Journal of Non-Crystalline Solids 358 (2012) 349–353

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Effect of stirring on striae in glass melts

Martin Jensen, Yuanzheng Yue *

Section of Chemistry, Aalborg University, 9000 Aalborg, Denmark

ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form 27 September 2011
Available online 26 October 2011

Keywords:
Melt homogenization;
Stria;
Stirring;
Retention;
Diffusion

ABSTRACT

Chemical striae have often negative effect on the glass properties, and hence, elimination of striae has been a key issue in glass science and technology. To produce highly homogeneous glasses, it is necessary to stir melts during the melting process. To explore the physical origin of the stria elimination during stirring, and to optimise the homogenisation process, both simulations of striation and homogenisation experiments are performed. The results show that stirring broadens the stria size distribution in the melt through conversion of larger striae into smaller ones. Only the striae with a size below half the diffusion length in the melt can be eliminated during the melting process. Stirring itself does not homogenise the melt, but enhances the stria elimination rate by generating small striae.

1. Introduction

The homogeneity of glasses is important to their physical properties [1,2], and hence, homogenisation of the melt is a crucial step in glass production. Inhomogeneitiy is a complex term since it is influenced and determined by several factors such as bubbles and striae. Some types of striae are of physical origin, i.e., difference in cooling rate, while others are of chemical origin, i.e., difference in the chemical composition and/or redox state. As a stria is a three dimensional amorphous domain within the glass matrix, the stria can be described by different parameters such as its volume (size), geometry and compositional difference. Due to the strong impact of inhomogeneities on glass performance, glass scientists and technologist have made considerable efforts in finding ways to characterise, understand and remove inhomogeneities from glass products [3–13]. Often the extent of striations in a glass melt is reduced by elevating the melting temperature and/or prolonging the retention time. Until the research of optical glasses began in Jena more than one century ago, glass technologists did not realise that application of a high temperature resistant stirrer during melting process is one of the most efficient techniques to achieve high homogeneity of a glass melt. Since then, studies have been conducted to elucidate the effect of stirring on the homogeneity of glass melts [14–18]. Most of those studies focus on the major source of inhomogeneity, namely, stria, which is also the object of the present study. Despite progress of earlier studies in improving the homogenisation process by stirring and in understanding its mechanism, some key questions are still not fully understood. What is the physical origin of the homogenisation enhancement by stirring? Is stirring during the entire melting process desirable or does a threshold for the homogeneity improvement by stirring exist? What are the individual roles of retention and stirring on the elimination of striae from glass melts?

To clarify those questions, we have designed and performed a simple set of stirring-retention combined experiments on a borosilicate model glass melt. Furthermore, through image processing we simulate the evolvement of striae, and directly reveal the influence of stirring on the stria size and the compositional difference to the glass matrix.

2. Experimental

2.1. Modelling

An image of a periodic striation with a stria length of 200 pixels was generated using the programme Gimp (GNU image manipulation programme). The stria was introduced by the blend function with a 0–255 linear grey scale gradient and a triangular wave repetition. As a grey value of 0 and 255 corresponds to completely black and white, respectively the colour of the simulated stria changes between black and white. The grey scale gradient was started at 0,0 pixel and ended at the position 50,50 pixel. The reasons for choosing a triangular wave are described in detail elsewhere [19]. The striation was subjected to 1, 2 or 3 stirrings of 360° by applying the whirl function in Gimp. For the stirring, a pinch amount of 0.5 and a radius of 1.3 were used.

2.2. Glass melting

Borosilicate glass with the composition (wt.%): 49.7 SiO_2, 20.5 B_2O_3, 2.0 Al_2O_3, 4.0 Li_2O, 7.8 Na_2O, 4.0 K_2O, 3.0 CaO, 9.0 ZnO was prepared and used for the homogenisation experiments. In addition, another glass with the same basic composition, but containing 0.4 wt.% CoO was produced. The addition of CoO to the batch causes intense blue colouring of

* Corresponding author. Tel.: +45 99408522; fax: +45 96350558.
E-mail address: yy@bio.aau.dk (Y.Z. Yue).

0022-3093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.09.040

the glass. After casting of the CoO doped borosilicate glass, it was crushed and the pieces with size of 1–2 mm were collected for further melting experiments.

150 g of the borosilicate glass melt were produced in a $Pt_{90}Rh_{10}$ crucible (diameter 7.3 cm, height 8 cm) in an induction furnace equipped with a 40 kW generator (Hüttinger, Germany). The batch was initially melted at 1120 °C for 1 h to obtain a homogeneous glass melt. At 1120 °C, the viscosity of the melt was measured by means of rotational viscometry, and was found to be 1.7 Pa·s. The viscosity was measured using a concentric cylinder viscometer under atmospheric conditions. The furnace was a box furnace (model HT 7, Scandiaovnen A/S, Allerød, Denmark) and the viscometer head was a Physica Rheolab MC1 (Paar Physica, Stuttgart, Germany). During the melting process, the platinum crucible was covered with an alumina lid to maintain a uniform temperature in the entire melt. After 1 h at 1120 °C, the alumina lid was removed and 0.75 g CoO doped glass grains with a size of 1–2 mm, were added to the 150 g glass melt. Afterwards, the glass grains were dissolved into the original clear glass melt in the crucible under the alumina lid for 2 min. After the CoO doped glass pieces were melted, a 15 min homogenisation process including a certain duration of stirring was initiated. Two series of homogenisation experiments were performed. For the first series, the melt underwent a period of stirring and subsequently a period of retention (denoted as the SR series) (see Table 1). For the second series, the opposite is the case, i.e., the melt first underwent a period of retention and subsequently a period of stirring (denoted as the RS series). For each melt sample in the SR and RS series a new batch of 150 g was prepared. The durations of retention and stirring in the SR and RS series are given in Table 1. During both the retention and the stirring period, the crucible was covered with an alumina lid. For the stirring periods the crucible was covered by an alumina lid with a hole for the stirrer. To stir the melt, a $Pt_{90}Rh_{10}$ stirrer with a propeller (height 2 cm and total width 4 cm) was used. The speed of the stirring was fixed at 20 rounds/min. After the 15 min homogenisation interval, the melt was kept at 1120 °C for another 5 min before casting

