Original Paper

Leached antireflection surfaces

Part 1. Characterization of the neutral solution process

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The kinetics of the formation of leached antireflective surfaces on borosilicate glasses by the neutral solution process is reviewed. The most important variables were found to be temperature, surface/volume ratio, concentration of network dissolution products in solution, and annealing rate. A pronounced mixed alkali effect was observed, indicating the importance of alkali/proton exchange in the formation of the leached layer.

Durch Auslaugung gebildete reflexionsmindernde Oberflächenschichten

Teil 1. Charakterisierung der Glasauslaugung durch neutrale wäßrige Lösungen

Die Kinetik der Bildung von reflexionsmindernden Schichten auf der Oberfläche von Borosilicatglas mit neutralen Lösungen wird betrachtet. Dabei zeigt sich, daß die wichtigsten Prozeßvariablen die Temperatur, der Quotient aus Oberfläche und Lösungsvolumen, die Konzentration der gelösten Netzwerkbildner in der Lösung und die Kühlrate des ausgelaugten Glases sind. Es wurde ein deutlicher Mischalkalieffekt beobachtet, der die Bedeutung des Austausches von Alkaliionen gegen Protonen während der Schichtbildung erkennen läßt.

1. Introduction

Antireflective (AR) surfaces on glass produced by chemical leaching methods have shown technical utility in specialized applications, primarily high energy laser optics. The particular treatment process under discussion, henceforth termed the Neutral Solution Process (NSP) [1], is a refinement of a technique originally developed by Schröder [2] and is currently being utilized to treat large (up to 110 cm diameter) laser optics [3]. Although the process is empirically well-defined, allowing uniform and reproducible operation, the precise chemical mechanism of the process has, thus far, not been discussed. A more detailed understanding of the mechanism of the NSP is useful, both for solving practical problems and limitations to its application and to provide further information on the fundamental mechanisms of glass corrosion in aqueous media. The following report presents a summary of the kinetics of the leaching process. Subsequent reports will detail characterization of NSP surfaces, give chemical release data and present a model of the leaching process which is consistent with the observed facts. For the sake of simplicity, the work described has primarily used the optical borosilicate glass BK-7.

2. Materials and methods

The solution used in the NSP consists of 0.035 M Na_2HAsO_4 or Na_2HPO_4 with $1 \cdot 10^{-3}$ M $AlCl_3$ in deionized water. Both arsenate and phosphate give identical rates of film formation. Because of the toxicity and higher cost of arsenates, the phosphate salt is the preferred material. The simple sodium phosphate solution has a pH value of 9.0 and its use alone does not result in film formation when glass samples are exposed to it; Al^{3+} incorporation is necessary for film formation. The effect of Al^{3+} concentration on film formation was previously reviewed by Schröder [4]. Below a critical concentration ($\approx 10^{-5}$ M) no film formation is observed. Above the critical concentration the film formation rate is not significantly affected by changes in Al content.

Addition of $AlCl_3$ to the phosphate solution reduces the pH value to 7.8 and results in the immediate formation of colloids as evidenced by turbidity. The structure and chemistry of the colloidal material has not as yet been evaluated in detail, but x-ray fluorescence analysis indicates that it contains primarily alumina. Titration of freshly prepared treatment solution indicates little buffering ability. However, the pH value has not been observed to change significantly during the leaching process ($\pm$ 0.5 units). Aluminum-free phosphate solutions, on the other hand, show noticeable increases in pH values with increasing exposure time when BK-7 glass is leached (9.1 to 9.4 after 120 h).

In order to reproducibly prepare AR surfaces on glass substrates, as many variables as possible must be kept constant in the treatment process. The "standard" set of conditions used in this laboratory are: a) surface/volume ratio fixed at 0.2; b) temperature fixed at 87 °C; c) only fine-annealed ($\leqq$ 0.5 K/h) glass

Received 14 November 1986.

is used, prepared with a standard and uniform grinding and polishing procedure [5]; d) solution composition in all cases as outlined above; and e) only inert materials are used in construction of the treatment apparatus (polyethylene, polypropylene, and teflon) to avoid contamination effects.

To stop the treatment process, samples are removed and soaked in distilled water for 2 min at 20 °C, rinsed in clean spectroscopic methanol, dried in an oven for 3 min at 80 °C, and allowed to cool to room temperature before measuring reflectance.

