

Oxide layer stability in lead–bismuth at high temperature

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Abstract

Materials protection by ‘in situ’ oxidation has been studied in stagnant lead–bismuth, with different oxygen levels (H_2/H_2O ratios of 0.3 and 0.03), at temperatures from 535 °C to 600 °C and times from 100 to 3000 h. The materials tested were the martensitic steels F82Hmod, EM10 and T91 and the austenitic stainless steels, AISI 316L and AISI 304L. The results obtained point to the existence of an apparent threshold temperature above which corrosion occurs and the formation of a protective and stable oxide layer is not possible. This threshold temperature depends on material composition, oxygen concentration in the liquid lead–bismuth and time. The threshold temperature is higher for the austenitic steels, especially for the AISI 304L, and it increases with the oxygen concentration in the lead–bismuth. The oxide layer formed disappear with time and, after 3000 h all the materials, except AISI 304L, suffer corrosion, more severe for the martensitic steels and at the highest temperature tested.

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1. Introduction

Lead bismuth eutectic has been proposed as coolant and as spallation target for Accelerator Driven Systems (ADS) due to its well suited nuclear and physico-chemical properties. However, lead–bismuth presents a high aggressiveness against stainless steels, which are considered to be structural materials for ADS. Nickel, chromium and iron, as constitutive elements of stainless steels show a high solubility in lead–bismuth that prevents their use as structural materials without any protection at temperatures higher than 400 °C for austenitic stainless steels and higher than 450 °C for martensitic steels. Steel corrosion in lead alloys depends on the concentration of oxygen dissolved in the liquid

metal. For oxygen concentrations in the liquid metal below the equilibrium concentration for the formation of protective layers, the structural steels will suffer dissolution attack. On the contrary, if the oxygen concentration is higher than necessary for the formation of oxide layers, the steel will experience an oxidation process [1]. Using the equilibrium $H_2 + 1/2O_2 \rightleftharpoons H_2O$ is possible to obtain the required oxygen potential at the temperature of interest for ADS systems [2].

An experimental work has been carried out to determine the influence of material composition, oxygen activity, temperature and time on the protection by ‘in situ’ oxide layer formation on structural materials in stagnant lead–bismuth.

2. Experimental development

The experimental device consists of a furnace with a quartz tube in which several alumina crucibles can be

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Table 1
Experimental matrix

Oxygen (wt%)	T (°C)	Time (h)			
		100	500	1000	3000
H₂/H₂O = 0.3					
3–4 × 10 ⁻⁷	535	–	F82H	F82H	All
3–4 × 10 ⁻⁷	550	All	F82H	F82H	All
8 × 10 ⁻⁷	600	F82H, T91	–	–	–
H₂/H₂O = 0.03					
3–4 × 10 ⁻⁶	535	–	All	–	All
3–4 × 10 ⁻⁶	550	–	All	–	All
8 × 10 ⁻⁶	600	–	All	–	–

All: F82Hmod, T91, EM10, AISI 316L and AISI 304L.

placed [3]. Several tests were carried out in this device in different conditions, according to Table 1.

Tests were carried out at 535, 550 and 600 °C for times from 100 to 3000 h. Five different materials were tested as-received: the martensitic steels F82Hmod, EM10 and T91, and the austenitic stainless steels AISI 316L and AISI 304L.

Tests were performed under flowing atmospheres with two different H₂/H₂O ratios: H₂/H₂O = 0.3, with a calculated oxygen concentrations in lead–bismuth of 3–8 × 10⁻⁷ wt% for the test temperatures, and H₂/H₂O = 0.03, with a calculated oxygen concentrations in lead–bismuth of 3–8 × 10⁻⁶ wt%. The oxygen content in both atmospheres is higher than the oxygen equilibrium pressure for the magnetite formation at all temperatures tested, according to the Ellingham diagram [4].

Longitudinal sections of the specimens were prepared without removing the adhered lead–bismuth for optical microscopy and scanning electron microscopy (SEM) examinations. Specimen analyses were performed by EDX (Energy Dispersive X-Ray Analysis). AUGER spectroscopy was used to analyse the composition of particular areas in some of the samples.

3. Results

Tests carried out on the martensitic steel F82Hmod at 535 and 550 °C, for 500 and 1000 h, in lead–bismuth eutectic under a gas atmosphere with a H₂/H₂O ratio of 0.3, were reported in [3]. After 1000 h testing, non-protective oxide layers were formed and material dissolution was observed at 550 °C, whereas at 535 °C an oxidation process took place. These results suggested the existence of a threshold temperature between 535 and 550 °C.

The influence of oxygen concentration in lead–bismuth and materials composition on this apparent threshold temperature was studied. Tests were carried

out with a higher oxygen concentration on F82Hmod and other steels.

Martensitic steels F82Hmod, EM10 and T91 were tested under an atmosphere with a ratio H₂/H₂O = 0.03, which corresponds to a calculated oxygen concentration of 3–8 × 10⁻⁶ wt%, for 500 h. These steels present an oxide layer with a thickness between 8 and 18 μm at 535 °C. This is a typical scale with an external oxide layer mainly formed by iron and internal one formed by a spinel with iron and chromium enrichment. At 550 °C, these steels also experiment an oxidation process, instead of the dissolution attack observed at the same temperature but under an atmosphere with a H₂/H₂O ratio of 0.3. At 600 °C, these steels suffer a severe dissolution, although some rests of oxide layers are detected on the martensitic steel surface. As an example, Fig. 1 shows the aspect of F82Hmod steel in these conditions.

