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ADDRESSING SOME ISSUES ENCOUNTERED IN LIQUID LEAD CORROSION TESTS OF CANDIDATE MATERIALS FOR FUTURE NUCLEAR REACTORS

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Heavy liquid metals (HLM), such as lead, Pb, are considered among the possible coolants in the development of Generation IV Fast Reactors. One of the objectives of this report is to make an overview of the first results obtained by RATEN ICN regarding the work in the liquid lead environment. Specifically, the paper deals with three issues of great interest in this field: developing of a testing capability in liquid lead for corrosion tests, testing a potentiometric sensor for measuring the dissolved oxygen concentration in this environment and the best way to remove the residual lead from structural materials without damaging the steel, when the material is pulled out from the melt. The installation implemented at RATEN ICN for performing corrosion tests in liquid lead in static condition behaved very well at a continuous operation of 1000 hours and at temperature of 550^{0}C. The potentiometric oxygen sensors with Pt/air reference electrodes performed well in oxygen saturated lead, having a signal response close to the theoretical one. Regarding the chemical cleaning solutions tested for lead removal, some of them based on hydrogen peroxide, acetic acid and alcohol (ethanol/propanol) were able to remove completely or partially the residual lead from the specimens without affecting the oxide layer or the steel structure.

Key words: (Lead-cooled Fast Reactor, corrosion test, potentiometric oxygen sensor, lead removal)

1. Introduction

Radioactive waste management is a major challenge for the sustainable use of nuclear energy and one of the goals for Generation IV Nuclear Systems. For high level radioactive waste, a feasible and socially acceptable solution is necessary. Even though deep geological repositories might offer a viable solution, the time scale needed for the radiotoxicity to drop to the level of natural uranium is too long, which is not acceptable for the public [1,2].

The Generation IV Reactor Integrated Materials Technology Program [3] was a start for performant materials selection based on specific criteria depending on the reactor system such as the Very High Temperature Reactor System (VHTR), the Molten Salt Reactor (MSR), the Gas-Cooled Fast Reactor System (GFR), the Sodium-cooled Fast Reactor System (SFR), Lead-cooled Fast Reactor

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System (LFR) and the Supercritical Water-cooled Reactor (SCWR). Each system presents its particular challenges, but it is to mention several common needs [4,5] such as safety to work with them, resistance to irradiation and corrosion including localized form such as stress-corrosion cracking, high dimensional stability and high thermal stress capacity, good behaviour at higher temperatures, irradiation flux, and aggressive corrosive environments, beyond the conditions of the current nuclear power plants. Mechanical properties such as strength, ductility, creep rupture, fatigue, are required as well but for different systems are more important in operating conditions. At present, from the beginning of the program, materials like ferritic–martensitic steels, austenitic stainless steels, Ni-base alloys, ceramic, refractory metals are considered promising materials for future power plant and the number of the investigations on their performance is increasing [6-10].

Among different heavy liquid metals (HLM), lead (Pb) and lead-bismuth eutectic (LBE: 44.5 wt.% Pb + 55.5 wt.% Bi) are considered at present as potential candidates for the coolant of new generation fast spectrum nuclear reactors and accelerated-driven systems and for liquid spallation neutron sources. The main problem of these coolants is a rather high corrosion rate of steels at high temperatures [11]. The conceptual design of lead/lead–bismuth cooled fast reactors (Fig. 1) have been developed to meet enhanced safety and non-proliferation requirements, aiming at both energy production and transmutation of nuclear waste.

