

THE DISSOLUTION OF CORDS IN MOLTEN GLASS

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Besides bubbles and solid inclusions, cords form a very important type of glass faults. With ever increasing demands on the optical quality of glass products, notably those of flat glass products and TV- and monitor screens, the behaviour of cords in the glass melt has become a very important theme.

However, the quantitative description of cord deformation and dissolution behaviour in the melt is still not well established. This presentation contributes to the description of the cord dissolution process in the glass melt. A model is presented which describes the simultaneous dissolution of a number of cords by diffusion. Recent advances in the methods to derive the diffusion coefficients of glass melt components will be discussed. The model and the diffusion coefficients are meant to be used in the 3D-models describing the complete glass melting process.

INTRODUCTION

Cords, glass inclusions - in glass with a slightly different composition as the base glass are an unwanted phenomenon in many glass products [1]. Especially products that have to meet the highest demands on optical properties (TV- and monitor screens, mirror- and automotive glass, camera lenses) have a very low tolerance for optical distortion. What is causing the trouble is that rays of light in the product are bent away by gradients in the refractive index [2]. In this respect refractive index gradients of 0.00001 mm^{-1} are already visible to the human eye. The visibility limit is associated with concentration limits of less than 0.1 wt% for most glass components, as can be estimated from models relating the refractive index to the glass composition [3]. This makes chemical (micro-) analysis of cords very difficult as a tool for cord diagnosis.

The demands for the optical homogeneity of Colour TV-screens and computer monitors has become ever stricter in the past few years, and the expectation is that this trend will continue in the near future. Better contrast and resolution, along with an increase in the number of image lines will undoubtedly make the screen more sensitive for optical distortion. For this reason, Philips Components has initiated studies to understand, control and suppress the formation of cords.

CORD SOURCES AND RELEVANT MECHANISMS

If we consider the glass melting process, we can discriminate a wide variety of possible causes for cords. These are roughly summarized in figure 1.

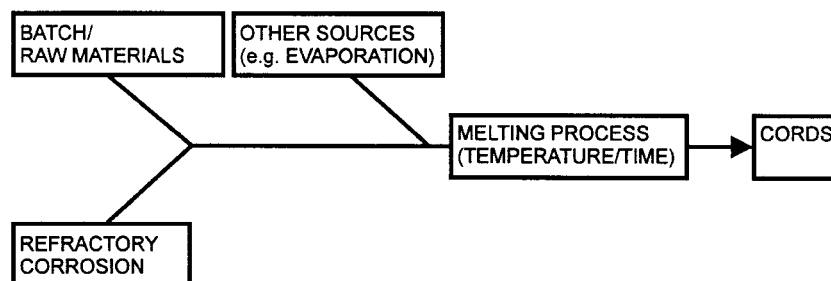


Figure 1. Ishikawa diagram cord sources.

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The main mechanisms related with cords in glass are [1]:

- batch melting: The residues of sand grains and other slowly dissolving components leave small areas with a composition that is different from that of the average of the glass melt. These areas are visible as cords.
- refractory corrosion: The corrosion of refractory materials causes the formation of a boundary layer that is enriched in the components of the refractory material (SiO_2 , Al_2O_3 , ZrO_2 , Cr_2O_3). When this boundary layer ends up in the bulk of the melt, it forms a cord.
- other mechanisms: besides batch melting and refractory corrosion there are a few other mechanisms, like evaporation that can cause variations in glass melt composition
- melting process: The cords that are formed in the melting process have to dissolve by diffusion and convection. Critical parameters in this respect are temperature, residence time and velocity gradients in the melt.

