Review Paper

Parameters affecting the workability of container glass

Part 1. Description of the problem – Melting history, rheology and influence of microstructure

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Poor workability designates sporadic cases in which the forming behaviour of container glass varies unpredictably, impairing quality, productivity and sometimes strength. The literature offers several plausible suggestions to explain such a poor reproducibility of the rheological behaviour, generally associated with physicochemical parameters of the glass which are not routinely analyzed and which are supposed to vary with "melting history" (temperatures, raw materials, melting atmospheres) and to influence viscosity by altering the structure of "flow units", while the analytical composition remains unchanged. Alternative hypotheses are based on various not properly controlled process parameters, such as gob temperature distribution or plunger and mould condition including lubrication.

Moreover, recent advances in rheology show that during the most critical stages of the forming process viscosity may change drastically with the deformation rate, providing a further plausible explanation for the observed irregular forming behaviour. One of the most promising physicochemical parameters is the possible presence of microstructure (phase separation, clustering, microcrystals). While in model glasses the correlation between microstructure and rheology is well-established, both at equilibrium and at high shear rates, there is still a lack of conclusive evidence about the presence of microstructure in industrial multicomponent glass.

Verarbeitbarkeit von Behälterglas und ihre Einflußgrößen
Teil 1. Beschreibung des Problems – Schmelzvergangenheit, Rheologie und Einfluß der Mikrostruktur

Der Begriff „schlechte Verarbeitbarkeit" bezeichnet die gelegentlich auftretenden Fälle, in denen das Formgebungsverhalten von Behälterglas unberechenbar schwankt, was sich auf Qualität, Packleistung und manchmal auch die mechanische Festigkeit nachteilig auswirkt. Die Literatur bietet verschiedene plausibel erscheinende Erklärungen für solch eine schlechte Reproduzierbarkeit des rheologischen Verhaltens an. Diese steht im allgemeinen in Zusammenhang mit physikochemischen Parametern des Glases, die nicht routinemäßig bestimmt werden, und von denen man annimmt, daß sie mit der Schmelzvergangenheit (Temperaturen, Rohstoffe, Schmelzatmosphären) schwanken und die darüber hinaus die Viskosität durch Veränderung der Struktur der „Fließeinheiten" beeinflussen, während die analytische Zusammensetzung unverändert bleibt. Alternative Theorien stützen sich auf verschiedene, schlecht kontrollierbare Herstellungsparameter, wie z. B. die Temperaturverteilung im Tropfen oder den Zustand und die Schmierung des Stempels und der Form.

Neuere rheologische Untersuchungen zeigen, daß sich in den kritischsten Abschnitten des Formgebungsvorganges die Viskosität in Abhängigkeit von der Verformungsgeschwindigkeit drastisch verändern kann. Auch dieser Umstand könnte prinzipiell die beobachtete Unregelmäßigkeit des Formgebungsverhaltens erklären. Einer der interessantesten physikochemischen Parameter ist das Vorliegen einer Mikrostruktur (Phasentrennung, Clusterbildung, Mikrokristallinität). Während bei Modellgläsern der Zusammenhang zwischen Mikrostruktur und Rheologie als gesichert gilt, sowohl im Gleichgewichtszustand als auch bei hoher Verformungsgeschwindigkeit, ist für industriell hergestellte Vielkomponentengläser das Auftreten der Mikrostruktur eher postuliert als nachgewiesen.

1. Introduction

1.1. "Bad workability" affecting the production of container glass

An accurate description of the syndrome called "bad workability" was given by Poole (1967, 1977). Apparently, without any deliberate change of the melting schedule molten glass sporadically undergoes some kind of modification which affects the forming behaviour (but not routine viscosity measurements at equilibrium), while the analytical composition remains constant. For a given period of time machine operators complain about abnormal variations of the efficiency and quality of production with increase in checks, splits, poor glass distribution or inadequate strength and find it difficult to adjust and maintain a proper machine setting. Essentially, under the term "bad workability" the following problems are grouped:

a) defects (checks, splits);
b) poor glass distribution;
c) difficulty to adjust machine setting;
d) strength losses.