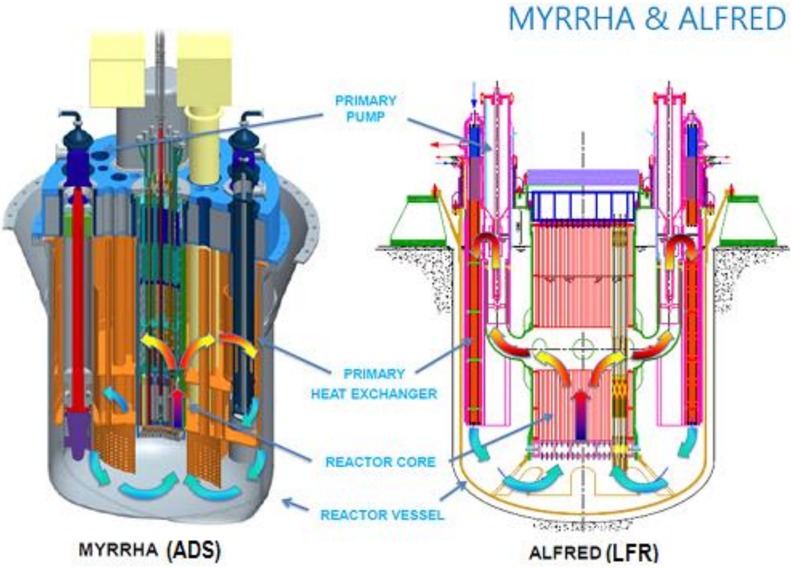


Fig. 1. Conceptual design of two nuclear systems cooled with heavy liquid metals [12]

Lead-cooled Fast Reactors (LFRs) and Accelerator Driven Systems (ADS) are studied in Member States to reduce the long-term hazard of spent fuel and radioactive waste, taking advantage of their incineration and transmutation capability.

The development of ALFRED Generation IV LFR requires a proper selection of the structural materials able to withstand the harsh environment of liquid lead. The compatibility of the structural materials with liquid lead is considered one of the critical issues in the development of LFRs. In a first stage, for the qualification of the materials it is necessary to perform specific tests regarding the corrosion resistance and mechanical properties in liquid lead environment. The Institute for Nuclear Research Pitesti (RATEN ICN) is involved in several European projects devoted to Generation IV research activities. For this reason, several small installations have been made for mechanical and corrosion tests in molten lead.

2. Experimental

The main issues that this paper addresses are the development of a testing capability in liquid lead, a potentiometric sensor for measuring at high temperature the dissolved oxygen concentration in this harsh environment and the best way to remove the solidified lead from structural materials without damaging the steel.

Installation for testing in liquid lead

One of the developing installations at RATEN ICN, aims to test the materials for corrosion in liquid lead at the operating temperatures of the LFR reactors. Fig. 2 shows the experimental installation which consists of a thermally insulated stainless steel furnace designed to expose different steels to stagnant liquid lead at temperatures up to 550^{0}C for long-term operation. The working crucible placed inside has a volume of approximately one litter and the lead used for the experiments weighs 10 kg which it is cut into small pieces from a 50 kg ingot. The lid of the furnace has inlets for the insertion of several components in the liquid metal bath (thermocouples, sensors, gases, etc.). Also, in order to prevent some gas leakage, it is used a seal and the lid is very well tightened by the furnace body with eight bolts and nuts. For data acquisition and recording of temperature and sensor output it is used a system from National Instruments and a LabVIEW 2016 software.

In the case of heavy liquid metals (HLM), Pb or LBE, materials corrosion undergo by the dissolution of the metal elements of the alloy: Fe, Cr, and mainly Ni. The solution rate and the solubility value of its elements are strongly dependent on the working temperature. Structural material oxidation can form protective oxide layers which prevent the corrosion and metallic diffusion processes. At temperatures up to ~480ºC, structural material protection is based on the in-situ formation of a thin and adherent oxide layer acting as a barrier [13].

Fig. 2. Installation for corrosion tests in liquid lead

Developing of an oxygen monitoring system in liquid lead

The mitigation for moderate operating temperatures (<450 – 480ºC) is based on active oxygen control where the precise amount of oxygen leads to the formation of protective layers of Fe-Cr and Fe_3O_4 oxides. The upper limit of oxygen concentration is limited by its solubility in the coolant and lower limit by thermodynamic stability of particular oxide [14].

In the case of ALFRED reactor, the working approach aims to work with a low and controlled oxygen concentration in the coolant. The range of oxygen concentration is reported to be between 10^{-6} and 10^{-8} % wt., which is much lower than the saturation limit at the minimum operating temperature of the reactor. Due to the importance of oxygen content, special sensors must be developed to determine the dissolved oxygen in the lead.

