Second Annual Report

GRADED INDEX ANTIREFLECTIVE COATINGS FOR GLASS

MASTER

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I. INTRODUCTION

M.I.T. is conducting research which will lead to a process for forming broad band antireflective (AR) coatings on glass. Use of these coatings increases the extractable heat from flat-plate solar collectors by 30-50% compared with their performance under equivalent solar flux, surface temperature and ambient conditions without broad band AR coatings. Conventional single layer or multilayer coatings do not reduce reflection losses significantly over the entire solar spectrum even though they are extremely effective in the narrower visible portion of the spectrum. Thus, they contribute very little added value and cause significant incremental manufacturing and maintenance costs. Graded index surface films can virtually eliminate reflection losses if controlled properly. We and others^(1,2) have demonstrated graded index films on a Borosilicate glass (Corning Glass Works No. 7740, PyrexTM). While glass treated this way exhibited adequate optical properties, the glass itself, cannot be fabricated by the float glass process because of excessive working temperatures, and consequently is too expensive for solar applications. The objective of our work is to define glass compositions and processing steps which will result in graded index surface films (which exhibit broad band AR characteristics) on glasses which can be fabricated by the float glass process. We have proceeded on the basis that the surface films must be characterized in detail and the absence of an adverse effect on long term strengths must be verified.

The mechanism by which these graded index surface films are produced on glass surfaces consists of preferentially etching one phase from a phase separated glass. The film which remains consists of a porous structure in which the fraction of solid phase increases continuously from the free surface toward the bulk glass. Scattering effects are eliminated by limiting the size of the pore structure to dimensions which are substantially less than the wavelength of light. With this structure, the local index of refraction is proportional to the fraction of solid phase which is present.

Our characterizations are intended to define the microstructural and chemical nature of the surface film throughout its thickness. We are defining the characteristic dimensions, the morphologies, the volume fractions and the chemistries of the phases (solid and pore) throughout the thickness of the film. Based on this information, optical characteristics can be calculated

and compared with observed results. The work at M.I.T. has focused on microstructural and chemical characterizations this year. The University of Massachusetts, under the direction of Prof. J.E. Ritter, has continued to study the mechanical characteristics of these glasses.

All of our work to date has been with borosilicate glass (CGW No. 7740). We regard this as a model glass which is extremely important to the program because so much work has been done on studying phase separation in this glass and also it is available in the large, uniform quantities needed for this program. Since the scale of the observations we are attempting to make on these porous surface films is generally beyond the current state of the art, it is extremely important to work with a glass host whose microstructural and phase characteristics are known. Once characterization techniques are verified, it will be possible to conduct compositional and process research with confidence.

II. RESULTS

A. MICROSTRUCTURE

Understanding the microstructural details of the process whereby a successfully anti-reflective surface is developed on glass necessitates investigation of two different, but interrelated aspects of the process; the phase separation heat treatment, and the selective etching treatment. We need firstly to verify the phase separation by direct observation, and to characterize the resulting microstructure in terms of scale, morphology, volume fractions and composition. Although a good understanding of the phase separation process is fundamental, it is not sufficient to yield a full description of the etched anti reflective structure. In particular, if the small scale topography is determined only by the as phase separated microstructure (and this requires adequate demonstration), what are the larger scale characteristics of the surface layer, e.g., its thickness and its surface topography? Solution of these problems will enable the variation of the "volume fraction porosity" with depth in the layer to be determined, a parameter of importance in forming a link to theoretical treatments of the optical behavior of the anti-reflective layer.

To avoid scattering the incident light, the scale of the microstructure must

be well below the wavelength of the incident radiation. Previous work^(1,2,3) on the model system (CGW No. 7740 glass) suggests a scale of order 20-200 Å. On this small scale, accepted techniques of microstructural characterization in such systems have been unsuccessful in yielding usefully, detailed information. Therefore, we have had to develop new techniques, and to use instruments at the limits of their resolution. Some discussion of the techniques we have applied, their evaluation, and their capabilities is presented below. Despite many problems, considerable progress has been achieved, as is detailed in the sub-section on results. We conclude this section with some discussion of these results and their significance for the present and future status of this work.

