

Oxygen activity measurement system for non-ferrous metals

INTRODUCTION

As most of the steps in the copper refining are oxidation - or reduction processes, control of the oxygen content of the liquid copper during every production stage is very important.

Already a few years ago Heraeus Electro-Nite has developed a control tool to assist the copper melter in his job of making a quality product at the best price. Celox®-Cu is a disposable immersion sensor, which gives within seconds the correct oxygen content in the copper bath.

The production of Celox®-Cu is following the procedures of ISO 9002.

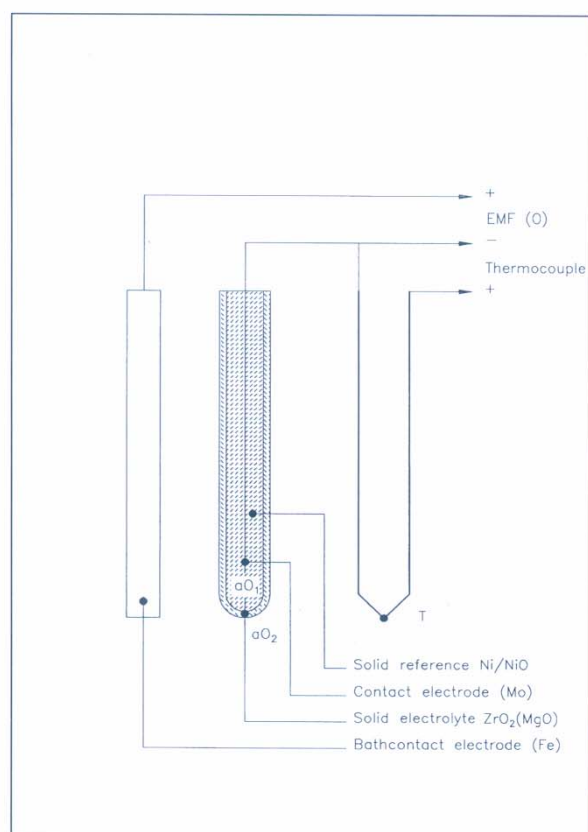


Fig. 2 : Celox®-Cu principle scheme.

Celox®-Cu



Fig. 1 : Oxygen sensor Celox®-Cu.

PRINCIPLE

The principle of oxygen activity measurement is based on the use of a zirconium oxide electrochemical cell. Because of different oxygen activities at both sides of the solid electrolyte, the cell produces an EMF which is defined by Nernst's law :

$$EMF = \frac{RT}{nF} * \ln \frac{p_{O_2}}{p_{O_1}}$$

p_{O_1} is known (cell reference). If the cell EMF and bath temperature are measured, then p_{O_2} (the oxygen activity in the copper bath) may be calculated.


Electro-Nite

TECHNOLOGY

The Celox®-Cu sensor is composed of a solid oxide reference cell, for oxygen activity measurement and a PtRh/Pt thermocouple, for temperature measurement.

These are assembled within a conical sand body, and protected by both copper and cardboard slag caps.

To complete the Celox®-Cu probe the sensor is attached to an expendable cardboard tube.

Whilst the operation of the thermocouple requires no explanation, operation of the cell may be represented by the expression :



in which :

Mo = negative reference electrode molybdenum wire.

Ni + NiO = oxygen reference material nickel-nickel oxide.

ZrO₂(MgO) = solid electrolyte ; magnesium stabilised zirconia in the form of a closed end tube.

a(O)_{Cu} = oxygen activity in the liquid copper, nickel or other metals.

Fe = positive electrode : steel tube in contact with the bath.

The Celox®-Cu sensor may be applied in liquid copper for a measurement of 0 to 10000 ppm under normal melt temperature conditions.

MEASUREMENTS AND ACCURACY

The relationship between temperature (°C) and oxygen activity, for Celox®-Cu is given by the following formula :

$$\log a_o = 7,64 - \frac{7\,943 - 10,08 (E - 7,8 + 0,0219t)}{t + 273}$$

with E in mV
t in °C

This formula is according to Larashi and Elliot for the standard Gibbs energy for solution of oxygen in liquid copper and corrects also for the Fe-Mo galvanic junction of the probe.