Reflectance spectra were taken using a double-beam recording spectrophotometer (model 330, Perkin-Elmer Corp., Norwalk, CT (USA)) at fixed incident angle of 6°. Aluminum mirrors with the front surface overcoated with MgF_2 were used for reference purposes.

Glasses prepared for evaluation of mixed alkali effects were melted in 0.5 l induction-heated platinum crucibles at 1400 °C and refined for 2 h at 1550 °C. The same lots of raw materials were used for all glasses. All test glasses were annealed with a velocity of 20 K/h and polished samples for leach tests were prepared using the grinding and polishing conditions described in [5].

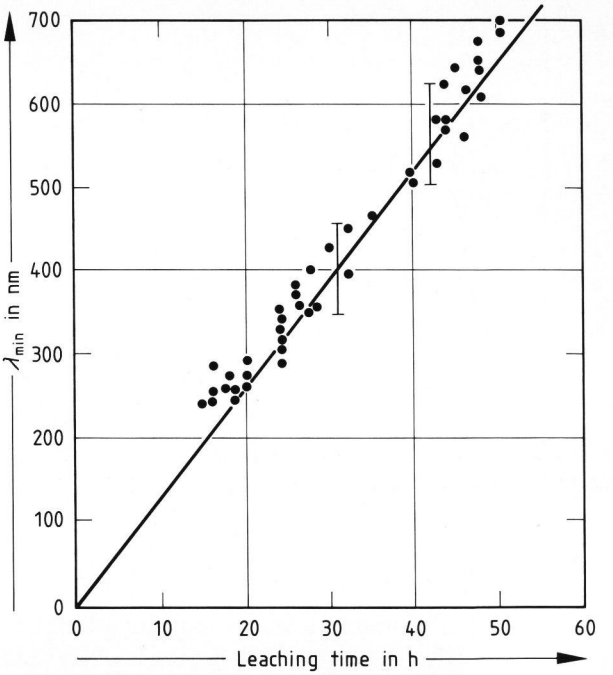

Figure 1. Wavelength of minimum reflectance vs. time for standard leaching conditions. (Brackets indicate bandwidth of < 0.2 % reflectance per surface.)

3. Experimental results and discussion

3.1. Film formation under standard conditions

BK-7 glass processed under standard conditions shows an initial linear rate of film formation based on plots of the wavelength of minimum reflectance (λ_{min}) vs. time (figure 1). At longer leaching times direct observation of the primary reflectance minimum is not possible, and film thickness is calculated using the formula given in [5]. A plot of calculated film thickness vs. time for the standard leaching condition is given in figure 2. A linear increase is observed until approximately 220 h after which the rate of film growth continuously decreases until a constant film thickness of ≈ 2.1 µm is approached. At or shortly after the steady state is reached, the surface layer is observed to peel off, exposing a second leached sublayer, whose calculated thickness at the time of delamination is ≈ 0.7 µm. The non-linear portion of the curve appears to follow $t^{0.5}$ kinetics although the data shown in this example is insufficient for confirmation. Measurements taken under other leaching conditions [5] show the same overall behavior, i.e., an initial linear rate, followed by $t^{0.5}$ kinetics and eventual stoppage of film growth, although in those cases delamination effects were not observed.

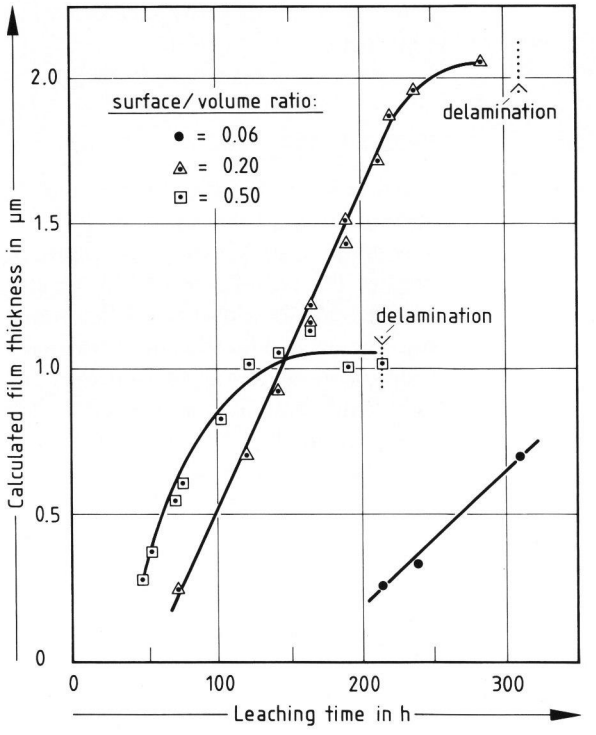

Figure 2. Film growth rate as a function of time for three surface/volume ratios.