Such problems may occur together or separately; the characteristic feature is the sporadic, cyclic occurrence, the fact that the problem comes and goes without apparent reason, without any intentional modification of either the glass composition or of the melting and forming process. The impression of machine operators that during such periods the forming behaviour of glass in the machine is altered is expressed by terms such as "brittle glass" and (in German and Italian) "trockenes Glas", "vetro secco" (= dry glass). The term "brittle glass" (sprödes,

fragile) is sometimes also associated with empirical reports of (unannealed) containers producing an unusual sound or showing an unusually fine fragmentation pattern when taken from the line and smashed on the ground.

It is not easy to formulate in scientific terms a working hypothesis which can justify such empirical observations, in particular the impression that the glass during bad workability periods "is different" or "behaves differently". It is normally assumed that the rheological behaviour of the melt may change due to uncontrolled variations of the "melting history", which somehow modify the nature and size of the "flow units", as will be explained in detail in section 1.3.

Viscosity variations may justify the defects and unstable machine setting; a low strength may be attributed to the presence of internal defects in the bulk glass (due to microstructure development or to structural changes), or considered as a secondary effect (due to a particularly defective surface). Several years after the first scientific reports the problem is still discussed and specific research programmes have been set up at national level or by major producers. Some technologists maintain that glass may behave differently when some normally neglected physicochemical parameter shifts due to variations of melting history. Others take a skeptical stand, considering the melting history theory as too scientific and attribute all the problems to the still unsatisfactory control over several aspects of the glass melting and forming process. Indeed, several "process inconsistency factors", exemplified below, may in principle cause the symptoms normally considered typical of bad workability:

- a poor temperature distribution in the gob may cause different types of forming problems;
- a high number of checks (associated with strength losses) may be caused by contact with cold metal parts on the line, particularly if the expansion coefficient of glass is high (Mills 1989, Wasylyk 1990);
- surface defects and poor glass distribution (causing strength losses) may be due to poor melting practice (thermal problems), improper swabbing practice or hot end lubricants (Wasylyk 1990); in such cases progressive wear and accumulation of solid residues (such as the ashes of mould lubricants) may justify an apparently erratic occurrence;
- strength losses may be due either to various types of surface defects (caused by plunger or mould problems) or to thermal and mechanical shocks on the line;
- the constant composition requirement is respected only nominally; in practice, the use of foreign cullet produces substantial oscillations (Mastaler 1990).

This short discussion anticipates the difficulty, experienced by many laboratories, to distinguish between "genuine" cases of poor workability (i.e., those where glass properties change due to melting history variations, while the oxide composition is constant) and the problems caused by the process-related factors exemplified before.

1.2. Rheological problems in the forming process

Production reports on bad workability are of an essentially qualitative nature. It is possible to analyze quantitatively the different stages of the forming process with the help of suitable rheological equations (Eirich 1956; Mills 1973; Poole 1977; Coenen et al. 1985; Manns, Brückner 1988; Simmons et al. 1988 and 1989; Hessenkemper, Brückner 1988, 1989, 1990 (b) and 1991).

The forming process (gob shearing, finish pressing etc.) is characterized by the application of very high (transient) stresses at high shear rates (Mills 1973, Poole 1977). Above some critical shear stresses glass exhibits non-Newtonian flow and melt fracture (resulting in checks and splits) can occur (Poole 1977; Manns, Brückner 1988; Hessenkemper, Brückner 1989; Coenen et al. 1985). Measurements at high shear rates based on various experimental setups (such as cylinder compression, fibre elongation, plunger penetration, cone-plate or parallel-plate rheometry, torsion or flection pendulum) provide a quantitative evaluation of flow (sometimes also of fracture) behaviour in conditions similar to the ones encountered in production (Mills 1973; Coenen et al. 1985; Simmons et al. 1988; Manns, Brückner 1988, Hessenkemper, Brückner 1989; Guillemet, Gyonne 1990). The conclusions reached by such studies can be summarized as follows. Viscosity at equilibrium (routine measurements, low shear rates, Newtonian behaviour) can be predicted from the chemical composition. High-shear rate measurements show that during forming the (non-equilibrium) viscosity may differ significantly from the equilibrium values (non-Newtonian behaviour). Production defects and a difficult machine setting can be attributed to changes of the non-Newtonian (or shear-rate dependent) viscosity according to Poole (1977); Simmons et al. (1988, 1989). In most cases a stress-induced viscosity decrease is observed beyond certain stress levels. The occurrence of such shear thinning is not necessarily detrimental for the process of container glass forming. In principle, the easier deformability of glass can be compensated by adjusting machine operation, or even be exploited to enhance productivity (Simmons et al. 1988). However, local application of different strain rates in certain parts of the container may give rise to thin spots, impairing the room temperature strength (Simmons, Simmons 1989). While shear thinning is a behaviour common

to all silicate glasses, for each temperature the conditions for its onset and its extent were shown to depend on load conditions and melt viscosity. In particular, the rheological study of Simmons and Simmons (1989), leading to an advanced model of glass container forming, suggests that the critical strain rate for the onset of shear thinning varies with composition, increasing as the alumina content increases or the soda content decreases.

