Online measurement of dissolved gases in secondary metallurgy

Bartek Wisniewski, Matthias Hölscher, Rajko Antonic,
Torsten Lamp

MINKON
German Technology

Online measurement of dissolved gasses in secondary metallurgy

Agenda

MINKON German Technology

Why to measure dissolved gases in the steel melt?

Oxygen and Hydrogen will degrade material quality

- Higher Oxygen concentration disturbs the solidification process by forming gas cavities (blowholes)
- Oxygen degrades material cleanliness by forming oxides inclusions
- Deoxidation allows to add alloying elements, other case Oxygen will react with additions
- Hydrogen promotes so called Hydrogen Embrittlement of the solidified material, which is very dangerous for special steel grades
- The gas measurement is important to control countermeasures like the level of vacuum degassing

MINKON German Technology

Oxygen Measurement – Basic principle EMF

Electrochemical measurement of electro motive force (EMF)

- In 1889 Walther Nernst described the electrical potential (EMF) as function of a concentration difference:

$$EMF = \frac{R * T}{n * F} * \ln \frac{c_{melt}}{c_{reference}}$$

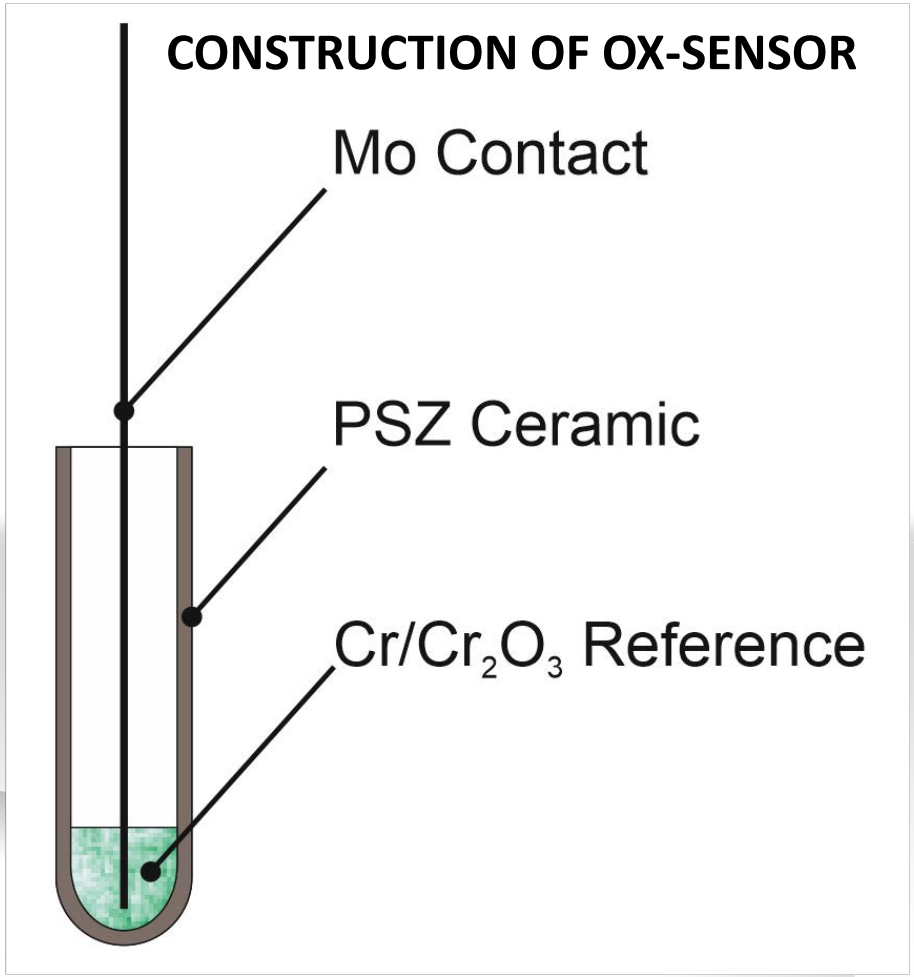
c = Oxygen concentration (= activity)

