TC 18 Project on
Bubble Nucleation in Glass Melts

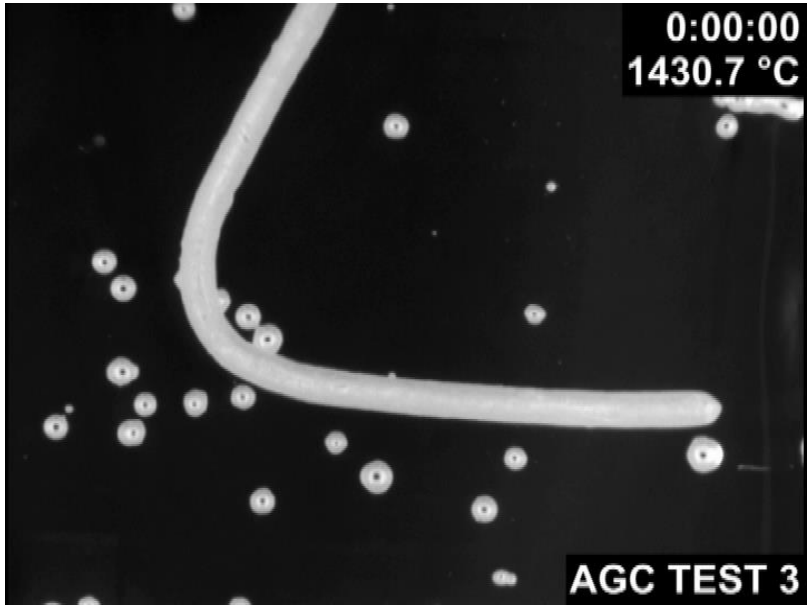
The aim of the project is to understand the mechanism and kinetics of bubble nucleation, to restrict bubble defects and to study the effect of bubble nucleation process on melting improvement.

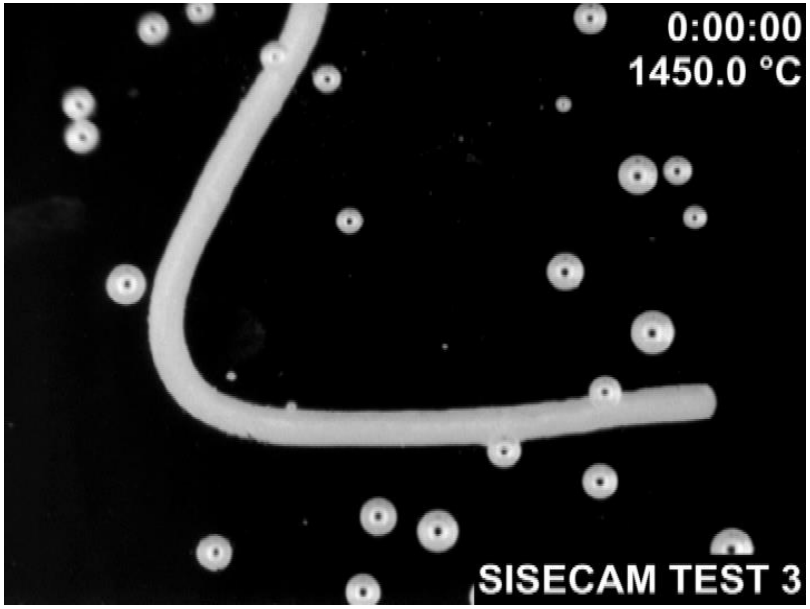
First step of the project involves the Round Robin Test on the determination of the nucleation temperature. The proposed method is based on high temperature observation of bubble nucleation on Pt wire immersed in the glass melt. Two samples of commercial float glasses delivered by AGC and Sisecam were chosen for the study.

The project is carried out in cooperation with TC14.

