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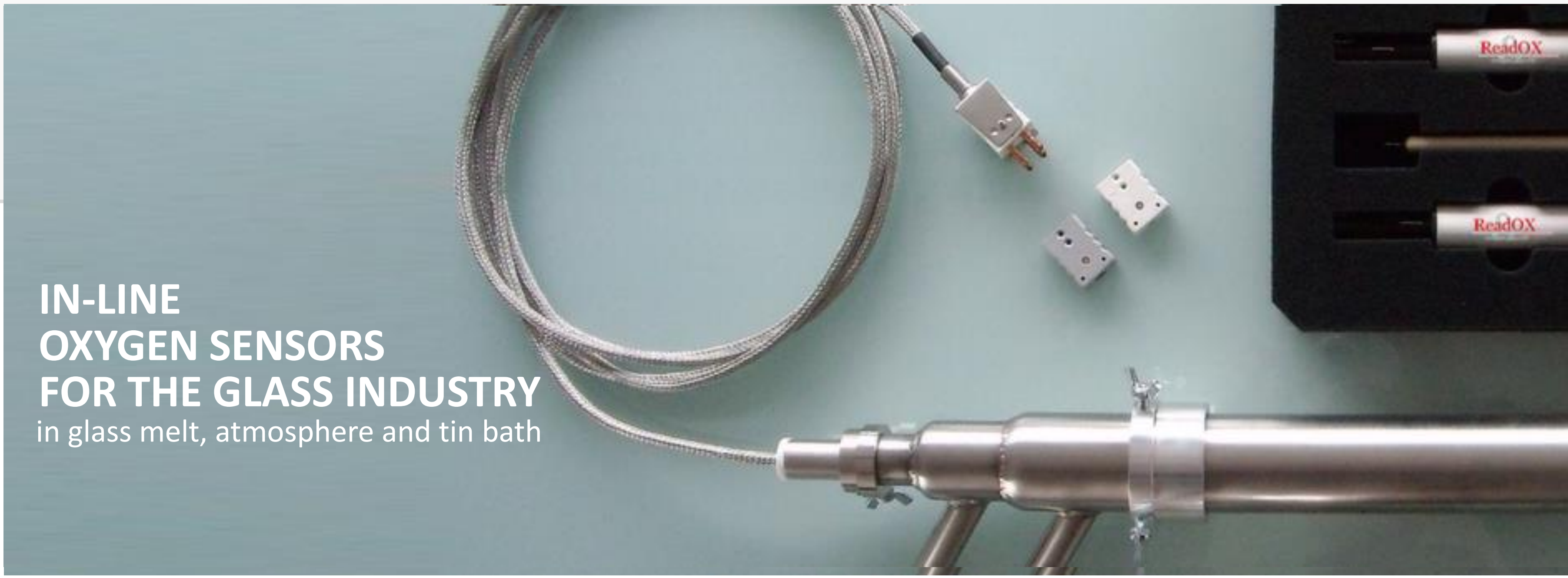

IN-LINE OXYGEN SENSORS FOR THE GLASS INDUSTRY

in glass melt, atmosphere and tin bath

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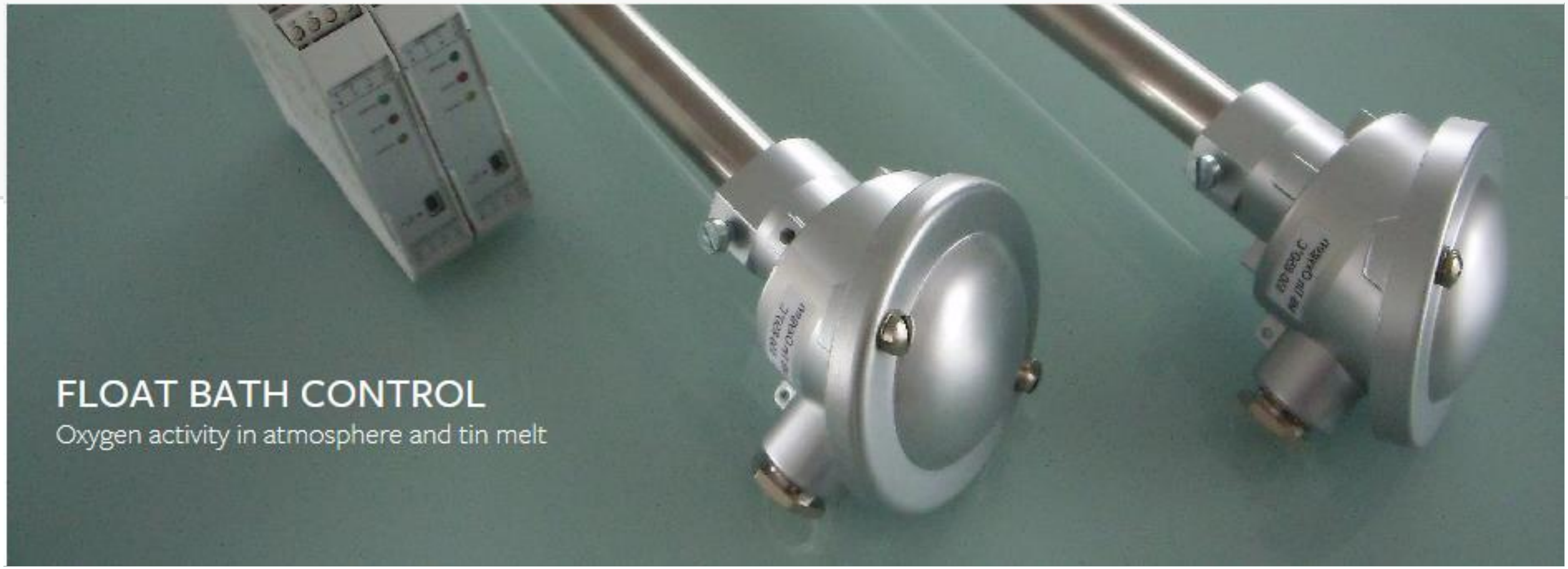
Tin bath oxygen sensors



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Introduction Float Glass Production

