JOURNAL OF MATERIALS SCIENCE 37 (2002) 5367–5369

Effect of distilled water on the optical properties and surface degradation of Zr-Ba based glass*

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Work has been performed to investigate the effect of distilled water on the optical properties and surface degradation of the glass known as ZBLAN, that could be employed as an optical fiber. Employing spectral techniques through the use of optical spectra, exposure of this material to an aqueous environment was found to cause weakening of the glass structure and a loss in signal transmission of the material. Also using methods normally applied in the corrosion of metals and alloys, like weight loss, our data has revealed that fluoride glass containing significant levels of Zr and Ba were highly unstable in the presence of water, produced a corrosion potential, and may possibly under go electrochemical rather than chemical dissolution, which in turn allowed formation of enriched Zr and Ba surface films. Presently the exact mechanism of degradation is unclear. This instability and degradation, showed an important deterioration in the optical properties of the glass, and brings into question the selection of Zr-Ba glass as optical fiber material or its use in electronic circuits where humidity may exist.

1. Introduction

In recent years, fluoride glasses have found many applications [1, 2]. However a new type of glass, ZBLAN, structured upon AlF_3, BaF_2 and ZrF_4 although discovered to have outstanding optical properties has poor chemical durability [3]. Due to the diffusion of water through protective cabling or changes in humidity leading to condensation, (for the above ground case), the optical properties of the fiber would be impaired. It was therefore felt necessary to collect data and analyze the behavior of ZBLAN in an aqueous environment. The study was conducted from two points of view, chemical and optical stability.

In the work carried out with the Zr-Ba-Al glass, corrosion behavior similar to that of a metal/alloy was discovered. Normally in water, glass is very stable, there is no measurable weight loss and a corrosion potential is not measured. However in our case, with ZBLAN, it was found that degradation could be monitored using techniques reserved for metals and alloys. In conventional glass water absorption is minimal [4], its surface resistant to acids [4], (except HF), and organic solvents have no great effect. It has been reported that the fluoride glasses possess remarkable properties, such as low refractive index, high transparency, low dispersion and Rayleigh scattering. Further fluoride glasses [5, 6] (with heavy metals) such as zirconium are transparent from 0.19 μm to 7.6 μm. However LiF, AlF_3 and in some cases BaF_2 dissolved at faster rates than either ZrF_4 or LaF_3.

2. Experimental

The experimental analysis was divided into two sections to see the influence of distilled water on the surface degradation of ZBLAN and optical properties. The composition of the glass, (ZBLAN), in disk form of diameter 15.2 mm, is given Table I.

Surface degradation analysis was carried by employing the following techniques;

1. Monitoring the corrosion potential of ZBLAN as a function of time. In this case, an electrical connection was made to the specimen which was then mounted in an araldite resin mould. The cross-section of the glass was then exposed for polishing and testing. Ag/AgCl (silver silver chloride, SSC) was used as the reference electrode. To prevent test solution contamination the reference electrode was placed in separate container,

*Work was carried out at the GIK Institute of Engineering Sciences and Technology.

TABLE I Glass composition (mol%)

No	Component	% in Glass
1	AlF_3	4.0
2	BaF_2	14.0
3	NaF	20.0
4	ZrF_4	56.0
5	LaF_3	6.0

also filled with distilled H_2O and connected to the test cell via a conducting bridge.

2. Measuring the weight loss of a given piece of ZBLAN after various exposure times up to 180 hours at 30°C. This was done down to an accuracy of 1 mg.

3. Scanning electron microscopy to see the effect of the liquid environment on the surface morphology of ZBLAN as well as changes in surface chemical composition. For conduction purposes specimens were carbon coated.

The optical characterization was performed using FT-IR (Fourier Transform - Infra Red) and Perkin Elmer Lambda - 19 spectrometer; [UV (ultra violet)/VIS (visible)/NIR (near infra red)]. This equipment was used to obtain transmission/wavelength spectra on individual disks of ZBLAN after exposure in distilled water for, 30 minutes, 1 hour, 2 hours, and 4.5 hours. A sample not subjected to distilled water was also tested.

For all tests ZBLAN was polished down to 1 μ, followed by degreasing in acetone and drying in hot air.

3. Results and discussion

Quite remarkably with ZBLAN a corrosion potential was measured which is unusual for glass type material. This implies that the mechanism for ZBLAN dissolution is unclear and could be electrochemical, chemical or involve both. When the same test was performed with ordinary or AlF_3 glass based glass containing no Zr or Ba no corrosion potential was measured.

Fig. 1 gives the variation of this potential as a function of increasing time. The data indicated that an anodic shift in potential over the first hour, from −9 mV to −6 mV occurred. For the next 11 hours the potential as shown in Fig. 1 then only drifted by 1.5 mV. The results suggest that over the first hour conditions were unsteady, where surface dissolution was initiating and spreading over the immersed glass. Beyond the second hour the minor change in potential shows that the dissolution process was now underway over the entire surface of the material and taking place under more steady state conditions. Evidence of this was gained when a white surface product showing uniform coverage was observed on the glass. A more detailed examination using scanning electron microscopy after exposure revealed the formation of a bulky loose surface product, consisting of cracked plates, where the interior of the plate contained rounded particles. Due to the presence of the product the optical transparency of the material was markedly reduced. This is illustrated by the spectra in Fig. 2, produced after various exposure times.

