

## 氟锆酸盐玻璃光纤预制棒表面处理

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**摘要** 管棒法加工的氟锆酸盐玻璃光纤预制棒表面和亚表面存在缺陷, 这会增加氟锆酸盐玻璃光纤的界面损耗并降低光纤强度。研究了一种非水有机溶液体系的表面处理剂, 其中溶剂是乙醇和戊醇的混合物, 酸是盐酸和草酸的混合物, 添加剂是二氧化锆和乙二胺四乙酸的混合物。相比于常规的水溶液体系的表面处理剂, 该处理剂能更有效去除光纤预制棒的表面和亚表面缺陷, 并且不存在水侵蚀表面引起的水化层和沉积杂质, 降低了光纤拉制过程中的析晶和失透风险, 可大幅增大光纤强度并降低光纤的损耗。光电子能谱(XPS)显示, 利用该处理剂处理过的氟锆酸盐玻璃表面和本体的组分含量更接近。原子力显微镜(AFM)观测结果显示, 利用该处理剂处理过的氟锆酸盐玻璃的表面粗糙度更低。实验结果表明, 由该表面处理剂处理过的光纤预制棒拉制的光纤损耗更低且抗拉强度更强。说明对于氟锆酸盐玻璃光纤预制棒而言, 非水有机溶液体系的表面处理剂比传统的水溶液体系表面处理剂更为合适。

**关键词** 材料; 表面处理; 光纤预制棒; 氟锆酸盐玻璃; 非水体系; 光纤损耗

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## 1 引言

中红外激光近年来在军事、通讯、医学、环境科学等领域得到了广泛的应用, 已成为发光领域的研究热点<sup>[1-5]</sup>。氟锆酸盐玻璃具有高稀土溶解度、相对较低的声子能量、较宽的光学窗口(0.3~7 μm)、低反射率、低分散率且易于加工制造等优势, 是中红外激光增益介质的基质玻璃, 在光纤激光器、上转换激光器和光纤放大器等领域有着广泛的应用<sup>[6-8]</sup>。

氟锆酸盐玻璃作为基质玻璃虽然优点突出, 但也存在一些缺点, 其表面的化学稳定性较差, 容易受到水分子的侵蚀, 如在潮湿环境中表面会产生半径为 0.5~1 mm 的霉斑<sup>[9-10]</sup>; 在水溶液或者含水的环境中, 表面则易生成难溶性的氢氧化物和氟氢氧化物并形成水化层<sup>[11-15]</sup>, 导致玻璃出现失透现象。氟锆酸盐玻璃光纤预制棒主要是采用管棒法制备的, 该方法属于光学冷加工, 会在表面留下离子型杂质并在亚表面产生微裂纹等微缺陷; 冷加工一般采用

水作为研磨介质的溶剂, 水会与氟锆酸盐玻璃光纤预制棒表面发生反应产生氢氧化物和氟氢氧化物杂质, 加大表面与本体的成分差异, 使光纤预制棒在拉制光纤时出现析晶或者失透现象<sup>[16-20]</sup>, 并且亚表面残留的抛光粉等颗粒性杂质可能会在光纤芯包层间的界面处形成散射, 增加光纤损耗, 杂质与微裂纹的存在还会降低光纤的力学性能, 这些问题已经引起了广泛的关注<sup>[21-23]</sup>。

目前所采用的表面处理就是对氟锆酸盐玻璃表面进行酸刻蚀或者通过等离子体对表面进行刻蚀, 但等离子体刻蚀方法受处理样品尺寸、形状以及价格等因素的限制<sup>[24-25]</sup>, 所以表面酸刻蚀是光纤预制棒的主要处理方式。Pureza 等<sup>[25]</sup>采用 0.2 mol/L 的硼酸水溶液作为表面处理剂, Schneider 等<sup>[26]</sup>采用 1 mol/L 盐酸水溶液+十二氧化锆添加剂的混合酸液作为表面处理剂, 对氟锆酸盐玻璃光纤预制棒表面进行处理, 有效提高了表面反应的均匀性, 但仍有部分水分子与氟锆酸盐表面发生侵蚀反应, 产生的难溶性产物影响表面质量。目前, 氟锆酸盐玻

