

Cation concentration profiles in float glass surfaces during corrosion in aqueous solutions

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The chemical composition of the thin surface layer of float glass is not homogeneous with respect to the concentration of some cations. This inhomogeneous cation distribution significantly changes if the glass surface comes into contact with aqueous solutions. Using ESCA significant changes in the distribution of magnesium and sodium cations were found on the "top" surface of float glass in static corrosion environment. The magnesium concentration increases in the thin surface layer, while sodium concentration decreases almost to zero. The relative amounts of calcium, silicon and oxygen appear to be nearly the same both in the original and the corroded surface layer. The change of magnesium and sodium concentrations as well as an electron micrograph of the glass surface indicate damage and hydration of the "top" surface layer of float glass.

The distribution of the elements does not show any significant change if corrosion proceeds in streaming water. Consequently, total dissolution of the basic glass network built by silicon and oxygen atoms appears to be the fundamental process in this case.

Kationenkonzentrationsprofile in Floatglasoberflächen während der Korrosion in wässrigen Lösungen

Die chemische Zusammensetzung der Oberflächenschicht eines Floatglases ist in bezug auf die Konzentration der Kationen inhomogen. Diese inhomogene Kationenverteilung ändert sich deutlich, wenn die Oberfläche in Kontakt mit wässrigen Lösungen kommt. Erhebliche Veränderungen der Magnesium- und Natrium-Kationenverteilung wurden auf der Atmosphärenseite des Floatglases in statischer Korrosionsumgebung mit Hilfe der ESCA-Methode gefunden. Die Magnesiumkonzentration nimmt in einer dünnen Oberflächenschicht zu, während die Natriumkonzentration auf annähernd Null sinkt. Die relativen Mengen an Calcium, Silicium und Sauerstoff in der ursprünglichen Oberflächenschicht scheinen denen in der korrodierten Schicht etwa gleich zu sein. Die Änderung des Magnesium- und Natriumgehaltes sowie eine elektronenmikroskopische Aufnahme der Glasoberfläche weisen auf die Bildung einer geschädigten und hydrolysierten dünnen Oberflächenschicht hin.

Die Elementverteilung zeigt keine wesentliche Veränderung, wenn die Korrosion in strömendem Wasser verläuft. Demnach scheint die vollständige Auflösung des aus Silicium- und Sauerstoffatomen aufgebauten Glasnetzwerkes der bestimmende Schritt in diesem Prozeß zu sein.

1. Introduction

The chemical composition of surface layers of float glass differs from the "bulk" composition [1]. The main difference is mainly caused by the tin content in the surface layers created by contact with molten tin (tin or "bottom" side) [2]. The relatively high content of tin in the glass surface layer is responsible for the increased chemical durability of this surface [3 and 4]. The opposite side therefore (i.e. the "top" side) from the point of view of float glass corrosion appears to be a limiting factor.

Concentration changes in glass surface layers caused by glass corrosion can be detected by determination of concentration profiles of some elements. Experimental data on the concentration distribution of some elements in corrosion surface layers of model glasses have been published by Richter [5] and Sprenger [6]. Recently, Yamanaka et al. [7] had measured concentration profiles in the "bottom" glass surface layer of float glass. Luo Jie et al. [8] used XPS analysis associated with argon ion

etching to determine tin oxidation states on the underside of float glass and found that tin is present in the +4, +2 and 0 valence states.

The aim of this work is to extend the published data by determination of the concentration distribution of some elements in the "top" surface layers of float glass after corrosion by water at static and dynamic conditions. The knowledge of concentration profiles can contribute to a better understanding of the corrosion mechanism, especially with respect to the formation of a damaged surface layer on the "top" side of float glass in static and streaming aqueous solutions.

2. Experimental methods

A 4 mm thick float glass sample, provided by Glavunion, Teplice (Czech Republic), was used to study glass corrosion by means of static and dynamic corrosion tests in water. The S/V (i.e. surface of glass to water volume) relation amounts to 0.1 cm^{-1} independent of the corrosion test applied. The static corrosion test consists of the treatment of the glass sample in 70 ml distilled water (initial pH value = 5.5) at a temperature of 95°C for

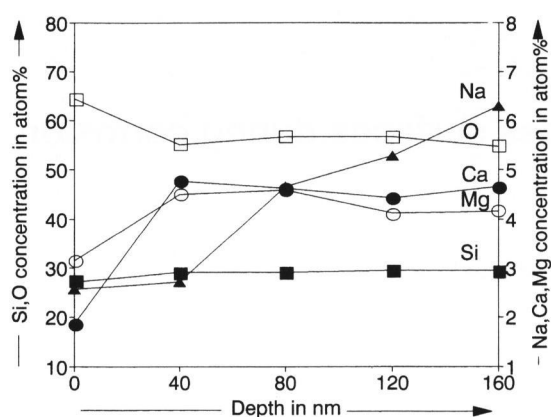


Figure 1. Concentration profiles of elements in the surface layer ("top" side) of the original float glass. Theoretical concentrations (in atom%) of bulk glass: 25.3 Si, 60.3 O, 3.0 Ca, 2.0 Mg, 9.3 Na.

