Chapter I

Introduction

1.1 Motivation, Objective and Scope

Glass batch melting has been studied by many researchers on various scales, and under various conditions, in an attempt to optimize and control the melting process. The interest in a deeper understanding of the batch melting process is high. Although many details of this process have been investigated, no comprehensive understanding has been reached, and predictive modelling is still based on unproven assumptions. Since batch melting is the first step of the glass melting process, it controls the overall rate of the melting process. So, the knowledge of batch melting process is very important in order to optimize, and enhance the pull rate in glass production. Earlier work was mainly focused on the thermochemistry and kinetics of the chemical reactions involved in batch melting. In mixtures containing soda ash, limestone, dolomite and quartz as major components, the reaction progress was measured on small samples in terms of CO_2 liberation and electrical conductivity. The occurrence of primary melt was found to be the key event significantly accelerating the entire process. One of the variables which has been found to have a large effect on batch melting is the different particle size of the batch components. Batch melting has been studied extensively on a small scale by DTA, XRD, etc.

The main purpose of DTA measurement is to identify reaction taking place in a batch or sub-system of a batch, e.g. under variation of the heating rate. Until today, an investigation on thermal behavior of batch blankets is still limited to this well-known differential thermal analysis method, which can not handle samples over 5 g. This is very important if related to the industrial scale, because, the reactions taking place in a large scale are controlled by boundary conditions significantly different from the microscopic scale. For example: Heat conductivity within the sample has always a big influence on a DTA experiment, while the impact of heat conductivity is negligible on the large scale. The problem is that none of the methods involved in small scale experimentation can be transferred to experiments on a large scale (>10 kg). Transferable methods are needed by which batch melting can be monitored on a large scale in a reliable way. The methods to be used in this thesis is the determination of local electrical resistivity. It is the objective of this paper to apply this newly established method to batches typical of industrial mass glasses, and to one- two- and three-component sub-systems of such batches, in order to identify the key mechanisms of batch melting. In doing this, the effects of heating rate, particle size, cullet addition and melt accelerants will be investigated. The method will be supplemented by conventional DTA experiments, by oxygen partial pressure measurements at the interface melt/batch, and by hot-stage XRD.

1.2 Literature Survey

The first stage of the melting process for soda-lime-silicate glasses is a series of solid-state reactions which includes the release of gases. These reactions are followed by formation of the first liquid phase in the batch. It is at this time that reaction rate significantly speed up. Batch melting is terminated when a so-called rough melt has formed. This is basically an established melt still containing residual quartz grains. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been the primary analytical methods for determining the reactions between the components during the early stage (Dinger and Sheckler,1990). Much of the research has been done on various binary mixtures. Wilburn and Thomassan, (1958), observed that varying the silica particle size distribution in soda ash-silica batch resulted in a shift in the temperature where the main loss of weight occurs and a change in the rate of CO_2 release. Their DTA work indicated that the intensity of the endothermic and exothermic peaks varied with particle size in the soda ash-silica system. The intensity of other peaks decreased as the particle size distribution of the silica was decreased.

Most of the existing models in glass systems focus on heat transfer and flow in glass tanks. A model formulated by Hrma (1982) focuses on glass batch melting, but it simplifies the melting process such that for a given composition, temperature is the only variable. The result of this model is the prediction of time to batch free liquid. Work by Conradt et al (1994) focuses on the local

temperature distribution and primary melt formation in a melting batch heap. The occurrence of primary melt was identified by a sudden increase of conductivities.

Other methods used for studying the glass batch melting process include hot stage microscope and X-ray diffraction. The hot-stage microscope is used to observe physical changes which occur in a glass melt as the temperature was increased. Conroy et al. (1963) and Manring et al.(1964) indicated that the melting process was a three-stage process when studied under a microscope. The first stage of the melting process includes the solid-state reaction which occur at less than 840 ^{o}C. The second stage is the formation of the first liquid phase around the other grains. The final stage is the dissolution of the silica grains into the melt.

Riedel (1962) observed the interesting detail that soda preferentially attacks the quartz grains in low heating rate tests, while it preferentially attacks the limestone high heating rate test.

Speyer et al (SPEYER, 1991-1993) performed thermal analysis of reactions, including the effects of particle size, on the fusion of soda-lime-silicate glass batches containing melting accelerants. They used DTA, DTGA, and XRD interactively. Their work indicated that the NaCl was found to be the most effective melting accelerants due to the formation of a $NaCl-Na_2CO_3$ eutectic liquid phase at approx. 636 ^{o}C, which effectively attacked the silica and lime relics. CO_2 gas release

terminated 80 K earlier with 1 wt. % NaCl additions, when compared to the base glass batch.

The recent investigations present large amounts of empirical observations. They also reveal the fact that even the knowledge on fundamental phase diagrams is very limited. For example, no phase diagrams of dolomite-soda ash, and only an incomplete version of $Na_2O-MgO-SiO_2$ are available.