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Corrosion experiments of steels in flowing Pb at 500 °C and in flowing LBE at 450 °C

Alessandro Gessi *, Gianluca Benamati [1]

ENEA CR Brasimone, 40032 Camugnano (BO), Italy

ABSTRACT

In accelerator driven systems (ADS), as well as in the next Generation IV reactors, one of the concerned issues is the material compatibility and corrosion in liquid Pb, which is considered a candidate coolant. Liquid metal corrosion of the structural materials can proceed via different processes: species dissolution and penetration of liquid metal along grain boundaries and metal. The occurrence of these corrosion phenomenon depend on the experimental parameters, such as temperature, thermal gradients, solid and liquid metal compositions, velocity of the liquid metal and oxygen activity in Pb. One possible technique to prevent any corrosive attack by the liquid metals is the in situ passivation of the containment steels. This technique is achieved through an active control and monitoring of the dissolved oxygen concentration. This paper summarizes the data gathered from the CHEOPE III loop, where passivation of T91 and AISI 316L steels is tested in pure Pb at 500 °C were carried out, comparing them with preliminary corrosion data, in LBE, gathered from the LECOR loop.

1. Introduction

The activities with heavy liquid metals at ENEA CR Brasimone have been performed since the beginning of the Vth Framework programme of the EU and several Italian Research and Development programs. Several facilities have been devoted to such studies in the last few years. Two of them LECOR (*LEad CORrosion*) and CHEOPE III (*CHEmistry OPEration*) have been performing two parallel experimental campaigns, the first one for compatibility tests in flowing LBE, the latter for in situ passivation experiments in flowing Pb.

The reference steels chosen for these experiments are T91 and AISI 316L. These two steels are commercial nuclear grade steels, chose both for their properties and for their availability on the market. They are considered for many components and parts of HLM cooled reactors, and subject to many compatibility tests.

2. Experimental

The corrosion tests were performed in the LECOR loop, in flowing LBE. As shown in Fig. 1, the plant has a ‘figure-of-eight’ configuration, typical for a corrosion loop, with a high temperature branch running from the economiser to the test sections, set at 450 °C, and a low temperature branch (at 350 °C) including the delivery and return pipes between the tank and the economiser, including the by-pass line. The vessel contains a mechanical pump, with submerged impeller, sized to provide the loop with a maximum liquid metal flow-rate of 1 m/s [1].

The three test sections TS1/2/3, containing the specimens to be investigated are placed downstream of the electrical heater and can contain up to 12 specimens each. Test Sections 1 and 2 contain the corrosion specimens; test Section 3 contains the solid Mg getter. The use of Mg is described later in the paper. In the steady state, the thermal power provided by the heater is equal to the power extracted by the forced air heat exchanger. This configuration enables a continuous transport of corrosion products from the hot region, where the test sections are located, to the cold region where they are partially released, simulating the actual behaviour of coolant fluid in a thermal production plant. The structural materials of the loop are as follows: the cold part is fabricated in austenitic steel, while the hot region is in ferritic steel representing a good compromise between the requirements of acceptable ductility and corrosion resistance in a liquid lead alloys.

During normal plant operations the total liquid metal flow-rate available to the test sections is adjusted through the by-pass line, while the liquid metal flow-rate in each test section is automatically controlled by electro-pneumatic regulation valves using feedback signals from electromagnetic flow-meters.

The CHEOPE loop (CHEmistry and OPErations) is installed in the ENEA Brasimone Centre too, has been used for the in situ passivation experiments in flowing Pb. CHEOPE III, is a part of a multipurpose facility, which has been used to perform passivation tests in a controlled oxygen environment (with high oxygen activity when compared to the one in the LECOR loop). The structure of this loop

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* Corresponding author. Tel.: +39 0534801273; fax: +39 0534 801250.

E-mail addresses: alessandro.gessi@brasimone.enea.it (A. Gessi), gianluca.benamati@brasimone.enea.it (G. Benamati).

[1] Tel.: +39 0534801423; fax: +39 0534 801250.