3.2. Factors influencing film formation

The important production variables described in section 2. were determined by systematically varying leaching conditions to assess influences on the rate of film formation. This was done both to determine what must be controlled in order to make this a technically useful treatment process for optics and to shed light on the mechanism of film formation.

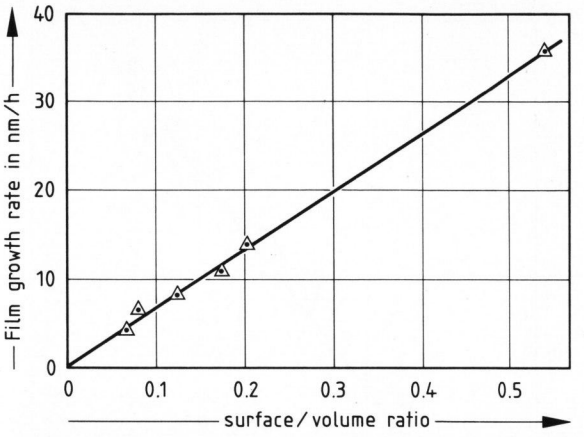

Figure 3. Film growth rate as a function of surface/volume ratio (short-time data).

3.2.1. Temperature

The rate of film formation shows a positive temperature dependence. Arrhenius' behavior is observed; an apparent activation energy of 84.6 kJ/(K mol) is obtained from a plot of $\log_{10}$ film formation rate vs. 1/T. The temperature normally used for treatment (87 °C) gives the most rapid treatment rate without excessive water evaporation losses or steam bubble formation on treated optics, both of which can lead to inhomogeneous surfaces.

3.2.2. Surface/volume ratio

A pronounced dependence of the film formation rate on the glass surface area/liquid volume ratio (S/V) is observed. This is shown graphically in figure 3. Despite differences in the initial rate of film formation, samples processed at different S/V ratios showed the same general kinetics as previously described. A comparison of behavior is shown for 0.06 S/V, 0.20 S/V and 0.50 S/V in figure 2. Of interest is the observation that although the initial rate of growth is higher at high S/V ratios, the final film thickness is substantially less than at lower S/V conditions. In addition to a positive influence on the rate, noticeable differences in the structure of reflectance spectra were also found. The observed trend is that high S/V ratios produce more highly reflecting surfaces, while samples produced at low S/V ratios show what appear to be stronger refractive index gradients in the surface layer, producing reflectance levels at maxima far lower than expected if the surface layers were of uniform refractive index [6 and 7]. A comparison of the reflectance spectra of three samples of equivalent optical thickness produced at differing S/V ratios is given in figure 4. The surface/volume ratio chosen for normal treatment (0.2) is high enough to give a convenient processing time while keeping the more desirable reflectance characteristics found at low S/V ratios. As mentioned

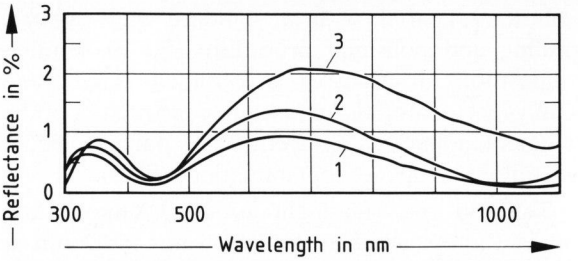

Figure 4. Effect of Surface/Volume (S/V) ratio on reflectance characteristics. Curve 1: 0.06 S/V, curve 2: 0.20 S/V, curve 3: 0.50 S/V.

in [5], the fact that reaction times are on the order of hours vs. minutes is advantageous when treating precision-finished optics as fluctuations in temperature, reactant or product concentrations, and flow will not lead to inhomogeneities during treatment.

Fixing the surface/volume ratio during treatment was a major factor in the smooth scale-up of this process from the 50.8 mm (≙ 2 in.) diameter research samples described here to the 110 cm diameter BK-7 optics treated at Lawrence Livermore National Laboratories [3]. Virtually identical reaction rates at fixed S/V were observed in both systems despite the difference in scale, and, presumably, in surface finish. No upper limits to scaling the process have so far been found.

