Applied Thermal Engineering 31 (2011) 1272–1278

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Simulation of tin penetration in the float glass process (float glass tin penetration)

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A R T I C L E I N F O

Article history:
Received 25 September 2010
Accepted 18 December 2010
Available online 25 December 2010

Keywords:
Tin penetration
Float glass
Numerical simulation

A B S T R A C T

The flat glass produced by the float glass process has a tin-rich surface due to the contact with molten tin. The penetration of tin into the glass surface is assumed to involve coupled diffusion of stannous (Sn^{2+}) and stannic (Sn^{4+}) ions. The diffusion coefficients of these ions were calculated using the modified Stocks–Einstein relation with the oxidation velocity of stannous ions depending on the oxygen activity in the glass. The ion diffusion was analyzed using a coupled diffusion simulation with a modified diffusion coefficient to compensate for the negative effect of the glass ribbon's stretching or compressing in the glass forming process. Tin penetration simulations for both green glass and clear glass show an internal local tin concentration maximum in green glass which is quite different from that in clear glass. The local maximum in the profile is associated with the accumulation of stannic ions where the greatest oxygen activity gradient occurs. Since more float time is needed in the manufacture of thicker glass plate, the tin penetrates to a greater depth with the maximum deeper in the glass and the size of the maximum larger for thicker glass.

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1. Introduction

Float glass has excellent flatness over a large area without polishing and the productivity is extremely high. The float process is the main method for manufacturing flat glass for architectural, automobiles and displays. 90% of the world's production of flat glass is formed using float technology [1]. The worldwide production of flat glass in 2007 was approximately 50 million tons with the market growing in volume at around 4 percent a year [2].

The basic principles of float glass manufacturing were developed by Pilkington [3]. The forming of the glass ribbon and its cooling take place in a tin bath. In the float process, a continuous ribbon of glass moves out of the furnace at a temperature of around 1373 K and drifts on a bath of molten tin. As the glass flows down the bath, the glass temperature is gradually reduced allowing solidification of the glass ribbon. During the production of the float glass, the tin ions diffuse from the underlying molten tin bath into the bottom surface of the glass. Consequently, the glass has two distinctly different surfaces with the properties of the tin containing surface significantly different from the top surface [4].

The glass ribbon enters the annealing lehr with a temperature of about 873 K after the forming process. At the lehr entrance, the bottom surface is sulfurized, forming a thin layer of sodium sulfate microcrystals to protect the surface in contact with the lehr rolls. After heat treatment in an oxidizing atmosphere, the oxidation of stannous ions at the tin containing surface will cause microscopic wrinkling and the phenomenon of bloom, a greyish haze which can be observed [5]. Thus, tin penetration is detrimental to glass quality.

Many experimental and theoretical studies have sought to understand the interaction between tin and the glass melt in the tin bath. However, the diffusion of tin in float glass is related to numerous variables such as glass composition, glass redox, ion exchange, tin bath atmosphere, temperature and float time [6]. Sieger [7] measured the tin depth profiles of clear float glass using EPMA (Electron Probe Micro Analysis) and observed the local tin concentration maximum (tin hump) phenomenon. Verita et al. [8] found that longer residence times on the tin bath resulted in a systematic increase of the tin penetration. Recent data using Mössbauer spectroscopy identified the charge states of the tin and iron [9]. The total tin concentration as well as the magnitude of the maximum in the tin profile was found to increase with increasing iron content. The data also showed that the Sn^{4+} percentage of total tin increased with increasing iron content and the maximum was associated with the accumulation of Sn^{4+} [9–14]. Johnston [15] studied the redox behavior of a variety of polyvalent metal ions in glass. Cook and Cooper [16] outlined a dynamic model for the observed reaction between the float bath and the glass melt. They found that the inward motion of Sn^{2+} is affected by its oxidation to Sn^{4+} in a redox exchange with Fe^{3+}.

Numerical simulation is an easy way to predict the tin profiles and to further optimize the float process for effective tin diffusion coefficient has been used to calculate the tin penetration profile in many

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doi:10.1016/j.applthermaleng.2010.12.030

studies. Wang et al. [17] and Shao et al. [18] assumed that an oxidized layer formed on the glass with adherent diffusion coefficient for the tin while the glass was being heated in an oxidized atmosphere. A one-dimensional finite difference model was used to predict the local tin concentration maximum in the tin profile. Paulson [19] used an equibrium thermodynamic model to describe the interactions between the glass and tin with the fraction of tin which oxidizes to Sn^{4+} found to be related to the temperature and oxygen activity. He assumed that the effective diffusion coefficient was constant, so the tin penetration profile could be predicted using the complementary error function solution to Fick's second law of diffusion.

Despite these efforts, the diffusion behavior of the stannous and stannic ions is still not well understood since the effective diffusion coefficient is not known. Also the diffusion coefficients of stannous and stannic ions are strongly dependent on temperature. Due to the wide range of temperature in the glass forming process, the application of a constant diffusion coefficient will significantly reduce the simulation accuracy.

