Properties of low cost, high volume glasses*

MASTEDM. A. Lind
J. S. Hartman
C. Q. Buckwalter

CONF-790838--6

Pacific Northwest Laboratory**
Battelle Blvd, Richland, WA 99352Abstract

The properties of new and weathered samples of low cost, high volume glasses have been studied to determine their usefulness for solar energy applications. Glasses of varying compositions produced by float, drawn, rolled, fusion, and twin ground techniques were examined. Spectral transmittance and reflectance were measured and solar weighted values calculated. Laser raytrace techniques were used to evaluate surface parallelism and bulk homogeneity. Compositional changes were examined with scanning electron microscopy, X-ray fluorescence, and Auger electron spectroscopy. These techniques were used in conjunction with ellipsometry to study the surface effects associated with weathering.

Introduction

The adaptation of inexpensive materials for use in solar energy conversion systems holds a high degree of interest in the solar community. One material system that has received considerable attention in recent years is the application of commercial second surface glass mirrors for use as solar reflectors. Until recently, the industry has produced mirrors designed for use primarily in interior applications. Little is known about the suitability and performance of these reflectors in a relatively hostile exterior environment. For a second surface mirror, one of the initial concerns is the performance of the glass superstrate which is metalized. The ideal superstrate will have superior optical figure, high solar transmittance, low manufacturing cost and possess superior weathering characteristics. This paper summarizes some of the physical properties of the high volume, low cost glasses that are currently available and discusses the techniques used to perform the characterizations.

Methods of processing

The properties of most high volume sheet glasses are a direct consequence of the methods used to produce the sheet. There are four processes in common use today for forming large continuous sheets of flat glass. These processes are designated float, rolled, drawn and fusion.

The float process is the most commonly used because of its relatively high production rates and good optical quality. In the float process the molten glass flows onto the surface of a molten tin bath. The sheet spreads to a uniform thickness as it is drawn off the bath. It passes through an annealing lehr before final cooling and cutting. The typical float line produces a continuous ribbon of glass 8-12 feet wide. Production volumes can run in excess of 100 million square feet per year.

Rolled glass is produced by allowing the molten glass to flow over a lip at the end of the mixing tank and pass between two rolls which form the sheet. The rolls may be patterned or flat. The patterned glass finds use in decorative applications. Before the introduction of the float process, rolled glass was ground and polished to produce high quality flat glass. Most of the high volume grinding and polishing lines in the U.S. have discontinued operations because of high cost of cleaning up the waste effluent to meet EPA requirements.

In the Colburn, Fourcault and Pittsburg processes the glass is drawn vertically from the melt to produce a continuous sheet. In the Colburn process the sheet is bent over a roll and passed over a horizontal flattening table before entering the lehr. In the Fourcault process a clay block with a longitudinal slot is placed on the melt. The glass extrudes as the block floats under a controlled load. The sheet is then drawn vertically through the annealing lehr and cut. In the Pittsburg process the slotted block is replaced with a submerged fire-clay form tapered to a narrow edge near the surface of the melt. The clay block produces a narrow zone of cooler glass of higher viscosity which is drawn off.

* Work performed for U.S. Department of Energy under Contract EY-76-C-06-1830.

**Operated by Battelle Memorial Institute.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ef

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

In the fusion process developed by Corning, the molten glass exits a forehearth through a refractory pipe into a refractory trough. The glass overflows this variable depth trough on both sides. The two gravity drawn sheets fuse together below the trough to form a single sheet with near pristine surfaces. Variable speed rollers in contact with the sheet control the vertical speed and thus the thickness.

Most of the processes described above are used to produce soda lime silica glass. The fusion process has been adapted to the production of aluminosilicate, borosilicate and other special composition glasses. Both the aluminosilicate and borosilicate glasses tend to be more durable than soda lime glass, as discussed later.

