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Dissolved oxygen control and monitoring implementation in the liquid lead–bismuth eutectic loop: HELIOS

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Abstract

A 12 m tall LBE coolant loop, named as HELIOS, has been developed by thermal-hydraulic scaling of the PEACER-300MWe. Thermo-hydraulic experiment and materials test are the principal purposes of HELIOS operation. In this study, an yttria stabilized zirconia (YSZ) based oxygen sensor that was hermetically sealed for long-term applications using the electromagnetically swaged metal–ceramic joining method, have been developed for high temperature oxygen control application over a long period of time. The rugged electrode design has been calibrated to absolute metal–oxide equilibrium by using a first principle of detecting pure metal–oxide transition using electrochemical impedance spectroscopy (EIS). During the materials tests in HELIOS, dissolved oxygen concentration was administered at the intended condition of 10^{-6} wt% by direct gas bubbling with Ar + 4%H_2, Ar + 5%O_2 and/or pure Ar while corrosion tests were conducted for up to 1000 h with inspection after each 333 h. During the total 1000 h corrosion test, oxygen concentration was measured by oxygen sensor. The result confirmed that the direct gas bubbling method is a viable and practical option for controlling oxygen concentration in large loops including HELIOS.

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1. Introduction

The lead and lead–bismuth eutectic (LBE) alloy are receiving growing attention as heavy liquid metal coolants (HLMC) and/or target material for nuclear waste transmutation systems such as accelerator driven system (ADS) or fast burner reactor to deal with spent nuclear fuels from water reactors [1–3]. Those lead or LBE-cooled nuclear systems, however, can have insufficient system life due to significant solubility and hence enhanced corrosion of structural metal constituents in HLMC. Typical system lifetime goal for those advanced liquid metal cooled nuclear power systems exceeds 40 years. Therefore, long-term corrosion resistance has been extensively sought worldwide to meet all the materials performance requirements [2].

According to earlier studies [3–7], the key element among environmental variables affecting LBE corrosion is dissolved oxygen concentration in LBE. At appropriate concentrations, protective oxide film formation on the metal surface provides a very effective barrier against long-term corrosive attack in LBE. Inadequate oxygen concentration may lead to degradation of passive film and to enhanced corrosion. Thus corrosion rates of various materials have been studied as function of dissolved oxygen concentration, temperature and LBE flow speed.

In this study, materials corrosion tests were conducted in the tall loop named as HELIOS (heavy eutectic liquid metal loop for integral test of operability and safety of PEACER). For this test, the dissolved oxygen concentration in LBE was controlled by the direct gas bubbling method and the oxygen concentration was monitored by YSZ oxygen sensors. This process for oxygen control in regarded as an inexpensive but rapid method for the dissolved oxygen control, when compared with the water

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vapor/hydrogen gas flow technique [4] and PbO pellet dissolution process [8,9].

2. The HELIOS LBE loop

HELIOS [10–12] was designed by scaling down from its prototype PEACER-300MWe (proliferation-resistant, environment-friendly, accident-tolerant, continual and economical reactor) [1]. Thermo-hydraulic experiment and materials corrosion test are principal purposes of HELIOS operation. To test the natural circulation capability of PEACER, the elevation difference between the heat sink (a heat exchanger) and the heat source (a mockup core) is kept the same as that of PEACER, at about 8 m with the total height of 12 m.

Fig. 1 shows the entire loop configuration generated by CATIA (a 3D CAD tool developed by Dassault systems) without showing support structure. It has been possible to utilize the natural circulation capability for corrosion test in flowing LBE, while bypassing LBE pump circuit.

3. YSZ oxygen sensor

Generally, oxygen sensors for application in LBE systems are based on the well-known oxidation and reduction reactions on the surface of the oxygen ion conductor made of YSZ membrane. Thus it is a kind of galvanic cell consisted as (A/AO)|YSZ|(B/BO), with A and B as metals, AO and BO as their oxide, respectively [7,13–16]. YSZ membrane acts as an solid electrolyte. While various combination of A and B can be employed, the (Bi/Bi_2O_3) |YSZ|(LBE/LBE · O) was selected in order to measure the dissolved oxygen concentration in LBE.

Fig. 2 shows the electrode design used in this work. Bi/Bi_2O_3 reaction has been employed as the reference couple that is placed inside YSZ tube. Mo wire was inserted into metal/oxide reference to transmit the electromotive force (emf) signal corresponding to oxygen activity in LBE. Ta wire was first considered instead of Mo but Ta was rejected because it has poor stability at high temperature due to surface oxidation.