T = absolute temperature

n = number of charge carrier here $n = 4$

R = universal gas constant $8.314\ J\ K^{-1}\ mol^{-1}$

F = Faraday constant $9.6485 \times 10^4\ C\ mol^{-1}$

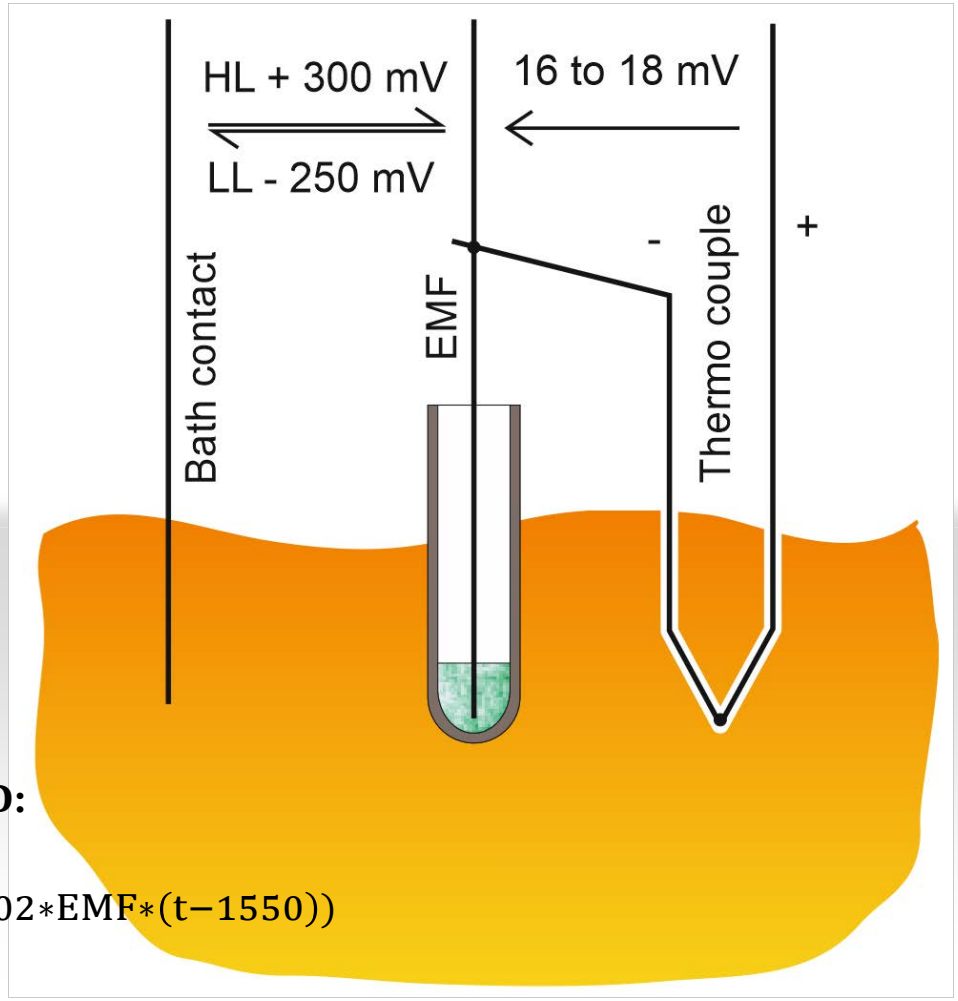


MINKON German Technology

Oxygen Measurement – Basic principle

Electrochemical measurement of electro motive force (EMF)

- Temperature measurement is made the same time as EMF measurement. The negative poles are combined.
- EMF represents Oxygen activity difference between reference powder and melt
- In steel two Oxygen levels are present:
  - high level (EMF up to + 300 mV)
  - low level (EMF down to – 250 mV)



OXYGEN CONETRATION IN PPM IS CALCULATED:

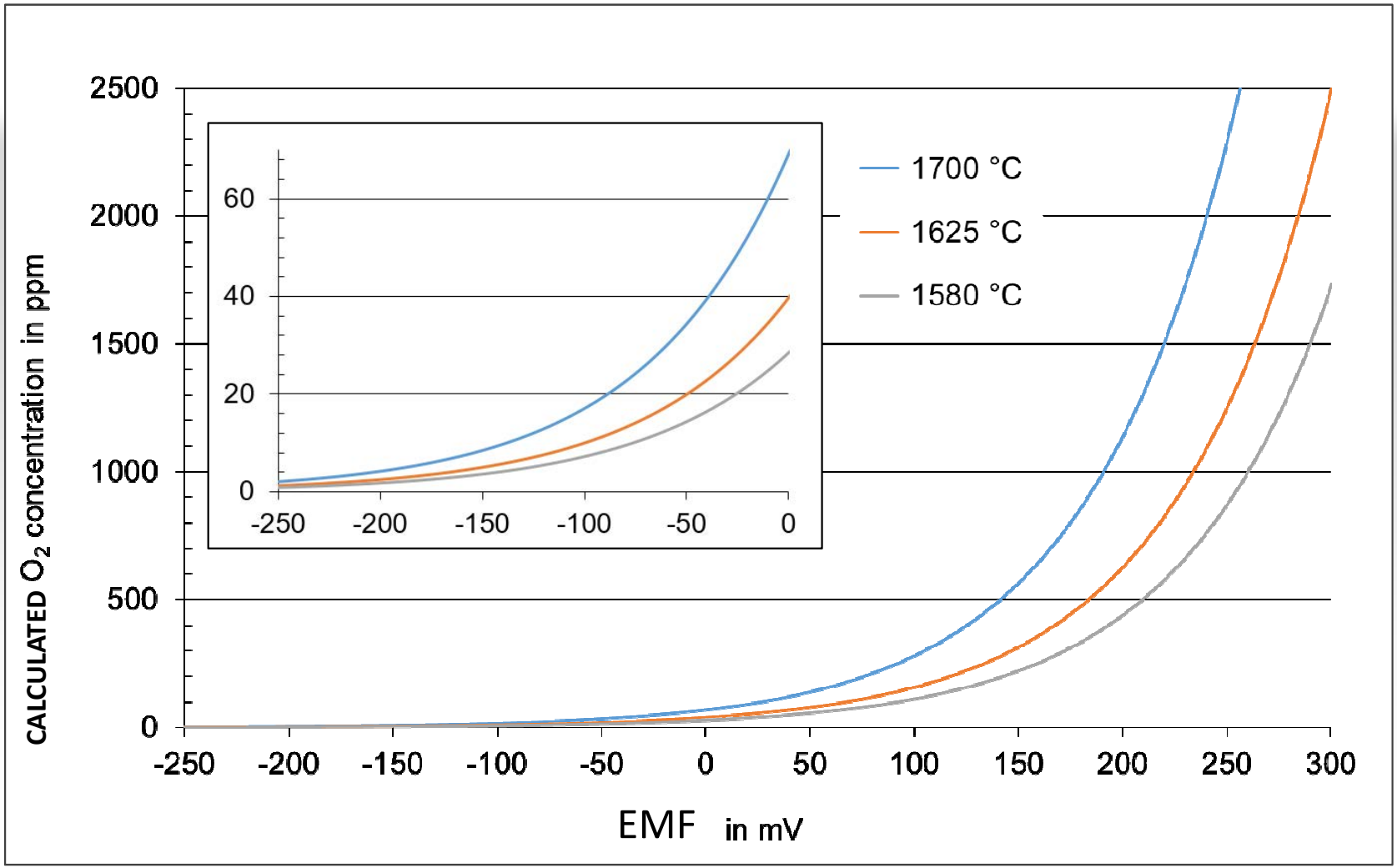
$$C_{Oxygen} = 10^{1,36+0,0059*(EMF+0,54*(t-1550)+0,0002*EMF*(t-1550))}$$

Where: EMF in mV; T in °C

MINKON German Technology

Oxygen Measurement – Basic principle

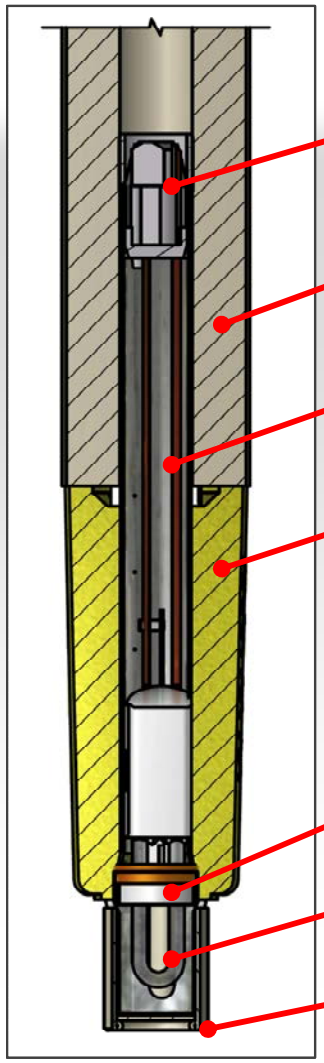
Exponential influence of melt temperature on concentration determination



MINKON German Technology

Oxygen measurement - application

The construction of the immersion probe



The connector to the wired lance

The lance protection cardboard tube

Internal thermocouple’s extension wires

Protective sand body of the probe

Bath contact, an electrode to metal

Thermocouple loop and EMF cell

Anti-slag protection cap

MINKON German Technology

Oxygen measurement - application

Easy to use dipping probes

- Different EMF cell types:

- high level application, BOF and EAF
  typically 600 to 1200 ppm

- low level application, VAC, LF, L, CC
  typically 1 to 10 ppm

- Used thermocouple types:
  - Type S 1750°C (standard)
  - Type R 1750°C (high accuracy)
  - Type B 1820°C (extended temperature range)