Glass characteristics

Transmittance

Differences in the spectral transmittance of the glass produced by any of the above methods is determined primarily by the amount of iron present in the raw materials (the sand, fluxing, and oxidizing agents) and by the thickness of the sheet. In the float process, where carefully controlled thermal mixing is used to homogenize the melt, a small amount of iron is usually added in order to increase the emissivity and promote convective mixing in the melt. This iron appears in the spectral transmittance as a broad Fe^{+2} absorption band centered around 1100 nm and a sharper Fe^{+3} band centered at 380 nm. In solar applications the Fe^{+2} band can reduce the solar transmittance appreciably as shown in Figure 1.

Figure 1. Spectral transmittance of low iron and normal float glass showing the Fe^{+2} and Fe^{+3} absorption bands.

Such an instrument, shown schematically in Figure 2, is designed to accurately measure the angular deviation of a collimated light beam reflected from one or both surfaces of the glass. Both the front and rear surface reflections can be examined independently by blocking the unwanted beam.

In other processing methods which do not rely as heavily on convective mixing and are amenable to mechanical stirring of the melt, the iron content can be lowered significantly to produce glass with low absorptance characteristics. These glasses can yield values for the solar transmittance approaching the theoretical maximum of about 0.92. This limit is determined by the bulk index of refraction and can be modified somewhat by using special surface treatments. Typical values for the solar transmittance of various glass types are shown in Table 1.

Flatness

The degree of flatness or the figure of the glass sheet is also determined in large part by the manufacturing process. The flatness as well as the parallelism of the two surfaces and the homogeneity of the refractive index can be evaluated using a laser raytrace instrument.

Table 1. Solar Transmittance Values for Various Types of High Volume Flat Glass

Type	Process	Thickness	Solar Transmittance*
Soda-lime-silica	Float	0.125"	0.83-0.88**
Soda-lime-silica	Rolled or drawn	0.125"	0.85-0.90
Aluminosilicate	Fusion	0.060-0.125	0.90-0.91
Borosilicate	Fusion	0.030-0.125	0.91-0.92

* Solar weighted using Moons AM2 terrestrial solar spectral distribution and a best fit interpolation routine.

** It should be noted the limited quantities of special run low iron float glass have been produced with a solar transmittance slightly greater than 0.89.

As seen in the figure, the beam reflected from the rear surface passes through two thicknesses of the glass sheet and is influenced by any index inhomogeneities within the sheet. The output from the linear position detector for a known system geometry allows calibration of the instrument for angular deviations of the reflected beam from the

Figure 2. Laser raytrace instrument for evaluating glass flatness.

Figure 3. Typical deviations from the 45° specular direction for three glasses. Both the first surface (top) and second surface (bottom) reflections are shown.

specular direction. Standard operation involves the translation of the glass sample under the beam which results in a linear plot of the angular variation in the specular beam versus position.

Typical traces for three glasses produced by different manufacturing processes are shown in Figure 3. These traces are indicative of the flatness across the width of the draw. The apparent increase in surface roughness in the second surface reflection for the float glass is due primarily to index variations in the bulk and not to actual surface irregularities. In general the glass tends to be an order of magnitude flatter along the line of the draw than across it. The exception is the twin ground glass, which is apparently the same in both directions.²

Figure 4. Relative flatness of selected glasses produced by different manufacturing processes.

A plot of the half angle deviation from the specular direction versus the fraction of glass surface area that deflects the beam by that angle is shown in Figure 4 for selected samples. The exact shape and magnitude of these curves vary with the manufacturing process as well as the individual production lines. This type of plot provides a convenient method of comparing flatness. It is especially useful in evaluating stray reflective losses when the glass is used as a second surface mirror superstrate.

