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Progettazione del sistema di monitoraggio e controllo dell'ossigeno
disciolto nell'impianto a metallo liquido HELENA

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PROGETTAZIONE DEL SISTEMA DI MONITORAGGIO E CONTROLLO DELL'OSSIGENO
DISCIOLTO NELL'IMPIANTO A METALLO LIQUIDO HELENA
A. Gessi - ENEA

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Sommario

This document describes the technical specification for the OCS (Oxygen Control System) to be implemented in the HELENA facility, with the goal to obtain very low Oxygen concentrations in HLM during the operation.

Note

This document is written in English

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Introduction

The need for an efficient Oxygen Control System in HLM facilities is connected with several aspects: Corrosion and passivation of materials, PbO formation control, various impurities control and, more generally, the control of non metallic elements in the melt itself. Electrochemical oxygen sensors currently used for measuring the chemical potential of oxygen in liquid lead alloys were investigated by five European laboratories, focussing on factors influencing the accuracy of the sensor output, the long-term performance in experimental facilities and methods of testing the sensors before installation and during operation in a plant.

Oxygen sensors

Based on the Russian work on important aspects of safe application of liquid lead (Pb) and lead-bismuth eutectic (LBE) as a coolant in nuclear reactors [1,2], it is generally accepted that maintaining a certain level of dissolved oxygen (oxygen potential) in these liquid metals significantly increases the compatibility with steels, the favoured materials of construction at temperatures below 650 °C. Efficient control of the oxygen potential requires devices for adding oxygen as compensation for the consumption that results from steel oxidation [3] and oxygen sensors for monitoring the actual level of dissolved oxygen in crucial positions within the reactor. Furthermore, such sensors are mandatory for characterizing the conditions in material tests targeting the performance of steels in the respective liquid metal. The high chemical stability of ceramics makes electrochemical oxygen sensors with oxidic solid electrolyte especially appropriate for application in liquid Pb alloys. The need to measure the oxygen potential on-line motivated several studies on the performance of electrochemical oxygen sensors in liquid Pb alloys in the recent past [4–12].

The principal components of an electrochemical oxygen sensor are (i) the solid electrolyte; (ii) the reference electrode which exhibits a known and, at constant

temperature, constant chemical potential of oxygen; and (iii) a second electrode (working electrode), the oxygen potential of which is to be measured. The electrodes are in intimate electric contact with opposing sides of the electrolyte that transforms the difference in the chemical potential into a difference in electric potential. This difference in electric potential is transmitted to a high-impedance voltmeter via the electric leads of the electrodes.

In the case of measurements in liquid metals, the electric contact of the working electrode is easily accomplished by submerging the electrolyte in the liquid metal. The required separation from the reference electrode is achieved, e.g., by using an electrolyte tube that is closed at one end. An auxiliary electric conductor positioned in some distance from the liquid-metal/electrolyte interface bridges the gap between the liquid metal and the connection to the voltmeter. The reference electrode that resides inside the electrolyte tube is formed either by (i) a partially molten mixture of a pure metal (liquid at operation temperature) and a thermodynamically stable oxide of this metal—and a submerged wire as electric lead—, or (ii) a gas with constant oxygen partial pressure combined with a wire contacting the internal electrolyte surface. Today, such oxygen sensors are routinely used for characterizing the conditions in experimental facilities operated with liquid Pb or LBE.

As part of the development of heavy liquid-metal technologies within the framework of several European programs, oxygen sensors currently used in European laboratories were investigated with regard to the accuracy of the observed chemical potential of oxygen and long-term performance in experimental facilities. Additionally, the appropriateness of methods suggested for testing oxygen sensors before installation and during service in the plant was addressed. Recommendations on the use of oxygen sensors in industrial-scale reactors are given on the basis of the extended state of knowledge resulting from these investigations, and the need for further improvement is evaluated.