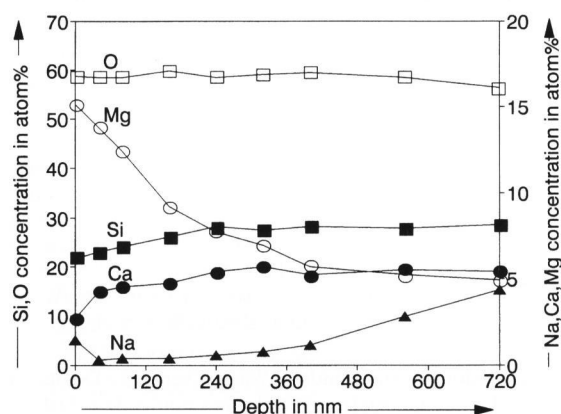


Figure 2. Concentration profiles of elements in the surface layer ("top" side) of the float glass after static corrosion test (11 d, 95°C). Theoretical concentrations (in atom%) of bulk glass: 25.3 Si, 60.3 O, 3.0 Ca, 2.0 Mg, 9.3 Na.

11 d. The glass samples (length: 2.2 cm, width: 1.0 cm) were fixed in a vertical position and placed in a polyethylene cylindrical vessel. A Soxhlet extractor with a 70 ml leaching overflow chamber, 250 ml boiling flask and reverse cooler (all chemically resistant Simax glass) has been used in the dynamic test. The volume of distilled water (initial pH value = 5.5) in the flask amounted to 200 ml. The glass sample was treated at the same temperature and time as in the static test.

Concentration profiles of some elements in a thin surface layer of the "top" glass surface before and after the corrosion test were determined by Electron Spectroscopy for Chemical Analysis (ESCA). The problems of chemical analysis of glass surfaces were recently treated by Pantano [9]. The experimental procedure used in that work was described in detail previously [10]. Determination of concentration profiles was based on the assessment of silicon, oxygen, sodium, calcium and magnesium spectra at different distances from the glass surface. Ionic etching by argon was used to remove very

thin layers of glass. Photoelectronic spectra were measured by means of the ESCA 3 MkII (VG Scientific) spectrometer using the AlK_{α} line ($h\nu = 1486.6$ eV). The pressure of the remaining gas in the sample chamber was 10^{-7} Pa. The voltage of 11.5 kV and the current of 20 mA were applied in the X-ray lamp used. The enter slit diameter was 4 mm and the passing energy $E_{\text{pass}} = 50$ eV. The photoemission lines of O(1s), Si(2p), Ca(2p), Na(1s) and the Auger line of Mg($K_1L_{23}L_{23}$) were used for quantitative analysis. The concentration profiles of the elements were obtained by Ar^+ ions beam etching. The energy of the Ar^+ ions beam was 4 eV and the pressure of argon in the preparatory chamber was $4 \cdot 10^{-4}$ Pa. The error of the concentration determination was estimated to be $\approx 15\%$. The element concentrations in the surface layer (except magnesium) were calculated by determination of peak area and using photoionization cross-sections according to Scofield [11]. The magnesium concentration was calculated using the intensity of the Mg($K_1L_{23}L_{23}$) Auger line. The concentration values calculated were corrected using a correction factor determined by MgO reference measurement. The Ca(2p) peak area was diminished by subtraction of the contribution of the Auger magnesium line. The modified program originally described by Hughes and Sexton [12] was used for fitting and concentration calculations. Binding energy values (in eV) were related to the Si(2p) energy value (102.80 eV), and so the influence of static charge was regarded.

Using an electron microscope (JEM 100B, JEOL, Tokyo (Japan)) a picture of the glass surface layer after corrosion was obtained. The glass surface of the sample studied was coated by a gold layer in vacuum and investigated while applying acceleration voltage of 40 kV at the angle of 40° .