Measurements related to material weight loss in distilled water, Fig. 3, show a decrease of 130 milligrams (mg) after 170 hours, where as with AlF_3 based glasses such serious chemical attack was not encountered [7]. The chemical composition at the surface of the glass, before and after exposure to distilled water is given in Table II.

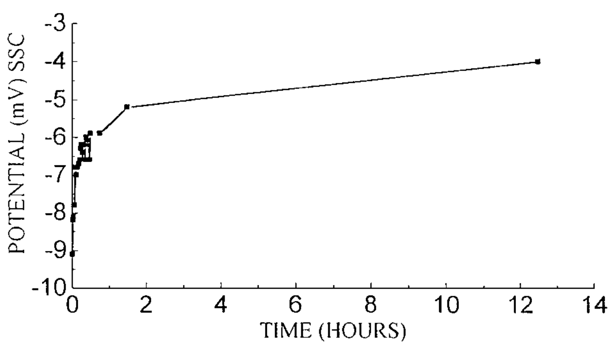

Figure 1 Corrosion potential as a function of time of ZBLAN in distilled water.

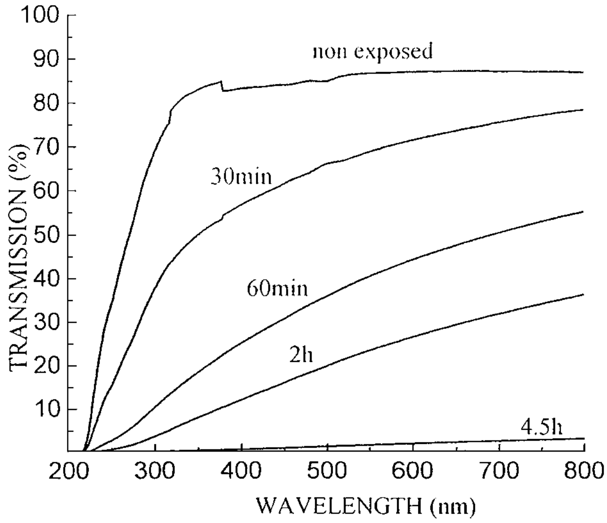

Figure 2 UV/VIS/NIR spectra for non exposed and exposed ZBLAN at various times.

TABLE II Surface composition of ZBLAN before and after exposure in distilled water

No	Element	% Before water immersion	% After water immersion
1	Na	16.67	Not detected
2	Al	5.25	Not detected
3	Zr	49.91	63.48
4	Ba	19.25	24.96
5	La	8.93	11.57

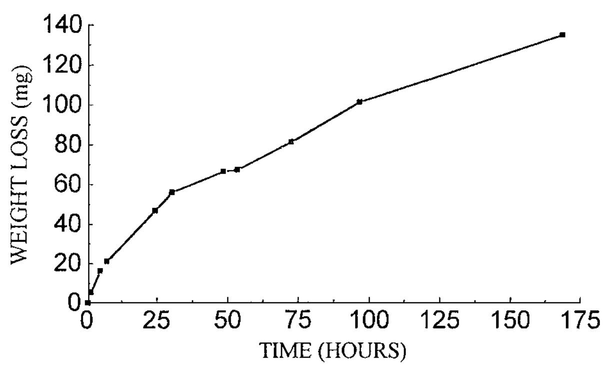

Figure 3 Weight loss versus time for ZBLAN in distilled water.

It is significant that as a result of water attack the only surface elements detected were Zr and Ba and La, and also with increased concentrations (La to the least extent). Based upon the above data it is thus suggested that the surface degradation of ZBLAN may have occurred through the electrochemical oxidation of Zr and Ba, balanced by the cathodic reduction of oxygen, and resulting in the formation of a hydrated zirconium/barium surface product. This mechanism implies that the material itself is conductive. The problem with this explanation is both these elements are already in their highest oxidation states. Thus the mechanism could involve a reduction in valence state followed by oxidation. Clearly further work must be performed to substantiate this claim.

4. Conclusions

1. It is believed that the surface degradation of ZBLAN occurred through an electrochemical mechanism, however presently this is not clear. Unusually the material produced a time dependent corrosion potential.

2. When immersed in distilled water ZBLAN underwent significant weight loss.

3. Dissolution of the glass produced a loose plate like surface product containing increased amounts Zr and Ba as compared to their bulk concentration before water immersion. Due to the formation of such films the optical and transmission properties of the fiber deteriorated.

Acknowledgment

The authors are grateful to the GIK Institute for the use of the laboratory facilities within the Faculties of Engineering Sciences and Metallurgy and Materials Engineering.

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Received 27 June 2000
and accepted 27 March 2002