Oxygen sensors currently used (in European laboratories)

Sensor components

Solid electrolytes applied in commercially available electrochemical oxygen sensors, e.g., for measurements in gas, are based on zirconia (ZrO_2) that is partially stabilized in the face-centred cubic (high-temperature) crystal structure by addition of yttria (Y_2O_3). Although the fully stabilized materials with ≥ 8 mole% (~ 14 mass%) Y_2O_3 promise a more favourable electronic behaviour, the partially stabilized grades with lower dopant concentration are preferred because of superior thermo-mechanical performance. Chemical incompatibility of yttria-stabilized zirconia (YSZ) with liquid Pb and LBE is not expected (and was not reported from earlier studies on electrochemical sensors for use in these liquid metals), because the oxygen potentials to be measured are much higher than the threshold for decomposition of the oxidic electrolyte. The microstructure of the electrolyte and, therefore, the specific electronic properties generally depend on the particular material that may contain additions of further compounds for improved mechanical and sintering properties, varying for the products offered by different suppliers.

The YSZ product used in the case of oxygen sensors for application in liquid Pb alloys basically is a slim tube that is closed at one end or, alternatively, a kind of thimble with more favourable ratio of length to diameter (with regard to structural stability). The electrolyte is combined with a metallic housing that provides the fittings for installation at the site of operation. For sensors operated in experimental facilities, tubes have been preferred, which allow for shifting the gas-tight joint between electrolyte and housing into some distance from the electrolyte tip that is submerged in the liquid metal and experiences high temperature. In this case, gas-tightness of the joint can easily be accomplished by a pressed fluoro-polymer ring with sufficient thermal stability up to a maximum temperature of $\sim 250^\circ C$ (or another polymer-based seal if the requirements on thermal stability are lower). Cooling fins on the housing of respective sensors ensure that the applicable temperature threshold is not exceeded. A steel sheath surrounding the electrolyte tube protects the fragile ceramic component from shear forces in flowing liquid metal. Perforating the steel sheath in the vicinity of the closed end of the electrolyte tube allows for the mandatory intimate contact between electrolyte and liquid metal. Coarse debris resulting from accidental cracking of the electrolyte during operation is retained inside the sheath, if the

respective end of the sheath is closed with either a grid or impermeable plate. When using a short thimble made of YSZ, the joint between electrolyte and metallic housing is immersed in the liquid metal during operation of the sensor, requiring a both chemically and thermally compatible sealant, e.g., based on glass ceramics [13].

The reference electrodes of oxygen sensors currently developed for use in Pb alloys are generally based on a metal/metal-oxide couple, for which mostly bismuth (Bi) and the bismuth oxide Bi_2O_3 is used, but also indium (In) and india (In_2O_3). The respective solids (at room temperature) are introduced into the electrolyte tube or thimble under practically oxygen-free atmosphere, along with a wire as electric lead. At operating temperature, the metal part of these metal/metal-oxide mixtures is liquid, which improves the contact with the electrolyte. The material chosen for the electric lead is molybdenum (Mo), primarily because of the presumably low solubility of Mo in the partially molten reference mixture. Long-term stability of the metal/metal-oxide reference electrodes in the assembled sensor requires that ingress of oxygen via the sensor housing is prevented, e.g., by sealing the gap between the electric lead of the reference electrode and the walls of the electrolyte tube or thimble with ceramic cement. Otherwise, there will be consumption of the metal part of the reference system. As Mo is chemically less noble than Bi, the oxide component of the Bi/ Bi_2O_3 reference electrode is prone to more or less pronounced decomposition in favour of MoO_2 formation. Therefore, regeneration of this particular reference system may be required after a certain time of sensor operation. In general, an initially solid metal/metal-oxide reference system may promote cracking of the ceramic electrolyte, because of

- (i) different thermal expansion of the metal part of the reference system and the electrolyte, and
- (ii) melting of the metal part of the reference system, which temporarily maintains a steep temperature gradient across the electrolyte if the respective melting temperature (Bi: 271 °C; In: 157 °C) is rapidly exceeded at the outer electrolyte surface (Pb-alloy/electrolyte interface).

Alternatively to the metal/metal-oxide reference systems, a gas with known and constant oxygen partial pressure can be used, e.g., air, combined with an electric lead made of an inert material like platinum (Pt). This type of reference electrode

considerably eases the assembly of the sensor. The sensor housing must provide openings for ingress of gas, which requires an appropriate safety concept for application of such sensors in a (nuclear) plant, e.g., for preventing contamination of the environment after cracking of the electrolyte. In the case of most experimental facilities, the Pt/gas reference electrode does not pose an important safety risk.