The distinction between high-temperature and low-temperature fracture behaviour is clearly outlined by Hessenkemper and Brückner (1989). Within the viscous range the occurrence of melt fracture is dominated by volume properties (possibly associated with structural changes or microheterogeneities). Accordingly, high-temperature strength values are quite high and of the same order as the theoretical cohesive strength of the material (Simmons, Simmons 1989; Guillemet, Gyonne 1990). After cooling, partially healed cracks (similar in appearance to checks or splits) are observed on the surface. Within the elastic and viscoelastic ranges cracks originating from surface faults (possibly including the already described discontinuities) lead to elastic fracture (causing destruction of the article at low strength values). The distinction between (high-temperature) melt brittleness and (room-temperature) elastic strength is particularly useful to avoid the confusion associated with the term "brittle glass" outlined in section 1.1.

Hessenkemper and Brückner (1990 (b)) suggested criteria to define and quantify an isothermal (or isochomal) workability of melts in correlation with their high-temperature fracture behaviour. In qualitative terms, a good isothermal workability is attributed to a glass which can accept strong deformations without cracking. Isothermal (or isochomal) conditions are selected in order to eliminate the influence of the temperature dependence of viscosity. A good isothermal workability is connected with a low relaxation modulus and low melt stiffness and a large high-temperature strength. All such properties happen to be typical of glasses with a small value of the constant B in the Vogel-Fulcher-Tammann (VFT) equation. On the other hand, the athermal workability is defined in connection with thermal properties such as the slope of the viscosity/temperature curve and the setting rate and seems to be coincident with the conventional concept of "ease of forming". In container glass production the isothermal workability seems to be the most important property to control the problems normally grouped under the definition of poor workability, particularly during the later stages of the forming process at relatively low temperatures and high viscosities.

The described high-shear measurements are affected by some limitations:
a) so far it was seldom possible to extend the temperature range above 800 °C (with ultrasonic techniques measurements up to 1300 °C could be performed; however, only within the linear viscoelastic range (Hessenkemper, Brückner 1991));
b) in most cases the sample must be remelted, thus modifying its physicochemical condition (microstructure, gas content, surface composition);
c) only a very accurate measurement setup and a complete understanding of secondary temperature effects can produce unambiguous results (Manns, Brückner 1988; Guillemet, Gyonne 1990; Varshneya et al. 1990), so that sometimes even experts disagree on the interpretation of the results (Takamori, Tomozawa 1990; Simmons, Simmons 1990).

Either because such problems suggest a cautious approach or because the investigations were kept confidential, so far no published examples of poor workability cases solved with the help of quantitative rheological measurements are available (with the exception of Coenen et al. (1985), whose results were however disputed by Hessenkemper and Brückner (1991)). Notwithstanding, such rheological measurements are at present the most important tool offering the possibility to quantify and to confirm objectively the reliability of production reports and to define the array of problems called bad workability or brittleness in terms of measurable properties.

A promising aspect of the obtained results is that the erratic occurrence of forming problems during a given job can in principle be attributed to operating conditions close to the critical rates beyond which shear thinning occurs. If, however, during a given job temperature, deformation rates and the (composition-related) Newtonian viscosity are kept rigorously constant, any behaviour instability must be justified by (melting history-induced) variations of microstructure, gas content or of other properties, as will be shown in section 1.3.