Method Description

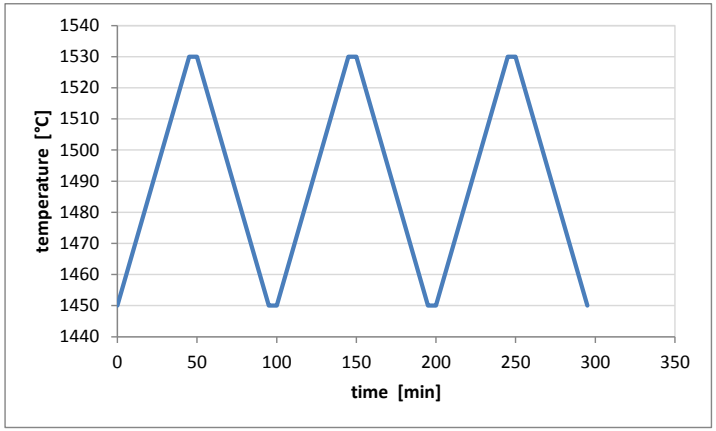
- **The determination of the nucleation temperature T_N**
  - The procedure based on high temperature observation of bubble nucleation on Pt wire immersed in the glass melt.
  - Before the observation, the silica glass observation cell containing the measured glass is heated at the temperature about 100°C lower than expected nucleation temperature to remove most of bubbles from the melt.
  - The glass sample is heated with a heating rate of 2°C/min.
  - Recorded pictures are evaluated by image analysis to measure temperature development of nucleated bubbles size. The nucleation temperature is obtained by linear extrapolation of measured experimental points to zero bubble size.
  - Common laboratory work of two participants, ICT Prague and Asahi resulted in the publication of the paper entitled:
    Vernerova M., Cincibusova P., Klouzek J., Maehara T., Nemec L. (2015): Method of examination of bubble nucleation in glass melts. Journal of Non-Crystalline Solids *411*, 59–67, doi:10.1016/j.jnoncrysol.2014.12.025





Test No.3

- repeated heating and cooling



RRT participants

Celsian (M.Hubert)

AGC (T.Maehara)

NEG (M.Kawaguchi)

UCT Prague (J.Klouzek)

Glass Service (F.Janos)

Results

AGC Sample		
Laboratory	T_N [°C]	St.dev. [°C]
UCT Prague	1490,7	3,5
AGC	1492,3	1,5
Celsian	1481,5	1,6
Glass Service	1480,1	3,8
NEG	1485,0	3,5

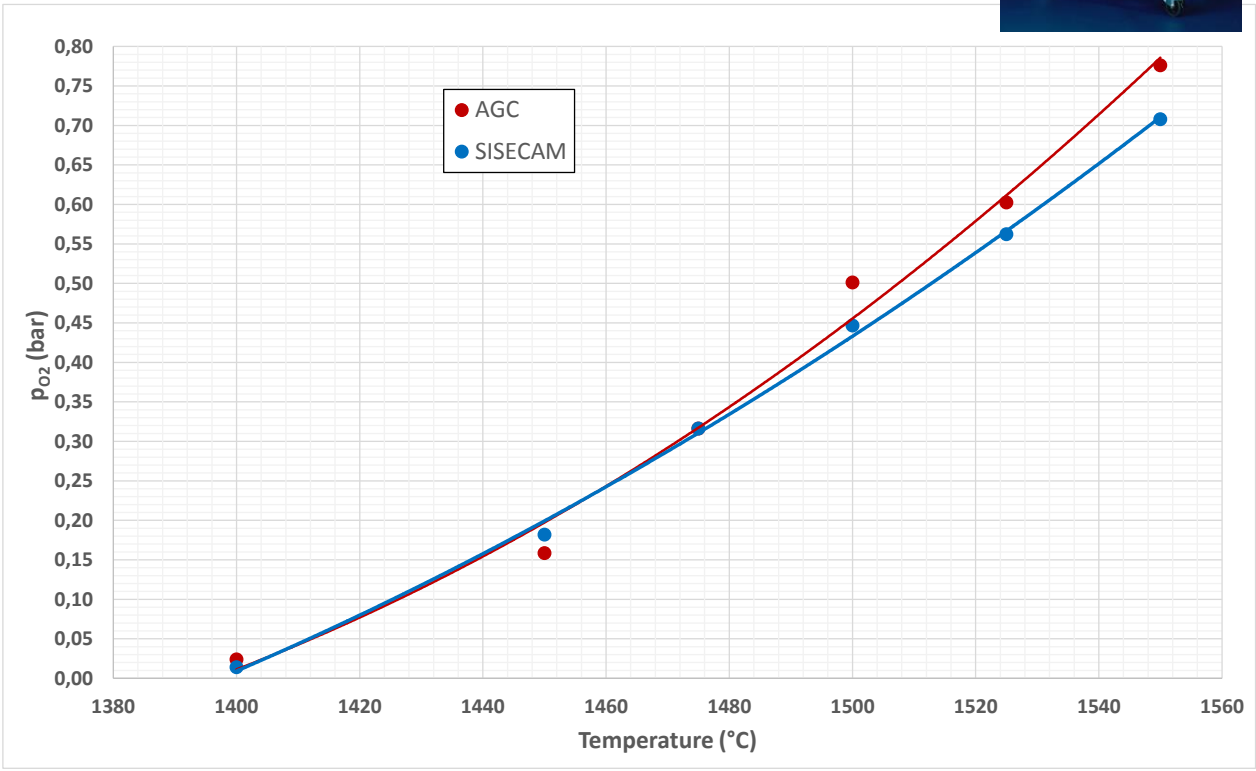
SISECAM Sample		
Laboratory	T_N [°C]	St.dev. [°C]
UCT Prague	1500,9	2,4
AGC	1500,1	2,0
Celsian	1484,9	8,5
Glass Service	1499,7	2,3
NEG	1501,0	1,9