- Cardboard tube protection from 500 to 1750 mm

MINKON German Technology

Oxygen measurement - application

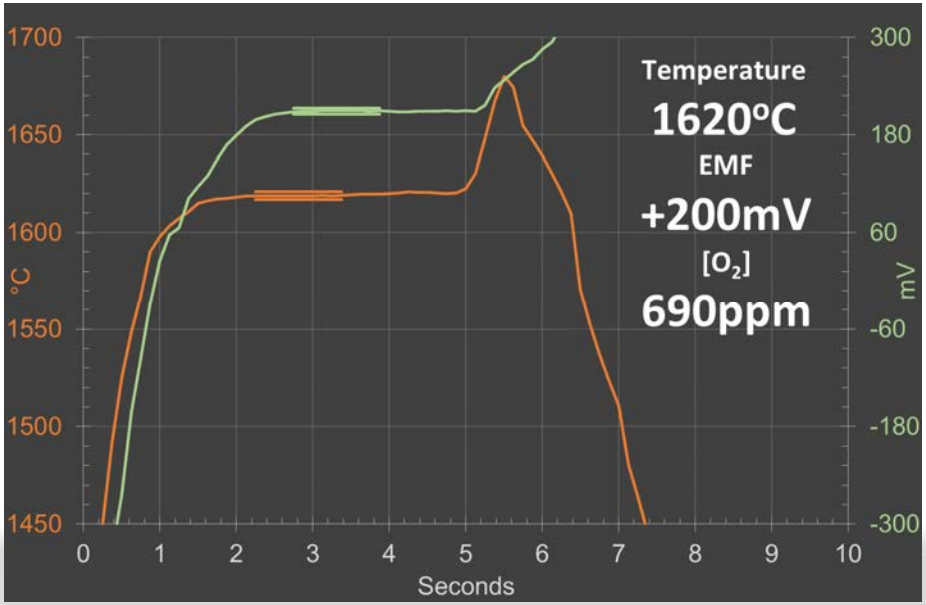
Instrumentation

- Computerized instruments with temperature, EMF recording and implemented functions for %Carbon and %Aluminium for Online calculations
- Typically connected to the steel plant process control system – LEVEL 2
- The very common equipment in every steel shop
- Additional equipment of:
  - Calibration units
  - Spare parts