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璃表面处理所采用的处理剂主要是以水作为溶剂,处理剂的成分设计思路是增强氟锆酸盐玻璃表面与处理剂反应生成的生成物在水中的溶解度,没有脱离水溶液体系,水与氟锆酸盐玻璃表面的侵蚀反应只是被限制或减弱而没有被消除,因此依然存在失透和析晶的风险。

基于以上研究,本文引入非水有机物作为溶剂。氟锆酸盐表面处理剂的组成为:乙醇和戊醇的混合物作为溶剂,酸为盐酸和草酸混合物,添加剂为二氯化锆和乙二胺四乙酸混合物。由于处理剂的主体以有机溶液为主,由相似相溶原理可知,有机溶液对氟锆酸盐玻璃表面不会产生侵蚀,同时草酸电离出的草酸根与氟锆酸盐玻璃的锆离子以及其他碱土金属反应生成可溶性络合物,添加剂中的乙二胺四乙酸也是良好的络合剂,能与金属离子形成络合物,从而增加金属离子的溶解度,使其不沉淀于玻璃表面影响刻蚀的均匀性,所以氟锆酸盐玻璃表面溶解反应的一致性不受影响。本文研究了经非水有机溶液表面处理剂处理过的氟锆酸盐玻璃表面的组成与形态的变化以及光纤预制棒拉制的光纤的损耗和强度,研究结论对改进光纤预制棒的表面处理工艺以及探索有机溶液在光学冷加工中的应用具有参考意义。

表 1 两种表面处理剂的组成

Table 1 Compositions and proportions of two surface treating agents

Surface treatment agent	Solvent	Acid	Additive
Non-aqueous organic solution	Ethyl alcohol with mass fraction of 70% + amyl alcohol with mass fraction of 15%	Hydrochloric acid with mass fraction of 4% + oxalic acid with mass fraction of 6%	Zirconyl chloride with mass fraction of 3% + ethylene diamine tetraacetic acid with mass fraction of 2%
Aqueous containing solution	Deionized water with mass fraction of 86%	Hydrochloric acid with mass fraction of 4%	Zirconyl chloride with mass fraction of 10%

## 2.2 实验测试

### 2.2.1 氟锆酸盐玻璃表面成分的测试

通过 X 射线光电子能谱(X-ray photoelectron spectroscopy, XPS)对 1# 和 2# 片状氟锆酸盐玻璃样品表面进行元素含量测试,然后与玻璃本体元素含量进行对比。测试过程中腔内保持  $5 \times 10^{-7}$  Pa 左右的高真空。

### 2.2.2 氟锆酸盐玻璃表面形貌的测试

采用原子力显微镜 (Atom Force Microscopy, AFM)测试对比 1# 和 2# 片状氟锆酸盐玻璃的表面粗糙度。

### 2.2.3 氟锆酸盐玻璃光纤损耗的测试

将傅里叶变换红外光谱仪输出的红外光通过

## 2 实 验

### 2.1 样品的制备和处理

氟锆酸盐玻璃的组成为  $54\text{ZrF}_4 \cdot 14\text{BaF}_2 \cdot 4\text{AlF}_3 \cdot 8\text{LaF}_3 \cdot 20\text{NaF}$  (ZBLAN),制备所使用的原料均为高纯化学试剂,其中  $\text{ZrF}_4$  是以  $(\text{NH}_4)_2\text{ZrF}_6$  的形式引入。称取原料并搅拌混合均匀后放入铂金坩锅中,采用惰性气氛保护措施,并在铂金坩锅上面加盖以减少组分的挥发。在  $1000 \sim 1050$  °C 的硅碳棒电炉中熔制 40~60 min,玻璃液高温澄清均化后,将其浇铸在预热过的石墨模具上,然后迅速移入到马弗炉中进行退火,退火温度为  $310 \sim 330$  °C,保温时间为 3 h,并以  $5$  °C/h 的速度降温至室温。将退火后的玻璃样品研磨、抛光,加工成  $10 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$  的玻璃片以及  $\varphi 10 \text{ mm} \times 100 \text{ mm}$  的光纤预制棒两种形状以作为实验样品。

