Laboratory of Inorganic Materials

University of Chemistry and Technology Prague
Institute of Rock Structure and Mechanics CAS
Technicka 5, 166 28 Prague, Czech Republic

Bubble nucleation and foaming in glass melts

Jaroslav Kloužek, Miroslava Vernerová
Lubomír Němec, Miroslava Hujová

The aim of the lecture

chemical reaction → saturation or supersaturation → bubble growth bubble nucleation → fining foaming dissolution

– to summarize reactions of sulfur taking place during glass melting process (function of the ratio carbon/sulfate added to the batch)

– to observe and evaluate the reactions of sulfur compounds in glass with water vapor in surrounding atmosphere

– to study the nucleation of bubbles in glass melts

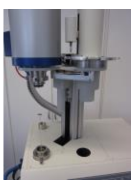
Experimental

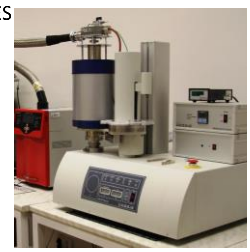
Evolved Gas Analysis

GC-MS: Hewlett Packard 6890A with 5971A
- sample (1 g) in silica glass test tube
- He flow rate 50 ml/min
- analysis of SO2, O2, CO, CO2, (N2, NO, NO2, CH4, …)

STA – MS

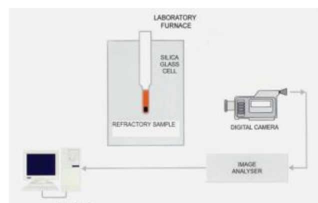
- Linseis STA PT1600 HIRES
- samples 50 mg or 1 g
- He flow rate 20 ml/min





High temperature observation

- sample placed in silica glass cell
- observation area ~ 30 x 20 mm



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Chemical reactions sulfate - carbon

- Active reducing agent, degree of the reduction

	C	CO $CO_2(g) + C(s) \leftrightarrow 2CO(g)$ $(700-1000\ °C)$
Reduction to SO_2	$2SO_4^{2-}(l) + C(s) \leftrightarrow CO_2(g) + 2SO_2(g) + 2O^{2-}(l)$ $(850\text{-}1150\ °C)$	$SO_4^{2-}(l) + CO(g) \leftrightarrow CO_2(g) + SO_2(g) + O^{2-}(l)$ $(900-1000\ °C)$
Reduction to S^{2-}	$SO_4^{2-}(s,l) + 2C(s,l) \leftrightarrow 2CO_2(g) + S^{2-}(l)$ $(650-900\ °C)$	$SO_4^{2-}(l) + 4CO(g) \leftrightarrow 4CO_2(g) + S^{2-}(l)$ $(700-1000\ °C)$
	$3SO_4^{2-}(l) + S^{2-}(l) \leftrightarrow 4SO_2(g) + 4O^{2-}(l)$ $(1100-1300\ °C)$	
Reduction to S_2	$2SO_4^{2-}(s,l) + 3C(s,l) \leftrightarrow S_2(l) + 3CO_2(g) + 2O^{2-}(l)$	$2SO_4^{2-}(s,l) + 6CO(g) \leftrightarrow S_2(l) + 6CO_2(g) + 2O^{2-}(l)$
Sulphate decompo-sition	$2SO_4^{2-}(l) \leftrightarrow 2SO_2(g) + O_2(g) + 2O^{2-}(l)$ $(1100-1550\ °C)$ $2SO_4^{2-}(l) \leftrightarrow 2SO_3^{2-}(l) + O_2(g)$ $SO_3^{2-}(l) \leftrightarrow SO_2(g) + O^{2-}(l)$	

Kloužek J., Arkosiová M., Němec L., Cincibusová P. (2007): The role of sulfur compounds in glass melting. *Glass Technol.: Eur. J. Glass Sci. Technol. A*, *48* (4), 176-182.