Float Glass Production Line

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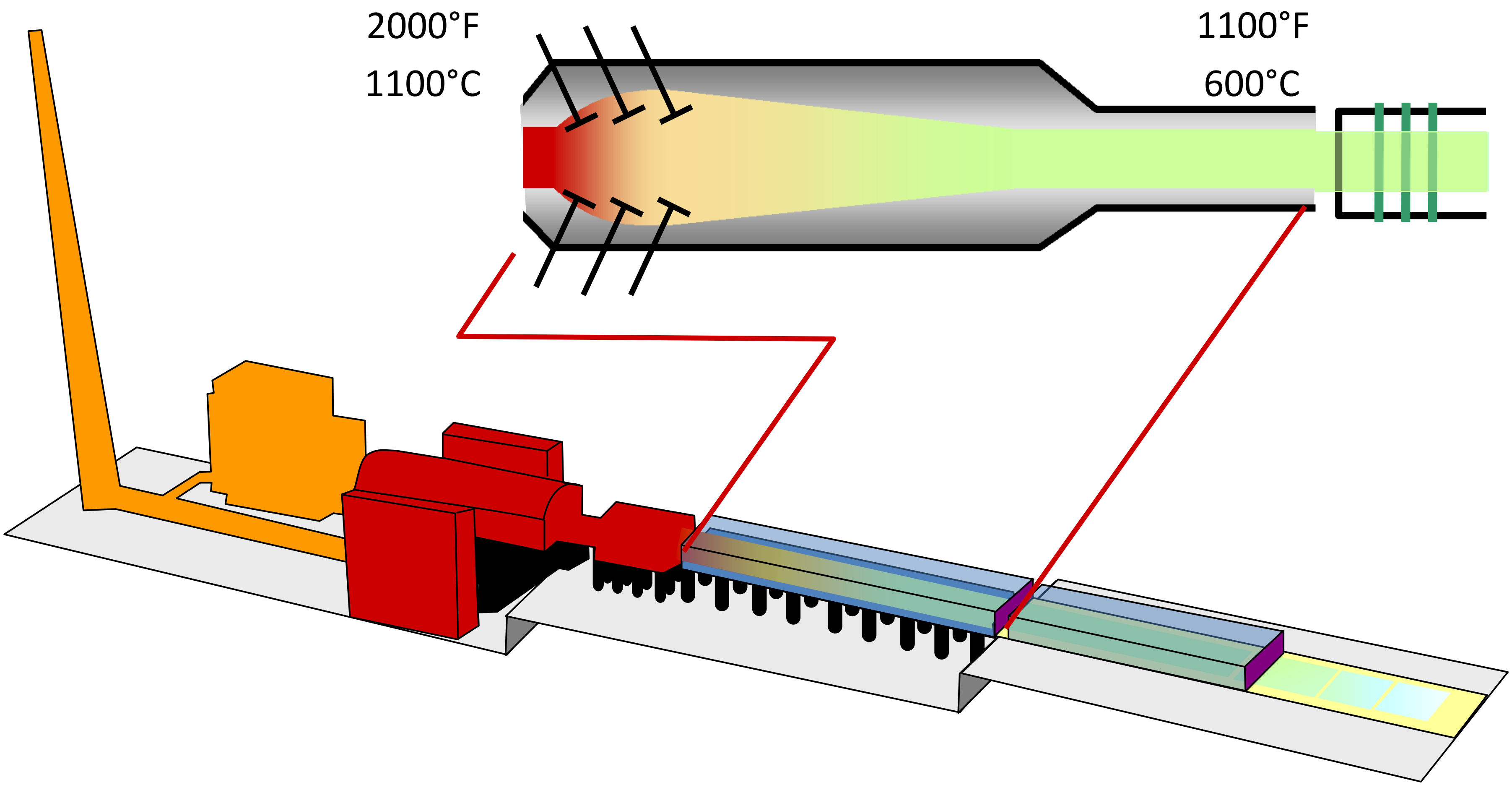
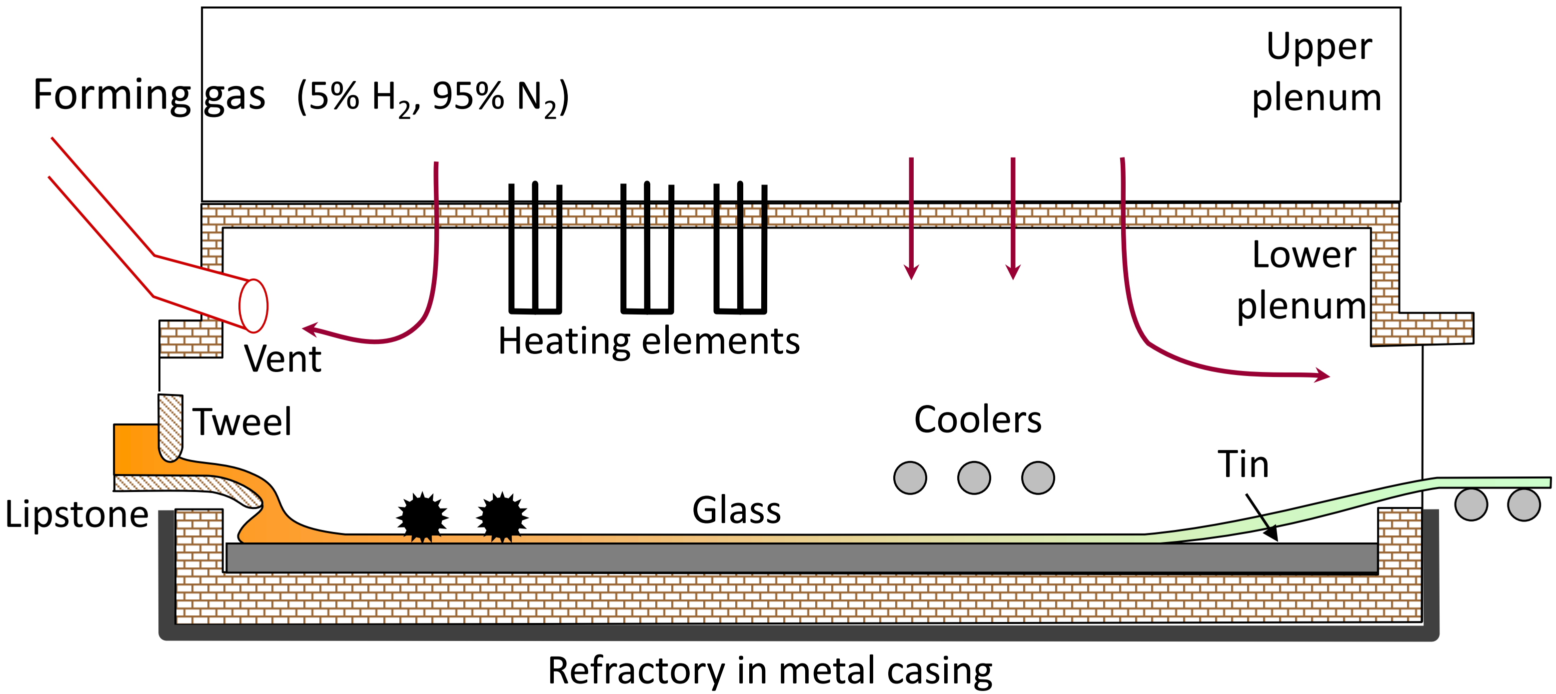
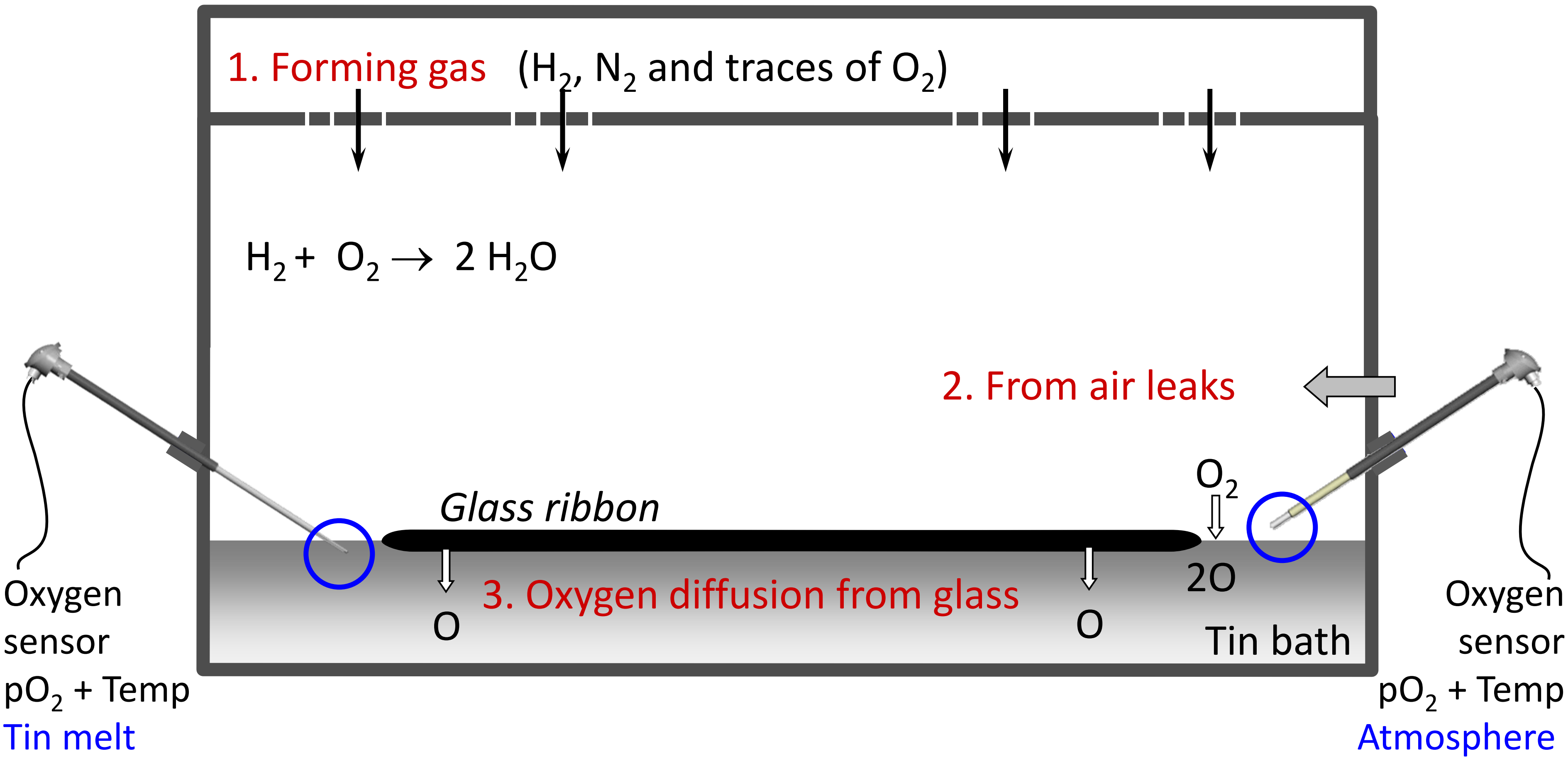


Schematic cross section Tin bath

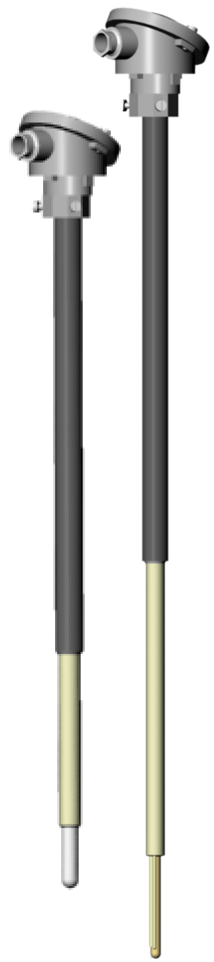


Tin Bath: three sources of oxygen



Tin Bath oxygen sensors

(tin melt and protective atmosphere)



- Continuous monitoring of oxygen content and temperature of tin melt and protective atmosphere
- Early warning of too high oxygen levels in the bath
- Reduced oxygen related surface defects:

  On glass bottom surface:
    - Tin pick-up (by dross formation)
    - Tin diffusion (bloom formation after bending or tempering)

  On glass top surface (top specs):
    - Cassiterite particles (SnO_2)
    - Tin drops
- Critical oxygen pressure for CVD coating inside tin bath
- As a pair: measuring driving force for tin deoxydation for optimal glass quality at lowest hydrogen consumption

Tin bath chemistry

In tin bath atmosphere : protective gas (5% H_2, 95% N_2)

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \qquad \log pO_2 \approx \log\left(\frac{pH_2O}{pH_2}\right)$$

During normal production:
$\log pO_2 = -15$ (hot end) to -25 (cold end)

Dissolution of oxygen in tin (Sieverts law)

½ O_2 (g) ⇆ O(tin)

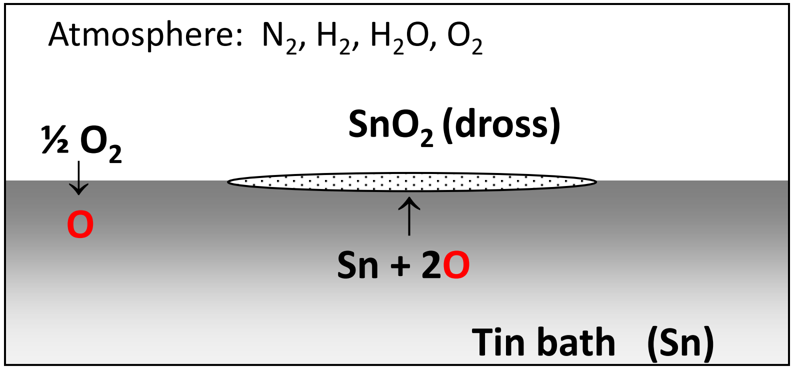
Maximum solubility reached:

Sn(*l*) + 2O (tin)→SnO_2(dross)

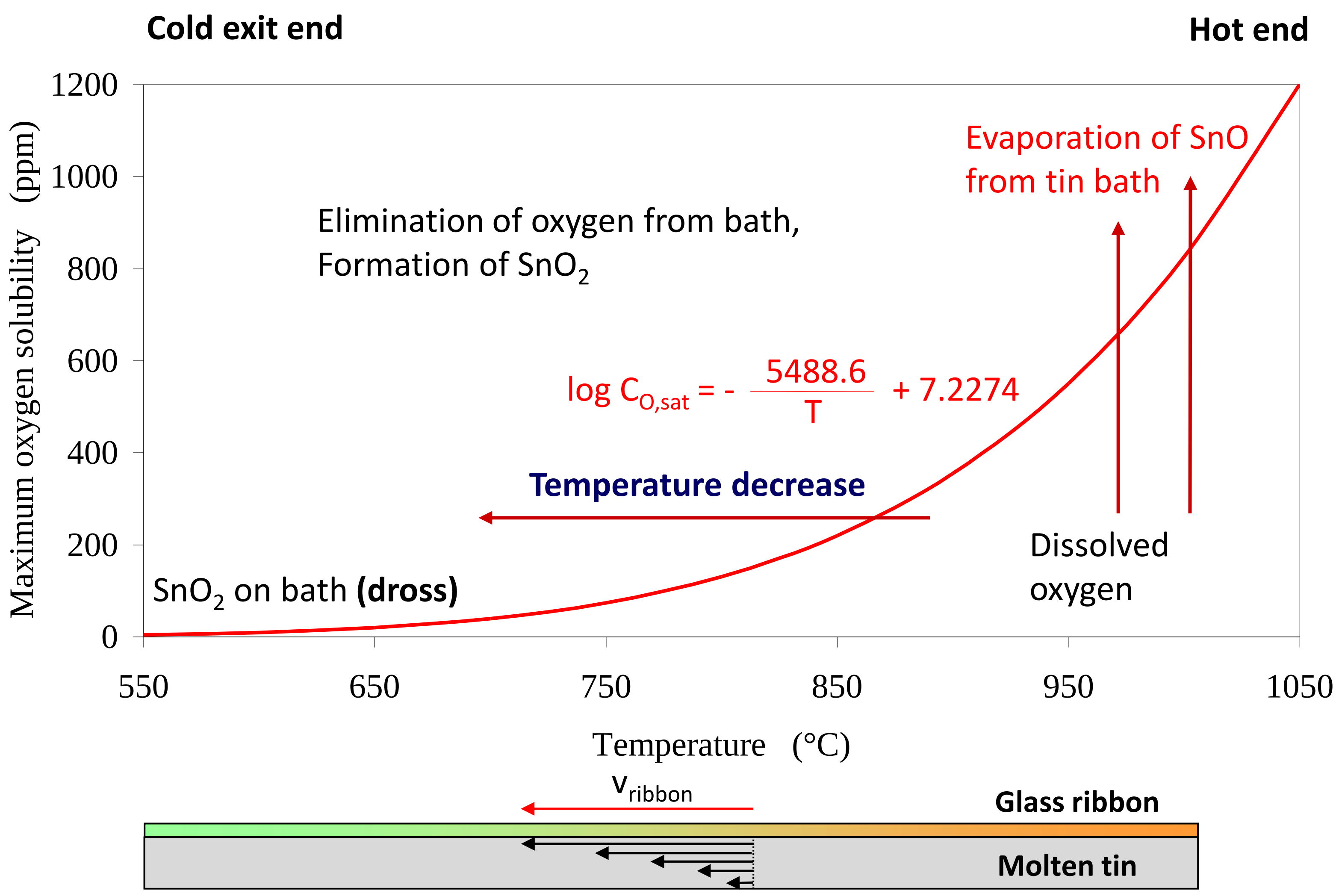
Maximum oxygen solubility is (very) temperature dependent

$$\log C_{O,sat} = -\frac{5488.6}{T} + 7.2274$$

$C_{O,sat}$ (ppm)
T (K)