将氟锆酸盐玻璃的片状和棒状样品分别用两种表面处理方式进行处理,利用高纯乙醇和丙酮超声清洗处理后的样品,再利用氮气干燥处理得到洁净表面。水溶液表面处理剂处理后的样品记为 1#,非水有机溶液表面处理剂处理后的样品记为 2#。两种表面处理剂的组成如表 1 所示。

透镜耦合到光纤中,光纤的输出端使用红外功率探测器进行检测,调整光路使功率探测器的光强达到最大值。测试方法采用截断法,光纤的截断长度为 2 m,光纤外径为  $200 \mu\text{m}$ ,芯径为  $80 \mu\text{m}$ ,测试了 1# 和 2# 棒状氟锆酸盐玻璃样品拉制的光纤损耗。

### 2.2.4 氟锆酸盐光纤抗拉强度的测试

采用拉力万能试验机测试光纤的抗拉强度,测试了 1# 和 2# 棒状氟锆酸盐玻璃样品拉制的裸光纤,拉伸速率为  $2 \text{ mm/min}$ ,光纤直径为  $200 \mu\text{m}$ ,光纤长度为 1 m,1# 和 2# 拉制的光纤各测试了 100 根。

### 3 结果与讨论

#### 3.1 两种表面处理方式对表面的影响

光纤预制棒的冷加工工序为粗磨-精磨-抛光。粗磨和精磨的目的是使块状玻璃加工成棒型,所用研磨介质金刚砂的粒径一般为  $7\sim 40\ \mu\text{m}$ ,会在玻璃

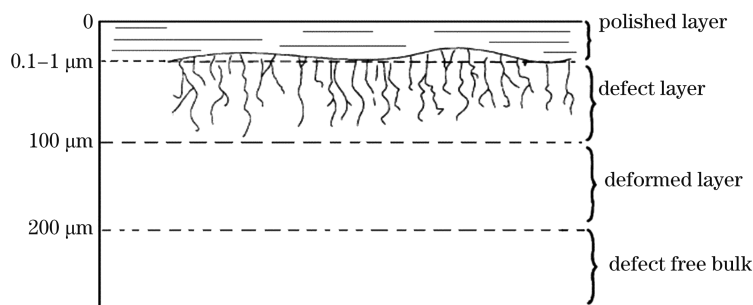


图 1 玻璃表面结构模型<sup>[27]</sup>

Fig. 1 Structure model of glass surface<sup>[27]</sup>

模型将表面分为抛光层、亚表面缺陷层以及变形层,表面以下  $100\ \text{nm}\sim 1\ \mu\text{m}$  区域是抛光物化反应形成的致密、高杂质浓度的抛光层,其构成了光学元件的光滑表面;抛光层以下  $1\sim 100\ \mu\text{m}$  区域是含有微裂纹和少量金属离子或金属氧化物杂质的亚表面缺陷层,微裂纹呈垂直表面向下延伸的树状结构特点;亚表面缺陷层以下为变形层和玻璃本体。抛光层的杂质主要来自于抛光液,一般为 Al、B、Ce、Fe 及 Zr 等抛光液中常见的元素成分<sup>[30-31]</sup>,随着深度的增加,杂质离子的浓度迅速减小;亚表面层的缺陷主要是微裂纹以及嵌入微裂纹中的抛光液的颗粒型杂质。一般采用酸刻蚀处理光学玻璃冷加工形成的表面缺陷(杂质和微裂纹),不同的玻璃体系对应不同的酸,如石英玻璃采用氢氟酸,钠钙硅酸盐玻璃采用氢氟酸,氟锆酸盐玻璃采用盐酸溶液,盐酸一般为水溶液。因此利用 XPS 测试对比了有机溶液表面处理剂和水溶剂表面处理剂对样品表面元素的影响,结果如图 2 所示,其中方法 a 为表面纳米  $\text{CeO}_2$  抛光,方法 b 为表面非水有机溶液处理,方法 c 为表面水溶液处理。