1. Techniques

a. Replication

The conventional method of studying phase separation and similar phenomena in glasses has been that of replication of a selectively etched surface and examination of the replica in the transmission electron microscope. In the initial stages of our microstructural investigation we made a careful and extensive evaluation of the replica method as applied to our system. Resolution of topographical features is limited, theoretically, by the grain size (commonly 50 Å) of the heavy metal layer used to 'shadow' the replica by evaporative deposition at some predetermined angle and the ability of the polymer to transfer small scale features. Our study showed that variation of the shadowing angle caused images to be produced that would be interpreted quite differently if seen separately. This in particular, but also other features of the method, for example the process of applying plastic film to the original surface and then stripping it off by pulling it with tweezers, caused us to doubt the accurate interpretation and reproducibility of this method, as commonly practiced, for feature sizes below the order of 1000 Å. This technique thus yielded to a large extent in favor of high resolution scanning electron microscopic examination. This followed demonstration to our satisfaction that both techniques were in agreement as to the microstructures observed.

b. Scanning Electron Microscopy (SEM)

The recent acquisition of a state of the art scanning microscope (an AMR 1000 A), with resolution approximately $70 \text{ \AA}$, gave the possibility of a more direct observation of the selectively etched glass surface than by the replication technique. Observation of the surface is not quite direct, as it is necessary to coat the surface with a layer having good electrical conductivity and secondary electron emission characteristics. Experimentation with different coatings was undertaken, and a two-part process involving deposition of a thin layer of a carbon ($20\text{-}40 \text{ \AA}$) followed by a layer of gold-palladium alloy ($100\text{-}150 \text{ \AA}$) has been selected as being most successful. The coating procedure is considerably simpler, and thus less susceptible to artifact introduction, than the many-step replication process, but may obscure very fine details, for example by 'filling in' small pores. We have verified that the structures observed are not solely coating artifacts.

c. Transmission Electron Microscopy (TEM)

Both the above methods give information on the topography of the etched surface, but neither have sufficient resolution to elucidate the small scale features in the 7740 glass system. Thin film TEM has ample resolution ($5 \text{ \AA}$ or less) to examine the detailed microstructure of the phase separation, but cannot be used to directly observe the anti-reflective layer topography. In this sense, the two techniques (SEM and TEM) are complementary. Direct transmission has its own problem, namely, development of sufficient contrast between the two phases. Because both phases are amorphous (precluding so called 'diffraction contrast' mechanisms) and their constituent elements have very similar scattering properties (so that the 'absorption contrast' is very small), it has not been possible to obtain contrast from as-thinned "phase separated" specimens (prepared using the ion milling technique). However, a technique has been developed in which the thinned specimens receive a light selective etch (ideally on one side only), allowing a simple mass-thickness contrast mechanism to reveal the microstructure, with good results. As in SEM, the specimens must be coated (from the un-etched side) with a thin carbon layer to eliminate charging effects, but unlike SEM, this layer does not contribute

to the development of contrast. The development of a technique capable of resolving fine scale phase separation in such glass systems is essential for this program and is of major interest to the scientific community.

d. Scanning Transmission Electron Microscopy (STEM)

The STEM may be used to obtain both TEM micrographs as described above, and also SEM micrographs (with possibly 20 Å resolution; this option will become available in the near future). Its most important contribution to the study, however, is in giving the possibility of chemical analysis of the separate phases. In this technique, a small electron probe excites a small portion of the glass, generating X-rays characteristic of the elements present. Unfortunately the light elements in the glass (Na, B, O) cannot be detected at present (a "windowless" detector will be installed soon) using the X-ray signal. Another detection mode has recently become possible namely, energy loss spectroscopy. Unfortunately, quantification of electron energy loss data is not yet possible. Because of these and other more practical difficulties (which have also nearly been solved), this type of chemical analysis of glass phases is in a primitive stage, but has prospects of rapid advancement.

