Sensors to Control Dissolved Oxygen Concentration in Heavy Liquid Metal Coolants

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Oxygen impurities control is of a paramount importance for providing structural steel corrosion resistance; and the current lead-based heavy liquid metal coolant (HLMC) technology rests to a large extent on it.

In the early period of HLMC development, in particular, Pb-Bi, a method of coolant sampling was used with the aim to control oxygen impurities in it, with the follow-up remote analysis of these samples. Later on, more effective and prompt methods of control were developed and used; they were based on electro-chemical sensors with solid oxygen-conducting electrolyte.

Based on the vast JSC "SSC RF – IPPE" experience in developing various control devices for the nuclear power industry [1, 2], an active development is currently under way of solid electrolyte sensors to control oxygen in lead and lead-bismuth coolants.

One of the sensors developed was conventionally called a "capsule-type" sensor due to a typical shape of its ceramic sensitive element (CSE). The CSE is the main component of the sensors designed to control thermo-dynamic activity (TDA) or contents of oxygen and hydrogen in melts that are based on lead and cover (inert) gas. As a result of studies performed by the SSC RF – IPPE specialists, it was determined that CSEs based on solid electrolytes made of oxide ceramics were capable of being in operation for a long time under the conditions of high temperatures and thermal shock in metal melts (in gas), they demonstrate stability of their conducting and mechanical properties, high thermal resistance and low gas permeability (Fig.1).

Figure 1 – Ceramic capsule-type sensitive elements

The conducted R&D work resulted in development of the optimal chemical and phase composition to give the CSE the above-mentioned properties [3, 4]. Justifying calculations and experiments were performed to substantiate the geometrical shape of the sensor ceramic sensitive element in terms of its best strength, thermal resistance and hydrodynamics in the melt flow.

Based on the CSE data obtained, the sensors of oxygen thermodynamic activity (OTDA) in HLMC were developed and fabricated (Fig.2), the sensor type was approved as a measuring tool and it was put on the State Register of Measuring Equipment. The OTDA sensors were subject to metrological certification. Thus, the developed sensors were certified, registered in the State Register of Measuring Equipment (№63266-16) and admitted for use in the Russian Federation.

Figure 2 – Oxygen activity sensors.

The principle of operation of the oxygen solid electrolyte sensor consists in generation of electric potential in the galvanic cell that includes a reference electrode, a solid oxide electrolyte and the material under analysis, which is a working electrode. The process of oxygen ions transfer from the electrode where its chemical potential is higher to the electrode with a lower chemical potential is a total potential-generating process. The oxygen TDA in the electrode under study can be determined by measuring the sensitive element temperature and EMF at the known chemical potential of the reference electrode:

$$E = \frac{RT}{nF} \ln \frac{a_B}{a_A},$$

where n – is a number of electrons involved in the reaction;
F = 96485 C/mole – Faraday number;
R = 8.314, a universal gas constant, J K^{-1} mol^{-1};
T – temperature, K;
a_A - OTDA in the reference electrode;
a_B -OTDA in the electrode under analysis.

<u>Oxygen sensor technical characteristics</u>

Oxygen activity measurement range	from 10^{-6} to 1
Pressure of the medium under analysis, MPa, not higher	from 0 to 0.5 MPa
Upper limit of the temperature of the medium analyzed, °C	up to 700
Limits of allowable relative deviation from the nominal static characteristic (NSC), %	±10
Ramp-up time after initial sensor installation into the medium under analysis, h, not more	10
Temperature variation rate, °C/s	to 100
Working medium	Pb, Pb-Bi

In compliance with ISTC contract №3687$_{P}$, for the CIRCE test facility (a nuclear pool-type target facility, the ENEA Center, Brasimone, Italy) a pilot specimen of an oxygen activity sensor with a length of 8 m (Fig. 3) was developed, tested and supplied as part of the HLMC oxygen potential control system.

Figure 3 – Oxygen activity sensor with a length of 8 m

As of today, the developed capsule-type oxygen sensors are used in dozens of experiments both in the pool-type test facilities that partially or completely simulate the conditions of pool-type reactor operation, and in the loop-type circulation facilities [5] in various SSC –RF IPPE divisions (Fig. 4), and in other institutions: NIKIET (Moscow), Central Research Institute of Structural Materials CRISM "Prometey" (St.Petersburg), TSKBM (Central Design Bureau of Machine Building**,** Sosnovy Bor, Leningrad region.). The lifetime of the first sensors that were put in operation has already covered the period of ~ 70 thousand hours.

Figure 4 – Testing of a 6-meter-long sensor at the IPPE test facility

The aim to improve reliability and safety in the operation of pool-type reactors and facilities that use Pb-Bi and Pb as a coolant requires development and upgrading of the devices capable of diagnosing the state of the coolant and detecting the risk of emergency conditions at an early stage.