The purpose of the present study is to develop a numerical method which can simulate coupled diffusion of both stannic and stannous ions based on the tin penetration mechanism. To improve the simulation accuracy, the model must properly predict the redox reaction between two kinds of ions and the influence of temperature on the diffusion process. The characteristics of the tin penetration profile observed in experimental data, especially the local tin concentration maximum in green glass, should be accurately reproduced by the numerical simulations. The influence of glass thickness on the internal tin penetration will also be analyzed.

2. Tin penetration mechanisms

2.1. Redox reaction

A sketch of the float process is given in Fig. 1. The tin bath is an airtight enclosure with a controlled atmosphere of nitrogen and hydrogen to avoid oxidization of the tin. The passage of the glass through the tin bath creates a glass ribbon. The glass ribbon is pulled by top rollers at the edges of the ribbon to achieve the proper thickness. All the float glass then passes through an annealing lehr immediately after it is removed from the tin bath to eliminate thermal stresses introduced during the float process. After annealing in air at a controlled cooling rate, the glass leaves the lehr at about 473 K.

During normal operation of a float line, the tin bath becomes contaminated with elements from the glass and the bath atmosphere which combine with the tin to form tin-containing species. The two most significant elements are oxygen which comes predominantly from air leaks into the float bath chamber and iron which comes from the glass itself [1].

During the heat treatments in the tin bath, the iron and sodium in the glass diffuse toward the surface. When the glass melt in contact with the tin in the tin bath, there is an immediate driving force for a redox reaction at the glass melt/tin interface with the Na_2O and other glass component cations reduced where the Sn is oxidized. The diffusion mechanism of tin into the glass during the float process is driven by the chemical potential for oxygen established in the glass by the surface redox reaction and the chemical inter-diffusion potential created by the addition of new cations from the oxidized float medium [16].

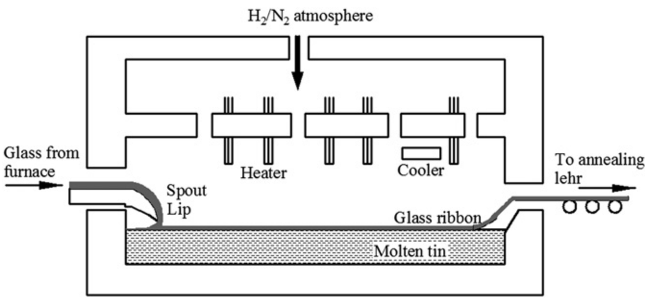

Fig. 1. Sketch of the tin bath.

The change in the Gibbs energy for this oxidation of Sn to SnO at the glass melt/tin interface is given by

$$\Delta G_{\mathrm{Sn:SnO}} = \Delta G^{0}_{\mathrm{Sn:SnO}} + RT\ln\frac{a^{2}_{\mathrm{SnO}}}{a^{2}_{\mathrm{Sn}}p_{\mathrm{O_2}}} \tag{1}$$

The dynamic processes in the glass melt that include the glass melt/tin interfacial reaction are illustrated in Fig. 2. The processes are inter-diffusion of $Sn^{2+,4+}$ions into the glass and Na^{+} and Fe^{2+} out of the glass. The reduction reaction in the glass melt occurs by the outward diffusion of O^{2-} with the charge compensated by a parallel flux of electron holes or the inward flux of divalent, network modifying cations and the inter-diffusion of cations.

Significant diffusion of tin results from the Sn^{2+} concentration decrease in the glass. No marked change in the tin concentration profile is observed for glass heat-treated in an Ar atmosphere. Therefore, the significant diffusion of tin is induced by oxygen diffusion from the atmosphere [11].

Near the float glass surface, the tin is incorporated as Sn^{2+}, but after some inter-diffusion, the Sn^{2+} is oxidized to Sn^{4+}. Since the Sn^{4+} acts as a network former, while the Sn^{2+} acts as a network modifier in the glass, the mobility of Sn^{4+} is some order of magnitudes smaller than that of Sn^{2+}. The stannous ions are more prevalent near the surface, while in the sub-surface tail of the diffusion profile, the stannic form predominates as verified by the Mössbauer experiments [10].

The experimental data shows two conspicuous internal peaks in the float glass, one for tin within its diffusion range and the other for iron at the end of the tin penetration. The significant diffusion of tin into the surface is slightly reduced by increasing the iron content in the glass since the iron in the glass reacts with tin as [6,20]:

$$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+} \tag{2}$$

2.2. Kinetic modeling

The governing equation for non-steady state diffusion with reactions is

$$-\nabla\cdot(D\cdot\nabla C) + \frac{\partial C}{\partial t} - G = 0 \tag{3}$$

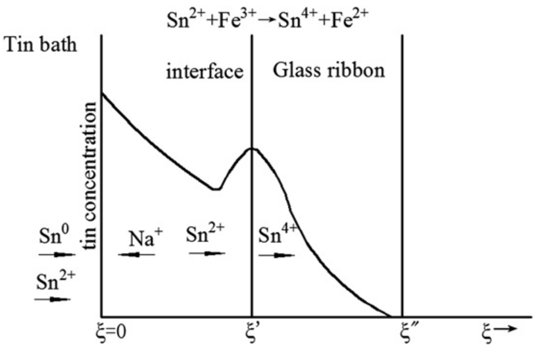

Fig. 2. Schematic diagram of the reactions in the float glass.

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