Sensors are based on the potential measurement method at null current for a galvanic cell built with a solid electrolyte: zirconia doped with either magnesia, calcia or yttria, as this doping element stabilises the ceramic into the tetragonal form that conducts oxygen ions under certain temperature and oxygen conditions. The choice of the reference system is critical. It greatly depends on various parameters, such as the oxygen partial pressure of the reference, which must be close to the partial pressure to be measured, the good knowledge of the equilibrium value of the reference system, a good buffering effect in case of slight disturbances to keep the partial pressure stable, and good compatibility between the lead wire and the reference systems [11].

Assuming pure ionic conduction in the solid electrolyte, and assuming that all transfers at the various interfaces developed in the electrochemical cell are reversible, the Nernst relation giving the theoretical electromotive force (EMF), noted E_{th}, can be written:

$$E_{th} = \frac{RT}{4F} \cdot ln \frac{p_{O_2(ref)}}{p_{O_2(Pb,LBE)}} \qquad (1)$$

well-known
(reference system)

to be evaluated
(working system)

with E_{th} in Volts, R the perfect gas constant (8.31441 J/mol/K), F the Faraday constant (96484.6 C/mol), T the temperature (Kelvin), and P_{O_2} the oxygen partial pressure in the lead alloy.

The potentiometric sensor used in the experimental installation at RATEN ICN, Fig. 3, monitors the oxygen content in the liquid metal. It is composed of an yttria partially stabilized zirconia (YPSZ) tube closed in one end (which works as the solid electrolyte), a Pt-air reference electrode inside the ceramic tube, and a 316 stainless steel clad that protects the YPSZ tube, which in addition is the working electrode.

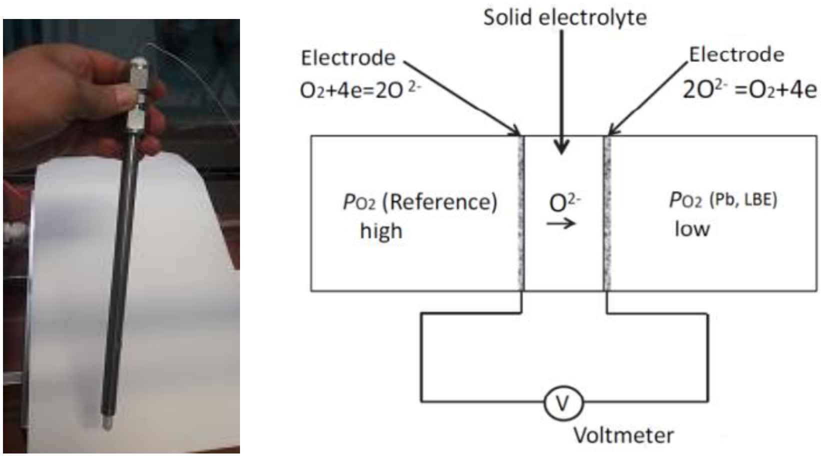


Fig. 3. Oxygen sensor and working principle

Residual lead removal

Another problem when testing the materials is the residual lead left on the specimens and on the sensor when removing them from the melt, because the lead solidifies very fast at temperatures below 321 ^{0}C. Furthermore, for the inspection of components removed from the reactor vessel it is very important to be able to clean the structural material from residual lead without damaging it.

Some methods which have been tested for the removal of residual lead from the austenitic steels are presented In Table 1.

Table 1

Solutions tested in different condition for lead removing

Specimen	Cleaning solution	Temperature (^{0}C)	Time (sec)
1	$HNO_3$20% (Sol.1)	75	900
2	4ml H_2O_2 30%+2ml CH_3COOH 96% (Sol.2)	75	180