3.2.3. Flow

It is clear that liquid flow has a strong effect on glass leaching reactions via its effects on ion movement from the surface [8] and on the rates of reactions which are affected by product concentration. There was some initial concern about the potential for flow-related inhomogeneities, especially on scale-up to large leaching volumes. In practice, no flow-related variations in leaching rate or surface uniformity were observed in either stirred or unstirred baths of 0.2 or 5.0 l volume. Very large optics treated in scaled-up treatment systems were, if anything, more uniform [3]. Again, this insensitivity to flow is largely a consequence of the slow reaction rate. It would appear that transport through the surface is the rate-determining factor in the leaching process rather than transport in the leaching solution.

3.2.4. SiO_2 content of leaching solution

The effects of high S/V ratios may be reasonably well duplicated by adding silicic acid to the treatment solution prior to use. Film formation rate increases directly with initial $Si(OH)_4$ content (figure 5), and the reflectance characteristics observed for samples prepared in silica-activated solutions at low S/V are remarkably similar to samples prepared at high S/V without silica additions. Additions of other glass

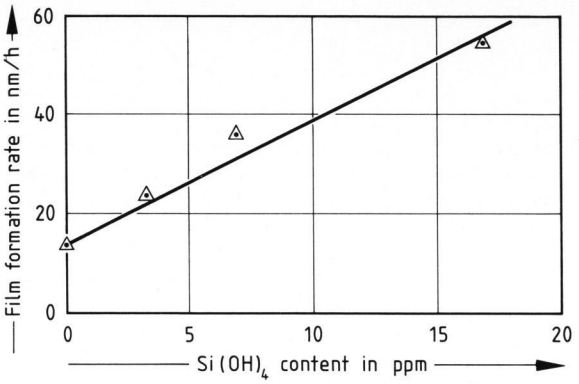

Figure 5. Film growth as a function of initial $Si(OH)_4$ content.

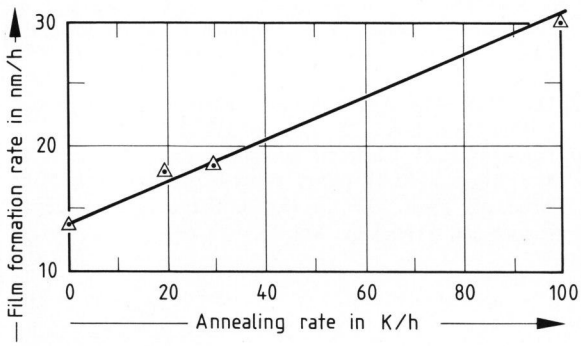

Figure 6. Film formation rate as a function of annealing rate.

constituents (sodium, potassium, boron) as neutral salts did not affect leaching rate.

The effects of both surface/volume ratio and silica addition are believed to be due to their effects on network dissolution reactions, which, in turn, would have a strong influence on both the rate of film formation and the physical/optical character of the surface layer.

3.2.5. Annealing rate and mixed alkali effect

A linear dependence of film formation rate on the annealing rate of the test glass was also found (figure 6). Unlike the case of leaching at high S/V ratios, the reflectance characteristics of rapidly annealed glasses were indistinguishable from samples annealed at rates of $\leqq 1$ K/h produced under standard conditions. Thus, while both S/V and annealing rate were found to activate the leaching process, the leached surfaces produced were not equivalent, suggesting that two very different activation processes were occurring.

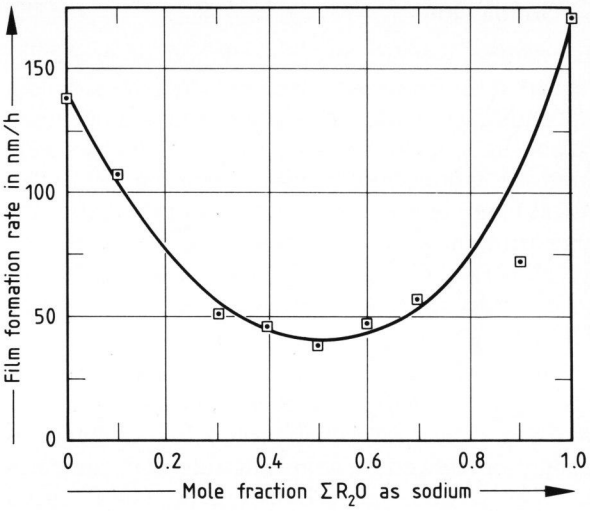

Figure 7. Mixed alkali effect on film formation for glass compositions given in table 1.