Oxygen solubility in molten tin



Top surface defects

Tin dripping by tin build-up on colder overhead equipment and roof

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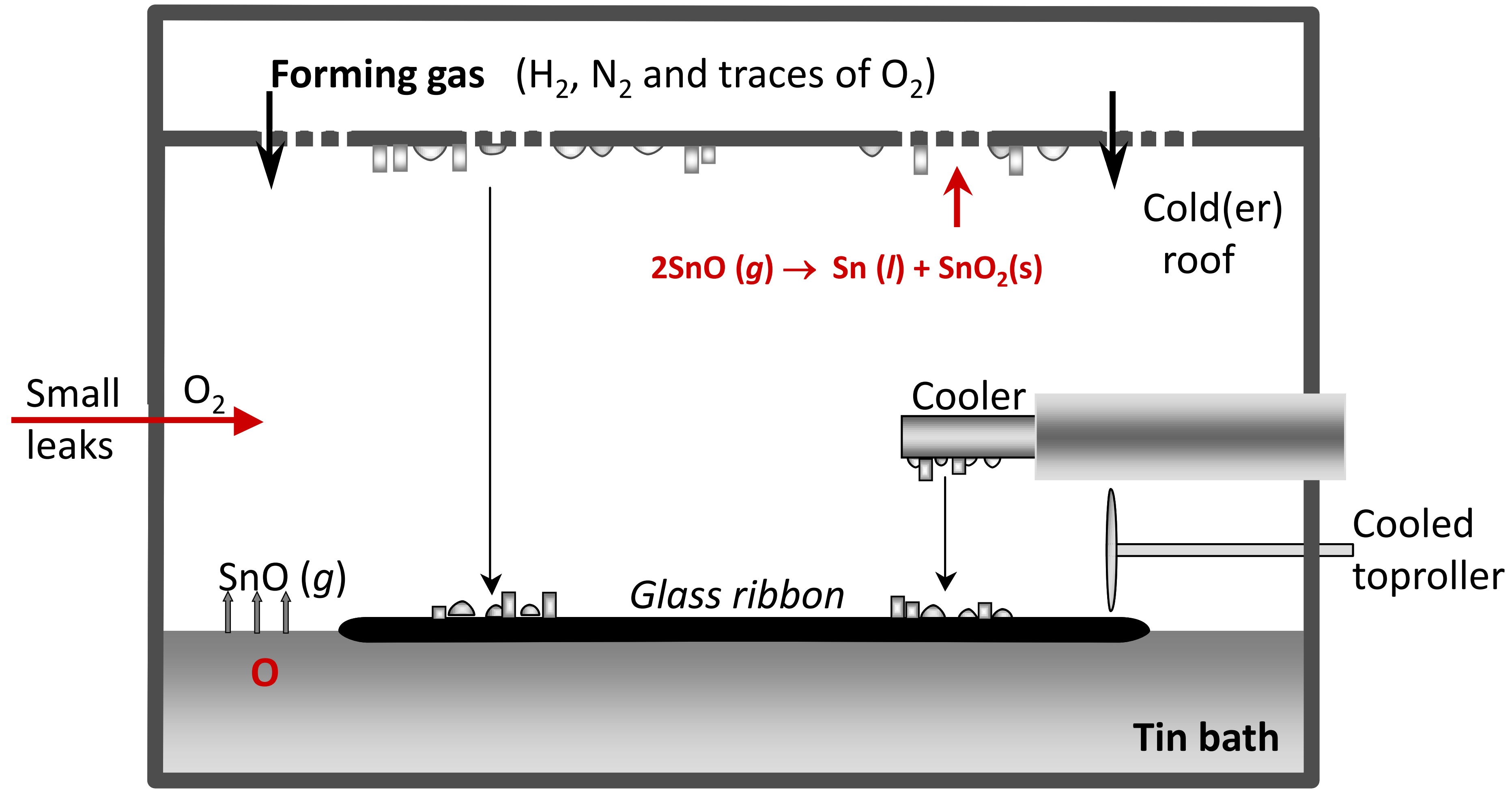
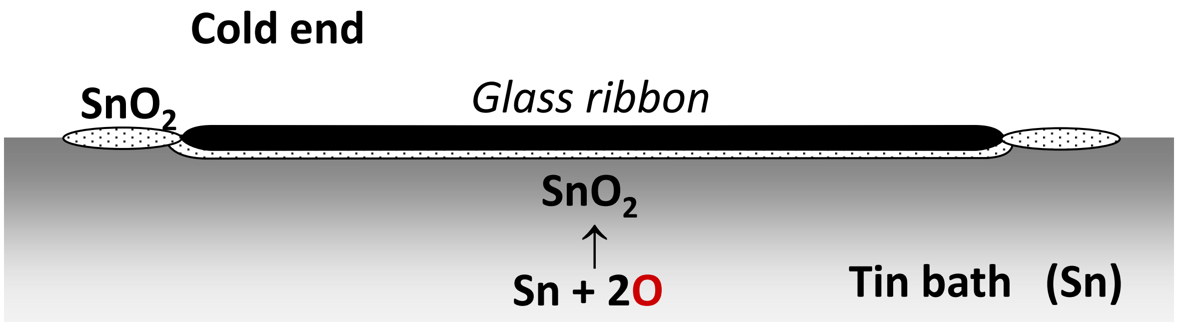


Bottom surface defects

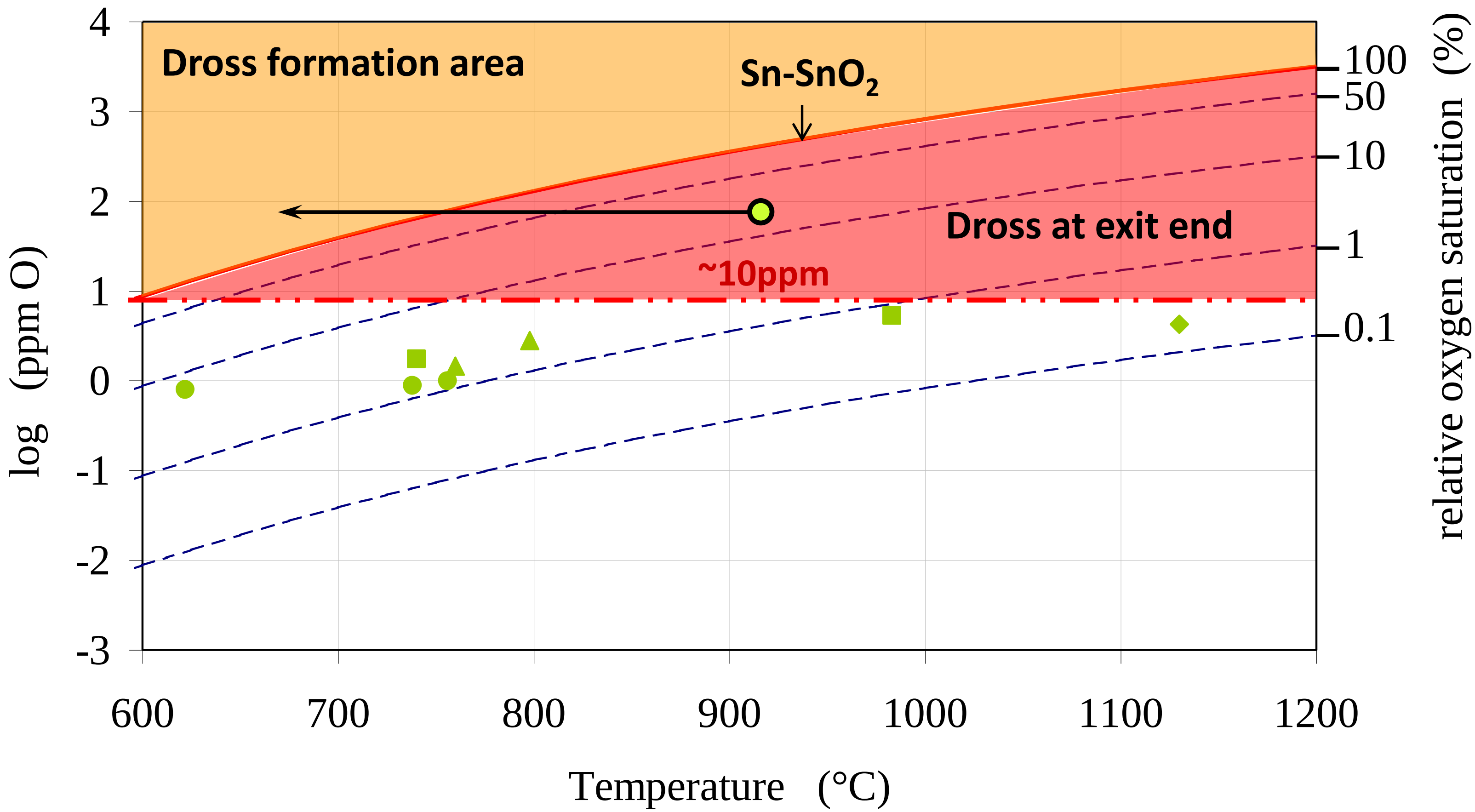
Dross



At low temperatures dissolved oxygen is expelled from the melt as SnO_2, which may adhere to the bottom surface of the ribbon

Oxygen levels in various tin baths

dross formation limit



High oxygen levels during start-up

after a shut down (removal of side walls)