2. Results

Perhaps the only characteristic of the anti-reflective layer that can be established by replication techniques with any confidence was that two levels of feature size existed: a larger pore-and-ridge structure of dimension 1000-2000 Å and a 'background roughness' of much smaller size, perhaps 100-200 Å. This has been corroborated by SEM observations, which show the pore-and-ridge structure but also cannot resolve the background roughness clearly. Recent TEM work has established the existence and form of the small scale structure. Through a combination of the SEM and TEM results, and chemical analysis (principally by selective etching rate measurements), we now feel that we have a good qualitative understanding of the microstructure development, and have begun to quantify relevant parameters. To summarize: 1. Heat treatment of the bulk glass at 600°C produces separation into two co-continuous phases (of approximately equal volume fraction). All our results are consistent with this taking

place by a spinodal decomposition mechanism, in which the microstructure slowly coarsens while the compositions of the phases move toward the equilibrium values.

2. Some separation may already have taken place in the as-received glass. This is difficult to determine with the etched sample in TEM as the compositional difference appears to be very small, and the 'boundaries' are not at all distinct.

3. The microstructural scale increases slowly with heat treatment time, and is of the order 80 Å after 3 hours at temperature. As the annealing time increases to 25 hours, the scale increases to approximately 150 Å. After 25 hours, the phase boundaries have become quite distinct. Small angle X-ray scattering measurements on the CGW No. 7740 glass (private communication by M. Tomozawa) gave a scale of 100 Å for 2 hours heat treatment, and 180 Å for 23 hours heat treatment. Both the magnitudes, and more importantly, the trend of these results agree quite closely. The X-ray measurements indicate a continuing increase in size with heat treatment time. 4. The selective etch treatment preferentially removes the high-alkali phase (confirmed by chemical analysis with STEM in the energy loss mode). Results of etch rate experiments and TEM observations are consistent with this occurring progressively faster, as the heat treatment time is increased. Progressively increasing selectivity may also occur if the compositions are moving only slowly toward equilibrium. This has yet to be confirmed. Hence, the depth and characteristic scale of the anti-reflective layer is thus quite a sensitive function of heat treatment time, for times less than about 10 hours. With increasing heat treatment time, and increasing layer depth, a larger-scale 'pore' or 'pore-and-ridge' structure develops. Presumably this is due to uneven removal of the high silica phase by the etching solution, after its exposure, and is imposed upon the finer scale sponge-like structure.

3. Discussion and Conclusions

It has not been an easy task to perform a detailed microstructural investigation in this 'model' system. At least three pieces of the work undertaken in the course of doing so are new developments which will ultimately be suitable for open publication: the critical evaluation of the replication technique; the new thin-film preparation technique; and the detailed confirmation of spinodal decomposition in this system. We now have a good

qualitative understanding of the microstructure development, and are rapidly quantifying that understanding. The two outstanding problems at present are achieving quantitative stereomicroscopy in the SEM for the large-scale pore sizes and depth, and quantifying the changes in chemical composition of the two phases. When this data is available, it should allow a close simulation of the optical properties by computation from a theoretical model. It should be emphasized that there is no single technique that will fully characterize the microstructure: a combination of both SEM and TEM is necessary now, and it appears that it will always remain so.

Extension of these characterization techniques to other systems is now possible. This should be straightforward for alkali-silicate glass systems, or to other systems where a 'quick survey' technique that will verify the existence of phase separation in any arbitrary system, since the separation of two glassy phases is a relatively subtle change in the material. The good agreement between our results and the small angle x-ray scattering results of Tomozawa indicate that small angle x-ray scattering might help survey materials for phase separation behavior. For the same reasons, etch rate and, possibly, viscosity measurements might also be of use, and would further indicate whether the phases are discrete or co-continuous.