3	2ml $H_2O_2$30% +2ml CH_3COOH 96%+ +2ml C_3H_7OH (Sol.3)	20	900
4	4ml H_2O_2 30%+2ml CH_3COOH 96% (Sol.4)	20	900
5	2ml H_2O_2 30%+2ml CH_3COOH 96%+ +2ml C_2H_5OH(Sol.5)	20	900
6	2ml H_2O_2 15%+2ml CH_3COOH 48%+ +1ml C_3H_7OH (Sol.6)	75	60
7	2ml $H_2O_2$30% +2ml CH_3COOH96%+ +2ml C_3H_7OH (Sol.7)	75	60
8	2ml $HNO_3$67%+6ml HCl37% (Sol.8)	75	300
9	2ml $H_2O_2$30% +2ml CH_3COOH96%+ +2ml C_2H_5OH (Sol.9)	75	90 180
10	2ml $HNO_3$67%+6ml HCl37% (Sol.10)	20	900
11	Electrolyte: 3,5g H_3BO_3 +3,8ml HF48%+ +45ml H_2O; 10V (Sol.11)	20	300
12	4ml $H_2O_2$30% +2ml CH_3COOH96% (Sol.2)	75	60
13	Electrolyte: 3,5g H_3BO_3 +3,8ml HF48%+ +45ml H_2O; 5V (Sol.11)	20	900
14	2ml $H_2O_2$30%+2ml CH_3COOH96%+ +2ml C_2H_5OH (Sol.9)	75	90 180
15	2ml H_2O_2 15%+2ml CH_3COOH 48%+1ml +C_3H_7OH(Sol.6)	75	90

3. Results and discussion

The installation implemented at RATEN ICN for performing corrosion tests in liquid lead in static condition behaved very well at a continuous operation of 1000 hours and at temperature of 550^{0}C. The thermal insulation must be very good as not to overload the heating resistance in order to ensure the working temperature inside. However, at first, a lot of heat was lost through the lid and the resistance was overloaded. After the thermal insulation was improved, the temperature on the heating element was not much higher than the one inside the working crucible.

The 316L austenitic steel after the preliminary tests performed in liquid lead at 550^{0}C for 1000 hours it is presented in Fig. 4A. Specimen presents a corrosion process in the matrix, as shown in cross-section in Fig. 4B. The corrosion penetration in the material was measured in several locations and was between 2.7 µm and 4 µm.

Regarding the oxygen monitoring system, the electromotive force of the oxygen sensor following temperature variation under the condition close to oxygen saturation in Pb was measured every second using an NI 9205 Voltage module on an CompactDAQ platform which has a 16 bits resolution and an absolute accuracy at full scale of 0.7 mV in the range ± 1V.

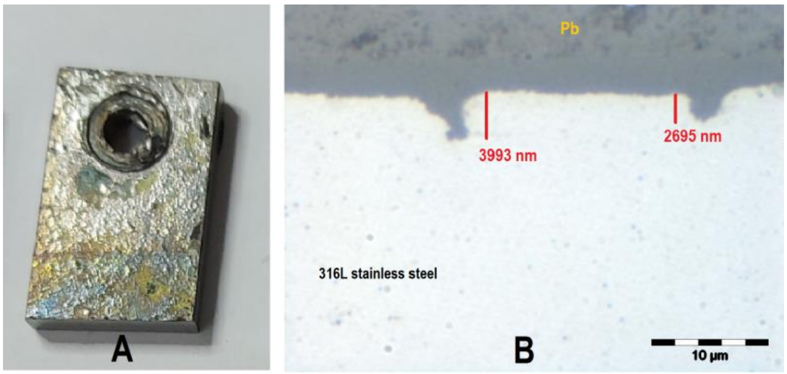
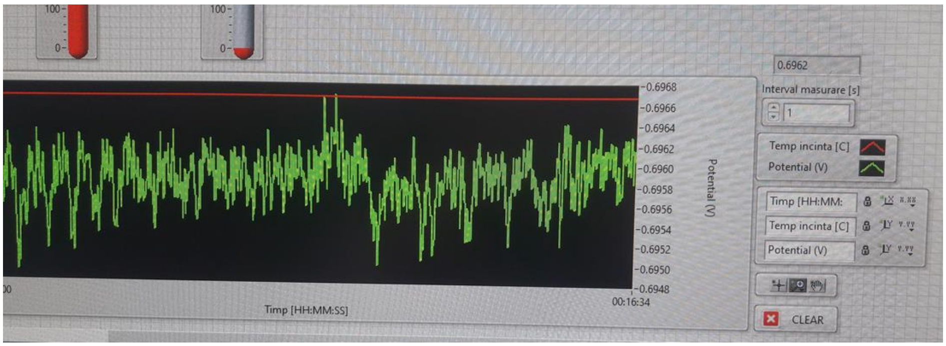


