the contacting fiber surfaces.

The reliability of optical connectors has become an issue because of their increased use in uncontrolled environments. A related issue to back-reflection is the reliability of stabilized zirconia ferrules to long-term exposure to humid and low-temperature (<100°C) environments. Low-temperature aging concerns the transformation of the stabilized tetragonal phase to monoclinic, which involves an increase in the unit cell volume of 4–5 vol%, as well as a shear displacement. Fujisawa *et al.*[6] studied low-temperature aging of zirconia for use as an implant material for hip joints. In that work, aging after 3 years at temperatures below 150°C resulted in some transformation, but with no significant loss of flexural strength. However, for zirconia ferrules, which have tight dimensional tolerances, maintaining a polished surface finish but not the mechanical properties is paramount to the long-term reliability of the connector. In this report, we summarize our understanding of the low-temperature aging of zirconia used for ferrules and the effect of aging on the surface finish. The degradation is related to stress relief during polishing, which accelerates hydrothermally activated aging in the zirconia.

II. Experimental Procedures

Various mated connectors were subjected to a series of high humidity thermal-cycling tests between minimum and maximum temperatures of −10° and 85°C, and humidity levels of 95% relative humidity (RH) or condensing environments. All the connectors were purchased from commercial vendors and therefore have proprietary compositions and processing histories. Nevertheless, the starting phase content was always 100% tetragonal zirconia and the stabilizer in all cases was yttria. The entire cycle was 90 d. These tests are described in detail elsewhere.[7] The connectors were inspected before and after testing by profilometry and optical and interferometric microscopy. Environmental scanning electron microscopy, with an energy dispersive spectroscopy X-ray analyzer for chemical analysis, and atomic force microscopy were used to image and analyze the entire endface.

Raman spectra were obtained using a Raman microprobe (Model U1000, Instruments S.A., Inc., Edison, NJ) with a CCD detector

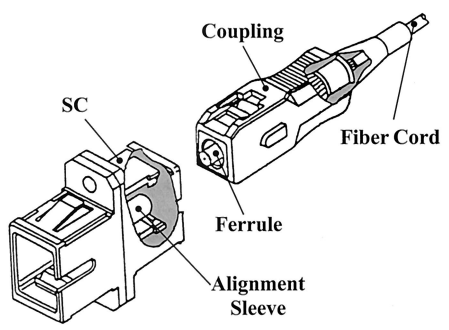

Fig. 1. Drawing of the SC connector; the ferrule in the center of the coupling device surrounds a single optical fiber.

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[*]Member, American Ceramic Society.
[†]Oak Ridge National Laboratory.
[‡]Rutgers University.
[§]Bellcore.
[¶]Now with Lucent Technologies, Murray Hill, NJ 07974.

(EG&G, Inc., Wellesley, MA). An Ar^+ laser (Model 2020-05, Spectra Physics, Inc., Mountain View, CA) operating at 5145 Å was used to excite the spectra. The average laser power at the ferrule surface was ~10 mW. The spot size was ~5 μm in diameter and the depth of field was 25 μm with a confocal aperture (CFA) and 50 μm without the aperture. All peak heights were determined by fitting the spectra with pseudo-Voigtian functions. The monoclinic volume percentage in the probed ZrO_2 was determined using the equation

$$V_m = \frac{I_m^{180} I_m^{190}}{F \nu I_t^{147} I_m^{180} I_m^{190}} \times 100 \quad (1)$$

where I represents the intensities of the Raman peaks with the superscripts and subscripts denoting the peak position (in cm^{-1}) and phase (t = tetragonal, m = monoclinic), respectively. Using a method used by Katagiri *et al.*,[8] the calibration constant F of Eq. (1) was measured to be 4.08, which compares well to previously reported values.[8,9] The technique was accurate to ~0.2 vol%, as determined by the limit of delectability of the two monoclinic peaks.

III. Results

Interferometric microscopy revealed a significant increase in the surface roughness after the temperature/humidity cycling test. Also, the endface of some of the ferrules appeared to flatten following testing. The flattening or deformation of the zirconia occurred in a circle concentric to the embedded optical fiber, which corresponded to the contact area of the two mated ferrules. Figure 2 shows a ferrule that exhibited both of these degradation mechanisms following aging.