B. CHEMICAL CHARACTERIZATION

The objective of the chemical characterization is to provide a basis for analyzing the optical characteristics of the anti reflecting film. We are trying to characterize the variation in composition as a function of depth into the film. Combining this information with our knowledge of the volume fractions of the two phases present in CGW No. 7740 glass will allow us to calculate the porosity gradient as a function of depth. A refractive index gradient function can be calculated based on porosity and compositional gradients. Reflectance and transmittance characteristics can then be calculated directly.

Two chemical characterization techniques have been used to analyze the surface films. In addition to Auger and Secondary Ion Mass Spectrometry which yield direct characterizations, we are beginning to analyze the materials removed during film formation to provide an indirect characterization.

1. Auger Electron Spectroscopy (AES)

AES analysis involves the bombardment of the sample surface with an incident beam of electrons. Subsequent radiationless de-excitation of an atom on the surface may occur by the emission of Auger electrons. Usually a cylindrical mirror analyzer (CMA) is used to measure the Auger electrons which gives the output in the form of a differentiated energy distribution function. Elements are identified by inspection of the presence of one or more peaks at particular characteristic energies. AES has high surface sensitivity with a depth resolution, typically 3-30 Å, determined by the Auger electron escape probability.

Generally, the peak-to-peak height of the differentiated Auger peak is proportional to the quantity of the specific element present at the surface. Thus, elemental identification as well as semi-quantitative information is provided. Sputtering with a positively charged inert gas like Ar^+ removes layers of atoms from the surface. Auger analysis coupled with ion milling enables us to evaluate a compositional profile as a function of depth.

Auger analysis for glasses is fraught with problems owing to their insulating nature and high mobility of alkali ions under the influence of the electron beam. The incident beam electrons must be provided with a conducting path through the sample otherwise a build-up of electronic charge results on the sample surface, disrupting the detection of Auger electrons. We have minimized charging problems by using a glancing angle for the incident electron beam relative to the sample surface. This results in an increase in the number of secondary electrons leaving the surface and establishes a relatively stable charging condition.

We have analyzed CGW No. 7740 glass in the as received condition and with anti reflecting films in the M.I.T. AES facility, (SAM 590A-Physical Electronics Ind.). We have observed all anticipated elemental species in the glass i.e. Si, B, Na, Al and O. Sodium is very mobile in glass under the electron beam and the Na Auger signal decays in a matter of a few seconds, rendering it very difficult to collect reliable data. One way to overcome this problem is to cool the sample stage to liquid Nitrogen temperatures. This decreases Na mobility allowing for a few minutes of analysis. We are in the process of setting up a liquid N_2 sample stage.

Sputtering with Ar^+ ions to do depth profiling presents a positive charging

problem due to the insulating characteristics of the glass. We have been successful in minimizing this source of positive charging by depositing a 300-400 Å layer of gold on the sample surface and having a 300-600 µm hole in the coating where the glass surface is exposed for Auger analysis. Gold coating tends to stabilize the positive charge build-up on the surface.

Relative concentrations of B, Si, and O have been profiled as a function of depth into the layer up to 1800 Å from the surface. Na could not be detected due to its high mobility and the Al content on the anti reflecting film surface was too low to be detected. Profiles of B, Si, and O remained essentially constant with depth. We expect the concentration of Si to remain constant throughout the film. In the selective etching process for the formation of the anti reflecting film, most SiO₂ present in the low silica (leachable) phase is left behind in the pores. We did expect B concentration to increase with depth and reach a constant level in the bulk glass. We are doing more experiments to resolve this anomaly.

The investigation of craters generated by ion milling using Interferometry and high resolution scanning electron microscopy shows that the bottom of the craters had a characteristic roughness and curvature across their diameters. These asymmetric crater profiles can lead to inaccuracies in Auger results. We plan to raster the ion beam to eliminate crater effects.