1.3. Possible causes of bad workability

The theoretical and experimental work described in section 1.2. allows to analyze and quantify workability problems, but does not offer a direct explanation of the factors causing them. Any perturbation of the rheological behaviour is generically consistent with "structural modifications". Here, the term "structure" is used in a broad sense, by analogy with what is known on polymer flow behaviour. Indeed, it is understandable that the viscosity of a melt may vary if any factor produces a change in the nature and size of its "flow units". However, it is not easy to single out exactly which type of modification is occurring in each specific case. Since the analytical composition is unchanged, it is logical to think of some physicochemical parameter normally excluded from routine controls. Apparently identical workability problems

were interpreted quite differently by various authors. Only in a few cases, mostly concerning simple glasses, it was possible to explain the rheological behaviour with some specific properties of the melts, such as gas content or microstructure (Simmons et al. 1989; Hessenkemper, Brückner 1990 (a); Habeck et al. 1990). In the following a schematic classification of the physicochemical parameters assumed to be the further variables (besides composition) which may affect glass viscosity and potentially influence workability is presented:

a) microheterogeneity associated with phase separation, devitrification or unmelted batch constituents (Rindone 1974, Poole 1977, Stewart et al. 1988);

b) oscillations in the content of chemically dissolved gases (Klein 1973; Coenen et al. 1985; Williams 1989);

c) changes in the structure of glass, possibly associated with a different coordination of cations and/or with a different ratio of non-bridging to bridging oxygens and/or with a different redox state of polyvalent ions such as iron, sulphur, chromium, etc. (Coenen et al. 1985; Hirashima et al. 1988; Williams 1989);

d) "macroinhomogeneity", due to an increased frequency and intensity of layers of glass (≈ 0.1 mm thick) with a different composition (Brückner 1962; Hense 1987).

Clearly, also possible interrelations between different causes cannot be neglected. For example, variations of the H_2O content or of the redox state may influence the nucleation and growth of microphases (Gonzalez-Oliver, James 1980; Rindone et al. 1982; Jewell, Shelby 1991); variations of the redox state may modify the glass structure, due to a different coordination of cations (Coenen 1985; Hirashima et al. 1988); structural modifications may act as precursors to phase separation (Rindone et al. 1983); chemically inhomogeneous layers (cords or reams) may show a different tendency to nucleate (or a different redox state) as compared to the matrix and so on.

Poole's definition of bad workability (1977) referred to cases with unchanged equilibrium viscosity. Rigorously speaking, some of the just mentioned parameters (e.g. water content) are known to influence viscosity also at equilibrium; therefore, their variations should be detected by routine controls. However, they are included in the present review for the following reasons:

1. they are often mentioned in connection with workability problems;

2. at present is not enough evidence to quantitatively predict their influence on viscosity measurements at equilibrium and in production;

3. routine viscosity measurements at equilibrium normally require remelting or conditioning, which

may modify the rheological behaviour of glass (due to dissolved gases, redox state, microstructure etc.). Ideally, viscosity measurements performed directly in the feeder (or at least on fibers drawn from the melt) would be more representative of the conditions of glass at the forming stage.

Finally, two further interesting hypotheses about the origin of workability problems − not connected with viscosity changes of the melt − were formulated by Poole (1967):

− the forming behaviour of glass containers might be due mainly to the rheological properties of the "skin", the outer layer of the gob and of the parison, whose composition (and viscosity) is likely to be altered by several factors such as atmosphere, lubricants, contact with metals etc.;

− if the radiant heat transfer properties of the glass vary for some reasons, the whole temperature distribution in the parison and the cooling rates vary accordingly. This modifies the forming behaviour even if the viscosity in the feeder or forehearth remains unchanged.

1.4. "Melting history" and reproducibility of the melting and forming process

In the industrial production of container glass the reproducibility of the melting and forming process is normally insured by a rigorous and frequent control of the glass composition. However, for a nominally constant composition in terms of oxides, variations in pull rates, jobs, fuels, temperatures, furnace atmosphere, use of bubblers and electrodes, cullet addition (both quantity, size and type), raw materials (grain size, crystalline form, hydration) etc. can in principle modify the physicochemical parameters of the glass (in terms of the factors listed in section 1.3.) and eventually give rise to poor workability events. The variables listed above are considered as practical examples of "melting history" (a sort of memory effect implying that the glass properties can be influenced by the melting conditions). In particular, it is assumed that unintentional modifications of melting history can justify apparently erratic variations of forming behaviour. In principle, also stress-induced (transient) variations of microstructure, structure etc. often suggested to take place instantaneously during forming can be included in this concept.

The effects of melting history on rheology, microstructure and mechanical strength have been demonstrated by various authors on a laboratory scale (McKinnis, Sutton 1959; Rindone 1969; Sproull, Rindone 1974; Olix 1978; Hsich 1979; Bobkova 1987). However, very little data is available on the corresponding behaviour of container glass in modern industrial furnaces.