如图 2 所示,利用方法 a 处理后,表面元素含量和本体元素含量非常接近,只有表面的碱金属 Na 含量相对本体有较明显的减少,这是由于抛光所用的是  $\text{CeO}_2$  水溶液,在水溶液中氟锆酸盐玻璃表面易形成水化层,表面的  $\text{Na}^+$  与水溶液中的  $\text{H}^+$  发生交换反应,从而表面  $\text{Na}^+$  含量减少<sup>[11-15,32]</sup>。在相同时间、温度、酸溶液浓度条件下,利用方法 c 处理后,玻璃样品表面元素含量相比方法 b 处理后的表面元素含量下降得更多,这表明其刻蚀程度较大,其中作

表面沿纵深方向产生微裂纹。抛光的目的是为了降低表面粗糙度以获得光滑表面,所用抛光介质氧化铈的粒径一般在纳米级别,其可以消除大部分微裂纹但无法完全消除,抛光粉、杂质以及金属氧化物等纳米颗粒会渗透嵌入微裂纹尖端并被表面的抛光层所覆盖,从而形成亚表面缺陷层<sup>[27-29]</sup>,如图 1 所示。

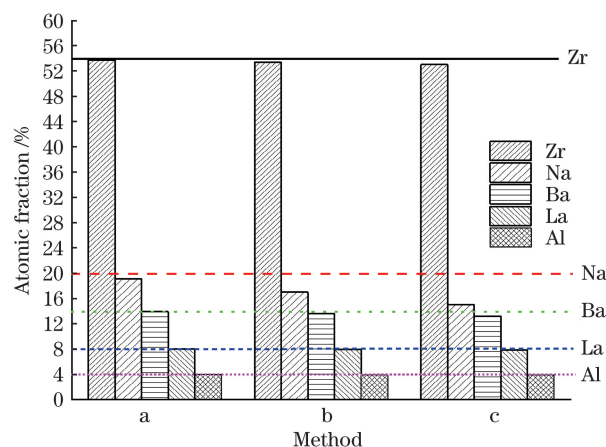


图 2 不同表面处理方式处理后氟锆酸盐玻璃的表面组成  
Fig. 2 Surface compositions of fluorozirconate glass treated by different surface treatments

为玻璃网络体的 Zr 以及作为玻璃网络修饰体的 Na 溶解的速度较其他 Al、La、Ba 更快,说明水溶液表面处理剂的刻蚀反应速度不均匀。水溶液表面处理剂处理后,表面元素含量变化最大的是与  $\text{H}^+$  发生交换反应而减少的  $\text{Na}^+$ ,其次是 Zr、Ba,这与文献<sup>[33]</sup>的研究结果一致。故相比于水溶剂表面处理方式,非水有机溶液表面处理方式处理后的表面元素含量与本体更加接近,说明有机溶液表面处理下反应更加均匀。

玻璃表面的粗糙度可以通过均方根粗糙度 ( $R_M$ ) 来表征:

$$R_M = \sqrt{\frac{1}{n} \sum_{i=1}^n Z_i^2}, \quad (1)$$

式中:  $Z_i$  代表每个点  $i$  相对于基线的高度;  $n$  代表测



试点数量。利用原子力显微镜对表面粗糙度进行测试表征,采用纳米  $\text{CeO}_2$  对一片状氟锆酸盐玻璃样品进行抛光,抛光后任取表面一个区域进行表面粗糙度测试,结果如图 3 所示。将该表面分为两部分,一部分涂上耐腐蚀材料,另一部分采用水溶液表面处理剂进行刻蚀,测试的表面粗糙度如图 4 所示。去除耐腐蚀材料,将经水溶液表面处理剂刻蚀的部分涂上耐腐蚀材料,再采用有机溶液表面处理剂进行刻蚀,测试的表面粗糙度如图 5 所示。