Alternatively, another auxiliary electric conductor, e.g., a Mo wire, submerged in the liquid metal or the walls of a metallic container can be used for transferring electrons to the head of the sensor housing that provides the connector for a voltmeter. schematically illustrates integration of a short YSZ thimble at the end of a long steel tube with the YSZ/steel joint immersed in liquid metal during operation. This concept is currently applied to oxygen measurements in a depth of up to 5 m below the surface of a liquid-metal pool. The YSZ for the thimble of the sensor has been developed specifically for this product on the basis of ZrO₂ doped with 3 mol% (5.3 mass%) Y₂O₃ [13]. The other sensors are equipped with commercially available YSZ products (tubes) shown in cross-section in Fig. 1 (a) and (b). The first is ZrO₂ doped with 4.5 mol% (8 mass%) Y₂O₃ and has been employed for sensors corresponding to Fig. 2. The material from which the longer electrolyte tubes of the sensors were produced are based on ZrO₂ with 4.8 mol% (8.5 mass%) Y₂O₃, containing alumina (Al₂O₃) in amounts < 5 mass% (> 95% mass% of 4.8-YSZ) for improved thermo-mechanical and sintering properties.

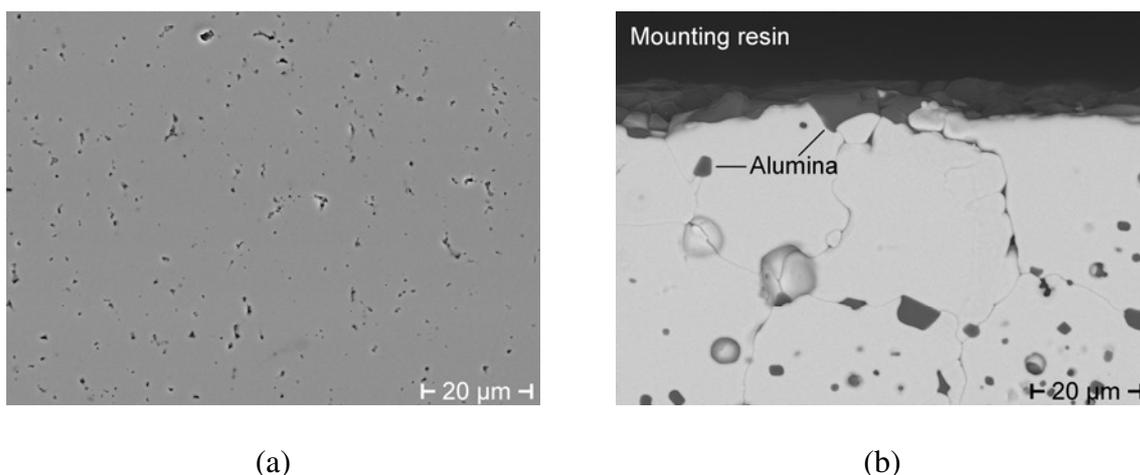


Fig. 1: micrographies of resins.

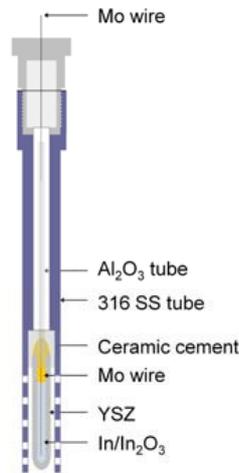


Fig. 2: wire connections.

Evaluation of the sensor output (voltmeter reading)

The starting point for the evaluation of the sensor output is the theoretical zero-current potential, E^* , of the oxygen-concentration cell formed by the sensor and the liquid metal. According to electrochemical principles, it follows that

$$E^* = \frac{(\mu_{O_2; Ref} - \mu_{O_2})}{4F}$$

with F denoting the Faraday constant ($F = 96485.31 \text{ C/mol}$).