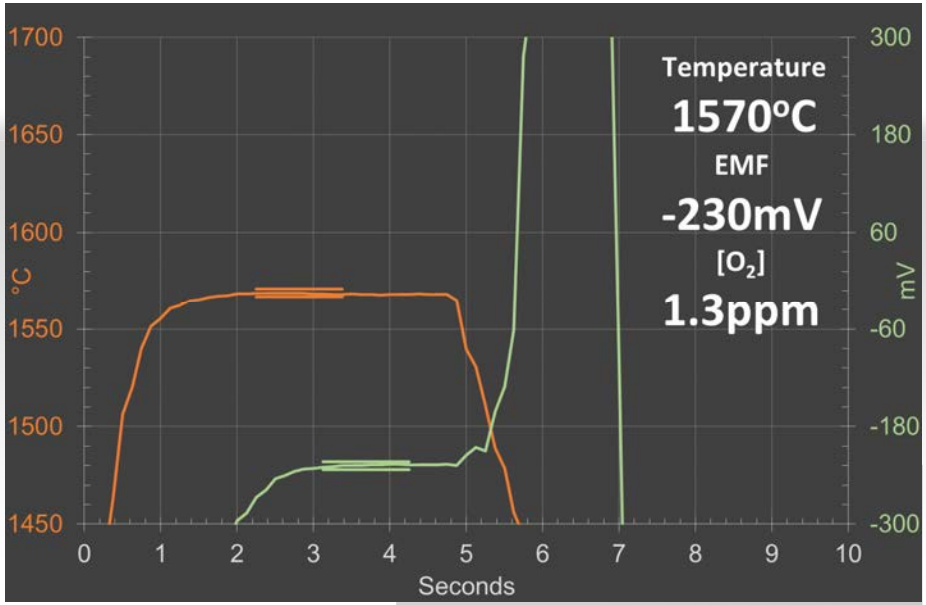
MINKON German Technology

Oxygen measurement - application

Individual examples of ox-probe usage at the steel shop application



High Level of oxygen content during melting in EAF



Low Level of oxygen content after secondary metallurgy treatment

MINKON German Technology

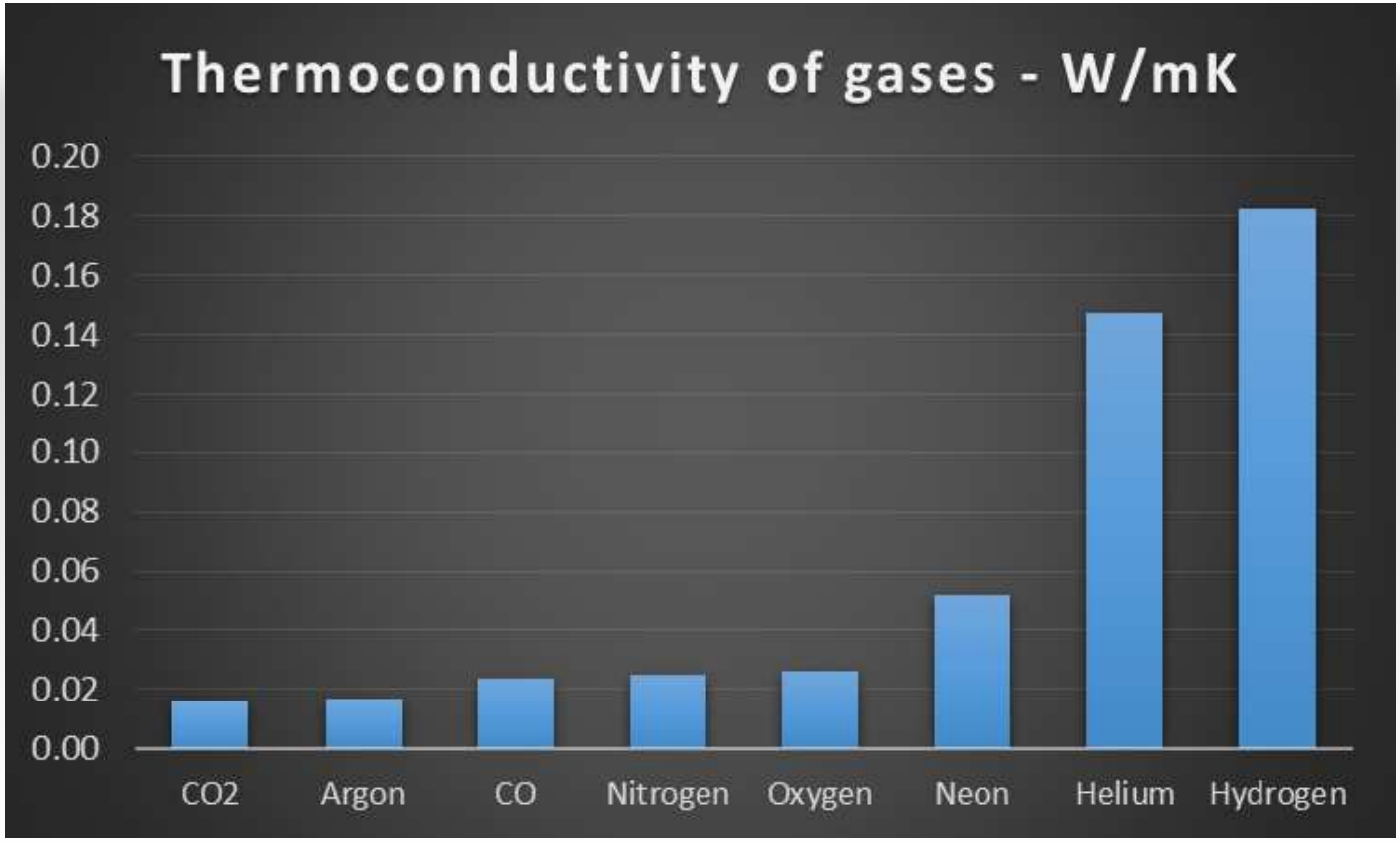
Oxygen measurement

Conclusions

- Electrochemical measurement method (EMF)
- For proper oxygen determination the precise melt temperature measurement is important as well as precise sensor accuracy
- Single dipping probes combine EMF and temperature measurement – Online info about %C and %AL
- High variety of probe types ensure optimum fit to measuring application