Yttria stabilized zirconia (YSZ) membrane that acts as an oxygen ion conductor has been widely used to measure the oxygen activity at very low partial pressure down to 10–30 atm [7,13–16]. However, current YSZ oxygen sensors

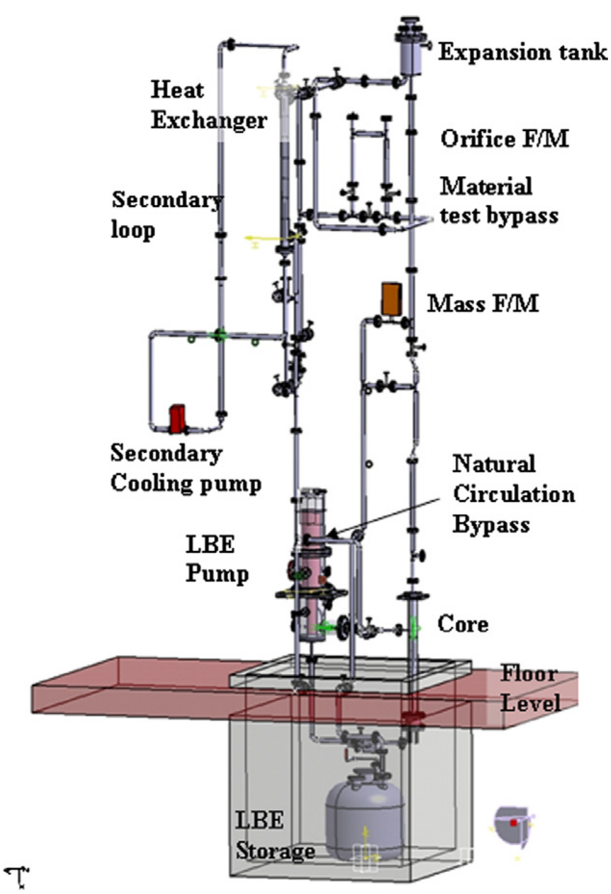

Fig. 1. 3D CAD drawing of HELIOS.

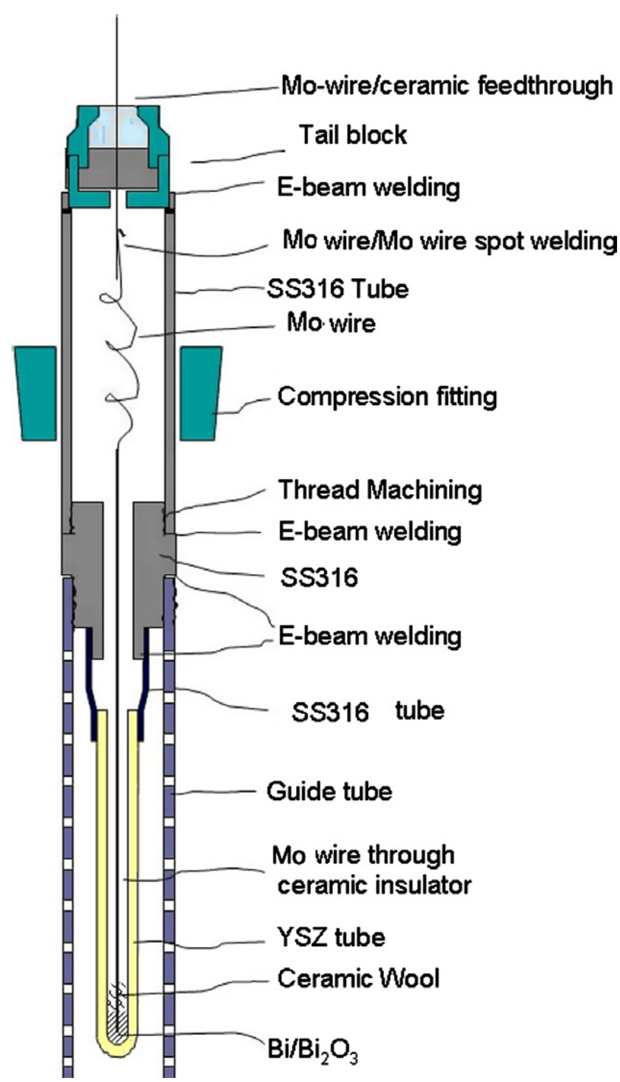

Fig. 2. Schematic of the YSZ oxygen sensor.

employed in LBE systems have several shortcomings, such as signal hysteresis during a heat-up and cool-down cycle, signal drift, external cooling requirements, etc., [6]. Signal instability may have been caused by leakage of the ambient air into the sensor reference junction through polymer or graphite seals that have limited tightness under thermal transients. The cooling requirement drives up the physical dimension of electrodes, making them unusable for many cases.