$\mu_{O_2; Ref}$ is the known chemical potential of (gaseous) oxygen at the reference electrode that is, by convention, connected to the high-voltage input of the measuring instrument. μ_{O_2} is the chemical potential of oxygen that corresponds to the oxygen content of the liquid metal. The dependence of the oxygen concentration, c_{O_2} , in the liquid metal on E^* follows the general equation

$$\log(c_o / \text{mass}\%) = C_1 + \frac{C_2}{T/K} - 10,080 \frac{E^* / V}{T/K}$$

with E^* in Volts and T in degrees Kelvin. C_1 and C_2 are constants that result from substituting the oxygen chemical potentials in Eq. (1) by (i) the oxygen partial pressure that prevails at the reference electrode at given temperature, (ii) the Gibbs free energy of formation of the oxide that precipitates first from the liquid metal at oxygen saturation, and (iii) the oxygen solubility in the liquid metal.

The observed zero-current potential, E , indicated by a voltmeter connected to the specific sensor may differ from the theoretical expectation E^* , possibly resulting from (i) non-ideal performance of the electrolyte, (ii) the presence of different electric leads in the non-isothermal electric circuit formed by the sensor and voltmeter, and (iii) a small electric current occurring during the measurement, which cannot be prevented completely when using modern digital instruments. If the solid electrolyte is not a pure ionic (oxygen ions, O_2^-) conductor but additionally allows for transport of electrons, E^* is reduced by a factor $1-t_e$, where $t_e < 1$ denotes the transfer number of electrons in the electrolyte. The unavoidable temperature gradient along the electric leads of the reference and working electrode gives rise to a thermoelectric voltage, U_{th} , that adds to the reduced value of E^* when different materials are used for these electric leads. The electric current that flows through the circuit is, according to Ohm's law, inversely proportional to the internal resistance of the voltmeter, R_V , reducing the sensor output in proportion to the ratio of R_V to the total resistance of the electric circuit. The latter basically is the sum of R_V and the resistance of the electrolyte, R_E , because the resistance of the electric leads and connections between the different components (summarized in ΣR_j) is probably negligible. The overall effect of these to some degree

predictable influences on the voltmeter reading E thus is

$$E = (1 - t_e) E^* + U_{th} \frac{R_v}{R_v + R_E + \Sigma R_j}$$

The significance of U_{th} for the oxygen measurement with the currently used sensors was investigated for a thermocouple formed by Mo and an austenitic stainless steel with composition similar to 316Ti (DIN W.-Nr. 1.4571), for variable temperature at the joint between two wires of the respective materials (T_1) and constant temperature $T_2 = 305 \text{ K}$ (32°C) at the cold end of these wires. The results of the measurements that were performed at T_1 ranging from 573 K (300°C) to 973 K (700°C) follow the well-established relation

$$U_{th} = C_3(T_1^2 - T_2^2)$$

with $C_3 = 1.251 \times 10^{-5} \text{ mV/K}^2$ when the Mo wire is connected to the high-voltage input of the voltmeter. The chosen set-up approaches the situation for oxygen sensors using a Mo wire as electric lead of the reference electrode (metal/metal-oxide sensors) and a stainless-steel sheath as electric lead on the liquid-metal side. Thus, thermoelectric voltages ranging from 3 to 11 mV occur in oxygen measurements with this type of sensor when operated at $300^\circ\text{--}700^\circ\text{C}$. The corresponding relative error of the observed cO is independent from the specific reference system and amounts – 11% and –23% at 300° and 700°C , respectively (according to Eq. 2). For Pt/air sensors using a stainless-steel wire with platinised tip as electric lead, thermoelectric voltages do not occur, as long as the wire of the reference electrode and the auxiliary electric lead of the working electrode are made of the same steel. Data on t_e of the YSZ electrolytes used for the regarded oxygen sensors is not readily available, but may be estimated from ZrO₂ ceramics stabilized with 8 and 10 mol%, respectively. These materials show $t_e < 10^{-4}$ at $< 800^\circ\text{C}$ [15,16], so that electron conductivity of the electrolyte is probably negligible in comparison to other factors potentially influencing the sensor accuracy, even if t_e of the employed YSZ materials is one order of magnitude higher. For minimizing errors resulting from electric currents occurring during the measurements, a voltmeter with $R_V \gg R_E$ should be chosen. Estimating the electrolyte resistance is however difficult, because R_E does not only depend on the chemical composition and microstructure of the electrolyte, but also on the

configuration of the reference electrode. The experience shows that a voltmeter (digital multimeter) with impedance $>1G\Omega$ is, in general, sufficient for eliminating a significant influence of electric currents in the case of oxygen measurements in Pb alloys.