MINKON German Technology

Hydrogen measurement
– basic principle THERMOCONDUCTIVITY



MINKON German Technology

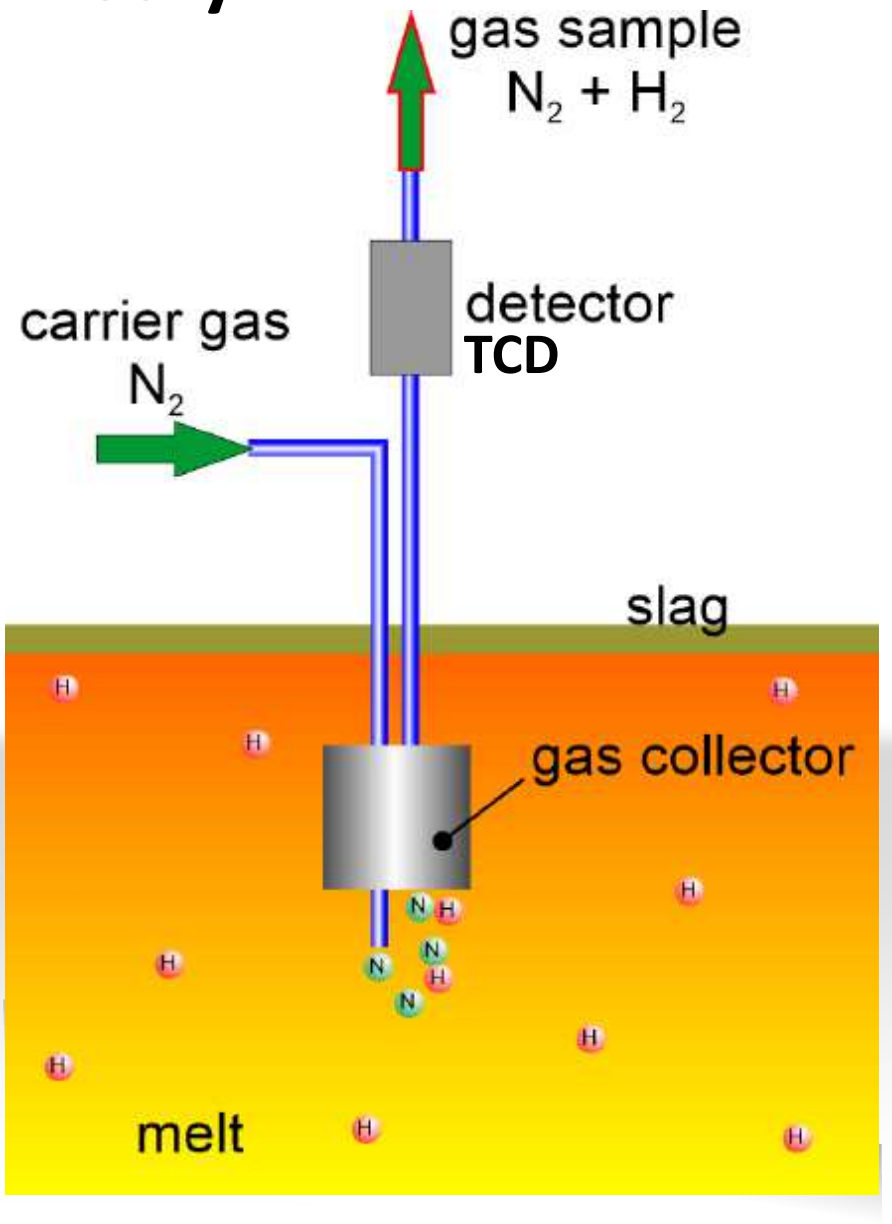
Hydrogen measurement – the theory

Gaseous sampling by using of carrier gas

- Input of carrier gas into the melt
- Collecting of raising carrier gas bubbles
- Determining of the H_2 partial pressure within the collected carrier gas
- Calculation of the H_2 concentration by using the Sievert equation:

$$H = K / f * \sqrt{PH_2}$$

with: H = Hydrogen concentration
K = equilibrium coefficient
f = Hydrogen activity
PH_2 = Hydrogen partial pressure



MINKON German Technology

Hydrogen measurement – the theory

K/f – factor of: $H = K / f * \sqrt{PH_2}$

- K : temperature dependent equilibrium coefficient

$$\text{Log } K_H(T) = -1900/T + 0.9201$$

- f : influence of alloying elements on Hydrogen solubility

$$\text{Log } f_H = 0.06\,[\%C] - 0.0022\,[\%Cr] - 0.0014\,[\%Mn] - 0.0023\,[\%Nb] - 0.0016\,[\%Ni] + 0.023\,[\%Si] - 0.019\,[\%Ti] + 0.0022[\%\,Mo] - 0.0074\,[\%V] + 0.0018\,[\%Co]$$

- standard value K/f = 0.750

Hydrogen - Two types of implementation:

Open or closed loop of carrier gas:

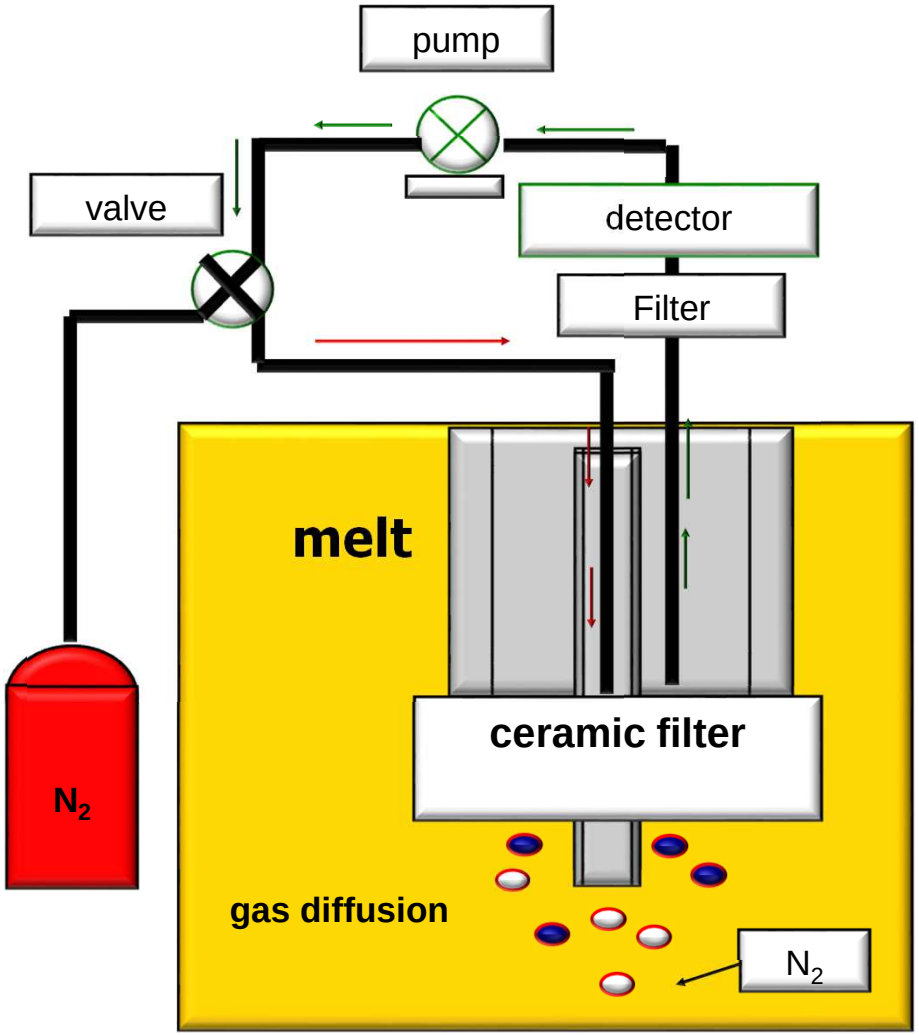
HydroKon CL

HydroKon OP

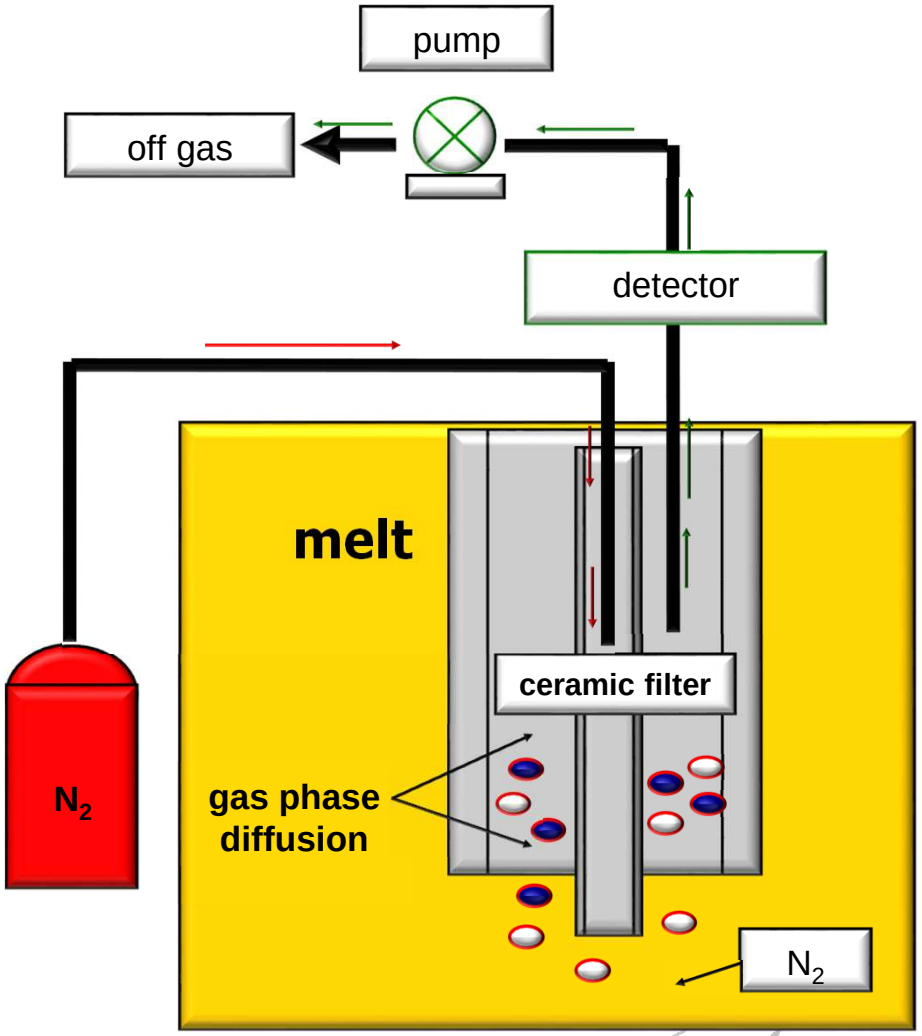
MINKON
German Technology

Hydrogen - Implementations

Closed loop



Open loop



MINKON German Technology

Hydrogen measurement – the systems overview

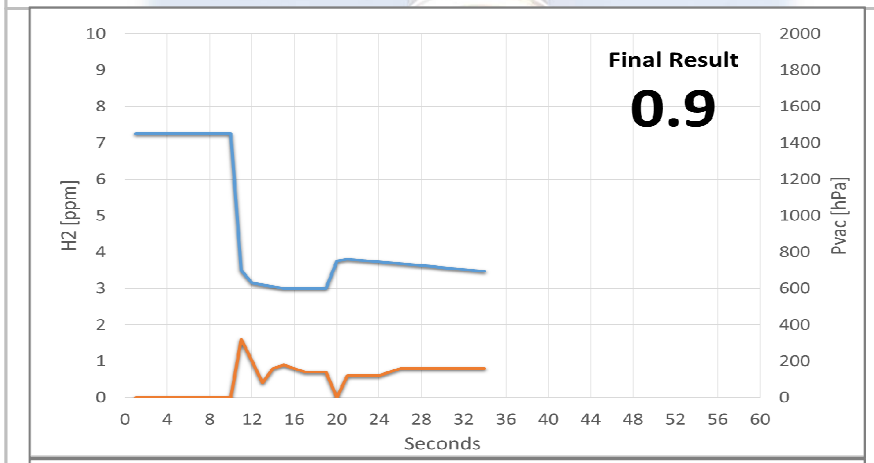
Overview

Closed loop	Open loop
▪ Range 0,5 to 20 ppm	▪ Range 0,1 to 10,0 ppm
▪ Accuracy 5% of meas. value, +/- 0,1 ppm	▪ Accuracy +/- 0,15 ppm
▪ High market penetration in Europe	▪ High alloyed grades and stainless steel grades do not disturb measuring
▪ Connecting hoses longer than 15 Meter possible	▪ Ti, S, Pb, Mn and Si have no influence on measuring
▪ Frequent filter change necessary	▪ No filter change

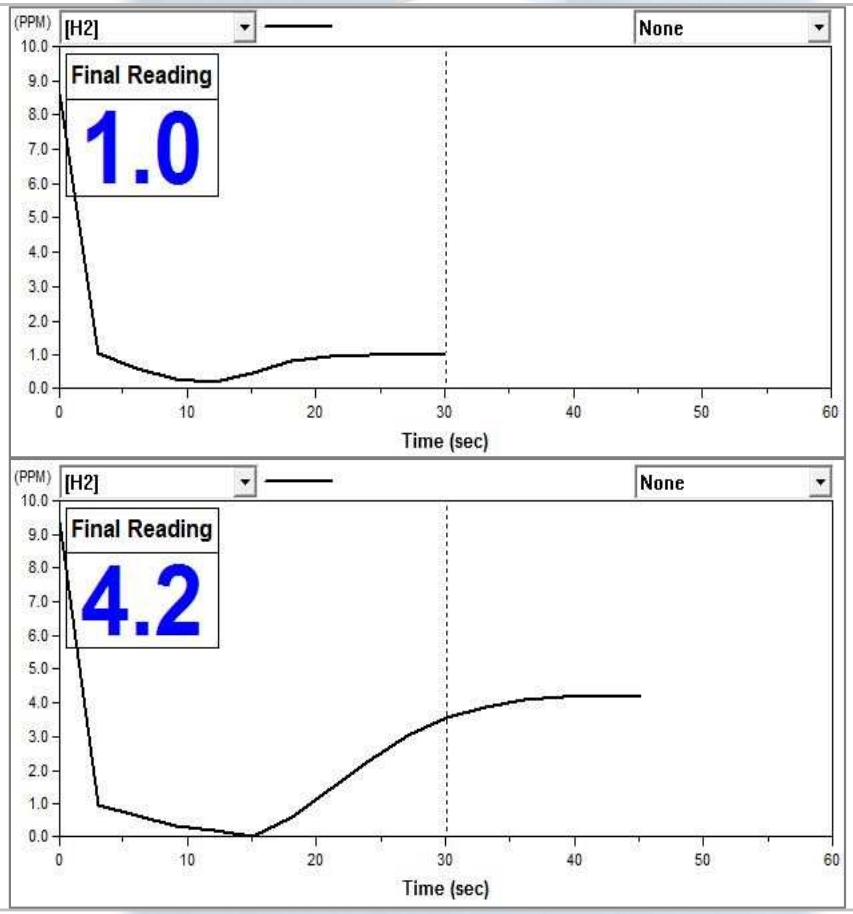
Hydrogen measurement – individual examples

Overview

Closed loop



Open loop



MINKON German Technology

Online measuring of dissolved gasses in high temperature melts

Conclusions

- Dipping probes provide an accurate an reliable online measuring method to determine Oxygen and Hydrogen concentration in the melt
- Allows to save the process operation time for the laboratory check
- The variety of probe types offer an optimal solution for nearly every application
- The deoxidisation process and vacuum degassing can be controlled more precisely with usage of online sensors

MINKON
German Technology

Thank you for your attention!

Contact

Minkon GmbH
Heinrich-Hertz-Str. 30-32
D-40699 Erkrath

Telefon: +49 (0)211 209908-0
Telefax: +49 (0)211 209908-90

www.minkon-international.de

MINKON German Technology