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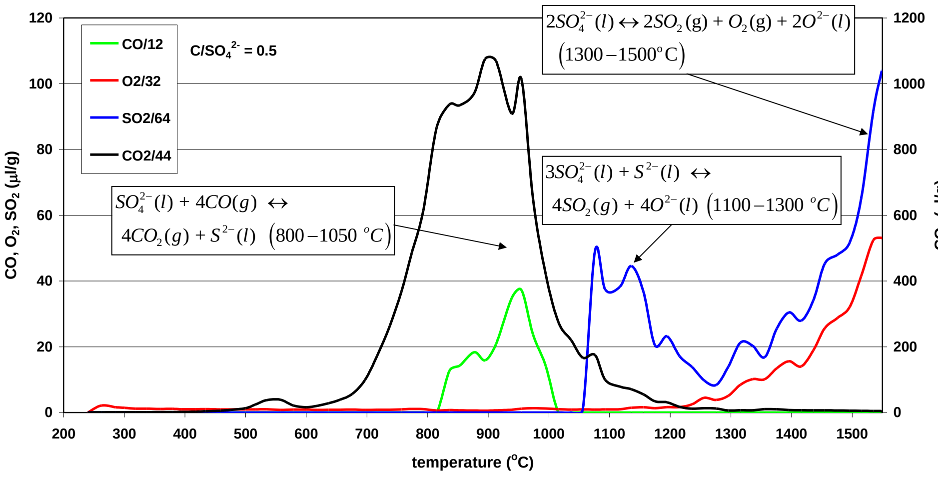
Evolved gas analysis

$Na_2O - CaO - SiO_2$ glass batch (16, 10, 74 wt.%), C/SO_4^{2-} = 0.5



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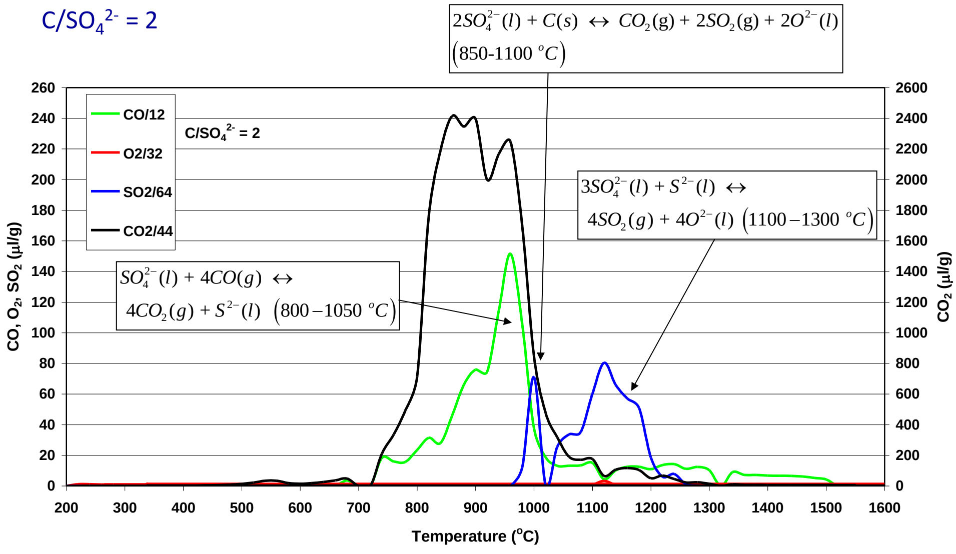
Evolved gas analysis

$Na_2O - CaO - SiO_2$ glass batch (16, 10, 74 wt.%)

C/SO_4^{2-} = 2



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Chemical reactions sulfate - carbon

- Significant reactions

$$3SO_4^{2-}(l) + S^{2-}(l) \leftrightarrow 4SO_2(g) + 4O^{2-}(l) \quad (1100-1300\ ^oC)$$
$$2SO_4^{2-}(l) \leftrightarrow 2SO_2(g) + O_2(g) + 2O^{2-}(l) \quad (1300-1550\ ^oC)$$

- Effect on partial melting processes
  - Bubble removal
  - Bubble nucleation
  - Foaming in glass melt