We have also analyzed the elemental compositional profiles in Auger by polishing through the anti reflecting film at a 5° angle. Ni was deposited on the glass surface prior to polishing to act as a fiducial. The wedge obtained though the surface increases the apparent films' thickness (from 1 to 10 µm) ten fold. The incident electron beam was scanned horizontally from the Ni-film to film-glass interface. Relative concentrations of Si, O, B, and Al were measured as a function of depth into the film. Analysis from the surface up to 4 µm in depth showed Si, O and B concentrations increasing with depth up to 1 µm and remaining essentially constant afterwards, whereas Al concentration showed no change from the surface into the bulk. The results obtained are anomalous and we are looking into possible artifacts which could have been introduced in polishing to resolve this problem.

In AES, the actual intensity signal of Auger electron current (I_i) is given by:

$$I_i = R \cdot I \cdot r \cdot \sigma_i \cdot w_{AE} \cdot \lambda_{AE} \cdot \bar{C}_i$$

where:

- Γ = Analyzer transmission
- I_p = Primary electron current
- r = Backscattering factor
- λ_{AE} = Mean escape depth of Auger electrons
- σ_i = ionization cross section
- W_{AE} = Probability of an Auger transition
= f (sensitivity factor)
- $\bar{C}_i$ = Mean volume
- R = Surface roughness factor

The primary ion current, I_p , is difficult to measure and the measurements made have a precision of $\pm 20\%$. The sensitivity factor is a function of the element and can be approximated using published data. Surface roughness factor has to be empirically determined and may vary from sample to sample depending on the surface topography. In view of the imprecision in the above measurements, AES is only useful for an order of magnitude estimate.

2. Secondary Ion Mass Spectrometry (SIMS)

In the SIMS technique the surface of the sample is impinged with a beam of ions. The energetic primary ions strike the surface, transfer their kinetic energy to the surface atoms causing them to be sputtered away. A portion of the sputtered atoms become ionized positively or negatively and these ions then are collected and analyzed by a suitable mass spectrometer.

We have performed extensive SIMS analysis on glasses using a Cameca IMS-3f Ion Microprobe-Cameca Instruments Inc. It uses O^- as the primary ion source, has a spatial resolution of 150-200 μm and the depth resolution is 0-50 $\text{\AA}$. The primary beam is rastered over a 500 μm square, whereas the secondary ions are collected from a 150 μm square which is concentric with 500 μm square. Mass spectra taken at the surface of as received CGW No. 7740 and anti reflecting film glass have shown the presence of all the major element species present in glass i.e. Si, O, B, Na and Al. Analysis of Na with reactive sputtering of O^- does not present a problem as was encountered in Auger analysis.

Compositional profiling as a function of depth was performed on as received CGW No. 7740, a fracture surface of as received CGW No. 7740 and

antireflecting film glass. We probed the as received glass up to a depth of 1000 Å monitoring relative concentrations of Si, B, Na and Al and saw no change with depth, which is what we expected. A plot of relative concentrations of Si, B, Na, Al and O for fractured as received glass also remained essentially constant with depth of up to 600 Å. Again, this is what we expected since we are in the bulk glass. We probed a depth of 5000 Å in case of antireflecting film glass. The plot of relative concentrations of B, Al, and Na showed a steady increase while concentrations of Si and O remained essentially constant as a function of depth into the film. These results are in accordance with our expectations. We are doing more work to improve our technique and interpretation of these results.

The sputtering rates for silicate glasses are very low i.e. approximately 30 Å/min. Removal of a 1.0 µm layer of glass will take about 5.5 hours. Controlling the fluctuations in the incident beam and instabilities in the system over a time period of this sort makes this analysis an extremely arduous task.