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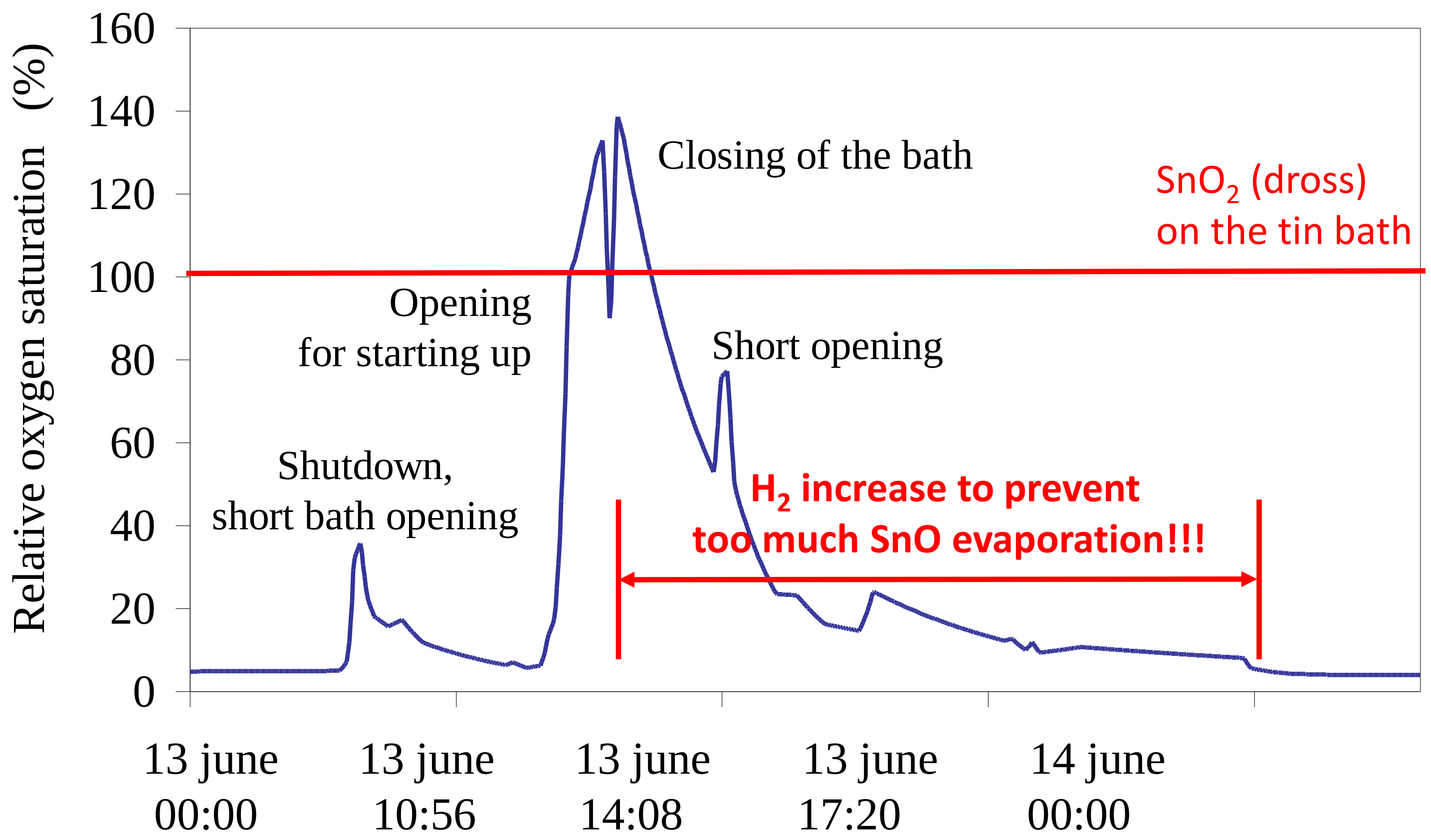
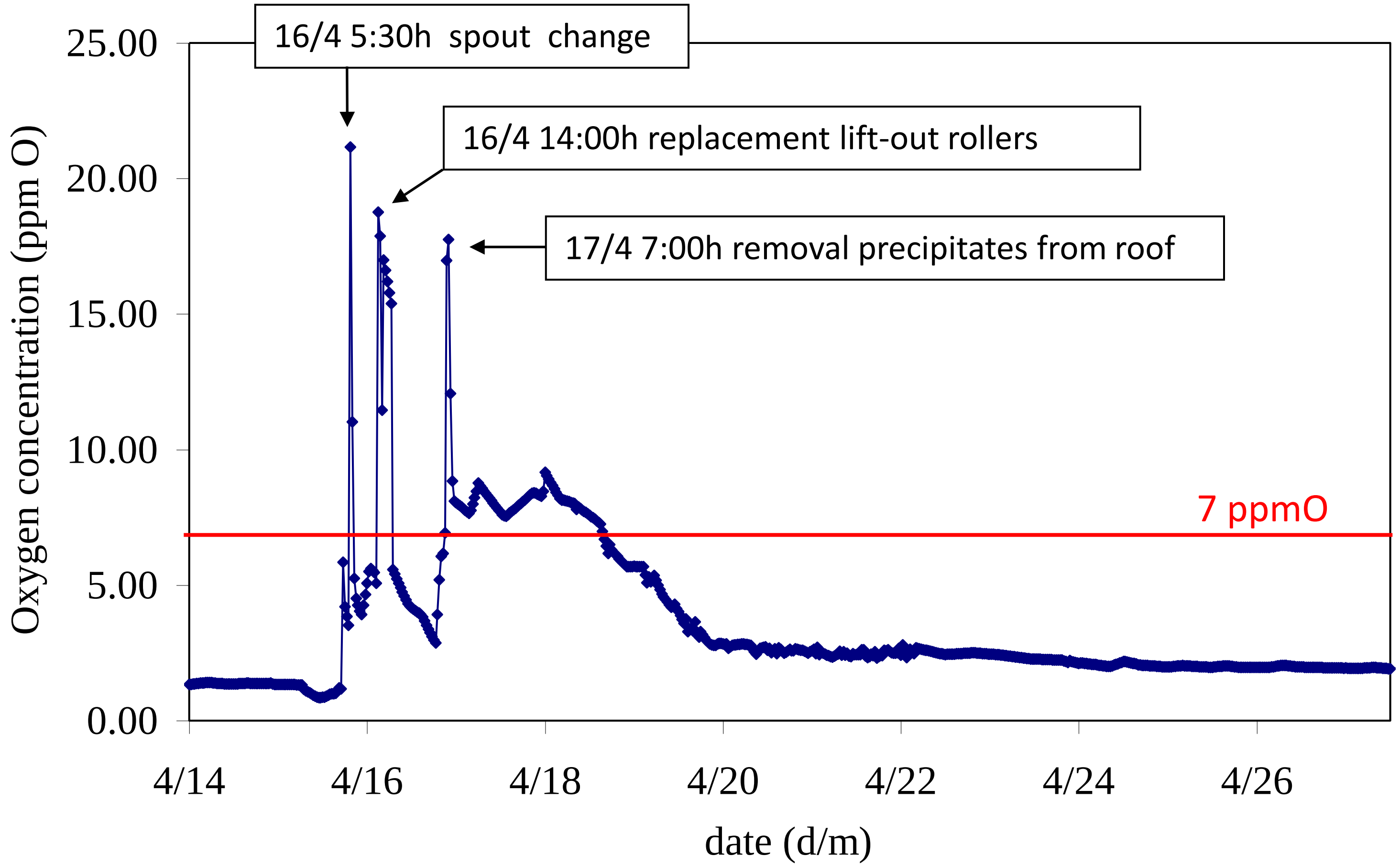


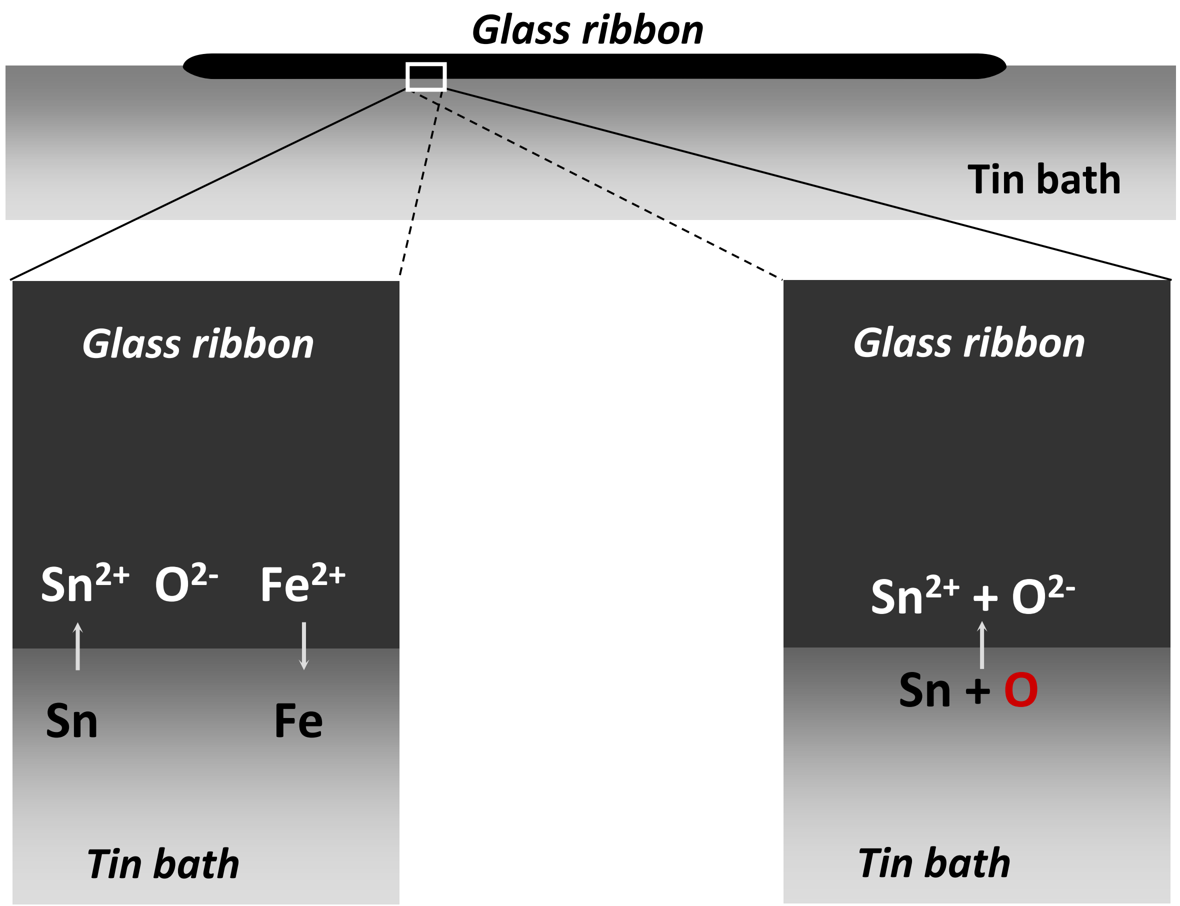
Oxygen content during maintenance activities

(cold end sensor, temperature 580 - 600°C)



Diffusion of tin into the glass ribbon

(causing bloom: haze on glass surface arising after bending or tempering)



Proposed by Hayashi *et al.*

Diffusion of tin into the glass ribbon

(causing bloom: Hayashi Y., Matsumoto, K., and Kudo, M., J. Non-Cryst. Solids 282 (2001) 188-196)