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THE THERMODYNAMIC MODEL OF SIMULTANEOUS REACTIONS

$$2SO_4^{2-}(l) \leftrightarrow 2SO_2(g) + O_2(g) + 2O^{2-}(l)$$
$$\frac{2}{3}SO_2(g) + \frac{2}{3}O^{2-}(l) \leftrightarrow \frac{2}{3}S^{2-}(l) + O_2(g)$$
$$CO_2(g) \leftrightarrow C(l) + O_2(g)$$

$$K_{SO_4^{2-}} = \frac{\left(\overline{c}_{SO_2} + 2x_1 - \frac{2}{3}x_2 + x_3\right)^2 \left(\overline{c}_{O_2} + x_1 + x_2 + x_4\right)}{\left(\overline{c}_{SO_4^{2-}} - 2x_1\right)} \qquad K_{S^{2-}} = \frac{\left(\overline{c}_{S^{2-}} + \frac{2}{3}x_2\right)^{\frac{2}{3}} \left(\overline{c}_{O_2} + x_1 + x_2 + x_4\right)}{\left(\overline{c}_{SO_2} + 2x_1 - \frac{2}{3}x_2 + x_3\right)^{\frac{2}{3}}}$$

$$K_c = \frac{\left(\overline{c}_c + x_4\right)\left(\overline{c}_{O_2} + x_1 + x_2 + x_4\right)}{\left(\overline{c}_{CO_2} - x_4\right)}$$

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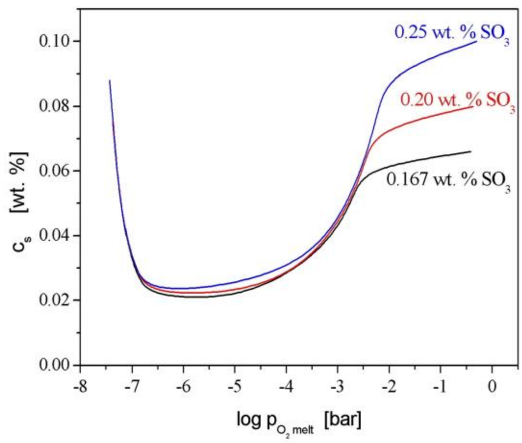
THE THERMODYNAMIC MODEL OF SIMULTANEOUS REACTIONS

1. The complete reaction between C and sulphate in solid phase

2. The reaction of generated S^{2-} with remaining sulphate in glass at 1300 °C

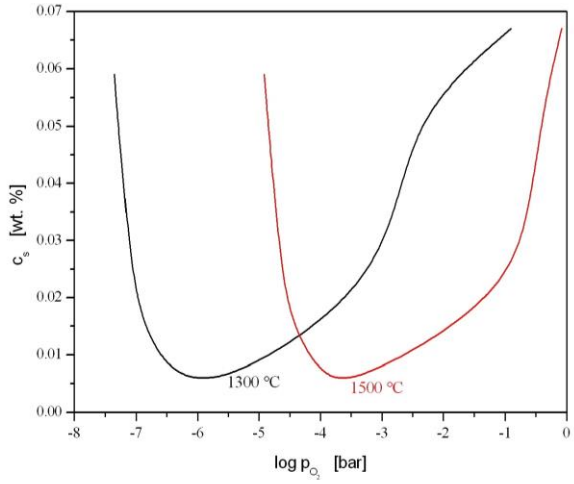
3. The heating of glass to refining temperatures