This equation is applicable to the Celox®-Cu unit with Ni-NiO reference taking into account the interaction coefficient e_o^o according to Taskinen.

$$e_o^o = 0,266 - \frac{613,9}{T} \quad (T \text{ in K})$$

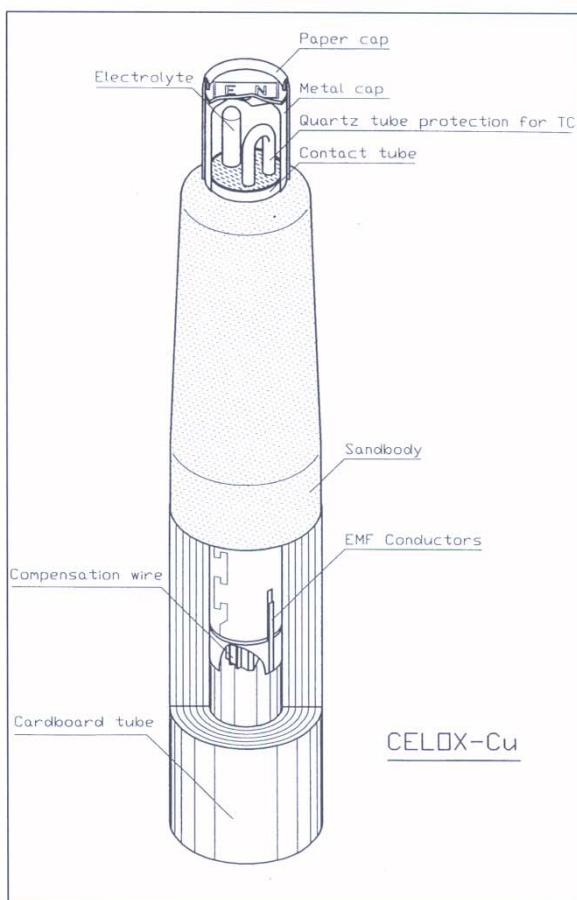


Fig. 3 : Celox assembly drawing.

Also corrections for other impurity elements in the copper, should be made as follows

$$\log f_o = e_o^o \text{wt \% (O)} + e_o^A \text{wt \% A} + e_o^B \text{wt \% B} + \dots$$

$$(\text{O}) \text{ concentration} = \frac{a_o}{f_o} \quad (\text{in ppm})$$

Interaction coefficients for different elements are shown in table 1.

The response traces of both temperature and oxygen signals exhibit stable plateaux and short response times.

In practical working conditions, reproducibility tests at 1150°C have shown a standard deviation of around 1.5 mV.

Measured values are within $\pm 10\%$ of lab analysis results over the whole range 0-10000 ppm.

Judging of the results is dependent on the accuracy of the comparative sampling and analysis of the copper.

Accuracy of the thermocouple wire is 0 to +4°C at 1554°C.

$$e_o^1 = a + b/T(K)$$

1	a	b	1	a	b
Ag	0,0072	-9,86	O	0,266	-613,9
As	-0,051	94,4	P	3,16	5790
Au	-0,0198	41,0	Pb	0,0396	-66,5
Bi	0,0502	-86,3	Pt	-0,0391	77,0
Co	0,717	-1310	S	0,285	-529
Cr	51,5	-94300	Sb	0,0205	-33,7
Fe	12,0	-22000	Se	0,172	-314
Ge	0,020	-35,4	Si	373	-68,3 x 10 ⁵
Hg	0,0053	-4,4	Sn	0,0300	-30,0
In	0,0734	-131	Te	0,0992	-177
Ir	-0,0494	95,6	Tl	0,0290	-47,6
Mn	37,22	-66280	Zn	3,00	-5490
Ni	0,148	-272			

Table 1 : The assessed dissolved-oxygen interaction parameters in liquid copper. (Ref. Report TKK-V-B21 (1983) Helsinki University, Pekka Taskinen)

PRACTICAL USE

The unit must be surely fixed on the lance and immersed quickly into the liquid metal to a depth of 10 to 20 cm below any slag.

The lance must be held rigid during the measurement.

Gas stirring (Ar, N₂, ...) has to be stopped during Celox-Cu® measurement. The recommended waiting time after stirring is 60 sec before use of Celox®-Cu. The electric power of the furnace has to be turned off during measurement.

Incorrect immersion may influence the quality of the measurement in terms of poorly defined or false measurements.

Immersion time is approximately 8-10 seconds for applications in copper melts. Celox®-Cu probes should be stored in a dry environment.

CELOX LANCE AND ACCESSORIES

Construction of the lance is extremely important. Care must be taken to guarantee an insulation of 2 Megaohm between :

- the positive and negative legs of both temperature and oxygen channels
- the two positive legs of temperature and oxygen
- all legs and earth

Polarity and colour coding of the contactblock, MI-cable, lance plug/socket, and compensating cable must be correctly maintained (see fig. 4).

The Heraeus Electro-Nite Celox®-Cu lance has been designed so that it may be used for temperature measurements only and for Celox®-Cu temperature and oxygen.

The use of a telescopic cardboard protection tube is recommended for applications in large converters or furnaces.