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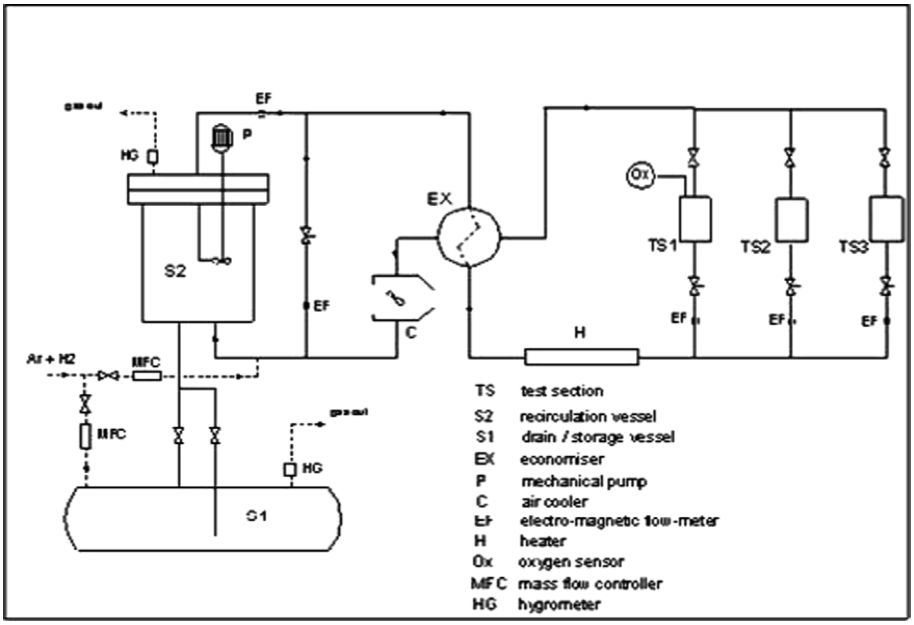

Fig. 1. The LECOR loop.

consists of a storage tank filled with 40 l of Pb, a test section, capable to host up to 18 specimens, and an oxygen sensor, directly put on the top of the test section. The flow chart scheme of this facility is shown in Fig. 2. The temperature of the test section was set at 500 °C and the flow-rate at 1 m/s, like the LECOR loop.

The use of Pb has been a great challenge for the operation of the facility. The monitoring of the temperature acquired a critical role, as well as the management of the temperatures in the gas phases. The pump vessel, which is the largest component of the cold leg, was kept at 420 °C, using a forced air flow cooler. The mechanical pump itself is inserted into a fully sealed chamber, without any rotating seal. The temperature of 420 °C is the maximum withstandable by the mechanical pump motor, placed inside the sealing chamber. During the first 2000 h, no mechanical problem was encountered.

The as-received materials were machined to cylindrical specimens with 10 mm diameter and 50 mm length. Before placing the specimens into the test sections of the loops, they were degreased and weighed. The dimensions of each specimen were measured. There was no additional heat treatment to them after machining. The specimens were fitted together in the test sections by fixing their ends with a double cone head.

The oxygen concentration in LBE were maintained in the range of 10^{-8}–10^{-10} wt.%., by means of solid stoichiometric Mg addiction