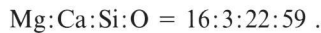
3. Results and discussion

Concentration profiles of some elements in a thin surface layer of the original float glass ("top" side) are depicted in figure 1. The original glass surface consists of a glass with undisturbed structure built by silicon and oxygen atoms. A lower content of calcium and magnesium was found in a very thin layer (up to 40 nm), while the zone with lower content of sodium displays a substantially greater thickness (of a hundred nanometers).

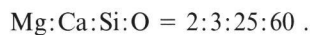
The basic glass structure built by silicon and oxygen atoms is not substantially changed by corrosion under static conditions (figure 2). More extensive changes were found in the case of magnesium and sodium distribution, which substantially changed in comparison to the original distribution. The changes were detected in the 360 nm thick surface layer. This relatively thick layer consists of silicon and oxygen atoms with an inhomogeneous distribution of magnesium concentration which increases towards the glass surface. The concentration of the most movable cations in this surface layer, e.g. Na^+ , appears to be negligible. This is in accordance with the

generally accepted assumption of preferential extraction of sodium ions from glass verified by many authors, recently by Richter et al. [5].

Considering that this layer practically does not contain any alkali ions, its chemical composition depends on the mutual relations of magnesium, calcium, silicon and oxygen concentrations. Using concentration values of these elements at the phase boundary between glass and corrosion medium the following relation can be written:



Taking into account corresponding average concentration values ("bulk" composition), this relation is as follows:



The comparison of these two relations shows nearly the same relative values of calcium, silicon and oxygen in the original and in the corroded surface layer.

Increased concentration of magnesium in the surface layer can be caused by back precipitation of Mg^{2+} ions released from glass into the corrosion solution. In such a case an additional layer should be formed on the original surface, probably consisting of magnesium and calcium silicates or magnesium hydroxide, i.e. of compounds with very low solubility in water. The pH value in the solution during static test increased fast from the initial value 5.5 to 8.5 and was approximately constant. The maximum SiO_2 concentration in the solution was $209 \mu\text{g} \cdot \text{cm}^{-3}$. Assuming the pseudocongruent dissolution of magnesium with respect to SiO_2 , the negative logarithm of the $\text{Mg}(\text{OH})_2$ ion activity product defined as

$$pI(\text{Mg}(\text{OH})_2) = -\lg(a_{\text{Mg}^{2+}} \cdot a_{\text{OH}^-}^2) \quad (1)$$

with a_i = actual activity of ion i , was calculated. Its value was about 10.9. The negative logarithm of the solubility product $pK(\text{Mg}(\text{OH})_2)$ was found to be 8.5 [13]. That means the solution is undersaturated with respect to $\text{Mg}(\text{OH})_2$. The atomic relation Me:Si:O (Me = magnesium, calcium) at the surface is near to the relation 1 : 1 : 3 in MeSiO_3 . The pI values for CaSiO_3 and MgSiO_3

$$pI(\text{MeSiO}_3) = -\lg(a_{\text{Me}^{2+}} \cdot a_{\text{SiO}_3^{2-}}) \quad (2)$$

were calculated considering the H_2SiO_3 dissociation equilibria in the solution



Assuming the maximum SiO_2 concentration $209 \mu\text{g} \cdot \text{cm}^{-3}$, the following pI values were calculated: $pI(\text{MgSiO}_3) = 7.1$, $pI(\text{CaSiO}_3) = 6.9$. For the SiO_2 con-

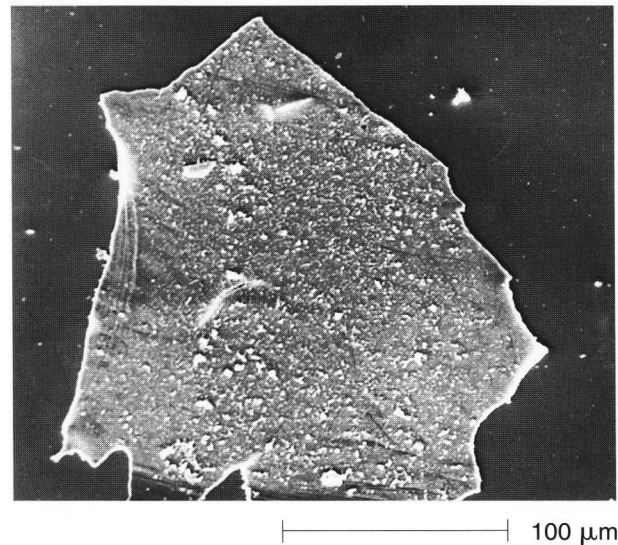


Figure 3. SEM micrograph of the glass surface ("top" side) after corrosion under static conditions (11 d, 95°C).