CALCULATED RESULTS



 Total sulphur concentration vs. redox state of glass(log p_{O2}), 1300°C

CALCULATED RESULTS



Total sulphur concentration vs. redox state of glass(log p_{O2}), 0.20% SO_3

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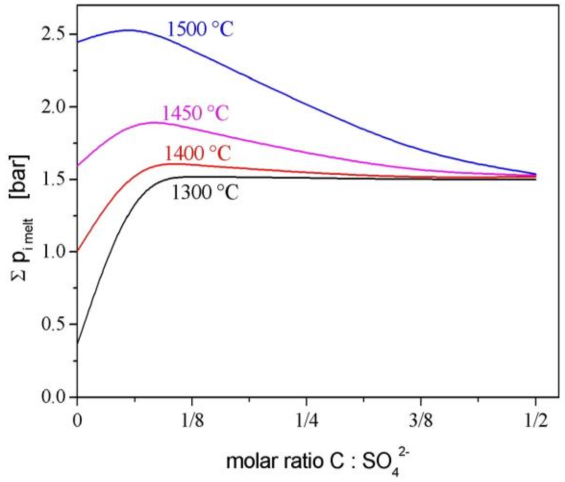
CALCULATED RESULTS



Refining potential (p_{O2} + p_{SO2}) vs. molar ratio C/SO_4(2-)

Glass melt without sulphites

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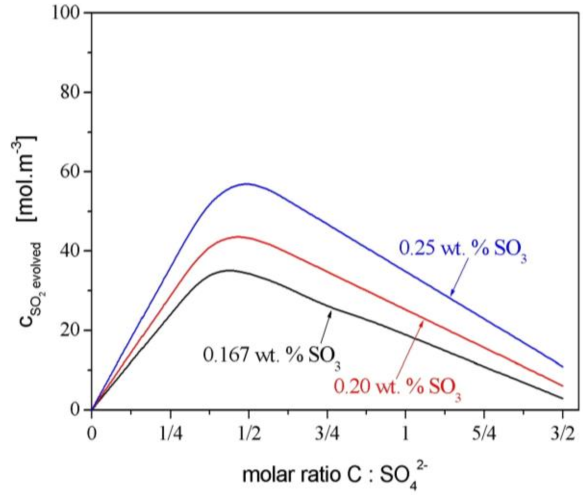
CALCULATED RESULTS



Evolved amount of SO_2 vs. molar ratio C/SO_4(2-), 1300°C

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Glass melt foaming

- Glass melt volume
  - reaction of sulfur compounds in the melt
  - bubble nucleation and growth
  - high bubble growth rate – packing available volume

- Glass melt level
  - reaction of sulfur compounds with water vapor
  - high initial bubble number
  - rapid bubble growth and rising velocity
  - also bubble nucleation on the level

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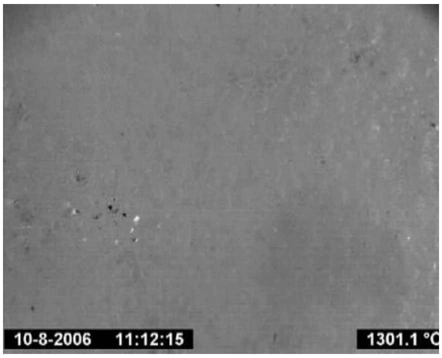
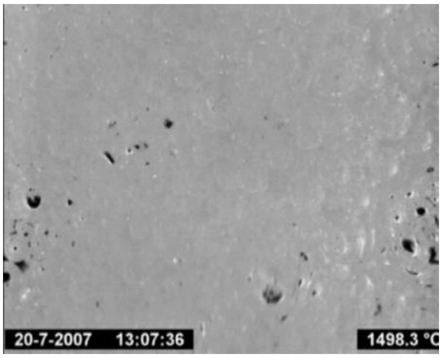
Foaming in glass melt volume



$$3SO_4^{2-}(l) + S^{2-}(l) \leftrightarrow 4SO_2(g) + 4O^{2-}(l)$$

- oversaturation of the melt by SO_2
- temperatures 1100-1300°C
- intensive bubble nucleation
- lower bubble growth rates



$$2SO_4^{2-}(l) \leftrightarrow 2SO_2(g) + O_2(g) + 2O^{2-}(l)$$

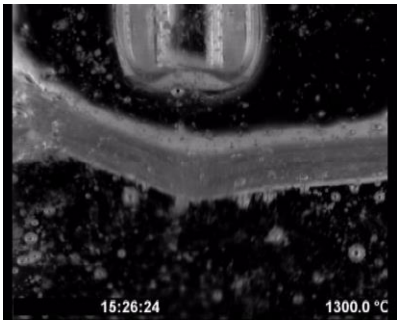
- over-saturation by SO_2 and O_2
- decomposition of remaining sulphate
- temperatures > 1450°C
- high initial bubble size
- high bubble growth rate