Because the primary effect of annealing was felt to be upon the diffusion rates of mobile glass cations (primarily alkali), it was expected that the process should exhibit a pronounced mixed alkali effect. A series of borosilicate glasses of composition similar to BK-7 was prepared in which the molar ratio K_2O/Na_2O was varied from a pure potassium to a pure sodium glass. Compositions melted are given in table 1. Polished samples (see section 2.) were then leached under standard conditions and the rate of film formation determined from reflectance data.

As can be seen in figure 7, a strong mixed alkali effect was observed, with the 1 : 1 K_2O/Na_2O composition giving the lowest leaching rate. This agrees with literature data [9 and 10] on mixed alkali effects on aqueous corrosion of glasses and indicates the importance of alkali/proton ion exchange in the formation of the leached layer.

Table 1. Mixed alkali test glasses, composition and some properties

SiO_2	in mol%	75	75	75	75	75	75	75	75	75
B_2O_3		15	15	15	15	15	15	15	15	15
Na_2O		10	9	7	6	5	4	3	1	0
K_2O		0	1	3	4	5	6	7	9	10
n_d		1.50205	1.50172	1.50272	1.50194	1.50250	1.50327	1.50366	1.50412	1.50355
V_d		65.60	66.20	66.52	66.65	66.70	66.59	66.85	67.22	67.23
density in g/cm³		2.397	2.392	2.398	2.394	2.397	2.4053	2.403	2.407	2.404
T_g in °C		560	564	559	565	565	563	567	573	602
$\alpha_{20/300}$ in 10^{-7} K^{-1}		58.2	60.1	61.4	60.9	62.2	64.2	65.4	70.7	66.5
film formation rate in nm/h		171	72	56.7	46.9	37.8	45.6	48.5	106	137

4. Conclusions

The neutral solution process method of producing leached antireflective surfaces was studied to identify important factors for reproducible and homogeneous use on a large scale. Several important variables were found to influence AR film formation, the most critical being temperature, surface/volume ratio, the concentration of network dissolution products, and annealing rate. Control of these variables enabled the process to be scaled up to treat precision optics of up to 110 cm diameter.

The variables mentioned above affect the two basic types of surface reactions occurring during corrosion. The first, alkali/proton ion exchange is strongly influenced by annealing rate and temperature. The second, network dissolution, is influenced by surface/volume ratio and additions of silica.

5. References

[1] Cook, L. M.; Mader, K.-H.; Schnabel, R.: Integral antireflective surfaces on silicate glass. US pat. no. 4 434 191. 28 Feb. 1984.

[2] Schröder, H.: Verfahren zur Durchlässigkeitserhöhung und Reflexverminderung von Glas od. dgl. Stoffen. German pat. no. 821 828. 18 Sept. 1952.

[3] Wirtenson, G. R.; Brown, N. J.; Cook, L. M.: Scaling up the neutral solution process. Opt. Eng. **22** (1983) no. 4, p. 450–455.

[4] Schröder, H.: Thin film formation on glass surfaces in chemical coating processes. In: Kunugi, M.; Tashiro, M.; Soga, N. (eds.): Tenth International Congress on Glass, Kyoto, Jpn., 1974. No. 8, p. 8-118–8-130.

[5] Cook, L. M.; Ciolek, S.; Mader, K.-H.: Integral antireflective surface production on optical glass. J. Am. Ceram. Soc. **65** (1982) no. 9, p. C-152–C-155.

[6] Cook, L. M.; Lowdermilk, W. H.; Milam, D. et al.: Antireflective surfaces for high-energy laser optics formed by neutral solution processing. Appl. Opt. **21** (1982) no. 8, p. 1482–1485.

[7] Marker, A. J.; Cook, L. M.; Mader, K.-H.: Light scattering in leached antireflection surfaces. Proc. SPIE **302** (1983) p. 143–148.

[8] Isard, J. O.; Allnatt, A. R.; Melling, P. J.: An improved model of glass dissolution. Phys. Chem. Glasses **23** (1982) no. 6, p. 185–189.

[9] Day, D. E.: Mixed alkali glasses – Their properties and uses. J. Non-Cryst. Solids **21** (1976) p. 343–372.

[10] Doremus, R. H.: Chemical durability of glass. In: Tomozawa, M.; Doremus, R. H. (eds.): Glass II. London, New York: Academic Press 1979. p. 41–69. (Treatise on materials science and technology. Vol. 17.)

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