Fig. 4. AISI 316L specimen tested 1000 hours in liquid lead at 550ºC
A) top view B) cross-section

Because other study [15] have shown that the input resistance of the voltmeter is important for the performance of oxygen sensor with Pt/air reference electrode, the voltage module was carefully selected in order to have an input impedance > 10GΩ. In Fig. 5 we can see that the signals measured by the potentiometric sensor in liquid lead at oxygen saturation and 530 ^{0}C were between 0.695 V and 0.696V. These values are very close to the theoretical value E_{th}=0.693 V, determined with the relation E_{SAT}(mV) = 1133.9 – 0.550 $T_{(K)}$ [11]. For a temperature of 500^{0}C the signals measured with the sensor (Fig. 6) were between 0.709 V and 0.711 V, which are almost the same with the theoretical value E_{th}=0.709 V.



0.6962

Interval masurare [s]: 1

Fig. 5. Voltage measured by the oxygen sensor with Pt/air reference electrode at 530 ^{0}C

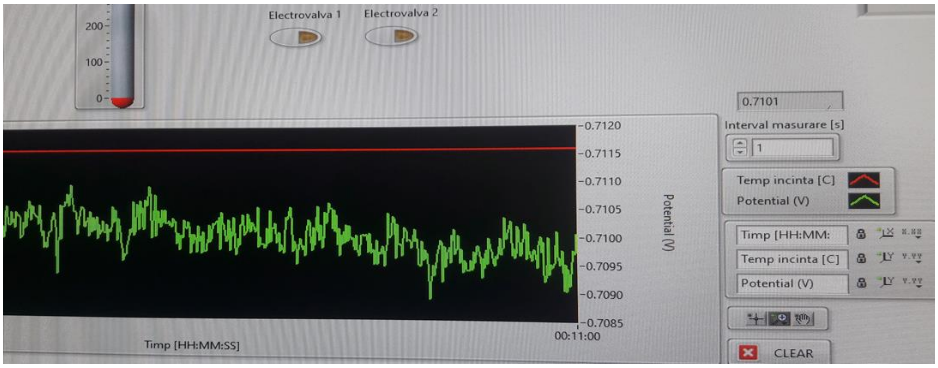


Fig. 6. Voltage measured by the oxygen sensor with Pt/air reference electrode at 500 ^{0}C

Lead removal from materials

Austenitic 316 stainless steel specimens tested 48 hours in liquid lead at 450 ^{0}C show on their surface a newly formed oxide layer. However, this layer is barely visible in certain areas, due to the lead that solidifies on the surface of the specimens when they are removed from the melt. Because of this, several methods for lead removal from the austenitic steels have been tested, and are presented in Table 1. In Fig. 7 we can see how the samples looked like covered with lead and then after testing them in different chemical cleaning solutions.

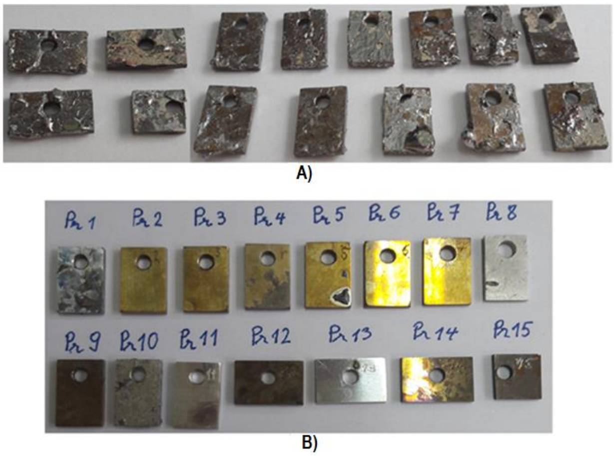


Fig. 7. Austenitic 316 stainless steels A) covered with lead B) after the chemical cleaning