Durability

The durability of glass is often rated by its resistance to water leaching. In fact the primary weathering mechanism for glass used in many exterior environments is due to the leaching effects of water. Although the reaction mechanism is not clearly understood, the evidence obtained implicates an ion exchange diffusion between the alkali ions in the glass and the hydrogen, H^+ , and or the hydronium ion, H_3O^+ . In the weathered portion of the glass the depleted Ca^{+2} and Na^{+} ions are replaced by H_3O^+ .³ The silicon skeleton structure of the glass remains constant compared to the more active

Ca^{+2} and Na^{+} ions. Eventually the hydroxide begins to attack the silicon structure. In the early stages of degradation however profiles of the alkali ions and hydrogen in the

leached area have been shown to be correlated with the age of the glass.⁴

Of the three types of glass of primary interest in solar applications soda-lime silicate, borosilicate, and aluminosilicate, the soda-lime silicate is the least durable. This can be illustrated by some simple leaching tests using a Soxhlet apparatus with pH4 and pH9 buffer solutions. By measuring the weight loss of the samples at prescribed time intervals the rate of ion leaching can be deduced. The test can be accelerated by crushing the plate glass to a -40 +60 mesh (U.S. Standard) in order to increase the surface to volume ratio.

The Soxhlet apparatus operates at 95°C and the sample, which is contained in a stainless steel bag is exposed to redistilled water every three minutes. The pH9 buffer solution is made from ammonium hydroxide and ammonium chloride and the pH4 solution from sodium acetate and acetic acid. Both the pH4 and pH9 solutions are maintained at 22°C in plastic bottles on a shaker table.

Table 2 shows the results of these leaching experiments for both crushed samples and 1/2"x1/2"-plate samples of typical soda-lime silicate and aluminosilicate glasses. Clearly the aluminosilicate has better resistance to leaching than the soda-lime. Unfortunately, to date, these accelerated tests have not provided very useful information on the kinetics of real time aging, but they are still useful as tools for ranking various types of glass.

Table 2. Percent Weight Loss Due to Leaching in Accelerated Tests

Sample	Crushed Soxhlet Leached 74 hrs @ 95°C	Plate Soxhlet Leached 72 hrs @ 95°C	Crushed pH 9 120 hrs @ 22°C	Crushed pH 4 120 hrs @ 22°C
Soda-lime silicate	24.5%	0.86%	0.18%	0.05%
Aluminosilicate	1.1	0.04	0.03	0.05

Composition

The two glasses tested above have also been examined using energy dispersive x-ray fluorescence to compare compositional differences. The technique employs an energetic electron beam to scatter electrons out of the atomic core levels. Other electrons from the conduction band or higher energy band states then decay into the core states that have been vacated. The decay emits a photon, typically in the x-ray region. The energy dependence of the emitted x-ray spectrum is characteristic of the elemental composition in the first micron of the material's surface.

The spectra for a typical soda-lime silicate glass and aluminosilicate glass produced by the float and fusion process respectively are shown in Figure 5. The surface of the soda-lime float glass contains a significant amount of tin not found in the bulk material. This tin is always present on the surface which is in contact with the molten tin bath during processing. As expected, both sides of the aluminosilicate fusion samples are identical and more representative of the bulk composition.

Figure 5. Energy dispersive x-ray fluorescence spectra of soda-lime silicate and an aluminosilicate glass plate

Aging

It is both interesting and instructive to examine the effects of actual weathering of a soda-lime silicate glass. A sample of 40+ year old glass retrieved from a south facing window of a deserted building on the Hanford reservation in south central Washington has been examined in detail. The semi-arid environment of this region is similar to the desert regions of southwestern United States in temperature and rainfall.

Figure 6 shows a scanning electron micrograph of a freshly broken edge of the weathered surface of the glass. The scanning electron microscope (SEM) employs a well focused electron beam (typically 100 Å diameter) which is rastered across the sample's surface. The electrons leaving the top 50 Å of the sample's surface (secondary electrons) are then collected using an applied electric field. This secondary electron current constitutes the major part of the SEM signal which is used to modulate the intensity of a CRT image scanning synchronously with the electron beam on the sample's surface. The morphology of the sample's surface (roughness, surface slope, shadowing, etc.) controls the image intensity. The value of the SEM is enhanced by the fact that the depth of field is far greater than for an optical microscope. Magnifications from 10X to 100,000X can be obtained.