Redox state measurement

AGC: p_{O2} = 0,33 bar (p_{O2} + p_{SO2} = 1 bar) at T = 1475°C

SISECAM: p_{O2} = 0,33 bar (p_{O2} + p_{SO2} = 1 bar) at T = 1480°C

- 15 – 20°C below T_N



- Sulphur content
- AGC: 0,22 % SO_3
- SISECAM: 0,19 % SO_3

NEG – analysis of nucleated bubbles

Bubble gas analysis

Table 4 shows results of bubble gas analysis. Figure 5 shows photos of a bubble on a platinum wire. Figure 6 shows photos of deposits inside a bubble. From bubble gas analysis, two types of bubble were confirmed. One contained SO_2. The other consisted mainly of O_2. It is highly possible that the former was generated by thermal decomposition of sulfate according to the following reaction.

$$SO_4^{2-} \rightarrow SO_2 + \frac{1}{2}O_2 + O^{2-}$$

There is a possibility that the latter was also generated by thermal decomposition of sulfate and SO_2 was consumed to form deposits of sulfate on the bubble surface. The other reason is that this O_2 bubble might be caused by reduction reaction of Fe_2O_3.

Table 4. Results of bubble gas analysis for AGC glass sample

No.	Longest diameter (mm)	Shortest diameter (mm)	Thickness (mm)	Diameter as spherical bubble (φmm)	Gas composition (vol %)					Internal pressure (kPa)
					CO_2	O_2	Ar	N_2	SO_2	
Bubbles on a platinum wire										
1	0.49	0.48	0.44	0.47	ND	93.8	ND	6.2	ND	6
2	0.23	0.17	0.16	0.18	12.4	ND	ND	45.2	42.3	8
Bubbles near glass surface (bubbles unattached to a platinum wire)										
3	0.48	0.46	0.46	0.47	5.0	ND	0.2	6.6	88.2	4
4	0.42	0.39	0.38	0.40	0.4	94.6	Tr	4.9	ND	25

*ND : not detected.

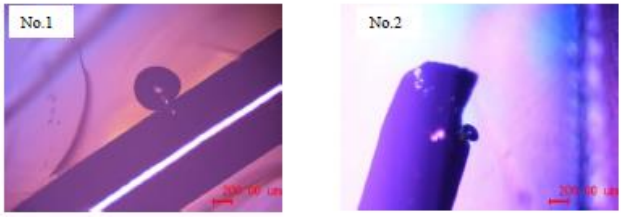


Figure 5. Photos of a bubble on a platinum wire.