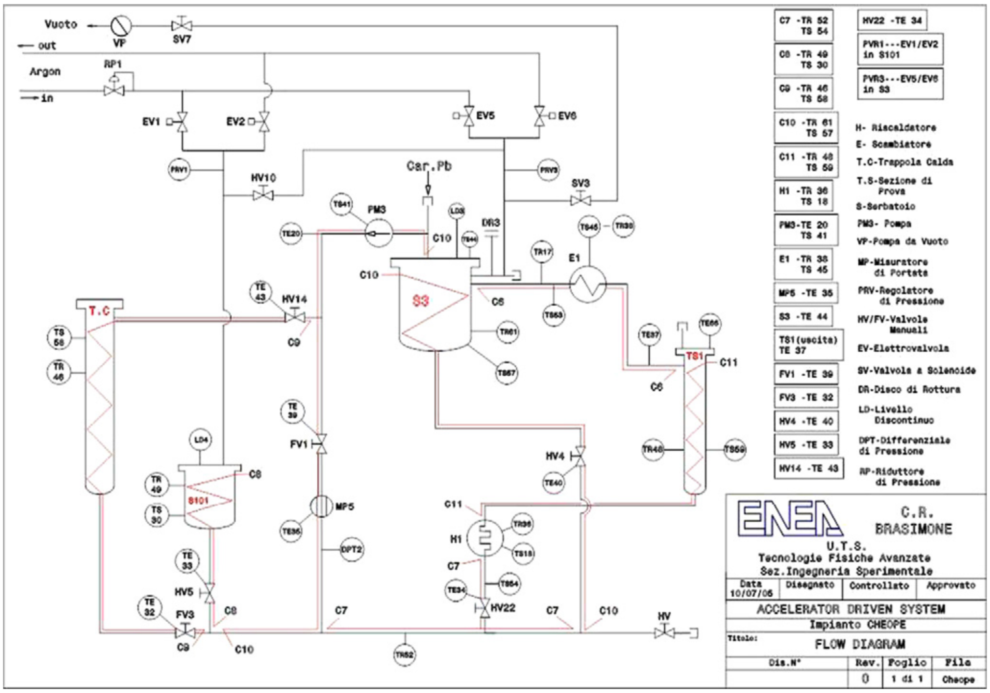

Fig. 2. The CHEOPE III loop.

(which acted as a oxygen getter) directly inside the test Section 2 and mixture of Ar/H_2 gas bubbling. The oxygen concentration was measured by an electrochemical sensor (Russian made at IPPE, Obnisk), placed in the TS1, winch gave a constant current output of 670–630 mV ca. corresponding to the above defined concentration range [2–4]. The correct amount of Mg was determined by checking the dissolved oxygen concentration using the electrochemical sensor. The total duration of the tests was planned for 4000 h. Three specimens were removed after the loop draining for analysis after 1000 h of exposure time form LECOR. The next time steps will be 2000, 5000 and 10000 h for both loops. The oxygen concentration in the CHEOPE III is being kept between 10^{-6} and 10^{-4} wt.% by means of gas bubbling. Again, the concentration is monitored by an electrochemical oxygen sensor, calibrated for Pb, which gave a constant output of 300–350 mV, corresponding to the required concentration.

After the LBE and Pb exposure tests, one specimens of each material has been immersed in a fresh solution ($CH_3COOH:H_2O_2:C_2H_5OH = 1:1:1$) at room temperature to remove the adherent LBE or Pb. Specimens were then cleaned and dried for visual examination and weight measurement. Specimens without cleaning were cut and polished for cross section examination by optical microscopy (OM) and scanning electron microscopy (SEM). Energy dispersion X-ray spectroscopy (EDS) was used to analyse the chemical composition of the adherent corrosion products and bulk materials.

3. Results

3.1. LECOR

The preliminary corrosion data shown in this paper are related to AISI 316L steel specimens. The EDS micrographs do not show deep LBE penetration into the steel matrix (Figs. 3 and 4). Only some areas seem affected by corrosion, with a maximum measured depth of 5 μm (Fig. 5). In none of the analyzed surfaces, LBE appears to stick to the steel surface (there are some detachments of thin steel layers, Fig. 5: AISI 316L specimen after 1000 h of exposure, LECOR. Slightly Cr enriched when compared with unexposed specimens due to elemental migration inside the matrix). It does not add any information The specimens are being weighted and weight variations will be parallely analyzed. In some areas, some residual, extremely thin, natural oxides can be observed.

3.1.1. CHEOPE III

The specimens extracted from the CHEOPE III loop after 2000 h of exposure in pure Pb in an oxidizing environment (analyzed trough the same analytical path), showed oxide scales formations over the steels' matrixes. On T91 specimens, three layered oxides scales (Figs. 6–8) were observed when cross sectioning the samples and analyzing them under SEM EDS microscopy. The average total thickness of the layers on T91 is 20 μm. The oxide scales appear detached from the steel surface and cracked along the interfaces. In several areas full detachments are clearly noticeable (Fig. 9). The composition of the different layers was defined by means of a Philips EDX spot probe, 2 μm diameter, and is depicted in Fig. 10. The three layers structure, with spinel/magnetite alternance, is expected from several past experiments [7].