A summary of the transformation behavior of the zirconia ferrules using Raman microscopy follows:

(1) The polished endface showed larger amounts of transformation to the monoclinic phase compared with the ferrule sides, which were not polished.

(2) The ferrules that exhibited only roughening showed only 1–2 vol% transformation, whereas ferrules that showed deformation (flattening) of the zirconia had as much as 40 vol% monoclinic at the surface, depending on the manufacturer.

(3) The amount of transformation was lower within the contact area (within 50 μm of the fiber), where the material was under compression after being mated, than outside the contact area. Figure 3 shows the distribution in monoclinic fraction moving away from the optical fiber on a ferrule endface. Outside the contact area, the monoclinic content is still ~10 vol%, but decreases rapidly as the contact area is approached.

(4) Transformation occurred only on the surface of the material. Figure 4 shows two spectra obtained from the same region on a ferrule that exhibited deformation (flattening). A CFA was used for one scan to limit the depth from which signal is obtained to ~25 μm, as opposed to ~50 μm without the aperture. The monoclinic content increased from 7.5 to 19 vol% after using the CFA, which shows that the transformation occurred primarily at the surface of the ferrule.

IV. Discussion

Unlike other applications that use transformation-toughened zirconia for its favorable wear resistance, high fracture strength, and toughness, in the case of zirconia ferrules, maintaining a polished surface finish and sample dimensions are the most important factors. An air gap as small as 0.02 μm can cause loss at the connector,[2] so even a small amount of transformation and the resultant surface deformation may significantly degrade the performance of the connector. Given a 4–5 vol% increase from completely transforming tetragonal to monoclinic zirconia, the transformation depth necessary to match this air gap would be ~1.3 μm. Because the ferrule end is curved with the optical fiber at the apex, it will require more transformation to actually cause separation of the mated ferrules. Nevertheless, for long-term exposure, even at room temperature, aging may become the significant factor limiting connector lifetime.

Our results show that polishing before hydrothermal exposure effectively accelerates aging of zirconia ferrules. It is unlikely that the transformation is associated with chemical attack during the polishing process because no monoclinic zirconia was observed in any of the samples before hydrothermal attack. Polishing has been associated with an increased rate of low-temperature aging relative to machined surfaces.[10,11] It is believed that machining creates a compressive zone that retards transformation, and that polishing relieves this stress, making it more thermodynamically favorable for transformation to occur.[12–14] In the samples studied here, the sides of the ferrules were only machined, and monoclinic zirconia was not found during hydrothermal exposure. Moreover, the transformation occurred entirely on the surface, which is typical for low-temperature aging.[14]

Compressive stress reducing the driving force for transformation also explains why the monoclinic content is lower within the contact area for samples that exhibited deformation (see Fig. 3). Material within the contact area is under compression to maintain contact between the two ferrules. The resulting compressive stress makes it less favorable to transform during hydrothermal exposure. The contact area may also restrict the attack of water, which would lower the amount of aging in this area. The flattening of the ferrule at the fiber

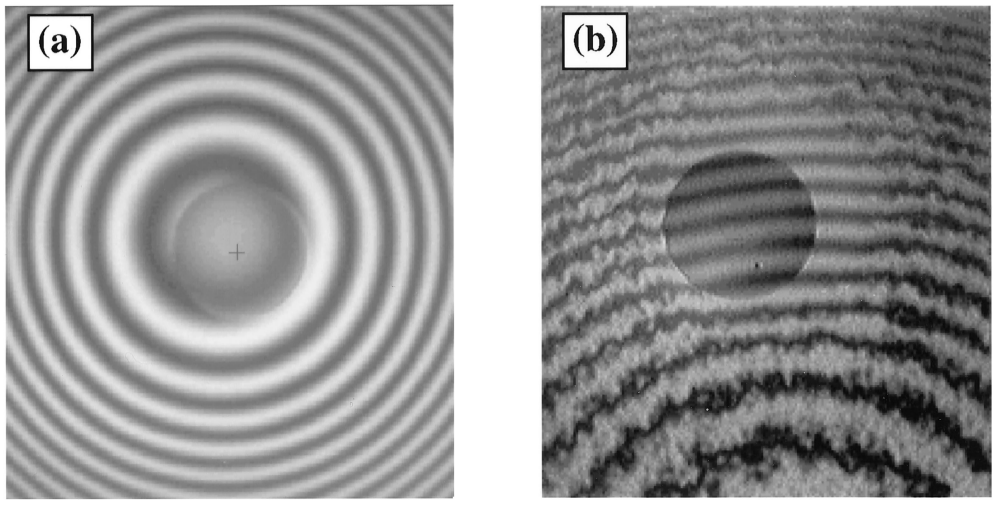

Fig. 2. Interferogram of a zirconia ferrule (a) before and (b) after aging in 95% RH at 85°C for 90 d; the circle in the center is the embedded optical fiber with a diameter of ~125 μm.