1.5. Role of the oxide composition

To complete this preliminary overview, it is necessary to shortly discuss the role of the glass composition. Most of the review which follows is dedicated to the influence of parameters other than the chemical composition, because it is commonly recognized that when poor workability is reported, only negligible oscillations of the oxide content occur. However, some authors suggest that within the range of container glass compositions, some might be particularly prone to suffer from poor workability. In principle, if the influence of parameters such as microstructure and dissolved gases on rheology is confirmed, a composition dependence may appear quite reasonable.

On the other hand, a high − composition-related − thermal expansion coefficient (and thermal conductivity) is known to increase the tendency to checking (Mills 1989) and may explain at least some of the surface defects observed, without the need to consider melting history effects. In his earlier paper Poole (1967) reported some empirical observations based on plant experience. Reducing the Al_2O_3 content, making small BaO additions and increasing the alkali level was found to be beneficial, while too high CaO levels led to checks and splits. In the 1977 paper the same author suggested that microstructure formation played a major role in influencing the viscoelastic behaviour of glass. Therefore, he suggested to select compositions with a low liquidus temperature, minimizing the tendency to give rise to devitrification and phase separation and stated that the previously formulated indications for composition changes were no longer actual, probably because the furnace construction and operation had changed radically in the last decade. Simmons and Simmons (1989) suggested that composition changes regarding alumina and alkali can cause large viscosity variations by modifying the critical strain rate for the onset of shear thinning and stated that the positive influence of alumina was in agreement with empirically found plant solutions, according to a recent personal communication by Poole (1989). Hessenkemper and Brückner (1990 (b)) found that the high-temperature crack-free deformation is better for glasses with lower values of the B constant in the VFT equation. Implicitly, this result suggests composition changes in agreement with this trend.

The contradictory statements found in the mentioned literature somehow reflect the difficulty to pinpoint exactly the factors and circumstances which cause poor workability in production. Some contradictions can probably be justified by the evolution of the melting practice; others reflect the fact that the parameter considered to be most influential by each author changes differently with composition. Anyway, at present there is no general agreement on the composition changes which should be undertaken to improve the workability.

1.6. Outline and aims of the paper

The purpose of the present review is to present and discuss the available evidence on the physicochemical characteristics of industrial soda−lime−silica glass (micro- and macroheterogeneity, dissolved gases, structure and surface composition) which are known or supposed to produce workability upsets by altering its forming behaviour in connection with variations of "melting history" (in terms of temperatures, raw materials etc.) as defined in section 1.3. Within the present context the term "bad workability" refers to the array of production problems listed in section 1.1. (including defects, unstable machine setting and low strength).

Some authors use the term workability in association with the ease of forming or productivity, quantified by parameters such as setting rate, working range etc. (Mills 1989). Such properties (which essentially depend on the slope of the viscosity/temperature curve) are beyond the scope of the present paper, dedicated to the factors which can cause shifts of the rheological behaviour for a constant oxide composition. Since poor workability is sometimes associated with a low mechanical strength, it was often suggested in the past that glass may become intrinsically brittle because its melting history produces microstructural or structural modifications which behave as defects. For brevity's sake the strength issue cannot be addressed systematically, because the practical strength of containers is influenced by a broad array of parameters, whose discussion is not possible in the present context. It is however worthwhile to mention that a thorough investigation conducted by AGR (American Glass Research, Inc., Butler, PA (USA)) on 18 plants located in different countries (Wasylyk 1990) showed that in most instances poor strength was caused by surface damage or surface stresses (generally caused by poor hot-end handling and poor moulding practice) rather than by glass quality. Indeed, Uhlmann (1982) remarked that submicrometer inhomogeneities are likely to affect the strength of pristine fibres, but not of commercial articles for which the critical flaw size is much larger.

Finally, the present review will concentrate on the soda−lime−silica glass composition, although problems of poor workability and low strength are known to occasionally affect also the production of fibres, tubing, pressed ware etc. In the present context, where attention is drawn on the specific physicochemical characteristics of melts, it appears safer not to generalize the results obtained for a given composition.