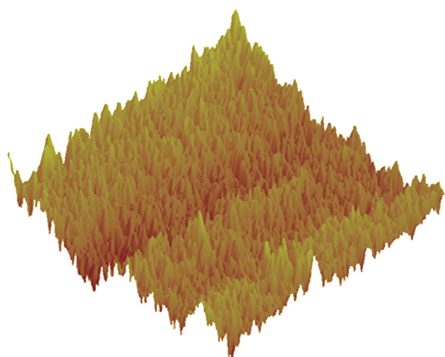


图 3 方法 a 处理后的样品表面粗糙度

Fig. 3 Surface roughness of sample after treatment by method a

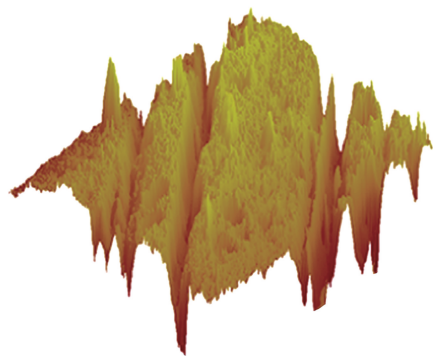


图 4 方法 c 处理后的样品表面粗糙度

Fig. 4 Surface roughness of sample after treatment by method c

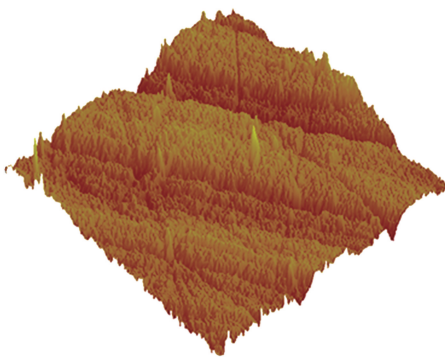


图 5 方法 b 处理后的样品表面粗糙度

Fig. 5 Surface roughness of sample after treatment by method b

对比图 3、4、5 可知,方法 a 处理后的  $R_M$  为 0.925 nm,方法 c 处理后的  $R_M$  为 8.971 nm,方法 b 处理后的  $R_M$  为 2.152 nm,可以看出,抛光所获得的表面粗糙度最低即表面平滑度最好,水溶液表面处理剂以及有机溶液表面处理剂对玻璃表面的作用只是单纯的化学作用,表面平滑度低于抛光表面。非水有机溶液表面处理剂处理后的表面粗糙度明显低于水溶液表面处理剂处理后的表面,说明非水有机溶液表面处理剂处理后的表面更平整。因此,相对于水溶液表面处理剂,非水有机溶液表面处理剂与玻璃表面的反应均匀性更好。

### 3.2 两种表面处理方式对光纤性能的影响

Sakaguchi 等<sup>[34]</sup>采用拉曼显微探针研究分析了氟锆酸盐玻璃光纤的损耗问题,认为散射源、杂质以及 O—H 等因素引起了光的散射和吸收,增加了光纤损耗,所以在玻璃原料的熔制、光纤预制棒的制造和加工以及光纤拉制等各个阶段都要杜绝这些因素的引入。在光纤预制棒的加工过程中,可能残留在棒表面的外来杂质主要为抛光液中的  $\text{CeO}_2$ 、杂质金属离子和氧化物颗粒;在光纤拉制过程中,金属离子可能会残留在芯包层间的界面处,形成吸收源,金属氧化物颗粒以及亚表面缺陷中嵌入的  $\text{CeO}_2$  抛光粉颗粒可能会残留于芯包层间的界面处,形成散射源,亚表面缺陷的微裂纹可能残留于芯包层界面或使界面产生气泡,从而降低光纤的抗拉强度;在加工过程中,水分子可能以 O—H 形式残留于光纤界面处,形成吸收源,且水分子会在玻璃表面形成水化层,水化层的存在可能使预制棒在光纤拉制过程中出现析晶现象,从而降低光纤强度。Hammer 等<sup>[35]</sup>采用 X 射线光电子能谱研究了水分子与氟锆酸盐玻璃表面的相互作用,认为水分子容易侵蚀氟锆酸盐玻璃表面,产生羟基氟化锆、氢氧化锆以及氟化钡和氟化镧。Pantano 等<sup>[32-33, 36, 12]</sup>研究了氟锆酸盐玻璃的水分子表面侵蚀机理,认为水分子对氟锆酸盐玻璃表面的侵蚀过程为:表面组分发生水解反应,  $\text{F}^-$  与水溶液的  $\text{OH}^-$  发生离子交换,溶液 PH 值降低,随着表面组分溶解物在溶液中的饱和,表面出现结晶现象并形成水化层,同时由于水分子的侵蚀作用,玻璃表面产生微裂纹。所以光纤预制棒拉制光纤前的表面处理有非常重要的意义,光纤预制棒的表面处理是去除表面的杂质以及钝化或去除微裂纹的有效手段。一般的表面处理都是采用水作为溶剂,加入不同的酸或添加剂,或者处理后再进行等离子刻蚀以去除水分子,本文利用了非水有机溶液表面处理