A significant scope of studies and developments was performed for this reactor design with the aim to improve solid-electrolyte sensors that control oxygen concentration in liquid metal coolant [5 - 7]. By now, the sensors for continuous and periodical monitoring of oxygen in the coolant have been developed and tested; they are designed for the use in advanced pool-type reactor units (Fig.5-6).

Figure 5 – The sensor with three sensitive elements for continuous oxygen monitoring, designed for advanced reactors.

The sensor designed for continuous monitoring of oxygen in HLMC may be 8 meters long and located in the area with the coolant temperature of 350 – 550 ^{0}C.

This sensor design employs three sensitive elements with different reference electrodes: ($Bi-Bi_2O_3$), ($Bi-Fe-Fe_3O_4$), ($Pb-Bi-Fe-Fe_3O_4$), which makes it possible to obtain different EMF conventionally within the same point of medium (Fig.6). The presence of $Fe-Fe_3O_4$ in the liquid metal electrode allows the OTDA level in the reference electrode to be maintained at the level of partial oxygen pressure in magnetite (Fe_3O_4). The use of Pb-Bi eutectics as the basis of one of the reference electrodes allows it to remain in the liquid state up to a temperature of ≈ 130 ^{0}C, which extends the temperature operation range toward low temperatures.

This design has the following advantages:

- Potentially improved reliability and durability of operation as compared to the currently used sensors with one sensitive element;
- Enhanced dependability of readings, i.e. all sensitive elements are located in one area, with the same TDA, the same HLMC temperature, i.e. the measurement is performed in one point;
- The sensor incorporating three sensitive elements that in terms of design are integrated into one housing, is more convenient in operation, because it needs only one seal assembly, which reduces the probability of loss-of-tightness and inleakage of air;
- Various reference electrodes make it possible to test the sensor by way of EMF measurement between potential pick-up terminals of different reference electrodes. In this case the EMF is independent of the thermodynamic activity level in the melt and is defined by the properties of the reference electrodes and temperature.

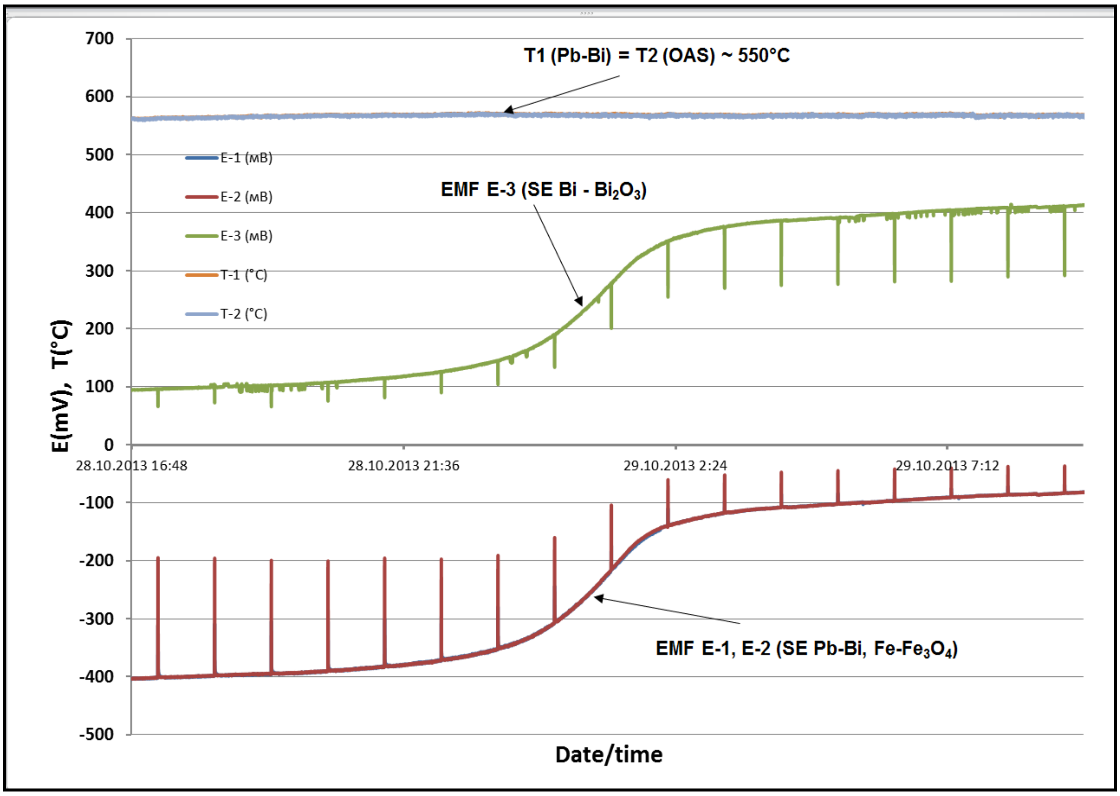

Figure 6 – Operation of a sensor with three sensitive elements within the oxygen TDA range from 10^{-6} to 1.