2. Microheterogeneity

2.1. Microheterogeneity and rheology

In the past several authors attributed workability problems to sporadic microstructure formation on the basis of electron microscopy studies. Normally the term "microheterogeneity" (or "microstructure") includes the effects of phase separation and devitrification (i.e., vitreous and crystalline inclusions, with size ranging between 1 nm and 1 µm). Some authors extend its meaning to include also refractory contaminants and batch-melting remnants, generally with micrometer size. The effect of microheterogeneity on glass viscosity is demonstrated by several studies on simple glasses such as alkali silicates or borates with phase separation (Mazurin, Porai-Koshits 1984; Simmons, Simmons 1989). Recently, Habeck et al. (1990) demonstrated the effects of microcrystals and phase separation on both the Newtonian and non-Newtonian viscosity. The separation of a new phase with a different composition (regardless of size) changes the composition of the matrix (at least in a surrounding diffusion zone) and, therefore, alters the rheological behaviour of glass. Also melting remnants of micrometer size and refractory inclusions might in principle produce similar effects due to interdiffusion; however, their practical relevance and impact on rheology is widely unknown. At the other end of the size scale, similar considerations apply to clusters and thermal density fluctuations (see section 2.3.2.). In the recent literature such inhomogeneities (1 to 10 nm) are classified as nanostructure or structural order on a middle-range scale (as opposed to short-range order, concerning interatomic bonds in the range up to 1 nm, and wide-range order, designating phase separation).

In the following a short review of the microstructural behaviour of soda–lime–silica glass (concerning both simple laboratory glasses and industrial compositions) is given, covering both middle- and wide-range order.

2.2. Analytical techniques

In view of the small particle size (sometimes down to a few nanometers) microstructural studies require very sensitive analytical techniques such as small angle X-ray or neutron scattering (SAXS or SANS), visible light scattering or transmission electron microscopy (TEM). The latter can also provide information on composition and crystallinity of the microphases. However, special precautions are required for sample preparation and data interpretation. For example Mazurin and Porai-Koshits (1984) give an excellent review of artifacts in electron microscopy due to sample preparation. A recommended precaution, when investigating a new or little known system, is to confirm the results with different techniques (Hsich 1979).

2.3. Evidence of microheterogeneity in soda–lime–silica glass

2.3.1. Vitreous and crystalline inclusions

Several examples of ternary soda–lime–silica glasses which give rise to phase separation, crystallization or even ceramization are described in the literature. Examples of phase separation for ternary compositions similar to those of commercial glasses (i.e. 76/13/11 wt%) were reported by Kumar (1976); Olix (1978); Rindone et al. (1982); Huntebrinker et al. (1989) using SAXS, TEM and visible light scattering.

Crystallization can be normally studied with optical or scanning electron microscopy after a reasonable crystal growth stage. High-sensitivity techniques are required in order to directly follow the nucleation stage. Homogeneous crystallization for soda–lime–silica compositions much lower in SiO_2 as compared to commercial glasses is described for example by Strnad and Douglas (1973); Kalinina et al. (1980); Gonzalez-Oliver, James (1980). However, as reported by several authors, if Al_2O_3 is added above trace amounts the tendency to immiscibility or homogeneous crystallization is lowered and nucleation rates dropped (Kumar 1976; Olix 1978; Rindone et al. 1982).

Indeed, the alumina-stabilized multicomponent soda–lime–silica glass is never mentioned by handbooks or reviews on phase separation (Mazurin, Porai-Koshits 1984; Vogel 1979). Moreover, it is a common experience in devitrification experiments on container glass to notice crystals only at the surface or at contact points with other materials (i.e., only heterogeneous crystallization is observed).

2.3.2. Clusters, middle-range order

The extension of the tendency to demixing from alkali silicates or borates to virtually all glasses, including industrial soda–lime–silica glasses, was postulated in the seventies by several authors, but experimental evidence is rare and no data on compositions or tielines is available. This lack of documentation was explained by the supporters of the universal microstructural theory with the suggestion that the inhomogeneous regions were extremely small in size and with diffuse boundaries ("clouds", "clusters" etc.) (Vogel 1971; Bobkova, Trunets 1973; Rindone 1974; Olix 1978). Some authors attributed the origin of such not well-defined inhomogeneities to incomplete melting of raw materials. According to others, clusters (formed by selective aggregation in the range just above the liquidus temperature and obliterated only by high-temperature treatments) or structural modifications produced by the melt atmosphere were precursors of full-scale phase separation or crystallization

(Rindone 1969; Rindone et al. 1983; Sproull, Rindone 1974).