INSTRUMENTATION

As instrument we recommend our Multi-Lab Celox. This is an industrial, programmable micro-computer based instrument with an outstanding measuring performance. For more detailed information please consult our particular catalogue Multi-Lab Celox.

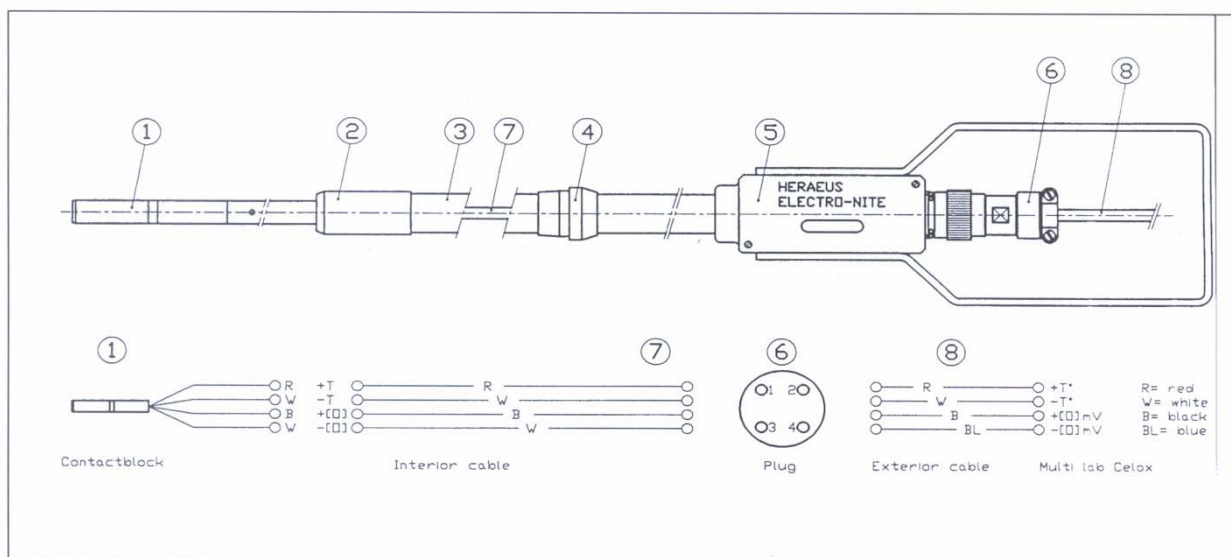


Fig. 4 : Celox immersion lance.

CELOX®-CU APPLICATIONS

- By using the oxygen sensor in the copper refining plant, a better control of the production process is possible and hence the production cost is lowered. An oxygen measurement in the converter permits to determine the endpoint of oxidation and prohibits from excessive blowing.
 - In the same way the Celox®-Cu can be used in anode furnaces. Removal of the impurities is achieved by oxidation into the slag and a first oxygen measurement (abt. 7000 ppm) may determine the endpoint of oxidation. Afterwards the copper is deoxidized by poling to an oxygen content of 500 - 2000 ppm to obtain a "flat-set" of the anodes and thus optimize electrolytic refining.
 - In the production of deoxidized copper the amount of deoxidant, e.g. phosphorus, can be accurately calculated by a direct oxygen measurement. By this way the amount of residual phosphorus is maintained very close to specification and a high quality casting is obtained (high conductivity, good deformability).
- Take care :
After a substantial addition of phosphorus, Celox®-Cu measurement is not possible.
- Celox®-Cu can also be used in other non-ferrous metals with specially adapted oxygen-formula.

ORDERING INFORMATION

CELOX®-CU SENSORS

Cardboard length (nominal)	Calibration Pt 10% Rh/Pt according to DIN 43710, IPTS 68
400 mm	CE 10210490
600 mm	CE 10210690
1200 mm	CE 10211290

TELESCOPIC CARDBOARD TUBES

Inside diameter	Outside diameter	Tube length	Part-number
31,5 ± 0,3	43,5 ± 0,8	1500 mm	RM 33012007
		1200 mm	RM 33012006
		900 mm	RM 33012005

CELOX IMMERSION LANCE (ref. Fig. 4)

1. Celox contactblock, 4 contacts
Cu-CuNi - Cu-CuNi : LC 23 016 002
2. Lanceholder
600 mm RM 33 016 010
900 mm RM 33 016 014
1200 mm RM 33 016 017
3. Cylindrical tube ¾" : RM 33 016 023
4. Arrest ring for telescopic tube : LC 33 016 077
5. Handle : LC 33 016 076
6. 4 pole connector : LC 33 016 075
7. Interior compensation cable, 4 wires
Cu-CuNi - Cu-CuNi : LC 33 024 008
8. Exterior compensation cable, 4 wires
Cu-Cu - Cu-CuNi : LC 33 024 007

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