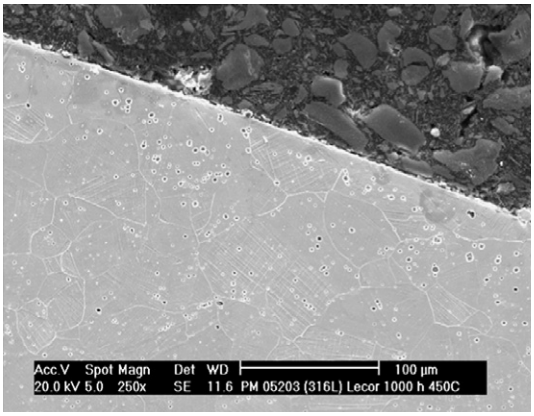

Fig. 3. AISI 316L specimens after 1000 h of exposure, LECOR.

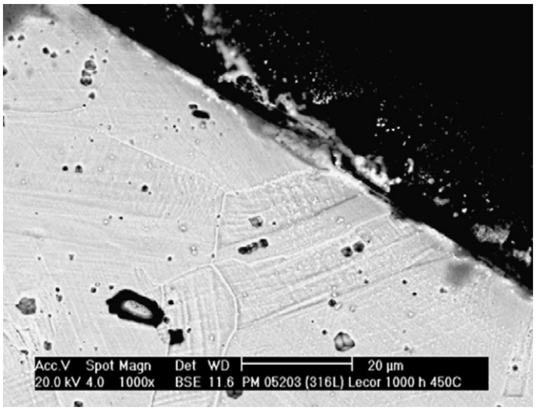

Fig. 4. AISI 316L specimens after 1000 h of exposure, LECOR.

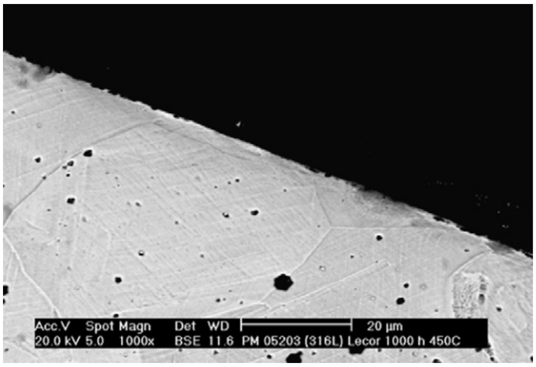

Fig. 5. AISI 316L specimens after 1000 h of exposure, LECOR.

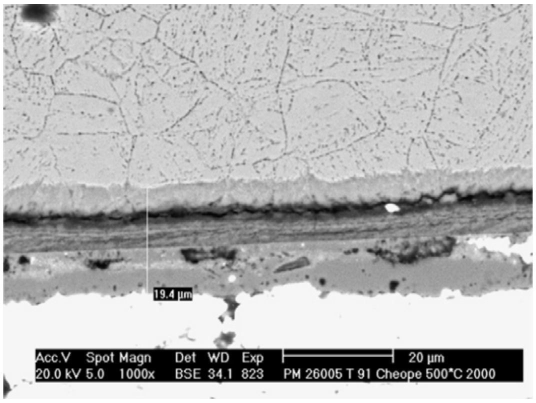

Fig. 6. T91 specimens exposed for 2000 h in pure Pb, CHEOPE III.

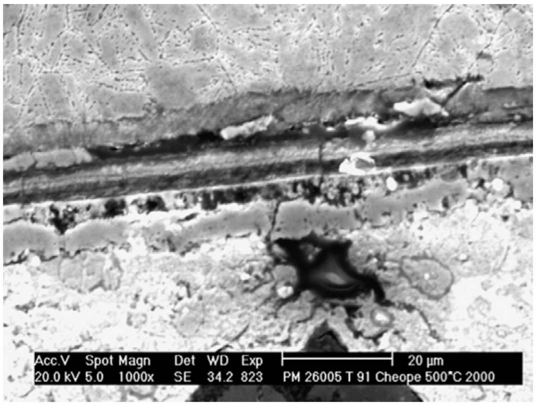

Fig. 7. T91 specimens exposed for 2000 h in pure Pb, CHEOPE III.