剂,二者处理后的光纤预制棒拉制的光纤损耗对比如图 6 所示,其中 A 为经有机溶液表面处理剂处理过的预制棒拉制的光纤损耗,B 为经水溶液表面处理剂处理过的预制棒拉制的光纤损耗。

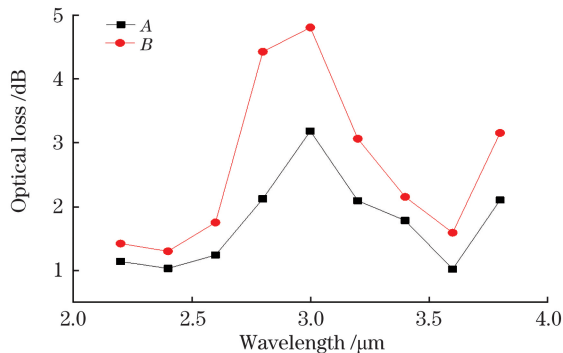


图 6 不同表面处理剂处理过的预制棒拉制的光纤的损耗  
Fig. 6 Optical loss of fluorozirconate glass fibres drawn from preforms after surface treatments with different solutions

可以看出,每个波长处的 A 都比 B 低,可见有机溶液表面处理剂对玻璃表面杂质的去除效果更好,所以光纤损耗更低。

光纤强度是光纤重要的力学性能,光纤强度及其分布取决于预制棒的质量,特别是表面质量,因为预制棒表面的杂质、亚表面的微裂纹及光纤拉制过程中残留在光纤表面的杂质会降低光纤强度。大多数裂纹以及杂质都是在光纤预制棒制作过程中出现的,所以在拉制光纤工艺之前改善预制棒表面质量是很有必要的<sup>[24,25,37-40]</sup>。预制棒的表面酸处理是应用最广泛、最有效的提高表面质量的手段之一<sup>[41]</sup>,石英玻璃预制棒一般采用氢氟酸水溶液,而氟锆酸盐玻璃预制棒则一般采用盐酸或者硼酸水溶液,虽然能去除或减少预制棒表面的杂质及亚表面微裂纹和杂质,但是氟锆酸盐玻璃易受水分子侵蚀,水分子以 O—H 的形式残留,会在玻璃表面形成水化层,使光纤在拉制过程中可能会出现析晶现象,既增加损耗又降低光纤的强度。本文提出使用非水有机溶液作为表面处理剂,二者处理后的光纤预制棒拉制的光纤断裂概率对比如图 7 所示,其中 C 为经水溶液表面处理剂处理过的预制棒拉制的光纤断裂概率分布,D 为经非水有机溶液表面处理剂处理过的预制棒拉制的光纤断裂概率分布。

光纤在拉力  $\sigma$  的作用下,其断裂累积概率  $F$  满足 weibull 双参数的分布<sup>[23,33,42]</sup>:

$$F(L, \sigma) = 1 - \exp\left\{-\left[\frac{L\sigma}{L_0\sigma_0}\right]^m\right\}, \quad (2)$$

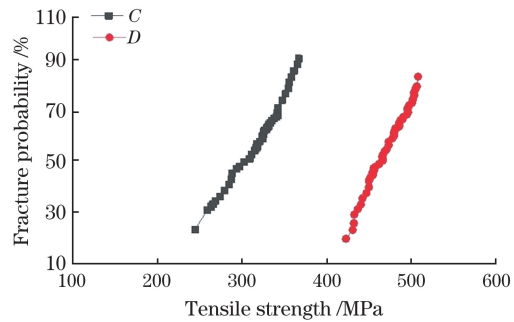


图 7 不同表面处理剂处理过的预制棒拉制的光纤断裂概率

Fig. 7 Fracture probabilities of fluorozirconate glass fibres drawn from preforms after surface treatments with different solutions

