SCIENCE FOR GLASS PRODUCTION

PRINCIPLES OF THERMOCHEMICAL SURFACE MODIFICATION OF COMMERCIAL SILICATE GLASSES

A. V. Gorokhovskii


The relationships between the structural parameters of surface layers, production conditions, and consumer properties of sheet glass examined in [1 - 4] enable us to take a novel approach to the thermochemical modification of the glass surface in the course of manufacture and secondary treatment. In particular, float glass has been found to have three surface layers differing in chemical composition. Moreover, these layers exhibit their structural features each in its own way, depending on the conditions in which the surface has been formed.

On the one hand, it is evident that control of the process variables involved in surface formation can serve as a method of thermochemical modification. In particular, this can be achieved through control of the hydrogen and oxygen content of the shielding atmosphere above the float bath.

On the other hand, the results obtained to date provide a basis for identifying the key mechanisms whereby the various reagents affect formation of the surface structures typical of each of the surface layers produced. The likely mechanisms responsible for modification of the surface structure in glass should thus be analyzed proceeding from the fact that commercial silicate glasses have three surface layers basically differing in the concentration of modifier ions and the connectivity of the element-oxygen network [4].

Somewhat arbitrarily, three key mechanisms can be identified.

1. Treatment that tends to reduce the diffusion of sodium to the freshly formed surface of the glass and inside the subsurface layers aligned parallel to the surface. The first subsurface layer produced in this way is depleted of sodium, and the resultant surface has a higher stability in a damp atmosphere. The second subsurface layer is less pronounced, and this reduces the probability for thermoelastic stresses to be induced at its boundaries. It has a more homogeneous structure, so the concentration of cracks inside the layer itself is reduced. All of this improves the thermomechanical properties of the glass.

The above treatment can be effected in the following ways:

- with reagents that would prevent the formation of ion-exchange centers on the glass surface;
- with reagents that would block the ion-exchange centers formed;
- with reagents that would promote processes tending to reduce the excess energy of the freshly formed surface.

2. Treatment with reagents able to leach the first surface layer of the glass.

The first surface layer produced by this kind of treatment is depleted of sodium ions and, if the treatment has been applied at temperatures above the annealing temperature range, its elemental oxygen network has a fairly high degree of connectivity. The second surface layer is then well-defined and impedes the diffusion of sodium from the bulk to the surface of the glass. The surface formed as described above has improved chemical stability, high adhesion, and high microhardness. As to strength characteristics, such a surface will obviously have high resistance to the action of abrasive particles. This will reduce the influence of the first level of

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strength (50 MPa), which is determined by the resistance of the surface to the action of abrasive particles. However, the high degree of structural inhomogeneity of the surface layers will lead to an increased concentration of microcracks in them. Because of this, the second level of mechanical strength (100 MPa) will be felt more strongly.

The above form of glass treatment can involve the use of reagents that fix the sodium of the subsurface layers into films at the surface, which can later be removed by water.

(3) Treatment with reagents that would only slightly affect the structure of the first and second subsurface layers, but would promote the formation, on the surface, of protective films whose structure and properties would subsequently govern the service properties of the glass.

The principal requirement to be met by the ways in which this kind of treatment can be applied is that the films it produces must make a tight union with the glass surface (the requirement of a strong adhesive contact).

A separate group of techniques can be mentioned, in which the surface of the freshly formed glass is given a combination treatment with several kinds of reagents, each acting on the surface properties of the glass via one of the mechanisms examined above.

Also, it should be borne in mind that the same reagent can sometimes affect the structural factors of the surface layers via several different mechanisms simultaneously.

The principles that one should take as a guide when one selects reagents for the thermochemical surface treatment of silicate glasses and glass products can be stated as follows. These principles are of a rather general character and can be of use both at glass works in order to control some particular consumer properties of the glass, and in developing new types of modifying reagents.

Above all, one should proceed from the fact that there is a rigorous pattern of relationships between the physicochemical and thermophysical conditions in which the glass is drawn and its surface is formed, the structural characteristics of the surface, and the specific service properties. In turn, these relationships owe their existence to the mechanisms by which the surface layers acquire their structure. The processes responsible for the structure that the surface of melt-drawn multicomponent silicate glasses acquires are outlined in Table 1. In turn, these processes determine how they can be controlled.

When choosing how to control the way a surface layer should acquire its structure, account must be taken of the link that exists between the controlled structural parameter and a specific service property of the glass. The pattern of relations most typical of sheet glass is given in Table 2, and the correlations between the key glass-drawing parameters and the processes responsible for the structure produced in the surface layers of thermally polished glasses are listed in Table 3. From a comparison of the data in the two tables, it is possible to predict how the service properties of glasses will change due to control of the process variables involved in glass-drawing.

From the listing below it will be clear how the processes responsible for the structure formed in the surface layers of multicomponent silicate glasses can be controlled by purposefully allowing certain chemical reactions to take place on the surface of freshly formed glass through changes in the atmosphere.

<table>
<thead>
<tr>
<th>Methods of control</th>
<th>Way to achieve the goal</th>
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<tbody>
<tr>
<td>Reduction of overall chemical activity of the surface</td>
<td>Greater role of reconstruction processes:</td>
</tr>
<tr>
<td>Formation of more connected and inert structures</td>
<td>increased inertness of the atmosphere</td>
</tr>
<tr>
<td>Neutralization of especially active surface centers, selective or global treatment:</td>
<td>longer residence of glass at temperatures above $T_c$</td>
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<tr>
<td>by gaseous acids</td>
<td>Neutralization of especially active surface centers, selective or global treatment:</td>
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<tr>
<td>by gaseous bases</td>
<td>by gaseous bases</td>
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<tr>
<td>by water vapor</td>
<td>by water vapor</td>
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<tr>
<td>Formation of oxide coatings</td>
<td>Formation of oxide coatings</td>
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<tr>
<td>Immobilization of modifier particles</td>
<td>Immobilization of modifier particles</td>
</tr>
<tr>
<td>Surface blockage</td>
<td>Surface blockage</td>
</tr>
<tr>
<td>Formation of active centers on the surface and subsequent treatment with:</td>
<td>Formation of active centers on the surface and subsequent treatment with:</td>
</tr>
<tr>
<td>surface-blocking reagents</td>
<td>surface-blocking reagents</td>
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<tr>
<td>surface property-changing reagents</td>
<td>surface property-changing reagents</td>
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<tr>
<td>Fixation of sodium ions: in surface compounds</td>
<td>Fixation of sodium ions: in surface compounds</td>
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<tr>
<td>in the structure of protective coatings</td>
<td>in the structure of protective coatings</td>
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**TABLE 1**

<table>
<thead>
<tr>
<th>Macroprocesses</th>
<th>Microprocesses</th>
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<tbody>
<tr>
<td>relaxation</td>
<td>formation of point active centers</td>
</tr>
<tr>
<td>reconstruction</td>
<td>formation of spatial active centers</td>
</tr>
<tr>
<td>Diffusion of SAS* to surface</td>
<td>Diffusion of SAS to regions of defect concentration</td>
</tr>
<tr>
<td>Thermodiffusion</td>
<td>Structuring at boundaries of inhomogeneities</td>
</tr>
<tr>
<td>Diffusion of adsorbates into the glass bulk</td>
<td>Surface crystallization</td>
</tr>
<tr>
<td>restructuring of the element-oxygen network of the entire surface layer</td>
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</tbody>
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* SAS stands for the surface-active components of the melt.