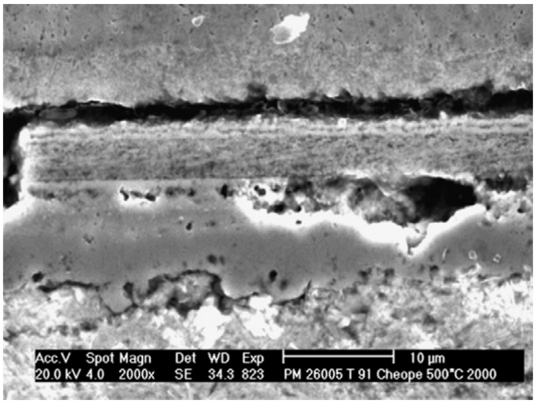

Fig. 8. T91 specimens exposed for 2000 h in pure Pb, CHEOPE III.

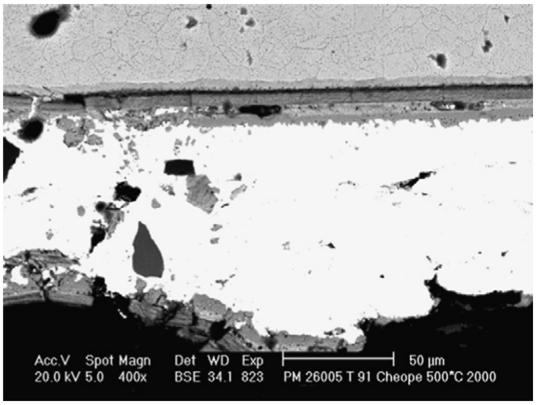

Fig. 9. Detachment of oxide scale from T91, 2000 h, CHEOPE III.

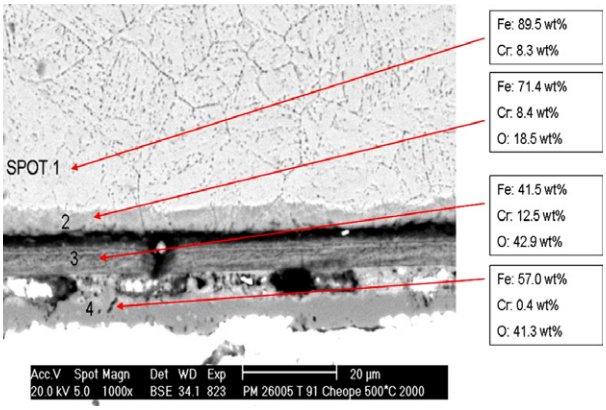

Fig. 10. EDS spots on T91 specimen, 2000 h, CHEOPE III.

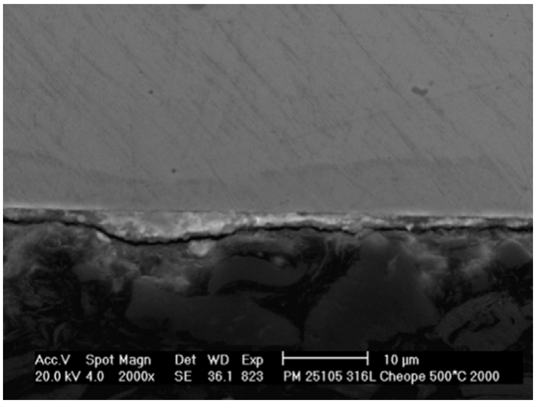

Fig. 11. AISI 316L specimens exposed for 2000 h in pure Pb, CHEOPE III.