式中:  $L_0$  为标准的光纤试样长度,其为常数;  $L$  为光纤测试试样的长度;  $m$  为 weibull 指数,是描述光纤强度分布的参数;  $\sigma_0$  为断裂累积概率  $F = 63.28\%$  时的应力,也称特征强度,是 weibull 函数的形状参数。当断裂累积概率  $F = 50\%$  时,对应的应力  $\sigma$  为光纤的中值强度,常用来对比不同批次光纤的强度。由图 7 可以看出,经水溶液表面处理剂处理过的预制棒拉制的光纤中值强度为 300~350 MPa,而经有机溶液表面处理剂处理后的预制棒拉制的光纤中值强度为 450~500 MPa,强度提高了约 50%。说明非水有机溶液表面处理剂对氟锆酸盐玻璃表面杂质和微裂纹的去除效果优于水溶液处理剂;在光纤的拉制实验过程中,相比于水溶液表面处理剂,经非水有机溶液表面处理剂处理后预制棒没有出现析晶现象。

## 4 结 论

以氟锆酸盐玻璃的表面为对象,研究了一种有机溶液表面处理剂,与常规的水溶液表面处理剂相比,经有机溶液表面处理剂处理后,氟锆酸盐玻璃表面的元素含量和本体的元素含量更一致,且表面粗糙度更低,说明有机溶液表面处理剂与氟锆酸盐玻璃表面反应的均匀性更好。光纤实验显示:经有机溶液表面处理剂处理过的光纤预制棒拉制的光纤损耗更低、抗拉强度更高,说明有机溶液表面处理剂能更有效去除预制棒冷加工过程中出现的杂质和微裂纹,降低了残留于芯包层界面处的杂质引起的损耗,有效去除了预制棒表面的微裂纹,增强了抗拉强度;由于没有水分子的存在,预制棒表面无法形成水化层,这降低了光纤拉制过程中的析晶风险。

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# Surface Treatment of Fluorozirconate Glass Fiber Preform Using Nonaqueous Solution

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## Abstract

**Objective** Fluorozirconate optical glasses are widely used as fibers because of their excellent optical properties, such as their transparency in the mid-infrared wavelength range around 8  $\mu\text{m}$ . These glass fibers show a wide range of military and industrial applications, such as in the ultra-low loss, long, and repeaterless optical communication links. They are typically fabricated from the fluoro-zirconate glass preform by the rod-in-tube method that allows for precise control of fiber dimension and geometry. To a large degree, the fiber quality depends on the quality of the preform. Before fabrication of the fluoro-zirconate glass fiber, the preform must undergo optical cold processing, including grinding and polishing. After shown in the structure model of the glass surface in Fig. 1, defects, such as impurities, scratches and microcracks, are introduced on the surface and subsurface of the fiber preform during this processing. During the fiber fabrication process, the defects end up at the core/cladding interface, decrease the strength of the fiber, and increase the optical losses. An acid treatment is an effective method to enhance the mechanical strength of the optical glass surface and eliminate the surface and subsurface defects. In general, the preform surface of the fluoro-zirconate glass fiber is treated with an aqueous acid solution, such as hydrochloric acid or boric acid. However, the fluoro-zirconate glass surface degrades rapidly upon exposure to aqueous media or humid atmospheric environments because of its poor chemical stability. Therefore, the conventional surface treatment of fluoro-zirconate glass fiber preform by etching with an aqueous acid solution increases the surface roughness and creates a hydrated surface layer. It also causes precipitation of crystalline dissolution products on the surface, which increases the optical losses, decreases the tensile strength of the fiber, and increases the risk of devitrification during fabrication of the fiber. Therefore, it is more optimal to treat the fluoro-zirconate glass surface using a nonaqueous solution.