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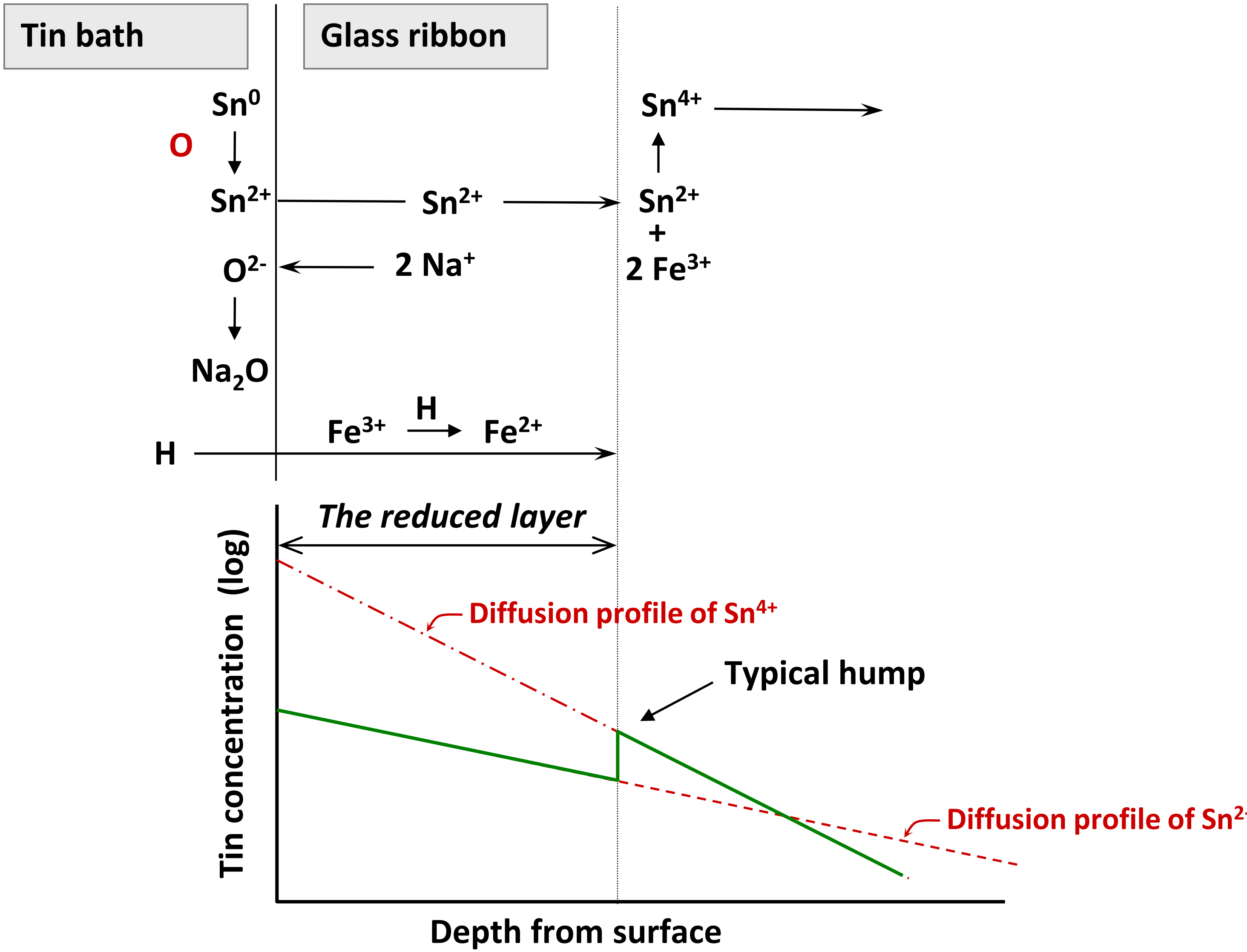
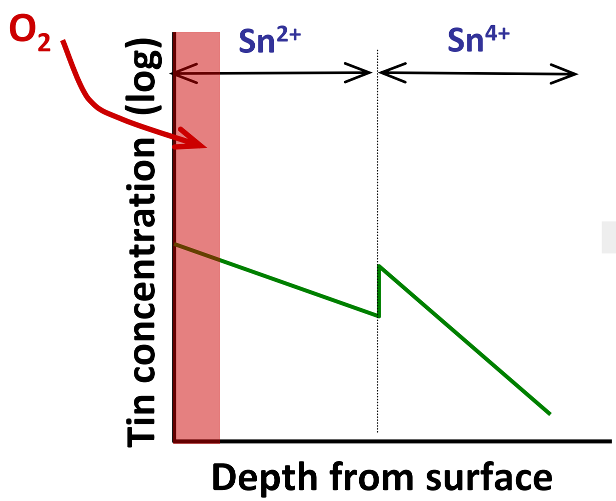
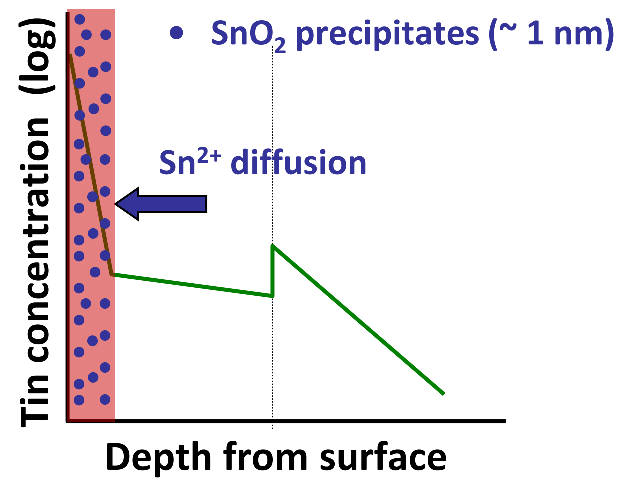


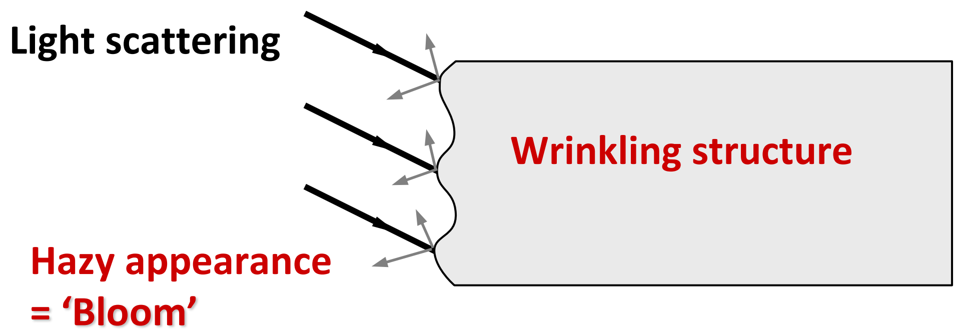
Diffusion of tin into the glass ribbon

(causing bloom: Takeda S., Akiyama, R., Hosono, H., J. Non-Cryst. Solids 311 (2002) 273-280)

O_2 penetrates the glass surface during heat treatment in air (bending or tempering)