For the first time in the HLMC oxygen activity measurement practice a sensor with a drive for vertical movement and submersion into coolant was developed.

Such a sensor is designed for periodic control of thermodynamic oxygen activity with the aim of testing operation of fixed sensors, and also as a replacement (backup) measuring tool for thermodynamic oxygen activity control.

The periodic control sensor is equipped with an electric drive, providing for periodic submersion of its sensitive elements under the coolant level and keeping the gas system out of service in the "cold" area. It provides for the sensor movement to the required distance – 200 mm at a velocity of up to 0.2 m per minute. Leak-tightness of a mobile sensor (separation of the gas volume of the facility and the working room volume) is provided by the use of a stainless-steel bellow assembly, Fig. 7.

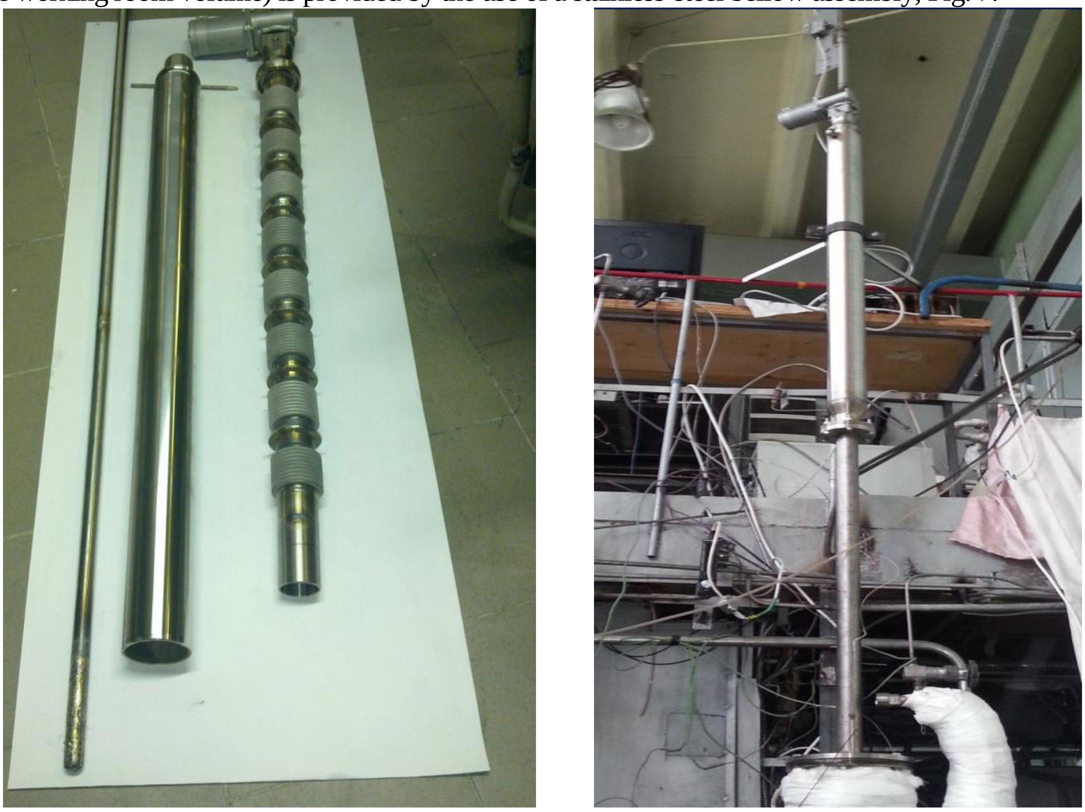

Figure 7. HLMC periodic oxygen control sensor

The need to apply the backup oxygen measuring tool is due to the importance and criticality of the oxygen control task in the NPP heavy liquid metal coolant. The backup sensor is needed for oxygen control system survivability; it eliminates the need of unscheduled change in the facility operating conditions (which even includes a reactor shut down) caused by replacement of fixed oxygen sensors.

Therefore, it can be stated that ceramic sensitive elements in the form of capsules for HLMC oxygen activity sensors have been currently developed at the SSC RF - IPPE. In addition, various sensors including those for pool-type reactors and facilities have been developed and fabricated in our organization with the use of the sensitive elements data. These sensors can be used both for continuous and periodic HLMC oxygen monitoring.

They represent one of the key elements (measuring element) of automated oxygen potential control systems for the NPP lead and lead-bismuth coolants and research facilities being developed in the IPPE, i.e. the systems implementing, on the one hand, corrosion prevention in HLMC structural steel, and on the other hand, preventing HLMC circulation loop slagging.

It is impossible to imagine the systems for HLMC preparation, preliminary cleaning and filling in the pool-type NPP primary circuits. Besides, these sensors are needed for non-nuclear lead (lead-bismuth) facilities designed for production of hydrogen, water steam, nanomaterials, etc.

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