**Methods** A nonaqueous organic solution composed of organic solvent, mixed acid, and additives (Table 1) was formulated to treat the surface of a fluoro-zirconate glass fiber preform. The organic solvent was composed of ethyl alcohol and amyl alcohol, which cannot corrode the fluoro-zirconate glass surface. Therefore, a corrosion layer cannot be created. The mixed acid component was a mixture of hydrochloric acid and oxalic acid with a small amount of water, which was further diluted with an organic solvent. The amount of water used did not cause chemical etching of the surface. The additives used were zirconyl chloride and ethylene diamine tetraacetic acid, which are metal complexing agents that increase the solubility of the etching products and prevent their precipitation on the surface. The nonaqueous organic solution could more effectively remove the surface and subsurface defects caused by optical cold processing, without creating a corrosion layer.

**Results and Discussions** To compare the two different surface treatments (using an aqueous acid solution and a nonaqueous organic solution, respectively), we have studied the surface compositions of the fluoro-zirconate glass using X-ray photoelectron spectroscopy (XPS). The composition variation of the fluoro-zirconate glass surfaces treated by these two surface treatments is shown in Fig. 2. It is evident that the compositions of the fluoro-zirconate glass surface etched by the nonaqueous organic solution were closer to those of bulk glass for the elements, Zr, Na, and Ba. Furthermore, it is clear that dissolution of the surface compositions etched by the aqueous acid solution was quicker than that by the nonaqueous organic solution, and the chemical etching by the nonaqueous organic solution was more uniform and did not create a corrosion layer or precipitation leading to opaque crystalline surface deposits. By using atomic force microscopy (AFM), we have studied the surface morphology of the fluoro-zirconate glass surface treated with these two methods. The surface root-mean-square (RMS) roughness of the fluoro-zirconate glass surfaces was 0.925 nm after polishing with nano-CeO<sub>2</sub> (Fig. 3), 8.971 nm after etching with the aqueous acid solution (Fig. 4), and 2.152 nm after etching with the nonaqueous organic solution. The surface roughness after etching with



the nonaqueous organic solution was lower than that after etching with the aqueous acid solution. Furthermore, the morphology of the surface etched by the nonaqueous organic solution was better than that etched by the aqueous acid solution. This means that the chemical reaction between the nonaqueous organic solution and the fluorozirconate glass surface was more stable, and with the lack of precipitation of the reaction products on the surface to affect the etching, the surface was smoother. Etching of the fluorozirconate glass fiber preform surface with the nonaqueous organic solution results in a higher surface quality, which is useful for subsequent fiber fabrication. Figure 6 shows the optical losses of the fluorozirconate optical glass fibers fabricated from preforms with the different surface treatments. The optical losses of the fluorozirconate optical glass fiber fabricated from the preform etched by the nonaqueous organic solution were lower at different wavelengths than those fabricated from the preform etched by the aqueous acid solution. It is evident that the fluorozirconate glass surface treatment with the nonaqueous organic solution was more effective at eliminating surface and subsurface defects and removing impurities, which increases the scattering and absorption losses compared to the traditional surface treatment using aqueous acid solution. The weibull failure probabilities of the fluorozirconate glass fibers fabricated from preforms with the two surface treatments are displayed in Fig. 7. The median tensile stress at failure is about 300 MPa for the fiber fabricated from the preform etched by aqueous acid solution and about 450 MPa for the fiber fabricated from the preform etched by nonaqueous organic solution. Therefore, it is shown that fluorozirconate glass preform surface treatment with nonaqueous organic solution was more effective in removing failure-producing defects than that with aqueous acid solution.

**Conclusions** In order to decrease optical losses at the fluorozirconate glass fiber core/cladding interface, the method to treat the preform surface using nonaqueous organic solvents is investigated. When comparing the surface quality of the preform and the performance of the resulted fiber after treatment with nonaqueous organic solvents or traditional aqueous acid solution, it is evident that the treatment with the former allows for the fabrication of an fluorozirconate glass fiber with lower optical losses and higher strengths than that with the latter.

**Key words** materials; surface treatment; fibre preform; fluorozirconate glass; non-aqueous system; optical loss

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