MODELLING THE DISSOLUTION OF CORDS

The first attempt to model the behaviour of cords in a full-scale glass melting tank was made by Geffken [4] and Becker [5, 6]. They considered the dissolution of isolated cords in molten soda-lime glass by diffusion and shear thinning. Their main assumptions were:

- cord dissolution is diffusion-limited; the diffusion coefficient is constant
- only one isolated cord is considered, diffusion is only considered in one dimension
- the velocity gradient in the direction of diffusion is the main cause of cord thinning

The conclusion of the work of Geffken and Becker [3, 4, 5] was, that the dissolution of cords in the melt is controlled by diffusion and by shear. Goldberg [7] reviewed the results of Geffken and Becker and concluded that the degree of homogenisation, defined as C/C_0 , where C is the concentration of the major cord component after dissolution and C_0 is its original concentration, is determined by a factor ϕ . This factor incorporates the effect of initial cord thickness, diffusion, residence time and shear, and is given by:

$$\phi = \frac{d}{4 \sqrt{(Dt^3 / (3 (dv/dz)^2))}} \quad (1)$$

where d - original cord thickness (m); D - inter diffusion coefficient ($\text{m}^2 \text{s}^{-1}$); t - time (s); dv/dz - velocity gradient in the direction of diffusion (s^{-1})

Later publications have considered how to incorporate the cord dissolution models in a 3D flow model [8].

However, the cord dissolution models that are currently used have one problem, that is especially important for batch cords. They all consider the behaviour of one single cord in an infinitely large glass melt, and they do not consider the interaction of neighbouring cords. By merging, these neighbouring cords tend to form larger cords, and thus become harder to dissolve. If one does not take this effect into account, the calculated dissolution time of cords becomes too optimistic.

THE NEW MODEL FOR CORD DISSOLUTION

In this paper a cord dissolution model is put forward that does take the interaction of neighbouring cords into account. The model is based on the use of the Einstein relation [9] for the movement of the particles that make up the cord in one dimension:

$$(\Delta X)^2 (\text{average}) = 2 D t \quad (2)$$

where $(\Delta X)^2 (\text{average})$ - mean squared displacement (m^2); D - inter diffusion coefficient ($\text{m}^2 \text{s}^{-1}$); t - time (s)

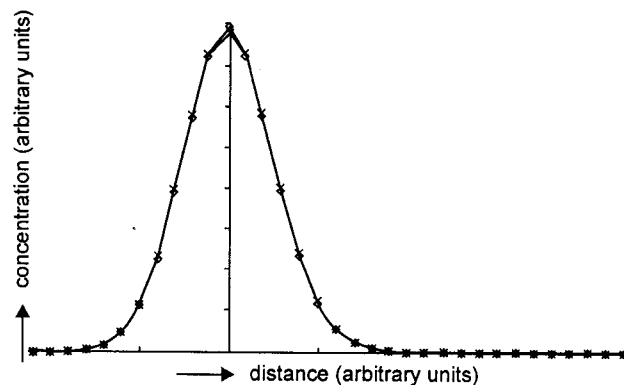


Figure 2. Diffusion simulation; 2 different methods originally a concentration pulse at $x = 0$, levelled out by diffusion.

x - numerical solution Ficks' law;
 ◇ - Gaussian peak $\sigma = \sqrt{2 D t}$

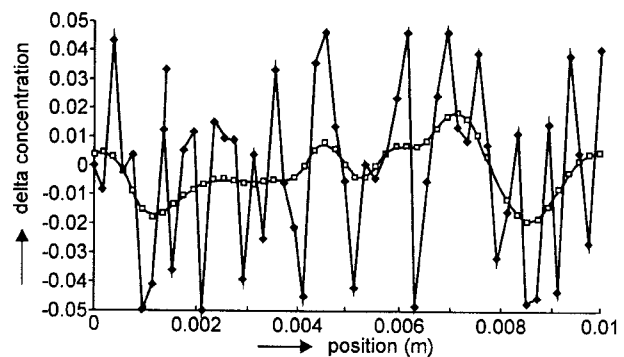


Figure 3. Model simulation diffusion in a stagnant melt Al_2O_3 , 1 day 1350 °C

◆ - original concentration; □ - end concentration.