In SIMS, the secondary ion current, I_s of a given element A measured at the collector is proportional to the primary ion current, I_p , the ion yield, ϕ_A = number of secondary ions of A / number of primary ions, C_A = the concentration of the element A, and Γ = the transmission of the mass spectrometer.

$$I_s = I_p \cdot \phi_A \cdot C_A \cdot \Gamma$$

I_s , I_p and Γ are measured in SIMS, so concentration of A can be calculated if the ion yield for A is known. Ion yield, ϕ_A has to be determined for each element and it may be a function of the matrix it is present in. Data on the ion yields and investigation of matrix effects in glasses is scarce because of the fact that the application of SIMS to glass analysis is a very recent development. So presently SIMS can, at best, give an order of magnitude estimate of concentrations.

3. Solution Analysis

We are in the process of performing Quantitative Atomic Absorption

Analysis on the etching solutions. By obtaining concentrations of each element released into the solution from the glass surface, we can determine the composition of the leached glass surface. A compositional profile can be established by measuring the concentrations of the elements released into the solution at different etching times.

We are also doing weight loss measurements for different heat treatment and etching conditions. An etching rate curve will allow us to determine the dissolution mechanism. The information obtained by the solution analysis when coupled with AES and SIMS should allow us to profile composition as a function of depth.

C. STRENGTH AND FATIGUE BEHAVIOR

To determine the effect that an anti-reflective coating has on the strength and fatigue behavior of a borosilicate glass (CGW No. 7740), test apparatus was constructed to measure the biaxial strength of specimens $3 \times 3 \times 0.125$ inches. This apparatus was designed to utilize two different biaxial loading configurations, concentric ring and 3-ball-piston.⁴ To measure the effect of the various processing steps on the glass strength, tests were conducted in mineral oil at a stressing rate of 3.12×10^{-1} MPa/s to minimize fatigue effects. The fatigue behaviour of the glass after a given processing step was determined by measuring the strength in distilled water at two different stressing rates, 3.12×10^{-1} and 3.12×10^{-4} MPa/s. From this dependency of strength on stressing rate, the fatigue resistance constant N^* was determined.⁵

Preliminary strength tests were first conducted to compare as-received specimens to those containing an anti-reflective coating. These results are summarized in Table I. It is evident from the concentric ring tests that the samples containing an anti-reflective coating are significantly stronger than the as-received specimens. This is undoubtedly due in part to the chemical polishing that the anti-reflective coated samples received as part of their processing. The fatigue resistance constant N for each of the glasses tested is given in Table II. These results show that although the samples containing an anti-reflective coating have nearly twice the strength of the as-received specimens, the fatigue resistance of the two glasses are similar. Also, the

* Greater fatigue resistance is signified by higher N values.

results show that the fatigue resistance is independent of the biaxial loading configuration; however, the strength measured in the 3-ball-piston test is greater than that determined by the concentric ring test because of the much smaller area of the glass that is placed in maximum tension. The fatigue resistance of these glasses ($N \approx 35$) compares favorably with previous results on Corning No. 7740,^{6,7} which indicates that the fatigue behavior is not affected by the anti-reflective coating. It should be noted that fracture in all of these specimens originated in the region of maximum stress with cracks radiating out from the fracture origin. This fracture pattern is quite typical of glass tested in biaxial loading.

A second series of tests were conducted to measure the strength behavior of the glass after various processing steps. These results are summarized in Table III. Comparing the tests conducted in mineral oil using the 3-ball-piston loading configuration, it is evident that processing significantly effects the strength. Heat treating increases the as-received strength from 278 to 454 MPa and chemical polishing further increases the strength from 454 to 610 MPa. The selective etch necessary to produce the anti-reflective coating caused a decrease in the strength from 610 to 356 MPa. The fully processed glass remained stronger than the as received glass even though in this test series there was an apparent decrease in strength as the process progressed. Since it is not expected that heat treating alters the strength controlling flaw, these results suggest that the phase separation that occurs during heat treating causes the glass to have a greater fracture toughness. Evidence for this hypothesis is shown in K_{IC} measurements (Table IV) where K_{IC} of the as-received glass is less than that of glass given the full processing treatment.* On the other hand, chemically polishing glass is well known to reduce the severity of the strength controlling flaws and this increases the strength as shown. Since the selective etch drastically reduced the strength of the glass, it is believed that the porous surface structure that is produced by this process must contain more severe strength controlling flaws. It is quite possible that the pores in the surface layers act as strength controlling flaws.