The melt was cast in a mould with a brass bottom and steel walls and was allowed to cool for ~10 s. Then the glass piece was transferred to an annealing furnace at 475 °C, i.e., the glass transition temperature of the glass, and was annealed for 0.5 h before the furnace was turned off.

2.3. Sample preparation

The obtained glass blocks were cut to pieces with a size of about 2×2 cm^2 with diamond coated blade using a Sectocom machine (Struers, Denmark). After cutting the samples were ground coparallel on a cast iron disk using water suspended SiC powder with ISO/FEPA grit size of 80, 220, 400, 800 and 1200. The samples were polished on an MD Plan cloth (Struers, Denmark) with 9 μm diamond paste and further polished on another MD Plan cloth with 3 μm CeO_2 powder humidified with water. After grinding and polishing, the samples had a thickness of 3–4 mm. From each melt, three glass pieces were prepared, which represent 15–20 wt.% of the glass melt.

Table 1
The homogenisation conditions of the studied glass melts, including the retention (R), and stirring (S) durations at 1120 °C. SR series refers to the glass series that underwent stirring followed by retention, whereas RS series refers to retention followed by stirring. For both series, the total homogenisation duration is fixed at 15 min. The number behind both SR and RS refers to the stirring duration.

SR series	SR2	SR4	SR6:	SR10:	SR15:
(S+R) (min)	2+13	4+11	6+9	10+5	15+0
RS series	RS4:	RS6:	RS9:	RS12:	RS15:
(S+R) (min)	11+4	9+6	6+9	3+12	0+15

2.4. Striae characterisation

The striae were analysed by means of image analysis, which is an effective method to characterise striae in various glasses [9]. The image acquisition was performed by an Epson Perfection V700 Photo scanner (Seiko Epson Corporation, Nagano, Japan) working in transmission mode at 8 bit, and at a brightness of −15 and a contrast of 40. Some of the glasses contain bubbles. Since the bubbles affect the stria characterisation, they were removed from the acquired image through image processing prior to the striae characterisation in the programme ImageJ [20] as described in details elsewhere [21]. The transmission of the sample was converted to a grey value on the acquired image during the image acquisition. The grey values of the image were recorded along an inserted line (line scan) in the image with a length of 2000 pixels, which at the applied resolution of 3200 DPI corresponds to 15.88 mm. The recorded grey values were converted into absolute transmissions by means of a transmission calibration standard (IT8, T070408, LaserSoft Imaging). To remove the effect of sample thickness on the stria characterisation, the transmission values were normalised to a constant sample thickness by applying the Lambert–Beer law. Thus the difference in transmission values reflects the change of the absorption of the sample caused by CoO. In the Lambert–Beer law, the extinction coefficient was set to unity. It is reasonable to assume a fixed extinction coefficient since only the concentration of CoO varies and concentration differences in CoO are rather small (maximum 0.4 wt.%). Therefore, it is possible to convert the grey values of the image into a relative stria concentration through the Lambert–Beer law. 500 lines scans were recorded from the sample and a blank foil and processed according to a method reported elsewhere [9].

3. Results

To explore the effect of stirring on striae in glass melts, we first perform simulation of stria formation and deformation of the striae through stirring. The image with the simulated striation shows a periodic structure due to a fixed stria length of 200 pixels (Fig. 1A). Through processing of the image with the striation, it is possible to simulate a stirring effect. The striation subjected to 1, 2 or 3 times stirring of 360° is shown in Fig. 1B–D. Upon stirring, a deformation of the stria occurs, implying that the stirred striation has lost the periodicity of the initial striation. The corners of the image are almost unaffected by the stirring, suggesting that these domains in a real glass melting furnace would be dead-zones under the applied stirring conditions. To quantify the apparent shift in stria dimension due to stirring, the grey value across the images in Fig. 1 is measured. For images of real samples, the grey value is a quantity that is proportional to the optical transmission of the glass and therefore, measurement of the grey value of images can be regarded as a transmission measurement. To study the grey value fluctuations on the images, a line scan is performed. During the line scan, the grey value of the image is recorded along an inserted line with a length of 2000 pixels. The length of the fluctuations in grey value is quantified by subjecting the line scan to Fourier transformation [19]. The Fourier transformation spectra of line scans on each of the four images in Fig. 1 are shown in Fig. 2. The unstirred striation (Fig. 1a) shows a sharp peak at 200 pixels identical to the stria size of the striation. After being subjected to one round of stirring (dark grey curve), the sharp peak at 200 pixels vanishes and instead multiple peaks at dimensions down to 30 pixels are observed (Fig. 2). Further stirring (grey and light grey curves) generates striae with dimensions below 30 pixels. From the four Fourier transformation curves it can be stated that stirring deforms the striations and this leads to the generation of both larger and smaller striae, i.e., to a broadening of the size distribution of striae. The area under the curve in the Fourier transformation spectra, which is a measure of the total stria content, is unaffected by the stirring.