To overcome these shortcomings, we have developed an YSZ-based rugged oxygen sensor by applying a new technique to join the YSZ ceramic into SS316 body structure. Pulsed electromagnetic force was used to compress metal tube on YSZ tube in order to form long-life hermetic seals (see Fig. 3). This method is found to be an effective way to drastically enhance the leak-tightness of the sensor by high residual sealing force over fairly large contact area, compared with conventional seals. YSZ-based rugged oxygen sensor by applying electromagnetic joining technology shows a good performance over 1000 h during material test.

All the metal parts described in Fig. 2 have been assembled by electron beam welding so that the welding heat effect can be minimized. Before the seal assembling, typically 3 g of Bi metal powder and 3 g of ground Bi_2O_3 fragments are mixed homogeneously. Then about 2 g of the mixture is inserted into the YSZ tube. A piece of ceramic wool was inserted atop to prevent the powder from spilling out of the tube during handling. The YSZ/SS316 tube is then connected with a Type 316 stainless steel (SS) adapter that is joined with SS tubing. The final assembly is attached onto the vessel by a commercial compression fitting. The length of electrode is adjusted for an individual application. The tail block at the end of the stainless steel tube is designed so as to weld with the metal/ceramic feedthrough.

Using the equations available in [6] among others, the measured emf sensor signal is converted into oxygen activity or concentration by using Eqs. (1) and (2):

$$\log a_{\mathrm{PbO}} = -\frac{10079}{T}(E - 0.1381) - 0.7173, \tag{1}$$

$$\log a_{\mathrm{PbO}} = \log C_{\mathrm{O}} - \log C_{\mathrm{s,O}} = \log C_{\mathrm{O}} - 1.2 + \frac{3400}{T}, \tag{2}$$

where a_{PbO} is the oxygen activity in LBE before forming lead oxide, E is the measured potential of YSZ electrode in volts, C_{O} is the oxygen concentration in LBE, and $C_{\mathrm{s,O}}$ is the oxygen solubility limit and T is the temperature of system in K.

4. Calibration of the oxygen sensor using electrochemical impedance spectroscopy (EIS)

Considering reported difficulties in obtaining reproducible signals from the YSZ sensor in LBE, each oxygen sensor needs to be calibrated in a rigorous manner prior to practical application [17,18]. Electrochemical impedance spectroscopy (EIS) is applied to pure metal specimen throughout oxygen gas titration, as shown in Fig. 4.

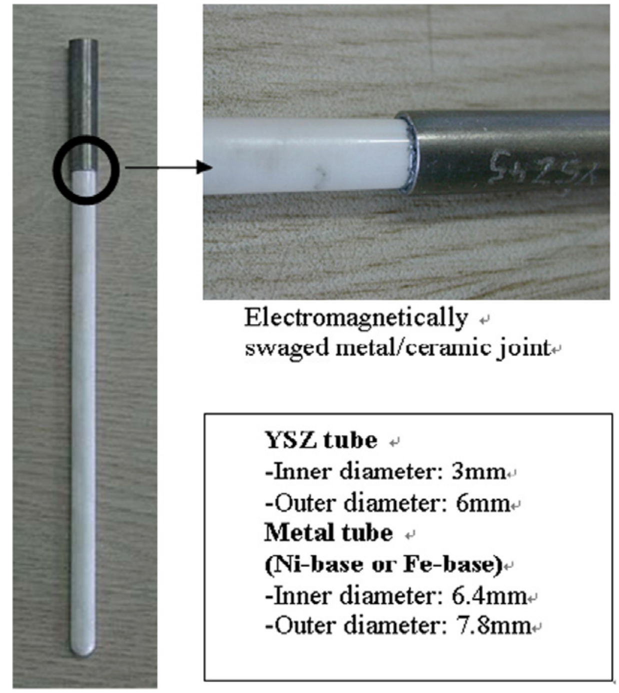

Fig. 3. Photographs showing metal to ceramic joint made by an electromagnetic swaging method (technical support by R.W. Bosch in SCK · CEN).