Chemical solutions based on hydrogen peroxide, acetic acid and alcohol (ethanol/propanol) were able to remove completely or partially the lead from the specimens without affecting the oxide layer or the steel structure. The speed for lead removal from the samples was significantly influenced by the temperature. Thus, the same solutions that cleaned the lead from the samples within 15 minutes at 20 °C, were able to remove the lead in just 1-3 minutes at 75 °C. The volume of solidified lead droplets from the material surface significantly influences the speed at which a solution manages to remove them. The higher is the volume, the lower the contact surface of the lead with the cleaning solution is. When the droplets are very big, the contact surface of lead with the cleaning solution is small and the cleaning speed decrease. Chemical cleaning solutions that have proven to be ineffective or have attacked the oxide layer and the austenitic stainless steel are: aqua regia, and fluoroboric acid.

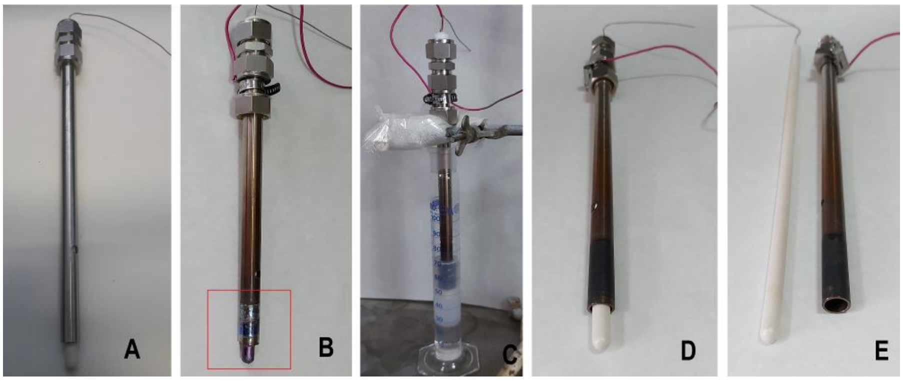


Fig. 8. Oxygen sensor A) initial B) covered with lead, C) tested in cleaning solution D) after cleaning E) cleaned and dismounted

Because the potentiometric sensor must also be cleaned for the residual lead, in Fig. 8 we can see how the sensor looked like before and after the cleaning procedure. To achieve this, a solution based on acetic acid, hydrogen peroxide and ethanol in a ratio of 1:1:1 was used for the first 60 minutes at room temperature. The biggest problem was the solidified lead between the ceramic body and the metal clad. In that area the contact with the cleaning solution is very small thus making it difficult to remove the lead. After this period of time, the sensor has not been completely cleaned, but the solid electrolyte could be removed from the clad. Next, the ceramic body was introduced into a 20 % nitric acid solution for 12 hours until no trace of lead was observed. Instead, the metal clad was kept in the same solution of hydrogen peroxide, oxalic acid and ethanol, until the solid lead was removed.

6. Conclusions

The installation implemented at RATEN ICN for performing corrosion tests in liquid lead in static condition behaved very well at a continuous operation of 1000 hours and at temperature of 550^0C. The corrosion penetration in the 316L steel matrix was measured in several locations and was between 2.7 µm and 4 µm after 1000 hours of exposure in liquid lead. Due to the importance of oxygen content, a special sensor was tested to determine the dissolved oxygen in the lead. The sensor response was very similar to that calculated under oxygen saturation (~10^{-3} % wt.) condition at several temperatures.

Because the ALFRED reactor is expected to operate at low oxygen concentration (10^{-6} – 10^{-8} % wt.), future works will be focused on this aspect and an oxygen control system will be implemented in the corrosion test facilities using a gas injection system with an argon and hydrogen mixture.

Chemical solutions based on hydrogen peroxide, acetic acid and alcohol (ethanol / propanol) were able to remove completely or partially the residual lead from the specimens without affecting the oxide layer or the steel structure. The same solutions that cleaned the lead from the samples within 15 minutes at 20 °C, were able to remove the lead in just 1-3 minutes at 75 °C. The volume of solidified lead droplets from the material surface influences significantly the speed at which a solution manages to remove them.

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