Figure 6. SEM micrograph of the surface of the aged Hanford glass

The SEM photograph shows the top layer of corroded glass is approximately 1800 Å thick. The dark band is an optical artifact and is part of the bulk, not part of the weathered layer. The Wallner lines introduced during the cutting of the sample are clearly visible in the bulk.

Both Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) have been used in conjunction with ion milling techniques to determine the elemental concentration variations at the surface of the glass as a function of depth. AES is based on the measurement of the current of Auger electrons that are emitted when an incident electron beam strikes the surface of the sample. The Auger process is initiated with the decay of a core electron into the vacant lower energy state and the simultaneous release of an x-ray. The x-ray is immediately absorbed by another electron in a higher core state which is then ejected from the first few monolayers of the sample's surface. The energy spectrum of the detected electrons is used to identify the elements present. SIMS is based on the measurement of the mass spectra of ions ejected from the sample surface when it is probed by an incident ion beam (usually helium, neon, or argon). The peaks in the ion mass spectra are related to the elements present in the first few monolayers of the surface. By carefully eroding the surface of the sample via ion milling, AES or SIMS can be used to determine depth profiles for the atomic constituents.

Figure 7 illustrates a depth profile for the weathered surface of the Hanford glass for several selected elements. SIMS was used to obtain the hydrogen data and AES was used for the heavier species. The diagram is intended only to show trends in the elemental concentrations. The vertical scales for each element are not the same. The data supports the model that, except for the first few hundred angstroms, the Ca^{+2} is leached out of the surface leaving a silica rich structure.

Ellipsometry provides a technique to obtain the complementary optical data required to fully understand the surface effects. Ellipsometry is based on the polarization sensitive differences in the reflection and transmission of light at a material interface. Light polarized parallel to and perpendicular to the plane of incidence will generally experience changes in both relative phase and amplitude. Therefore, a linearly polarized incident beam will generally become elliptically polarized after reflection. Ellipsometry provides a method of accurately determining the relative changes in both phase and amplitude of the input and output beams. The observed polarization changes can

Figure 7.

in a complex refractive index of $(n-jk)_{\text{interior}} = (1.502 - 0.036j)$. These results are consistent with unaged glass samples so this index was taken as the bulk value in later calculations. The same analysis (bulk model) of the weathered surface data yielded $(n-jk)_{\text{exterior}} = (1.404 + 0.109j)$. Two features of this result for the exterior surface should be examined. The real component of the apparent index is lower than its counterpart for the bulk index. This is consistent with a surface that exhibits a density lower than the bulk. Secondly, the imaginary index component is negative which corresponds to a negative absorption coefficient. This interpretation is not physically allowed indicating the bulk model is not appropriate for the weathered surface. Analysis of data recorded on polished quartz surfaces have shown similar behavior as a result of residual surface damage from the abrasive polishing.

Single film and multi-film stack models were also applied to the data recorded on the weathered surface. The multiple angle of incidence data was used to reduce the uncertainty in selecting unique solutions for the structures. The single homogeneous film model resulted in estimated film parameters of 1.34 and 2250 Å for the real index and thickness, respectively. The imaginary component of the index was essentially zero. It is interesting to note that, although this model does not contain sufficient freedom to accurately approximate the smoothly varying glass properties, the film thickness is comparable to values that might be estimated from either the SEM photomicrograph (Fig. 6) or the AES/SIMS depth profile data (Fig. 7). Further the reduced refractive index is consistent with what would be expected for a partially filled material matrix (fill factor < 1) analyzed with the Maxwell-Garnett theory.

The actual surface layers would be represented better by a multilayer model that takes into account the open structure of the silica gel at the surface and the gradual transition to bulk properties at greater depth. Such a model is being examined where the use of five homogeneous layers are used to form a histogram approximation of the actual sample. The structure of the AES data (Fig. 7) was used to select discrete regions of the sample that will allow a first order estimate of the system. Iterative calculations can be carried out by adjusting the indices and thicknesses of the layers until agreement is found with the actual ellipsometer data. Multiple angle of incidence data will again be used as a cross-check during these iterative calculations.