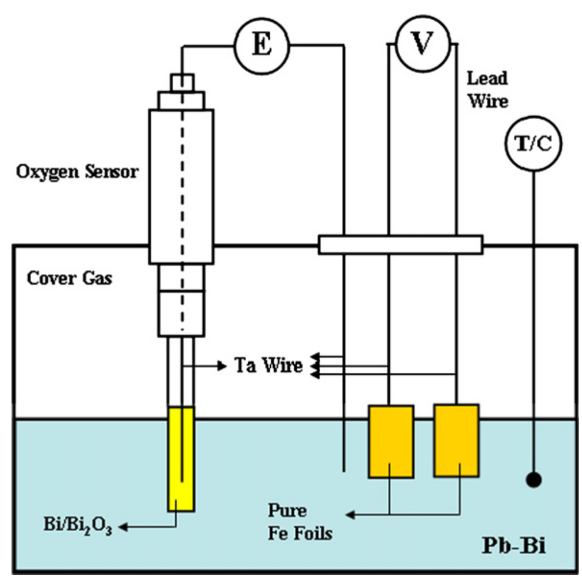

Fig. 4. Schematic of the YSZ sensor calibration in static LBE cell using EIS.

The calibration was conducted under static condition at the temperature of 350 °C. All the sensors and metal specimens were inserted into an alumina crucible within a vacuum furnace. A 99.9% purity tantalum wire having 0.5 mm diameter was used as an electrical lead wire for each of YSZ electrode, Fe foil specimen as well as LBE liquid electrode. A 99.999% purity iron foil of 0.25 mm thick was cut into one piece of 13.8 mm × 9.47 mm foil and another piece of 17.8 mm × 9.55 mm foil for use as Fe specimens. Total mass of LBE (99.99% purity) in the crucible was 1.4 kg. A gas injection tube was positioned just above the top of the crucible through which the carrier gas with hydrogen or oxygen was introduced and vented, to function as a rudimentary oxygen control system (OCS).

With the oxygen control system, it is possible to gradually increase the oxygen activity in LBE starting from a very low value below the metal/oxide equilibrium line of a reference metal. As the oxygen activity in the cover gas is increased, so does the oxygen activity in LBE.

When dissolved oxygen concentration is sufficient to oxidize the submerged metal wires or plates in LBE, the capacitance of the metal specimens will develop with the oxide film growth on the metal substrate. By measuring AC impedance and hence the electric capacitance of the oxide film, we can get the information of whether the oxide on the metal surface is formed or not.

The emf variations are also measured during the calibration test. Therefore, the exact emf value when metal/oxide transition occurs on the metal specimen can be determined. The oxygen sensor signal to this exact oxygen activity at this metal/oxide transition line can be compared with the thermodynamically calculated value.

If the oxide is formed on the metal specimen, electrochemical impedance spectroscopy (EIS) result shows a typical semi-circular capacitor signal in a complex impedance plane (Nyquist plot) as shown in Fig. 5.

Three EIS signal was measured around the Fe/Fe_3O_4 equilibrium potential. Rectangular mark was obtained at the value of 481 mV. After some time lapse, the impedance spectrum (circular mark) was measured again to confirm the reproducibility.

By purge the $5\%H_2 + Ar$ gas, the semi-circular impedance signal disappeared. In a clear contrast with semi-circular Nyquist spectra at emf value of 481 mV, the EIS

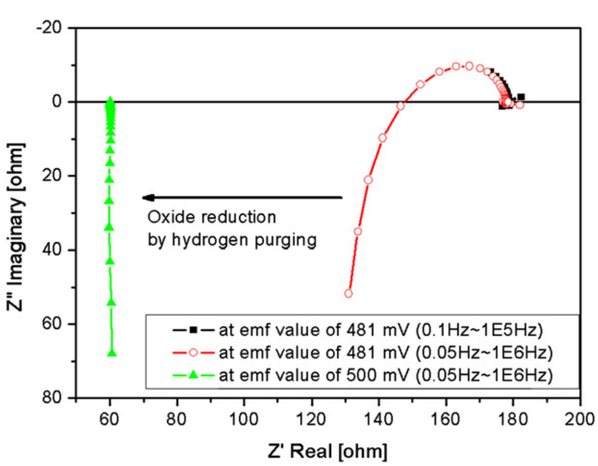

Fig. 5. Complex EIS plot for Fe specimens during the oxide reduction transient at 350 °C.

result at the value of 500 mV did not show any capacitive feature but revealed a fully resistance nature.

Because both emf potential of oxygen sensor and EIS signal were measured by using Solatron 1287 (a potentiostat) and Solatron 1260 (an impedance analyzer), emf potential and EIS signal cannot be measured at the same time. Triangular mark in Fig. 5 was measured after 2 min later at the potential value of 500 mV.

This is consistent with thermodynamic prediction [6] that the oxide formed on the specimen surface was reduced to metallic iron. From the experience, pre-oxidation of metal specimen for the measurement of impedance is recommended.