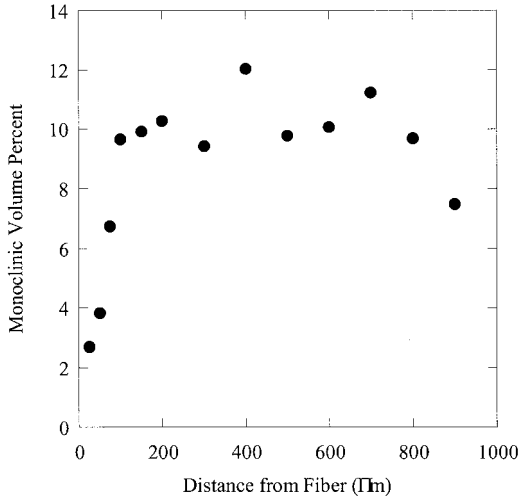

Fig. 3. Monoclinic volume percentage, measured along a line moving away from the fiber to the ferrule edge.

may eventually result in an air gap between the two mated fibers, similar to a withdrawal of the fiber into the ferrule, which would dramatically decrease light transmission.[1,2,15]

The increased roughness of the polished ferrule surface, as seen in Fig. 2(b), has been reported by other researchers studying low-temperature aging.[16,17] Jong-Kook *et al.*[16] measured surface upheavals following isothermal phase transformation after aging at 250°C for just 5 h. Chevalier *et al.*[17] measured small surface upheavals <10 nm in height after 3 h at 134°C resulting from the increase in crystal size from the t → m transformation. Microcracks also have been observed on the zirconia surface following aging caused by the dilation accompanying transformation.[18] Most studies of low-temperature aging of stabilized zirconia measure changes in fracture strength, not surface finish. More work needs to be done to improve our understanding of the relationship between surface deformation and polishing procedure. In this study, a large variation in performance was discovered between ferrules from different manufacturers, suggesting that with the appropriate polishing, surface deformation can be minimized or even eliminated.

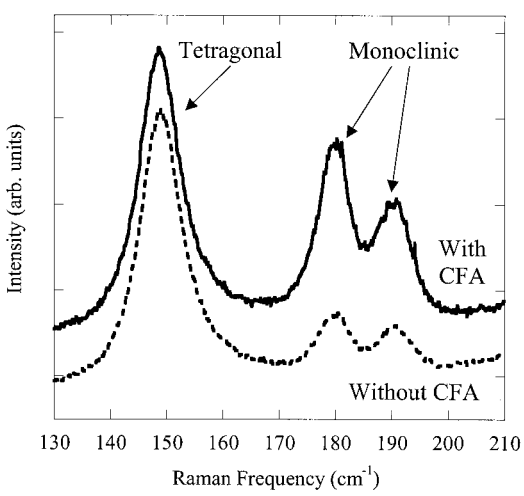

Fig. 4. Raman spectra obtained from the ferrule endface with (solid line) and without (broken line) a CFA.

V. Conclusions

Telecommunication networks are only as good as their interconnects, which comprise only ~0.2% of a typical network. In the future, fiber-to-the-home networks will require 600 million connection points.[5] Therefore, ensuring long-term reliability of optical connectors used in different service environments is crucial. Here, the effect of environmental degradation on zirconia ferrules and its possible effect on optical connector performance was investigated. Raman microscopy was used to quantify the tetragonal-to-monoclinic transformation of zirconia. The response of the ferrules varied between manufacturers, but some basic trends were observed. Polished surfaces exhibited more degradation than machined surfaces, and the transformation occurred only on the surface. It is believed that polishing relieves compressive surface stress resulting from machining, which makes transformation more favorable.

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