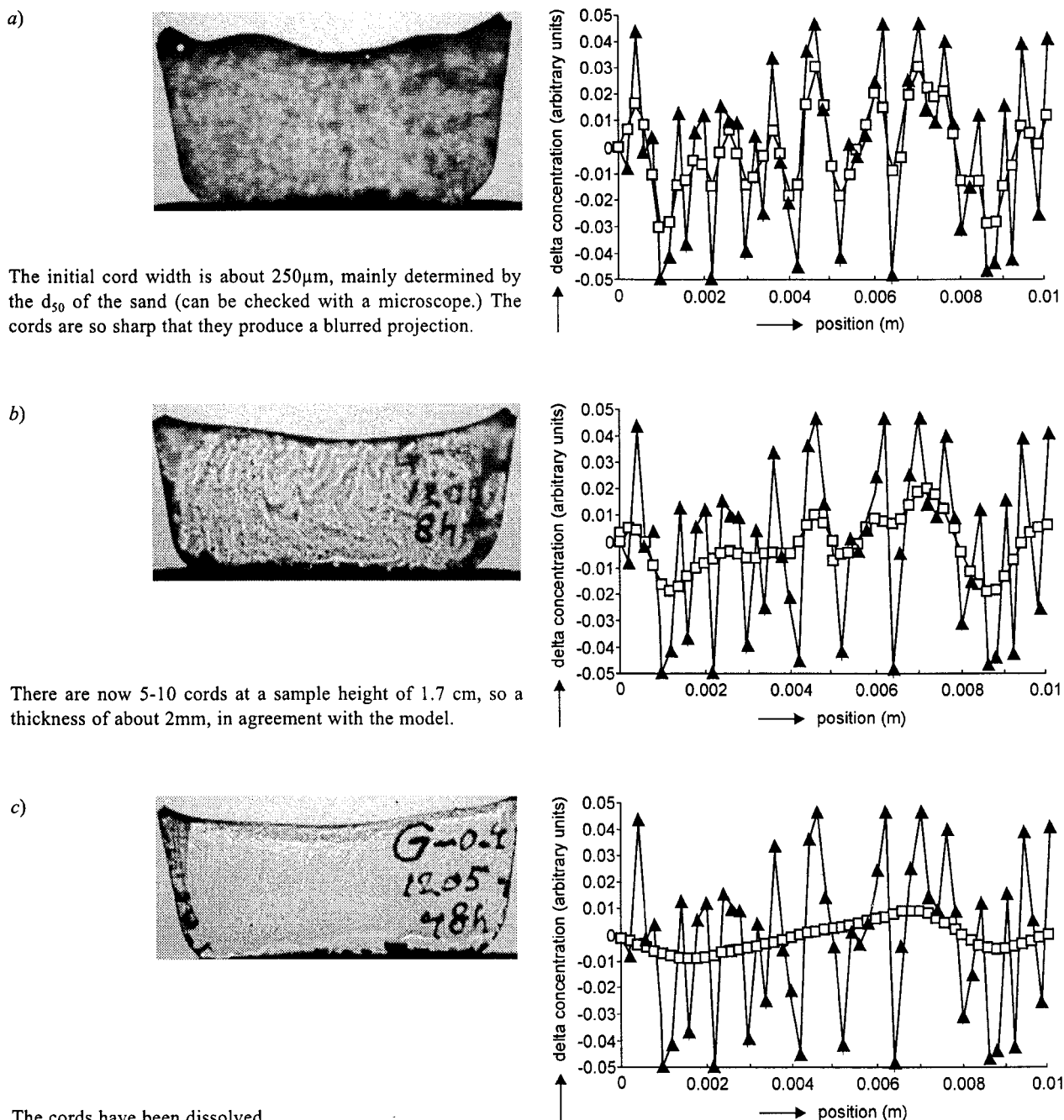


Figure 4. Cord projection images and model simulations of the dissolution of batch cords in CTV-screenglass melt.