5. Oxygen concentration control and measurements in HELIOS

Materials corrosion tests of various metals (SS316, EP823, T91 and HT9) were conducted for up to 1000 h with inspection after each 333 h at 450 °C. The flow was controlled about 0.4 m/s only by the natural circulation. Oxygen concentration was controlled about 10^{-6} wt% by using the direct gas bubbling of $Ar + 4\%H_2$, $Ar + 5\%O_2$ and pure Ar. All the gas was injected at a constant flow rate of 40 cc/min.

Various methods for controlling oxygen concentration in LBE such as cover gas control method (using the OCS or switching-off the gas injection) and direct gas bubbling method were considered. However, in case of cover gas control method using gas/liquid equilibrium, quite slow process was expected because the quantity of LBE in HELIOS is substantial (~1800 kg) in comparison with the gas/liquid contact area (<1 m^2). Because of that, a direct bubbling method that greatly enhances the gas/liquid area was preferred.

By direct gas bubbling with $Ar + 4\%H_2$, $Ar + 5\%O_2$ and/or pure Ar, the oxygen concentration of the test section was controlled at about the intended condition of 10^{-6} wt%. During the corrosion tests, dissolved oxygen concentration was measured by two YSZ oxygen sensors as shown in Fig. 6. At about 100 h, hot leg sensor showed meaningless signal because destroyed sensor uses a Ta wire as a lead wire inside the YSZ tube. Oxidation of Ta wire in the hot furnace confirmed that Ta wire can be easily oxidized and powdered above 450 °C. During the first suspending time for the inspection at the time of 333 h, Hot-leg sensor was replaced to a new one which uses a Mo as a lead wire.

The hot leg sensor was located at the test section under 450 °C and the other cold leg sensor was located next to the heat exchanger under 320 °C. The measured emf signals show fluctuating features due to the change of temperature at the test section. In Fig. 6, ①, ② and ③ indicate $Ar + 5\%O_2$, pure Ar and $Ar + 4\%H_2$ gas injection respectively. During the injection of pure Ar, oxygen concentration was scarcely changed. Therefore, dissolved oxygen in the loop was maintained by direct gas bubbling of Ar.

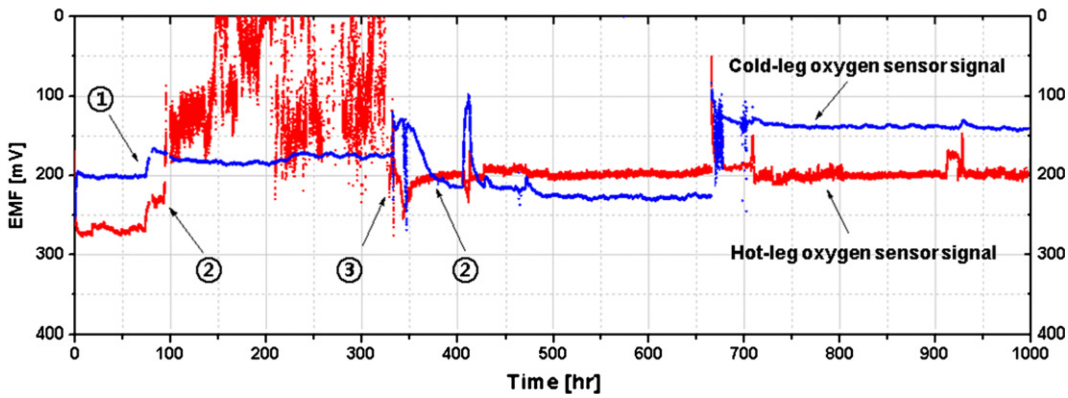

Fig. 6. Measured emf sensor signal [mV] during total 1000 h corrosion test.

6. Conclusion

Materials corrosion tests were conducted in the HELIOS controlling the oxygen concentration by direct gas bubbling method. The dissolved oxygen concentration in LBE was also monitored by two calibrated YSZ oxygen sensors located at different places and different temperatures.

To increase the oxygen concentration in LBE, Ar + 5%O_2 gas was injected as shown in Fig. 6 and Ar + 4%H_2 gas was injected to decrease the oxygen concentration. In case of pure Ar gas injection, oxygen concentration was maintained at a constant value.

Three oxygen concentration control experiences confirmed that the direct gas bubbling method is a viable and practical option for controlling oxygen concentration in large loops including HELIOS.

For the future work, more corrosion test will be conducted to test the characterization of sensor life time and effectiveness of the metal to ceramic seal.

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