Foaming on the glass melt level

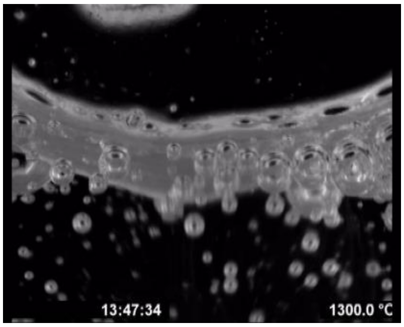
Experimental conditions

- temperatures 1300°C - 1500°C; C/Na_2SO_4 = 0 - 9; p_{H2O} = 0.3 - 1 bar

C/Na_2SO_4 = 0, p_{H2O} = 0.8 bar



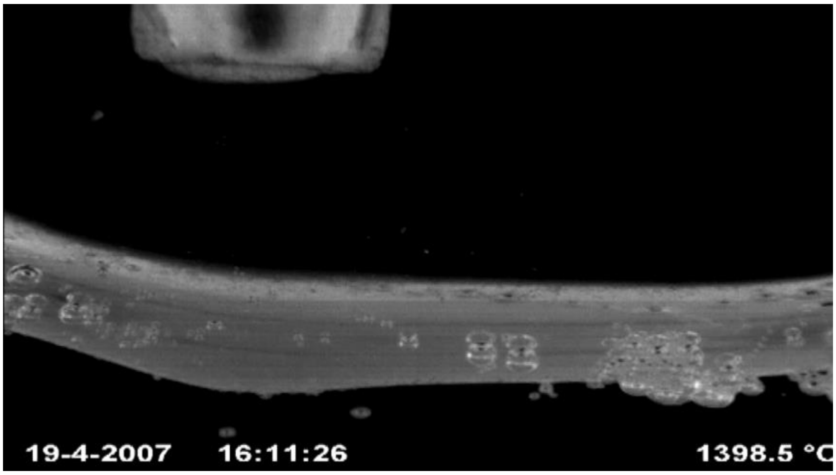
C/Na_2SO_4 = 6, p_{H2O} = 0.8 bar



Vernerová M., Kloužek J., Němec L. (2015). Reaction of soda-lime-silica glass melt with water vapour at melting temperatures. *Journal of Non-Crystalline Solids* , *416*, 21-30. doi:10.1016/j.jnoncrysol.2015.02.020