Temperature 1205 °C;

Δ - original concentration; $\square$ - concentration after diffusion;

a) - 2 hours; b) - 8 hours; c) - 48 hours.

From equation (2) one can derive that the particles that are originally present in one fixed position (a concentration pulse at $x = 0$) will, after some time, show a Gaussian distribution of their position with a standard deviation in position of $s_x = \sqrt{2 D t}$. The diffusion coefficient in (2) is the same as the one in Fick's first law. This is graphically represented in figure 2.

A set of concentration pulses next to one another will level out as Gaussian curves of concentration versus position. The resulting concentration profile can be found simply by adding the resulting Gaussian curves of all original concentration pulses. Figure 3 shows the result of such an exercise on a concentration profile that was constructed from random numbers, as a simu-

lation of a typical cord pattern in a melt directly after batch melting (the simulation in fig. 3 is concerned with Al_2O_3 cords at 1350 °C).

In figure 3 it is clearly visible that neighbouring cords tend to merge into larger ones as time progresses. This effect is not taken into account by the models of Geffken and Becker [3, 4, 5].

As input, the model presented in figure 3 requires the correct value of the diffusion coefficient of the major glass melt component that makes up the cord. The model presented in figure 3 does not take velocity gradients into account.

MODEL VERIFICATION WITH LABORATORY MELTS

The model can be verified for stagnant melts by making polished cross-sections of laboratory melts after a series of dwell times at a fixed temperature. In these cross-sections, the cords can be made visible by cord projection [2]. The photographs in figure 4 show how the cords caused by batch melting (generally assumed to consist of differences in silica content of the glass melt) slowly dissolve with time. (TV-screen glass batch, 1205 °C). The model simulation for silica cords in the same glass at the same temperature are presented as well. The required dissolution time, which is visually observed, is about the same, as the time needed to eliminate the short-range chemical inhomogeneity (the inhomogeneity within a scale of around 1 mm distance). The cord width increases, and the cords become less distinct as both model calculations and visual observation show.

CONCLUSIONS

In this paper, a model is presented for the dissolution of large groups of cords in stagnant molten glass, notably those related with batch melting. Unlike the model of Geffken and Becker, the one that is currently most widely used, this model takes the merging of neighbouring cords into account, but not the effect of a velocity gradient.

When comparing the results of this new model semi-quantitatively with the observations on laboratory melts, the model predictions seem reasonably realistic.

FOLLOW-UP

The main interest in cord dissolution is not concerned with stagnant melts, but full-scale glass production units. In order to cope with the complication of convection, the model should be extended. This can be done by allowing the stretching and/or compression of the distance scale alternatingly between diffusion steps. Extending this simple model to realistic 3D conditions with convection will lead to a much more complicated model, but with the presented model for a stagnant situation an important step has been taken.

In order to be able to use this model for the prediction of the required dissolution time of various cord types, the diffusion coefficient of the main glass melt and/or refractory components must be known. Obtaining these diffusion coefficient by measurement or by an estimation method is the subject of a study that is currently being performed at Philips Display Components. The first results of this study, reviewing the literature available on melt phase diffusivities have been published in [10].

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ROZPOUŠTĚNÍ ŠLÍR VE SKLOVINĚ

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Kromě bublin a pevných inkluzí tvoří šlíry velmi časté vady skla. Se stále rostoucími požadavky na optickou kvalitu sklářské produkce, zejména plochého a televizního skla, se chování šlír stává důležitým tématem. Kvantitativní popis deformace šlíry a jejího rozpouštění však stále není dostatečný. Tento příspěvek přináší popis procesu rozpouštění šlíry ve sklovině. Je prezentován teoretický model popisující rozpouštění souboru šlír difúzním mechanismem. Dále je diskutován pokrok metody získávání difúzních koeficientů jednotlivých složek skla. Model rozpouštění šlír a hodnoty difúzních koeficientů budou použity v třírozměrném matematickém modelu popisující kompletní tavící proces.