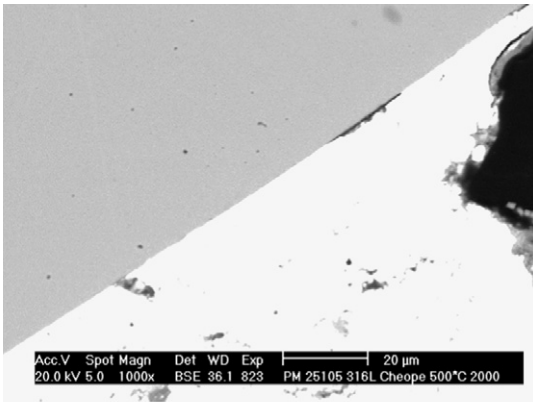

Fig. 12. AISI 316L specimens exposed for 2000 h in pure Pb, CHEOPE III.

On AISI 316L stainless steel, only the start of an oxidative phenomenon can be observed. Only in few areas of the specimens an extremely thin layer, below 1 μm appears to be forming. Due to its extremely small dimensions, it is, at the status, impossible to perform any analysis (Figs. 11 and 12).

In no steel, any elemental variation in the alloy is observed. There is no area where the liquid metal penetrated inside the matrix.

On the extracted specimens, weight variation has been measured, even though it is still not meaningful being only a first time step extraction. The weight gain (due to oxide scales) of the T91 specimens lays averagely at 0.020 g ± 0.0005, where for AISI 316L is 0.001 g ± 0.0005.

4. Discussion

4.1. LECOR

The behaviour shown by the AISI316L steel can be defined as expected. When comparing the EDS micrographs with the ones obtained after the 400 °C test, a similar corrosion effect is observed [5–7]. In both cases the reducing medium started a slow corrosion process, consisting in an elemental dissolution, function of the different steel elements solubility in LBE. Thus, in the 400 °C test a clearer ferritization was evidenced [6,7], while in this new experiment the process seems only about to start. This evidence can be related to the smaller time step, (1000 h instead of 1500) that was chosen, in order to acquire a better knowledge of the early phenomena. Small elemental concentration variations, for example, for Ni, Fe or Cr can be considered as the result of the different diffusivities and solubilities of the elements.

The LBE did penetrate inside the steel, but without any obviously noticeable preferred path. Again, this behaviour is found also in the former 400 °C experiment.

4.1.1. CHEOPE III

The in situ passivation in pure Pb of T91 and AISI 316L steels showed predictable results, on the basis of former experiments in LBE. No corrosion mechanisms were observed, but the formation of oxide scales on both materials. On T91, the oxide layers, clearly separated in Iron oxides and mixed Iron Chromium spinels, they appeared relatively thick, especially when considering the short exposure time (2000 h) but also fragile and detached from the steel surface . Moreover, inside the steel matrix, an inner precipitation process of mixed oxides can be observed (Fig. 8) with a different stoichiometry from the outer spinel layer. These experimental data suggest that the in situ oxidation of T91 steel is feasible and controllable in flowing Pb, leading to an effective protection from corrosion based on elemental dissolution. On the other hand, the steel matrix forms oxide scales that appear thick and fragile: longer exposures will provide more evidence for this phenomenon, thus indicating the possible need of future development of the steel itself.

On the other hand, on AISI 316L ss, the oxidation process proceeds slowly, forming thin and adherent oxide scales. The composition of the formed layers is not detectable after the firs exposure due to the extremely small dimensions. The slight weight gain, together with the absence of interface ferritization due to Cr and Ni dissolution, suggests the effectiveness of this protection from Pb corrosion.

5. Conclusion

The main conclusions are summarized as follows:

- After 1000 h of exposure in the LECOR loop, with low dissolved oxygen, a corrosion process based on elemental dissolution has started.
- In these samples, only very few areas the LBE penetrated into the steel matrix, down to a maximum of 5 μm, but without preferential paths.
- The comparison with previous experiments gave quite good consistency, even though a direct comparison will be more consistent with a bigger time scale.
- The active control/monitoring system for the loop gave again good results, confirmed also by the micro analyses.
- The in situ passivation of T91, in the CHEOPE III loop creates thick oxide layers, that appear fragile and easily removable by the LM.
- The in situ passivation of AISI 316L ss is a very slow mechanism, forming thinner layers over the steel surface.
- The active oxygen control and monitoring systems gave good results also when implemented in pure Pb.

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