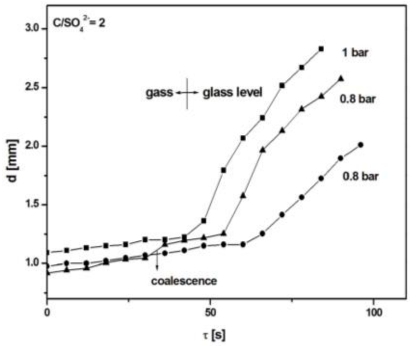
Foaming on the glass melt level

- Bubble nucleation temperature 1400°C; C/Na_2SO_4 = 6

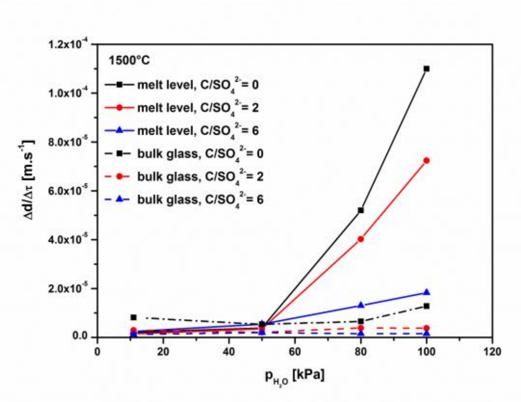


Foaming on the glass melt level

1500°C; C/Na_2SO_4 = 2



Change in bubble size when reaching the glass melt level



Bubble growth rate on the glass melt level and in the bulk glass

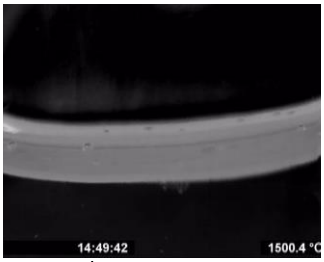
Foaming on the glass melt level

- high growth rates of bubbles reaching the glass melt level
  - dissolution of water vapor in glass melt at the top level (bubble lamellas)
  - chemical reactions of sulfur compounds with water vapor

$$SO_4^{\ 2-} + H_2O \leftrightarrow SO_2 + \frac{1}{2}O_2 + 2OH^-$$

$$S^{2-} + 2H_2O \rightarrow H_2S + 2OH^-$$

  - transport of sulfate to the level
    - rising bubbles
    - convection induced by gradients of surface tension
      - sulfate consumed by the reaction
      - evaporation of alkali component



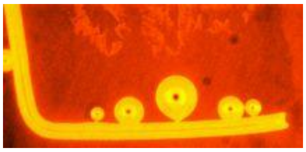
$$SO_2(g) + \frac{1}{2}O_2(g) + O^{2-}(l) \leftrightarrow SO_4^{\ 2-}(l)$$

Němec L., Kloužek J. (1998): Interaction of gas mixtures containing SO_2 and O_2 with glass liquids. *Journal of Non-Crystalline Solids, 231*, 152-160.

- nucleation of bubbles
  - over-saturation of glass melt by reaction products

Bubble nucleation

- **The aim of the study**
- to develop the set of experimental method for the examination of bubble nucleation in glass melts



- the interpretation of the results on thermodynamics basis

Vernerová M., Cincibusová P., Kloužek J., Maehara T., Němec 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

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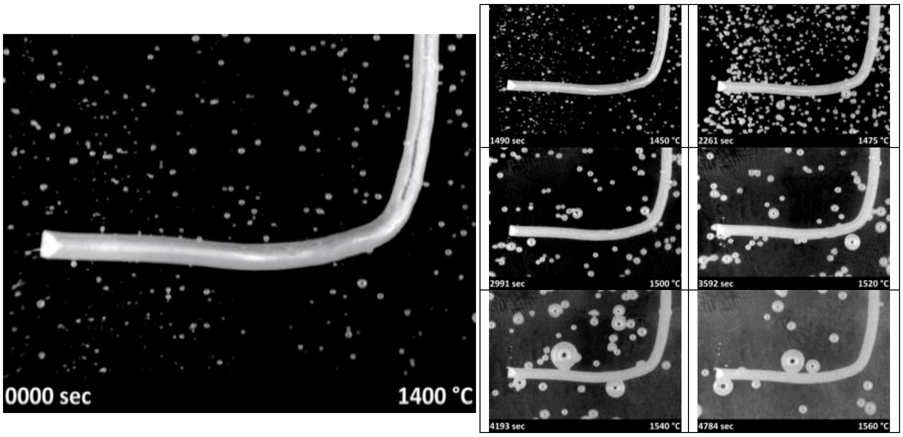
Bubble nucleation - Experimental

- **Samples – flat glasses containing 0.185 and 0.250wt.% SO_3**
- **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.
  - The method is tested within the round robin test of ICG TC18 and 14