The fatigue resistance constant of the glasses in this second series is summarized in Table V. Unfortunately, there appears to be no consistent trend in the results with N values ranging from 6.9 to 28.7.

* Since K_{IC} is measured by propagating a large crack through the glass, it is not believed that the anti-reflective coating of the fully treated glass effected the K_{IC} determination.

Table I. Summary of Strength Results From First Series of Tests

Processing Treatment +	Loading Configuration	Test Environment	Stressing Rate (MPa/s)	Strength (MPa)	Coefficient of Variation	No. Samples
A-1	concentric ring	water	1.25×10^{-1}	48(+ 10) [†]	0.21	25
	concentric ring	water	1.25×10^{-3}	42(+ 8)	0.17	25
A-1	3-ball-piston	water	3.12×10^{-1}	96(+ 11)	0.11	25
	3-ball-piston	water	3.12×10^{-4}	81(+ 13)	0.16	25
A-4	concentric ring	water	1.25×10^{-1}	83(+ 12)	0.14	25
	concentric ring	water	1.25×10^{-3}	73(+ 12)	0.16	25

+ A-1 signifies as-received and A-4 signifies heat treatment followed by chemical polish, followed by selective etch.

† Number in parentheses represents one standard deviation.

Table II. Summary of Fatigue Resistance (N) Results From
First Series of Tests

Processing Treatment	Loading Configuration	Test Environment	N
A-1	concentric ring	water	31.7
A-1	3-ball-piston	water	40.1
A-4	concentric ring	water	35.3

Table III. Summary of Strength Results From Second Series of Tests

Processing Treatment +	Loading Configuration	Water Environment	Stressing Rate (MPa/s)	Strength (MPa)	Coefficient	No. Samples
B-1	3-ball-piston	mineral oil	3.12×10^{-1}	278 (+ 84)	0.30	50
		water	3.12×10^{-1}	216 (+ 57)	0.26	50
		water	3.12×10^{-4}	167 (+ 45)	0.27	50
B-1	concentric ring	water	3.12×10^{-1}	102 (+ 15)	0.15	25
		water	3.12×10^{-4}	43 (+ 15)	0.35	25
B-2	3-ball-piston	mineral oil	3.12×10^{-1}	454 (+ 212)	0.47	10
		water	3.12×10^{-1}	241 (+ 22)	0.09	20
		water	3.12×10^{-4}	155 (+ 37)	0.24	20
B-3	3-ball-piston	mineral oil	3.12×10^{-1}	610 (+ 171)	0.28	10
		water	3.12×10^{-1}	224 (+ 42)	0.19	20
		water	3.12×10^{-4}	176 (+ 23)	0.13	19
B-4	3-ball-piston	mineral oil	3.12×10^{-1}	356 (+ 64)	0.18	50
		water	3.12×10^{-1}	203 (+ 47)	0.23	50
		water	3.12×10^{-4}	162 (+ 29)	0.18	50
B-4	concentric ring	water	3.12×10^{-1}	95 (+ 13)	0.14	21
		water	3.12×10^{-4}	73 (+ 11)	0.15	20
B-5	3-ball-piston	mineral oil	3.12×10^{-1}	426 (+ 130)	0.31	45
		water	3.12×10^{-1}	261 (+ 37)	0.14	50
		water	3.12×10^{-4}	191 (+ 69)	0.36	49

+ B-1 signifies as-received; B-2 heat treatment only; B-3 heat treatment followed by chemical polish; B-4 heat treatment followed by chemical polish, followed by selective etch; B-5 over age heat treatment followed by chemical polish, followed by selective etch.