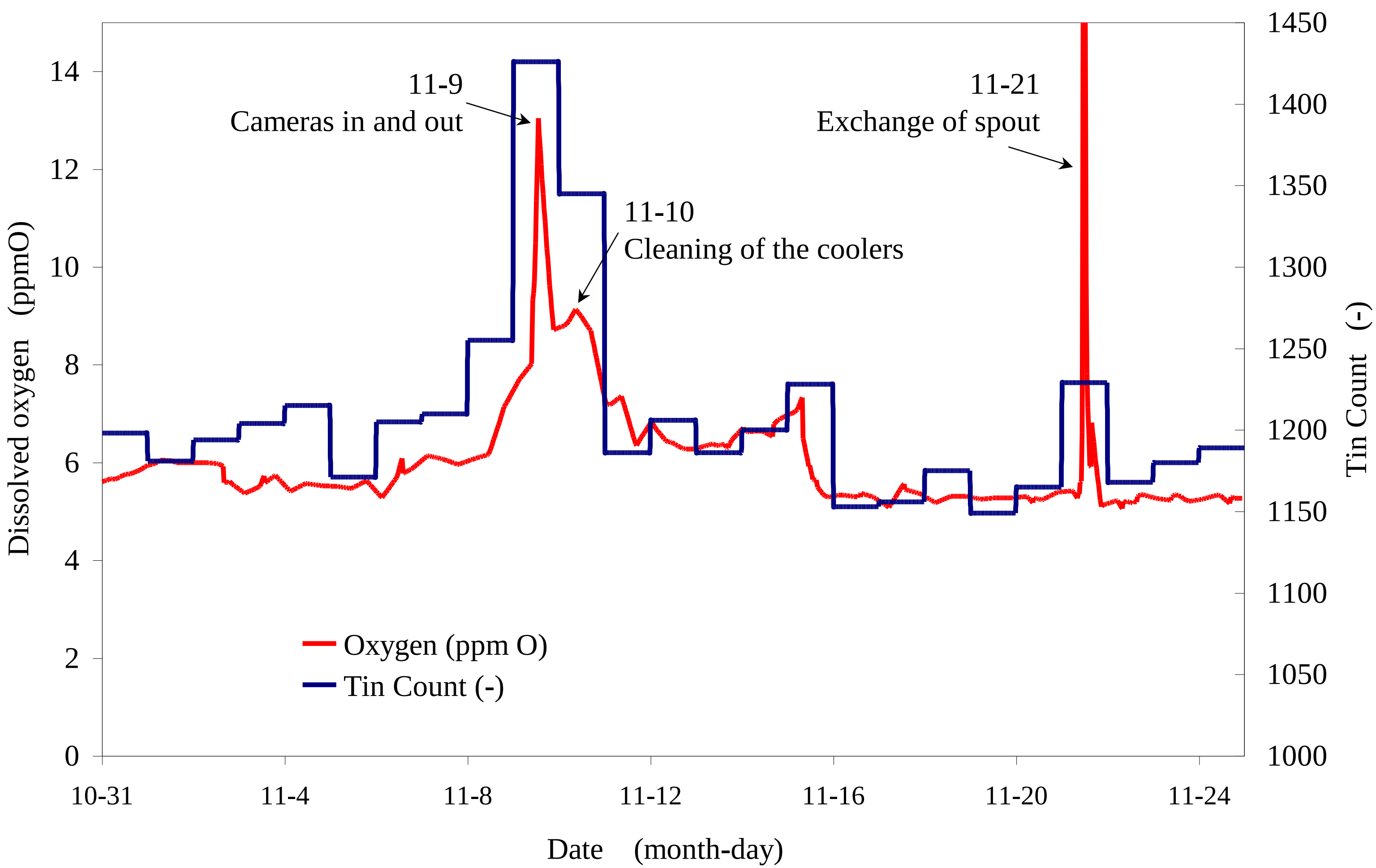






Tin count versus oxygen content

hot end sensor, temperature around 1000°C



Atmosphere oxygen sensor

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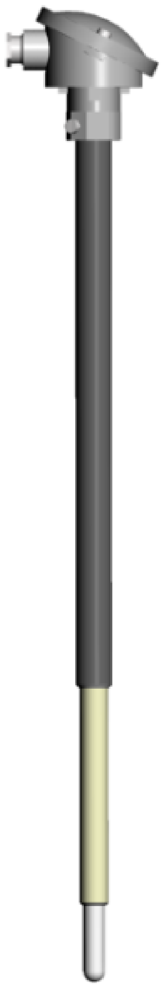
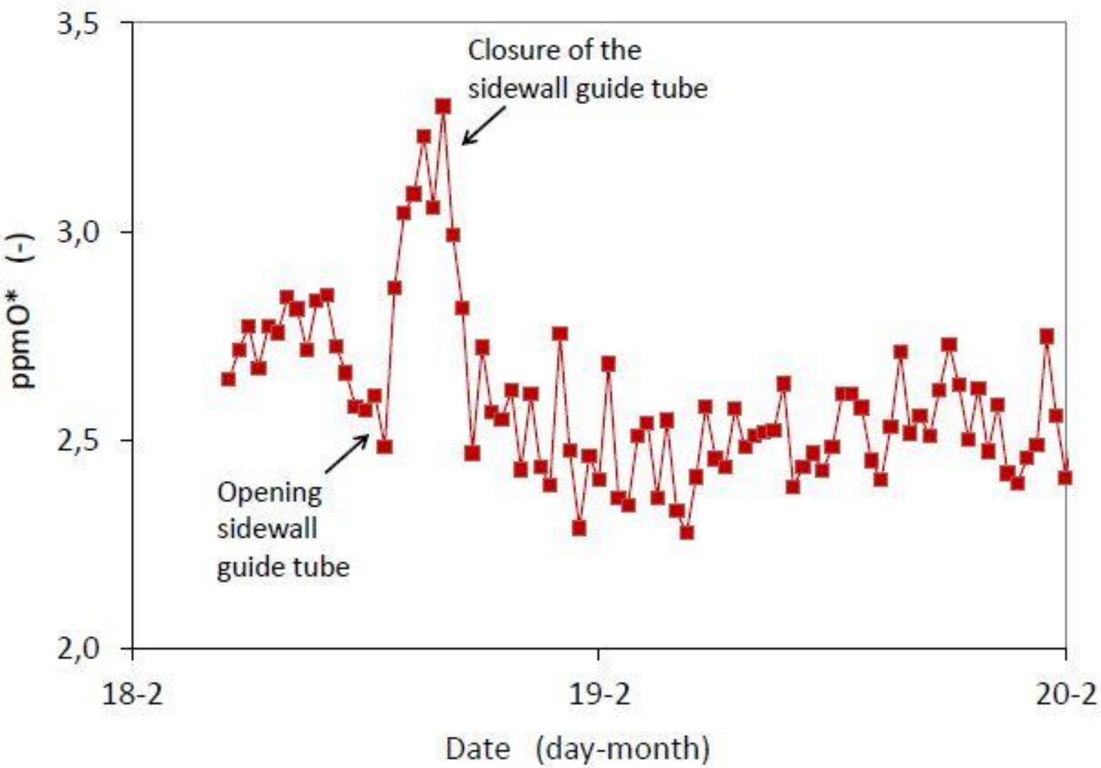


- Very sensitive to the smallest amounts of oxygen leaking into the bath atmosphere

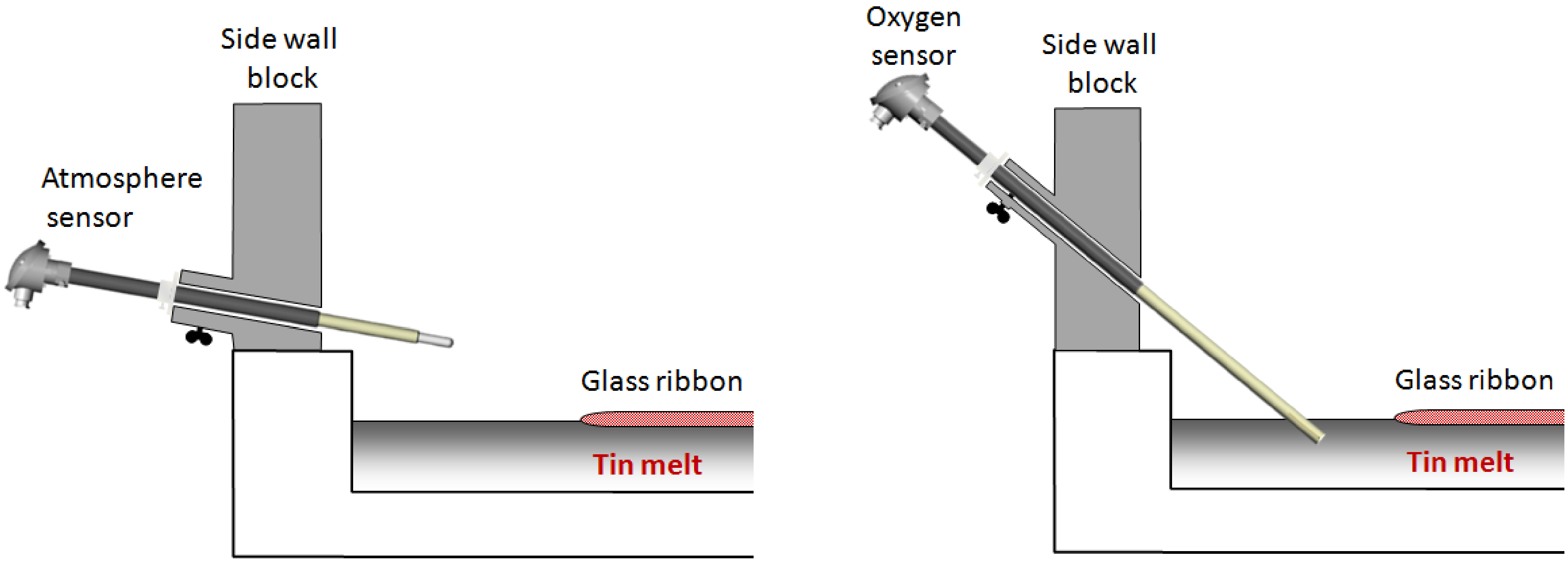


- It is an ideal tool for detecting small air leaks. Fast feedback of effectiveness of sealing activity

Oxygen control in tin bath

Simultaneous measurement of tin oxygen and atmosphere oxygen

Monitoring of driving force for deoxidation of the tin melt by measuring the $\Delta \log pO_2$ between tin and atmosphere



Oxygen control in tin bath

Simultaneous measurement of tin oxygen and atmosphere oxygen

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Monitoring of driving force for deoxidation of the tin melt by measuring the $\Delta logpO_2$ between tin and atmosphere

Oxygen control in tin bath

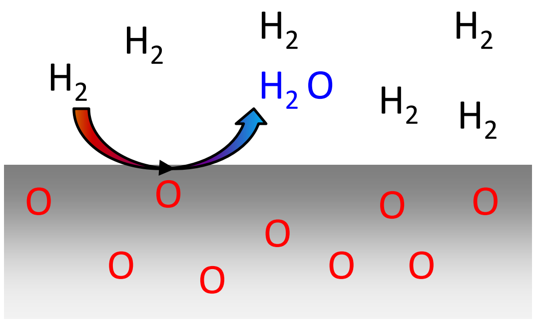
Driving force for deoxidation of tin melt

Atmosphere and tin sensor measurements:

$pO_2(Sn) > pO_2(atm)$

$H_2(atm) + O(Sn) \rightarrow H_2O(g)$

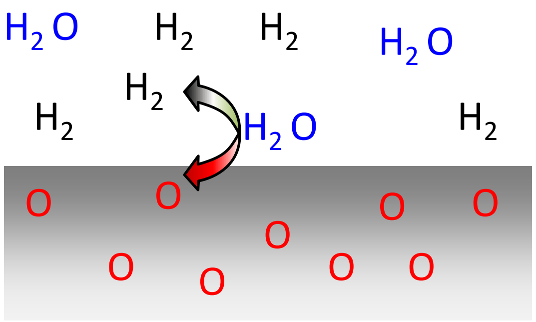
$\Rightarrow$ Oxygen is removed from tin



$pO_2(atm) > pO_2(Sn)$

$H_2O(g) \rightarrow O(Sn) + H_2(atm)$

$\Rightarrow$ Oxygen level of tin increases



Oxygen control in tin bath

Driving force for oxidation/deoxidation of tin melt

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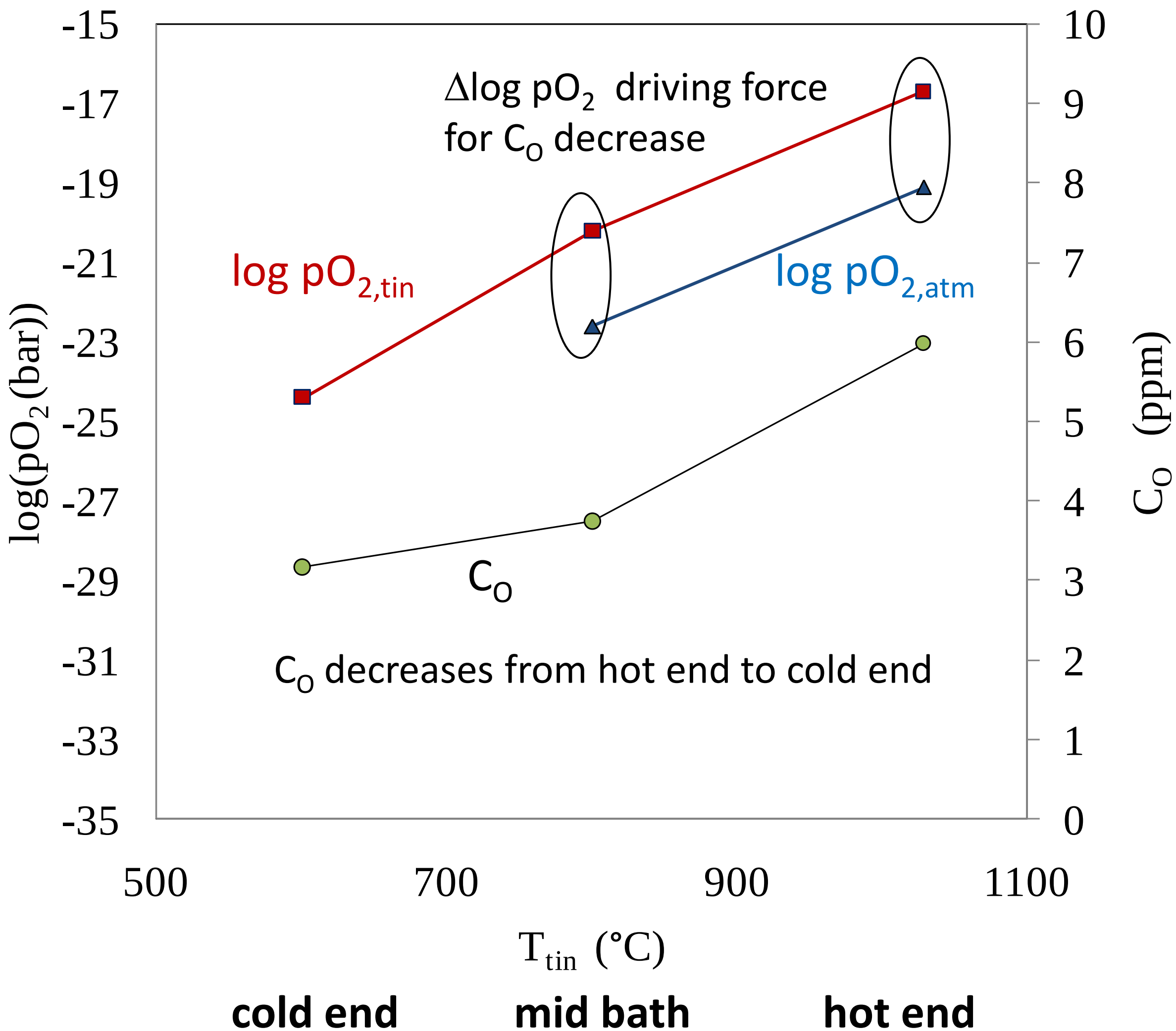