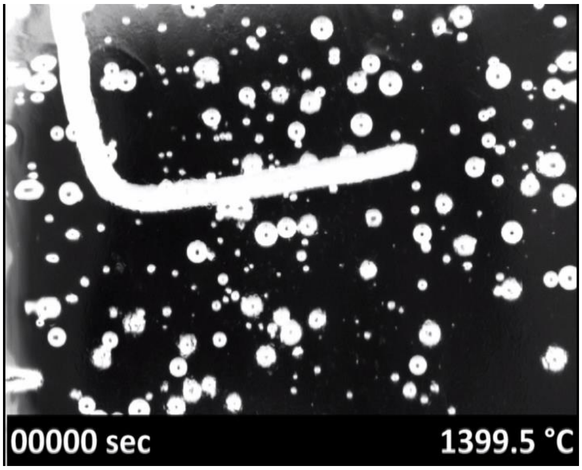
Bubble nucleation - Experimental

- **The determination of the nucleation temperature T_N**



Bubble nucleation - Experimental

- **The measurement of bubble nucleation intensity above the T_N**
  - constant temperature
  - the number and size of nucleated bubbles



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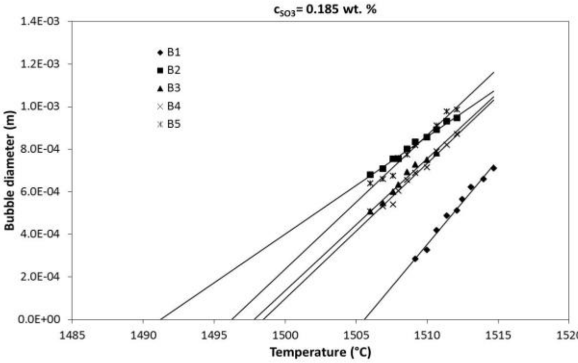
Bubble nucleation - Results

The nucleation temperature T_N



0.185wt.% SO_3: $T_N = (1502.6 \pm 7.5)°C$

0.250wt.% SO_3: $T_N = (1501.0 \pm 6.2)°C$

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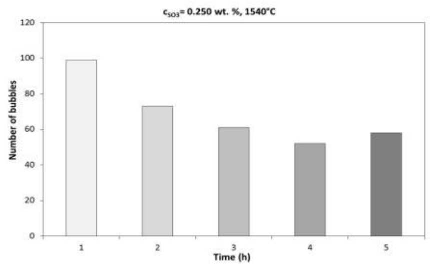
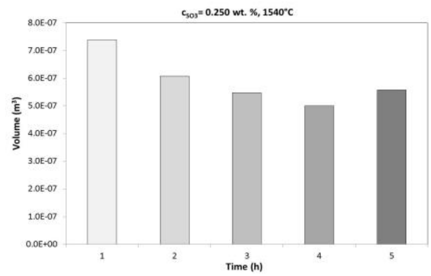
Bubble nucleation - Results

•**The bubble nucleation intensity above the T_N**



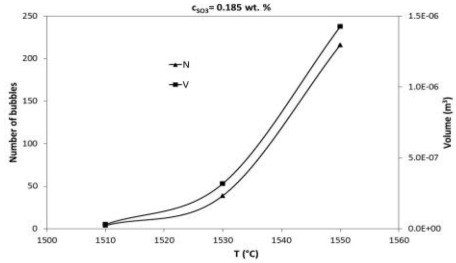
The numbers of bubbles per 1 hour nucleated on the horizontal part of the Pt wire immersed in the float glass at a temperature of 1540 °C. The sample with 0.250 % of chemically dissolved SO_3

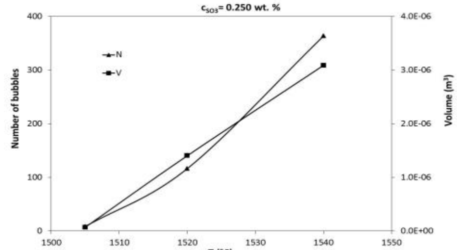


The volume of gas per 1 hour released from the melt into bubbles nucleated on the horizontal part of the Pt wire at 1540 °C. The sample with 0.250 % of chemically dissolved SO_3 (first experiment).