The HELENA Oxygen Control

The main goal of the HELENA OCS system is to reach extremely low Oxygen concentration. The LECOR loop, servicing in Brasimone since 1999, is designed to reach a concentration of $10^{-6}\text{wt}\%$, thus allowing in situ passivation of the tested materials. The new approach of HELENA is to go beyond this, reaching $10^{-8}\text{wt}\%$, allowing the exposure of newly developed materials and coating to a lower oxidizing environment.

The above depicted Oxygen sensors will be used to monitor the method, which is summarized in the following table.

| Step | Operation | Goal |
|--|---|-------------------------------|
| HLM purification in the storage tank | Ar/H ₂ bubbling, 3% | First O lowering |
| Mechanical filtering during loop filling | PORAL [®] 20 μm mechanical filter | Eventual slags filtration |
| HLM purification-maintenance | Ar/H ₂ bubbling, 3%, continuous, cold leg | Large pollution prevention |
| Oxygen gettering | Adsorption trapping in bypass line, continuous | $10^{-8}\text{wt}\%$ reaching |

Details

- HLM purification in the storage tank. Usually, the HLM are put inside storage tanks with a fusion procedure. The transfer from the fusion device to the tank itself could introduce casual pollution from flanges, operations etc. The need of a preventive purification has demonstrated to be a viable tool to clean up the HLM at a first step.
- Mechanical filtering: the possible presence of microscopic PbO slags is not avoidable by means of gas bubbling only. A mechanical filter with a thick mesh avoids the transfer of them into the actual loop.
- HLM maintenance. There are several possible pollution sources: O-rings, flanges, the pipes themselves by permeation phenomena. Keeping a continuous reducing mixture bubbling has demonstrated to be very effective in minimizing such kind of problems
- Oxygen getting. There are many possible candidate getters for Oxygen reduction: from alkaline metals to refractories. As an example, Mg has demonstrated to be a valuable Oxygen getter, given its extremely favourable free Gibbs oxidation Energy, but very tricky in its usage. The formed MgO (magnesia) is indeed very volatile and could represent a possible solid pollution itself. On the other hand, Ta could be even better, but much more expensive and consumable. Several experiments on the choice of the getter are on the run

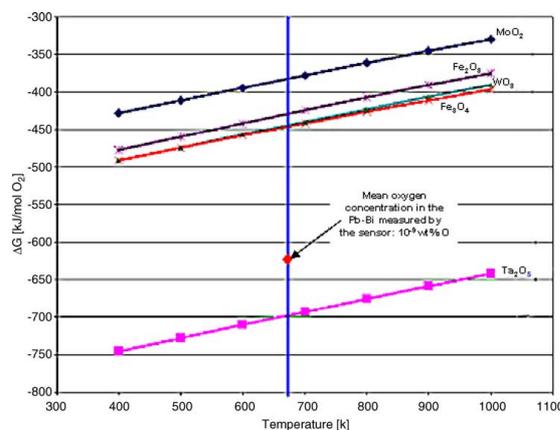


Fig. 3: Free Gibbs oxidation energy for selected materials

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Conclusion

Even though still not industrialized, Oxygen sensors have been thoroughly tested in the frame of several activities. They still are experimental, but results appear promising. A very small experience exists in the frame of Oxygen gettering. HELENA will be a very important facility to test different tools. The goal of achieving very low Oxygen concentration is connected with the choice of the right material for the LFR structures and components. Also, using 10^{-8} wt% means staying 4 orders of magnitude below the saturation of PbO. Enlarging the distance from cooling solidification is a good safety direction.

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