Ellipsometry is therefore a powerful tool that is sensitive to the optical effects on the sample's surface and can provide a very important complement to the standard surface analysis techniques (AES, SIMS, SEM, EDAX, etc.). But the development of an accurate surface model will generally require the use of insights gained from the other techniques. The use of an incorrect model for data analysis will produce answers but they will represent set of "effective" parameters for that model and may bear very little resemblance to the actual system.

then be related to the optical properties of the structure using Maxwell's equations and the appropriate boundary conditions.

The significance of the final results depends on the suitability of the optical model used for the sample. This is illustrated by the effects of the growth of a thin oxide layer on a metal substrate. A 25 Å oxide layer on copper will cause errors in the refractive index ($\Delta n/n_0 = 0.029/0.270$ and $\Delta R/R_0 = 0.058/9.1$) determined using a bare substrate model. But very useful data can be obtained on simple systems (discrete thin films, etc.) or on more complex systems where complementary data exists on the material structure. In this study, insights into the surface structure were taken from AES and SEM examination.

Ellipsometry data were recorded at $\lambda = 6328 \text{ Å}$ on both the weathered exterior window surface and on the unweathered interior surface. The exterior surface was measured at six locations and data were recorded at each for a variety of incident angles. The analysis of the interior surface data using an uncoated, bulk substrate model resulted

Conclusions

Some general conclusions can be drawn regarding the suitability of high-volume glasses for use in solar mirrors based on the data obtained from samples made by several different processes. These conclusions are based on the current technology which might be subject to rapid change if sufficient market incentive existed.

The float process is capable of producing acceptable glass for even the long focal length (~500 m) mirror systems. The process has the advantage of being a very high volume low cost operation. The principal disadvantages are the low solar transmittance (<0.86) due to the Fe^{+3} absorption in the bulk and the current practice of manufacturing only the less durable soda-lime glass. It should be noted, however, that limited quantities of 0.118 in. low iron float glass have recently been produced with solar transmittances over 0.89.

The fusion process has recently yielded both aluminosilicate and borosilicate glasses that are nearly as flat as the float glasses. The costs of these glasses are slightly higher and the production capacity lower than for the float process. The process is capable of yielding glass less than 0.5 mm in thickness with solar transmittances greater than 0.91.

Roller or drawn glass has unacceptable flatness characteristics for use as solar mirrors. The solar transmittance can approach 0.92 for a 3 mm thickness, however. This makes these glasses desirable for flat plate collector application.

Finally, twin-ground glass has the potential of being the highest optical quality glass. Difficulties associated with the process may continue to make this type of glass too expensive for solar use.

Although soda-lime glass does show the effects of aging it still appears to provide a relatively inexpensive and durable optical material for use in solar mirrors. Further research is under way to confirm the degradation mechanisms and determine if the interface between the glass and other materials such as silver is stable for long-term applications.

Acknowledgments

The authors wish to thank D. Knittle of the Stanford Research Institute for the excellent SEM photograph showing the degraded surface layer on the Hanford glass and G. McVay of PNL for his many informative discussions on glass degradation. The authors also gratefully acknowledge M. T. Thomas, L. Peterson and D. Baer of PNL for the Auger and SIMS data.

References

1. Moon, P., "Proposed Standard Solar Radiation Curves for Engineering Use," Journal of the Franklin Institute 320, 604, 1940.
2. Lind, M. A. and J. M. Rusin, "Heliostat Glass Survey and Analysis," PNL-2868/UC-62.
3. Das, C. R., "Theoretical Aspects of the Corrosion of Glass," The Glass Industry, pp. 422-427, Sept. 1969.
4. Clark, D. E. et al., "Aqueous Corrosion of Soda Silica and Soda-Lime Silica Glass," The Journal of American Chemical Society, 59:1-2, 1976.