Table IV. Summary of Fracture Resistance (K_{IC}) Results
From Second Series of Tests

Processing Treatment	K_{IC} (MN/M ^{3/2})	No. Samples
B-1	0.74 (<u>+</u> .109)	8
B-4	1.130(<u>+</u> .371)	3
B-5	1.26 (<u>+</u> .411)	5

Table V. Summary of the Fatigue Resistance (N) Results
From Second Series of Tests

Processing Treatment	Loading Configuration	Test Environment	N
B-1	3-ball-piston	water	25.0
B-1	concentric ring	water	6.9
B-2	3-ball-piston	water	15.1
B-3	3-ball-piston	water	28.1
B-4	3-ball-piston	water	28.7
B-4	concentric ring	water	23.6
B-5	3-ball-piston	water	22.4

A close examination of the fracture patterns in this second series of tests revealed a number of abnormal fracture patterns where the fracture sometimes did not originate in the area of maximum stress. Also, in these abnormal fractures the cracks did not always propagate parallel to the cross-section but sometimes twisted out of plane. Thus, the absolute strength of this second series of specimens must be viewed with some caution; although on comparing specimens of this second series with those tested under identical conditions in the first series (Table I and III), it appears that the strength of the second series is greater. Unfortunately, small inaccuracies in the measured strength can cause significant changes in the fatigue resistance parameter N and this probably accounts for the wide variation observed in N for this second series of tests. However, the strength changes measured as a function of processing for this second series are thought to accurately reflect the trend in strength between the different processing steps.

III. FUTURE WORK

During the first 18 months of this 36 month program, we have concentrated on verifying characterization techniques with a model glass. Some work is required to resolve remaining problems in this area; but overall, we feel that useful, reliable information about the surface films can be derived now. Therefore, we will begin to emphasize research with new glass compositions.

Glass compositions near the soda-line window glass compositions have been identified which are known to phase separate. We will make small samples of various compositions to map out annealing time-temperature cycles which result in phase separation. X-ray low angle scattering will be used to determine the presence and scale of the phase separated structure. Once this portion of work has identified means to produce the desired structures, selective etching techniques will be developed to produce the desired AR characteristics.

After reviewing the literature, we are now convinced that it is necessary to refine analytical models of the optical characteristics of graded index films. This work will be completed by September 1980.

The University of Massachusetts will continue to investigate mechanical properties of these phase separated glasses. In the immediate future he will reexamine the strength characteristics of CGW 6640 since present results are not

as definitive as we would like although they do indicate that both short and long term strengths are not adversely effected by the surface treatment. Later, we will study other glass compositions.

At present, we believe that we will successfully accomplish our research objectives by the end of the 36 month program.

IV. Publications

K. Jakus and J. E. Ritter, Lifetime Prediction for Ceramics Under Random Loads, to be published Res. Mechanica 1980

J. E. Ritter, K. Jakus, A. Batakis and N. Bandyopadhyay, Appraisal of Biaxial Strength Testing, to be published in Proceedings of XII International Commission on Glass, Albuquerque, N.M., July 1980

Theses

A. Batakis, A Study of Biaxial Strength Testing of Brittle Materials, Thesis submitted in partial fulfillment of M.S. Degree in Mechanical Engineering, University of Massachusetts, May 1980.

A. Iqbal, Determination of Surface Chemistry of Graded-Index, Anti-Reflection Films on Glass, Thesis submitted in partial fulfillment of M.S. Degree in Materials Science and Engineering, Massachusetts Institute of Technology, to be published in 1980.

Presentations

S. C. Danforth, J. S. Haggerty, D. Imeson, A. Iqbal, J. B. Vander Sande, Microstructural Analysis of Broad-Band Anti-Reflective Films on Glass, presented at University of Massachusetts, Department of Engineering Seminar, November, 1979.

S. C. Danforth, J. S. Haggerty, D. Imeson, A. Iqbal, J. B. Vander Sande, Microstructural Analysis of Broad-Band Anti-Reflective Films on Glass, presented at the American Ceramic Society, Annual Meeting and Exposition, Chicago, Illinois, April 27-30, 1980.

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