Bubble nucleation - Results

•The bubble nucleation intensity above the T_N

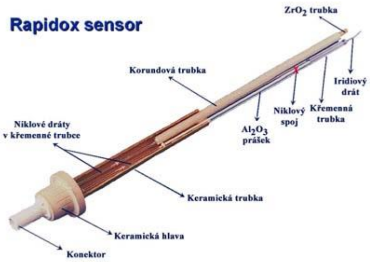




Bubble nucleation - Experimental

The measurement of the glass redox state

Electrochemical method using Rapidox system - 1250-1500 °C



Nucleation - results interpretation

The TURNBULL’s theory of nucleation

$$I = I_0 exp\left(-\Delta G_{crit}\frac{(2+cos\theta)(1-cos\theta)^2}{4}/kT\right)exp(-\Delta G_D/kT)$$

Thermodynamics barrier

ΔG_{crit} - Gibbs energy of the critical (stable) nucleus formation

$$\Delta G_{crit} = \frac{16\pi\sigma^3}{3\Delta G_V^2}\frac{(2+cos\theta)(1-cos\theta)^2}{4}$$

ΔG_v – Gibbs energy bound with the arisen new gas phase (bubble)

$$\Delta G_V = \frac{\Delta H(T-T_s)}{T_s}$$

T-T_s – overheating as driving force of the nucleation

$$\Delta G_V \approx -\frac{p_a ln\frac{c_b}{c_s}}{1-ln\frac{c_b}{c_s}}$$

c_b/c_s – oversaturation of the melt by the gas

Nucleation - results interpretation

- **I** - the buble nucleation rate [number/volume.time]

$$I = I_0 exp\left(-\Delta G_D/(kT)\right) exp\left\{-\frac{16\pi\sigma^3}{3}\left[\frac{T_s}{\Delta H(T-T_s)}\right]^2 \frac{(2+cos\theta)(1-cos\theta)^2}{4}/(kT)\right\}$$

$$I = I_0 exp\left(-\Delta G_D/(kT)\right) exp\left\{-\frac{16\pi\sigma^3}{3}\left[\frac{1-ln(c_b/c_s)}{p_a ln(c_b/c_s)}\right]^2 \frac{(2+cos\theta)(1-cos\theta)^2}{4}/(kT)\right\}$$

T_N and p_{O2} measurement

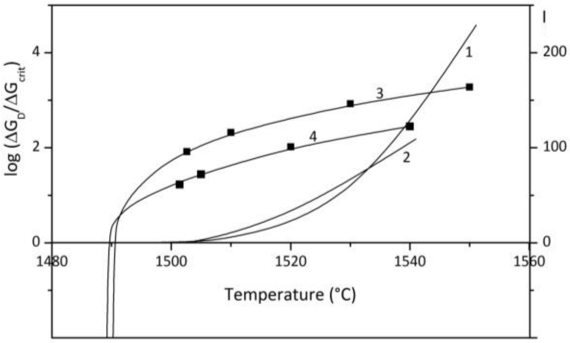
0.185 wt.% SO_3: T_N = 1503°C p_{O2} =0.490 bar

$\frac{p_{SO_2 melt}}{p_{O_2 melt}} = 2$ p_{sO2} =0.333 bar T_s = 1490°C

T_N - T_S = 13°C c_b/c_s = 1.47

Nucleation - results interpretation

- **I -** the buble nucleation rate [number/volume.time]
- **ΔG_D and ΔG_{crit} –** kinetic and thermodynamics barrier



- 1: **I** 0.185wt.%SO_3
- 2: **I** 0.250wt.%SO_3
- 3: **log (ΔG_D/ ΔG_{crit})** 0.185wt.%SO_3
- 4: **log (ΔG_D/ ΔG_{crit})** 0.250wt.%SO_3

The kinetic barrier overcomes the value of the thermodynamic barrier at temperatures closely above T_s. At experimental temperatures, the kinetic barrier surpasses the thermodynamic one by between two and three orders.

Conclusions

Impact of of sulfur compounds reactions on the glass melting processes

Foaming of glass melt - the reactions of sulfur compounds in glass with water vapor in surrounding atmosphere

- high bubble growth rates of rising bubbles reaching the glass level
- bubble nucleation

Nucleation of bubbles in glass melts

- the combination of the measurement procedures of T_N, I, and p_{O2} makes possible theoretical description of the bubble nucleation in glass melt