Recently, with the progress of experimental techniques and modelling, middle-range order features such as atomic clustering (due to a nonstatistical distribution of modifiers); equilibria between silicate rings and chain fragments with different lengths; complexation of polyvalent ions; thermal density and concentration fluctuations etc. are raising growing interest (Porai-Koshits et al. 1982; Kavka, Novotný 1984; Goodman 1985; Greaves 1985; Karlsson et al. 1990). Clearly, for such features the distinction between inhomogeneity and structure becomes quite blurred and the classification a matter of convenience.

Probably due to experimental difficulties, so far the occurrence of clusters and other nanostructural features in soda−lime−silica glass (both ternary and multicomponent) has been rather postulated than verified. No data is available about their possible size, shape, distribution and growth conditions. An influence on rheology was qualitatively predicted by Rindone (1974) and Greaves (1985) but without reporting experimental results.

2.4. Evidence of microheterogeneity in container glass

The glass container composition is typically within the following range (in wt%): 70 to 73 SiO_2, 13 to 15 $Na_2O + K_2O$, 11 to 13 $CaO + MgO$, and 1 to 2 Al_2O_3.

According to Poole (1977) most cases of bad workability were found to be correlated with microheterogeneity. Some TEM micrographs showing phase separation (spherical shape, high contrast, 50 to 100 nm in size) were shown in the paper. No details about composition or frequency of occurrence were given. Microstructure formation was attributed to low temperatures in the melting/forehearth system or to raw material particle size.

More details on microstructural studies performed on cases of container glass with bad workability were reported by Rindone (1974). Several TEM micrographs were published indicating the presence of four types of microstructure:

a) melting remnants (undissolved batch) less than 1 μm in size;

b) microcrystals, identified by selected area diffraction as $4Na_2O \cdot 3CaO \cdot 5SiO_2$ with a spherical shape and diameters <100 nm. They are secondary crystallization products formed by devitrification in the diffusion zone around the type a) stones;

c) acicular crystals, less than 10 nm in size, uniformly distributed, composition unidentified;

d) droplet-type phase-separated regions, which in some cases appear to be precursors for devitrification type c).

Examination of several cases revealed a correlation between poor workability and the presence of microstructure for both flint and amber glass. A study of samples taken from the different stages of the forming process, unannealed and annealed, showed that during periods of bad workability a droplet structure (type d)) appeared in the annealed gob, unannealed and annealed parison, and the unannealed and annealed bottle, while only melting remnants could be detected in samples taken from the refiner.

Recently, Stewart et al. (1988) investigated a workability problem in green container glass where poor distribution was the major defect. TEM micrographs of samples from the acceptable and the objectionable production, respectively, revealed the presence of microinhomogeneities in all types of glass, with a significant increase during periods of poor forming. The observed microstructure was described as "droplet" or "cluster" patterns, the latter including crystalline material. No indications about the composition of the observed features could be obtained from the study. The problem was solved by improving the temperature distribution both in the melter and the forehearth and by changing the composition towards a lower liquidus temperature. The occurrence of such microstructure-related workability problems was considered anomalous by the authors. Apparently in the eighties the occurrence of microstructure-related problems had become quite seldom, thanks to an improved melting practice.

Finally, a paper by Hsich (1979) suggests a relatively simple empirical test to assess the presence of microstructure in container glass. Glasses having the same composition but different melting histories are expected to show different apparent liquidus temperatures (as measured microscopically after treatment in a gradient furnace), since in an insufficiently melted glass the presence of melting remnants or inhomogeneity is likely to change the thermodynamic and kinetic parameters of crystal nucleation and growth. This principle was checked on laboratory melts: The insufficiently melted glass showed a significantly higher apparent liquidus temperature, as compared to good workability (microstructure-free) glass from the plant.

2.5. Evidence of microheterogeneity in flat glass

The composition range of soda−lime−silica flat glass is very close to container glass. Evidence of microstructure is found mainly in the literature of the seventies. For example, Sakaino et al. (1974) measured a commercial sheet glass by Small Angle X-ray

Scattering (SAXS) and found microheterogeneities of the order of 2 nm in size, while Bobkova and Trunets (1973) found microheterogeneities in window glass molten at a range of different temperatures. On the other hand, Williams et al. (1981) found commercial plate glass (and microscope slide glass) to be completely homogeneous by SAXS. According to Kavka and Novotný (1984) sheet and float glass, heat-treated for long times below T_g, showed an increase of anomalous birefringence and of an endothermic DTA peak. The observed behaviour was attributed to the growth of (cluster-like) microheterogeneities whose composition varied progressively as compared to the matrix.