centration $50 \mu\text{g} \cdot \text{cm}^{-3}$ representing the earlier stages of interaction follows $pI(\text{MgSiO}_3) = 8.3$, $pI(\text{CaSiO}_3) = 8.1$. The values $pK(\text{MgSiO}_3) = 43$, $pK(\text{CaSiO}_3) = 10$ were calculated using thermodynamic data published by Paul [14]. These values are valid for 25°C. They could be smaller for 90°C but it is probable that the solution is strongly supersaturated with respect to MgSiO_3 and supersaturated with respect to CaSiO_3 . The assumption of precipitation of silicates is in agreement with other authors [15 and 16]. The glass-water interaction then consists of the

- $\text{Na}^+ - \text{H}_3\text{O}$ interdiffusion resulting in a gel-like layer in the glass surface,
- partial dissolution of the gel layer,
- precipitation of MgSiO_3 and to smaller extent of CaSiO_3 on the glass surface,
- diffusion of Mg^{2+} ions through the gel layer towards the bulk glass.

Another explanation is that the surface layer is created by a partially damaged and hydrated silicate network which may to some extent have a gel structure with reabsorbed Me^{2+} ions [17 and 18]. Figures 3, 4a and b show a part of such a corrugated surface layer after corrosion. The damage of the surface is not homogeneous and its intensity varies in different places. Mg^{2+} and Ca^{2+} ions are concentrated in isolated particles which are spread on the surface of the basic glass matrix (figures 4a and b). The exact form in which magnesium and calcium are bound in the damaged surface could be better described if a molar composition of all components in the surface layers were known. A similar structure of the surface damaged by corrosion was also reported by Lodding et al. [19].

Figure 5 represents the concentration distribution of some elements in the glass surface layer exposed to streaming water in a Soxhlet apparatus. In such a case,



a) |-----| 100 μm



b) |-----| 100 μm

Figures 4a and b. X-ray images showing the distribution of two different elements in the same area as in figure 3. (The white spots indicate the location of the element.) a) Calcium, b) magnesium.

the concentration profiles of elements after corrosion are practically identical with the original ones. This phenomenon can be explained by pseudocongruent dissolution of glass as a whole, characterized by a continuous shift of the boundary between the glass and the corrosion medium. Total dissolution of the basic silica glass network built by silicon and oxygen atoms appears to be a fundamental process during corrosion in streaming water, while interdiffusion of alkali and hydrogen ions does not substantially affect concentration changes.

4. Conclusions

Concentration distribution of sodium, calcium, magnesium, silicon and oxygen atoms in a thin surface layer of a float glass sample ("top" side) was investigated

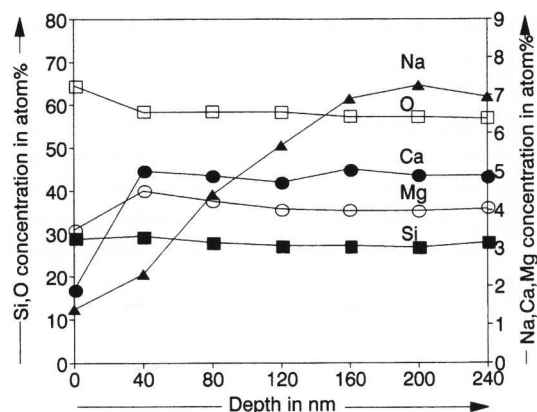


Figure 5. Concentration profiles of elements in the surface layer ("top" side) of the float glass after corrosion test in the Soxhlet extractor (11 d, 95°C). Theoretical concentrations (in atom%) of bulk glass: 25.3 Si, 60.3 O, 3.0 Ca, 2.0 Mg, 9.3 Na.

using ESCA. The original glass surface and also the surface layer exposed to corrosion in aqueous solution were studied by this method.

If the corrosion process proceeds in streaming water, the distribution of elements does not show any significant change.

In the case of magnesium and sodium especially corrosion in a static aqueous solution causes some changes in concentration distribution. Magnesium concentration increases, while sodium concentration decreases practically to zero in a thin surface layer, the thickness of which amounts to about 360 nm. The relative amount of calcium, silicon and oxygen appears to be practically the same both in the original and in the damaged glass surface layer.

The magnesium and sodium concentration changes as well as electron microscope investigations indicate formation of a surface layer deteriorating the "top" side of float glass exposed to static aqueous corrosion.

5. References

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