$\log pO_{2,atm} < \log pO_{2,tin}$

⇒

Oxygen is removed from the tin melt

Oxygen control in tin bath

Control of hydrogen supply to various sections of the bath

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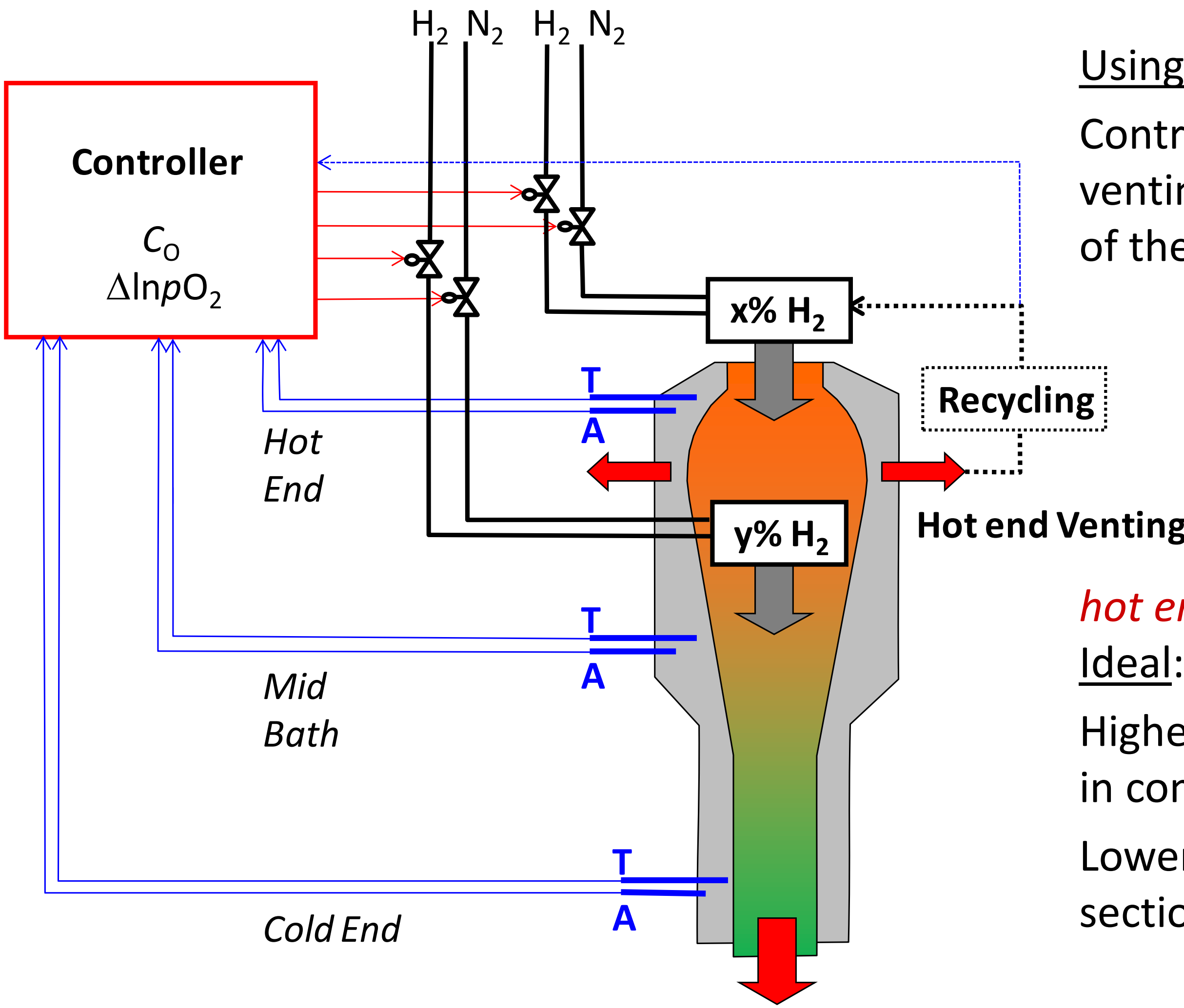

<u>Using sensor pairs in various bays</u>:

Control of hydrogen content and venting rate in various sections of the bath

hot end is most critical

<u>Ideal</u>:

Higher H_2 level in hot end section in combination with intensive venting

Lower H_2 level in mid bath/cold end section

Oxygen control in tin bath

pH_2O and D.P. of atmosphere in equilibrium with tin containing ***1 ppm O*** *(at 5%H_2)*

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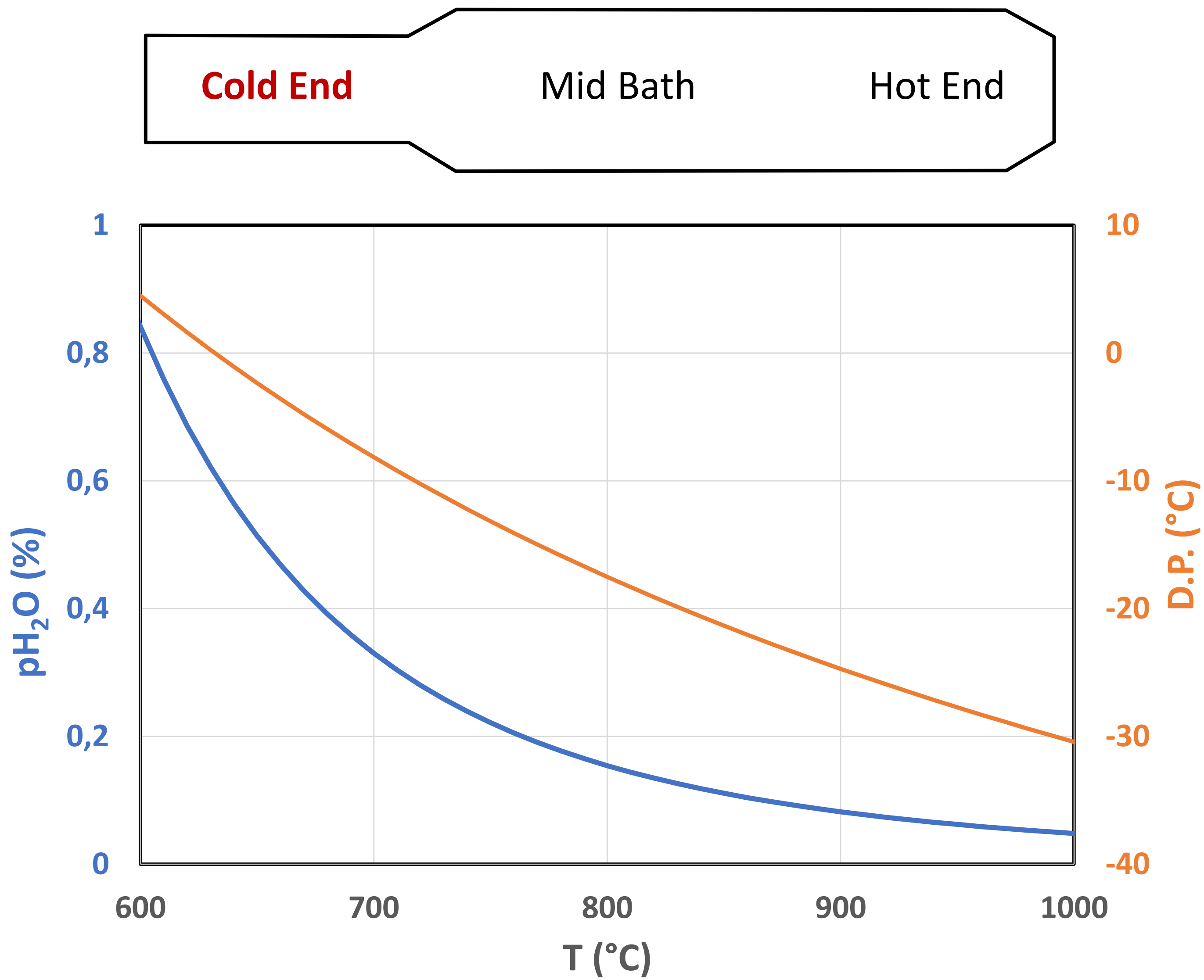

Oxygen control in tin bath

*pH_2O and D.P. of atmosphere in equilibrium with tin containing **1 ppm O** (at 5%H_2)*

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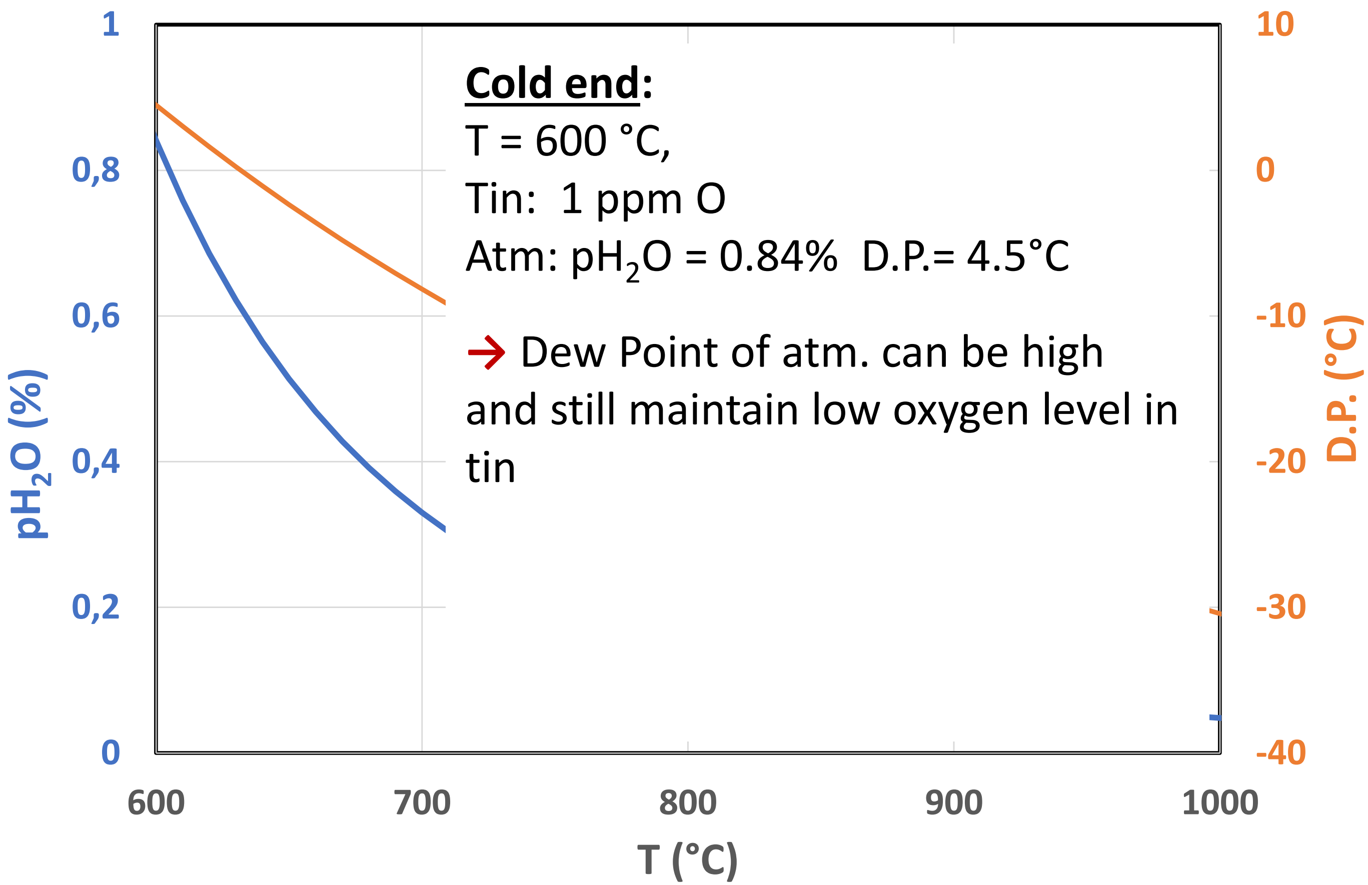