In a recent study of the dynamic flow behaviour of industrial soda−lime−silica glass (float glass and DGG standard glass I featuring a similar composition) Hessenkemper and Brückner (1988) observed a particular effect. By plotting the stresses at which non-Newtonian flow behaviour starts to be observed against the equilibrium viscosity, a nonmonotonous course was observed with a maximum corresponding to the conditions of measured maximum nucleation rate of devitrite crystals. The authors commented that even though this coincidence might be fortuitous, a model correlating formation and dissolution of devitrite nuclei with the observed behaviour (stress-induced nucleation) could be easily set up. It is interesting to compare this result with Hsich's suggestion (1979) to correlate workability and microstructure with the apparent liquidus temperature of container glass.

2.6. Open questions

The papers by Poole (1977), Rindone (1974), and Stewart et al. (1988) suggest that microstructure (due to phase separation and/or melting remnants) may develop occasionally in some relatively cold parts of the furnace and affect both rheology and strength. The sporadic occurrence of the problems is attributed to variations of pull, temperature distribution and raw materials or cullet size. The microstructural hypothesis is apparently supported by the observation that workability problems occurred preferentially in furnaces with cold spots and poor insulation (or when the temperature was lowered or the composition simplified) and the situation improved by raising the temperatures or by increasing the alumina content (Poole, pers. comm. 1989). Moreover, it appeared promising to attribute the associated strength losses to the presence of internal defects, by analogy with the studies on the correlation between microstructure and strength by Watanabe and Moriya (1961); Sproull and Rindone (1974). As the review shows, the available literature provides contradictory evidence, which is not sufficient to confirm or dismiss such suggestions. Several essential points, summarized as follows, are still unclear.

a) In spite of the growing interest for workability problems and glass quality and of progress in the analytical techniques, so far the occurrence of microstructure in container or flat glass was investigated only sporadically. No results based on SAXS or light scattering measurements are available to confirm the TEM results on which the three mentioned papers were based. Personal communications by the authors indicate that the sample preparation technique involved crushing in the laboratory, but never under vacuum. Moreover, the published studies leave several unanswered questions about the nature and composition of the microphases and the distribution in the container (localized or diffuse, superficial or internal (Fenstermacher, Rouda 1982)). There is no published evidence of the possibility to reproduce the observed phase separation under controlled laboratory conditions (thus obtaining information on composition, tielines and conditions for nucleation and crystal growth). According to the recent literature, phase separation or homogeneous crystallization might occur (in reasonable times) only in glass pockets with an extremely unlikely composition for modern melting practice (such as $Al_2O_3 < 300$ ppm or $SiO_2 \approx 55$ %).

b) Devitrification measurements for industrial soda−lime−silica glass (nucleation and growth rates, liquidus temperature) mostly refer to heterogeneous or surface crystallization. Virtually no data is available on bulk crystallization. On the other hand, recent rheological studies showed that workability problems are associated with modifications of the behaviour of the whole bulk of glass, where nucleation is unlikely. The only thinkable nucleation sites are the "melting remnants" and microscopic refractory particles mentioned by Rindone (1974); Hsich (1979); Stewart et al. (1988). However, the effects of viscosity variations observed under load by Hessenkemper and Brückner (1988) are commented in association with mass flow but correlated with heterogeneous crystallization data.

c) Published laboratory studies on phase separation were performed in static conditions. There are some indications that also shearing the melt may provide the driving force necessary for a structural rearrangement of the glass (Hessenkemper, Brückner 1988; Simmons, Simmons 1989; Varshneya et al. 1990). This would imply a temporary microstructure formation, which can be determined only in situ, at high temperatures and under strain, with obvious analytical difficulties (Straty 1989). In particular, Simmons and Simmons (1989) having observed on borosilicate glass fibers that the rates of phase transformation can be accelerated under shear, suggest that during container forming phase separation or crystallization might take place under high strain rates, despite the lack of such effects in unstrained samples.

d) Only vague indications are available about the occurrence of clusters and density fluctuations (middle-range order) in container glass. In particular, it is not known how far such characteristics can vary as a function of the melting conditions and eventually influence the forming behaviour.

In view of all the reported uncertainties and considering that the furnace construction and the use of cullet were suggested to be significant variables, it seems important to check with careful experiments the relevance of microstructural problems in the container glass of the nineties.

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