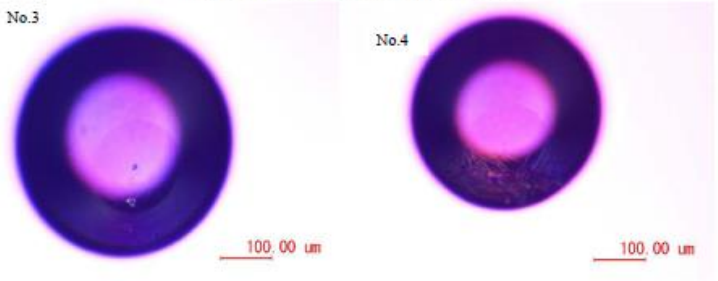


Figure 6. Photos of deposits inside a bubble.

Behaviour of nucleated bubbles during cooling

- Bubble nucleation in glasses containing sulphur with different redox state

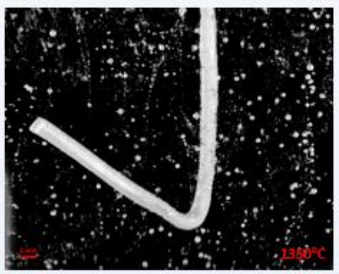


Fig. 1. The typical picture of the oxidized glass melt with the Pt wire, C/SO_4^{2-}= 0. The bubbles did not nucleate.

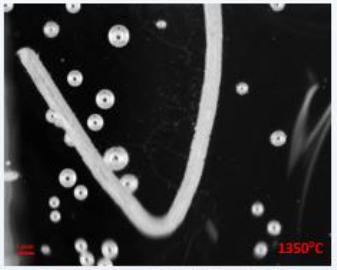
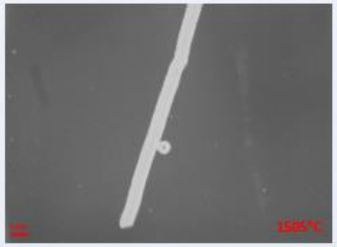
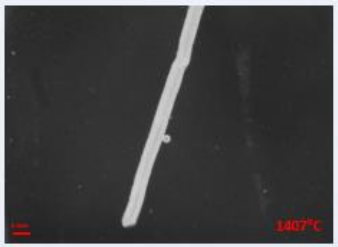


Fig. 2. The typical picture of the slightly reduced glass melt with the Pt wire , C/SO_4^{2-}= 3. The bubbles did not nucleate.

Fig. 3. The typical picture of the reduced glass melt with the Pt wire and nucleated bubbles, C/SO_4^{2-}= 9.





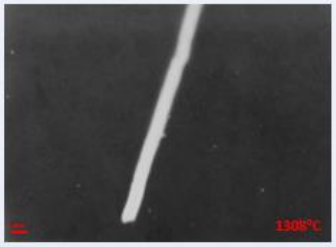
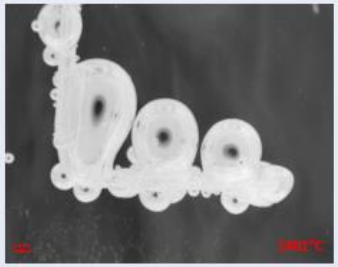


Fig. 4. The observation of the bubbles contraction during temperature drop, C/SO_4^{2-}= 0. Bubbles in oxidized, sulphate containing glasses quickly dissolved in the melt.



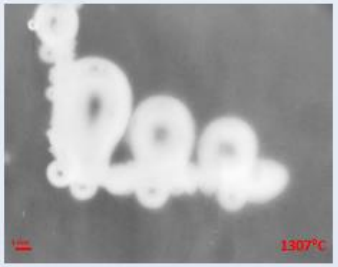


Fig. 5. The observation of the bubbles contraction during temperature drop, C/SO_4^{2-}= 9. Bubbles in reduced amber glasses did not dissolve in the melt.