Oxygen control in tin bath

pH_2O and D.P. of atmosphere in equilibrium with tin containing ***1 ppm O*** *(at 5%H_2)*

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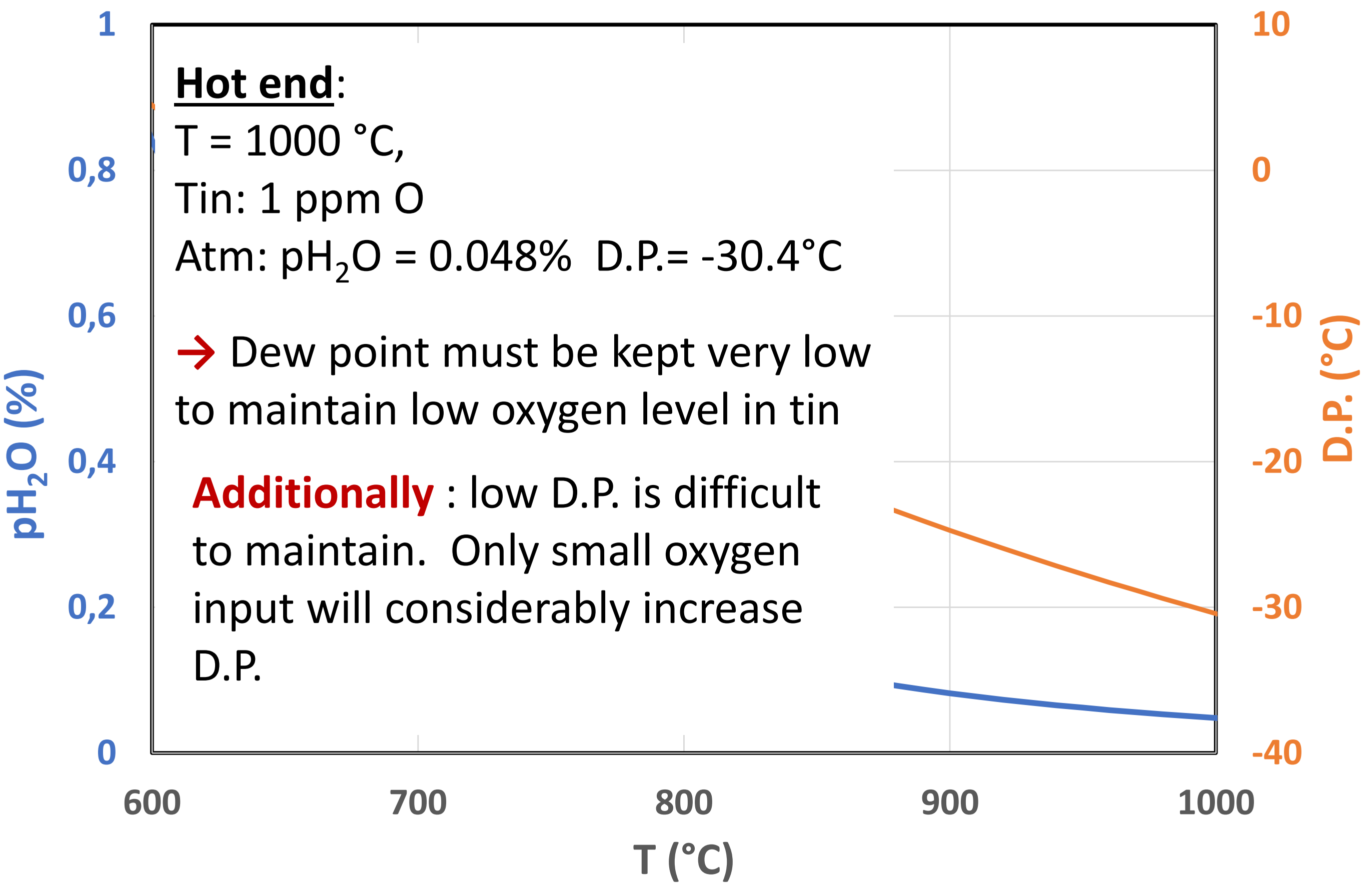


Hot end:
T = 1000 °C,
Tin: 1 ppm O
Atm: pH_2O = 0.048% D.P.= -30.4°C

→ Dew point must be kept very low to maintain low oxygen level in tin

Additionally : low D.P. is difficult to maintain. Only small oxygen input will considerably increase D.P.

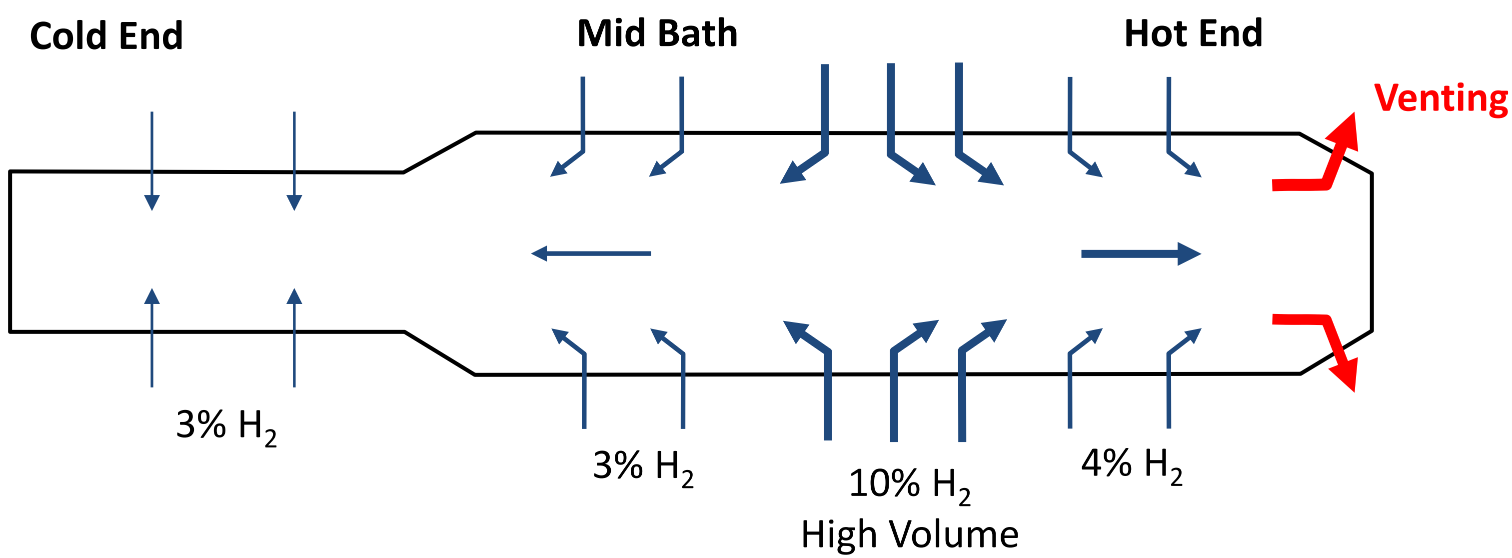
Oxygen control in tin bath

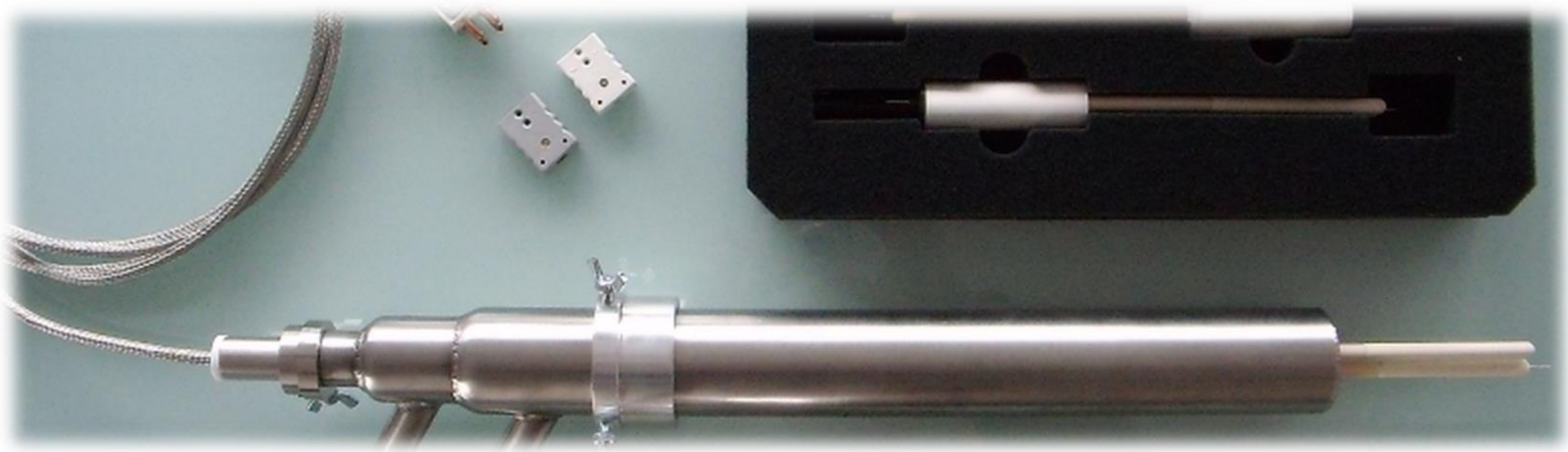
Venting: intensity and hydrogen levels in various sections of the bath

- Most oxygen enters bath in HE *(diffusion out of hot glass ribbon, air leaks at high T)*
- High oxygen content (high D.P.) of atmosphere is most harmful in HE because:
  - ➢ *At high HE temperatures a low D.P. is required for low ppm O in tin*
  - ➢ *D.P. rises rapidly on small oxygen input*
  - ➢ *At high HE temperatures SnO evaporation is most intense*

Measures to keep oxygen content in HE low :

- Intense venting in HE (high volume and high %H_2)
- Optimise atmosphere volumes and flow direction in various bays to prevent backflow from CE atmosphere:





Thank you for your attention !

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