The austenitic steels AISI 316L and AISI 304L were tested under the same conditions. On one hand, AISI 316L steel presents a similar behaviour than martensitic steels (Fig. 2). At 535 and 550 °C, a thin layer covers the entire surface, thinner for 550 °C. However, at 600 °C, no oxide layer was observed and a quite severe dissolution, up to 55 μm, was detected, mainly due to high solubility of nickel in lead–bismuth. On the other hand, AISI 304L present a different behaviour. At 535 °C, neither dissolution nor oxide layer is observed by SEM. At 550 °C, this material presents an almost intact surface with some isolated oxide nodules, with a thickness of 11 μm. At 600 °C, instead of the dissolution attack observed for the rest of the steels tested, AISI 304L steel presents the same behaviour than at 550 °C, an intact surface with isolated oxide nodules, but thicker and more numerous. Fig. 3 shows the general aspect of AISI 304L at 535 °C and the isolated oxide nodules observed in some areas at 550 and 600 °C.

In order to study the time evolution of oxidation/dissolution process, long time tests were carried out up to 3000 h under the two H₂/H₂O ratios, 0.3 and 0.03. For

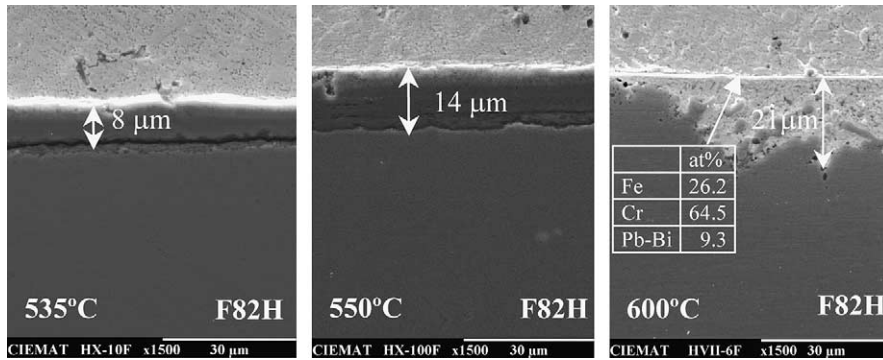


Fig. 1. Martensitic steel F82Hmod tested in lead–bismuth under an atmosphere with a H_2/H_2O ratio of 0.03 at 535, 550 and 600 °C for 500 h.

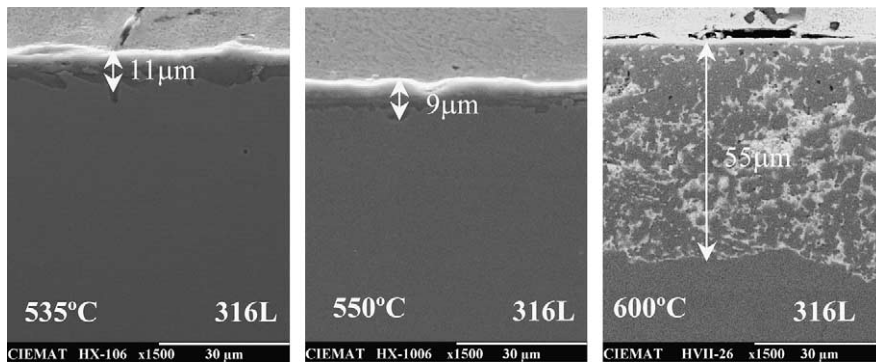


Fig. 2. Austenitic steel AISI 316L tested in lead–bismuth under an atmosphere with a H_2/H_2O ratio of 0.03 at 535, 550 and 600 °C for 500 h.

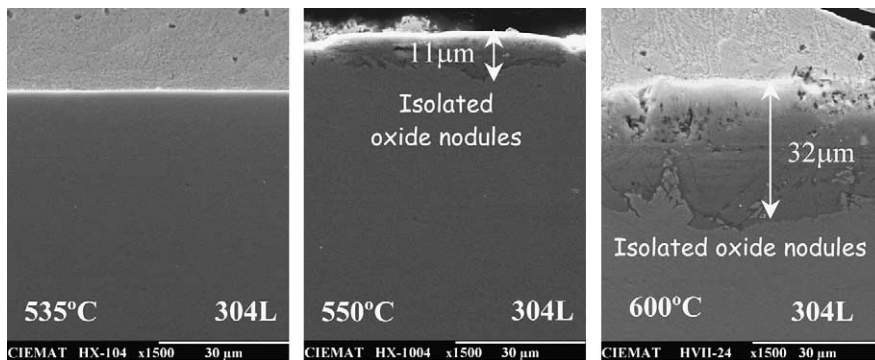


Fig. 3. Austenitic steel AISI 304L tested in lead–bismuth under an atmosphere with a H_2/H_2O ratio of 0.03 at 535, 550 and 600 °C for 500 h.

both oxygen concentrations, oxide layers formed on the F82Hmod steel surface after 500 and 1000 h are not stable with time, since they disappear after 3000 h testing, even at 535 °C. After this time, rests of oxide layer still exist, since chromium enrichment was detected at some surface zones (Fig. 4). Dissolution process becomes

more severe with temperature. Similar results have been found on the other two martensitic steels, EM10 and T91, tested under similar conditions.

AISI 316L tested at the same temperatures and H_2/H_2O ratios presents a similar behaviour than martensitic steels after 3000 h. However, AISI 304L presents an

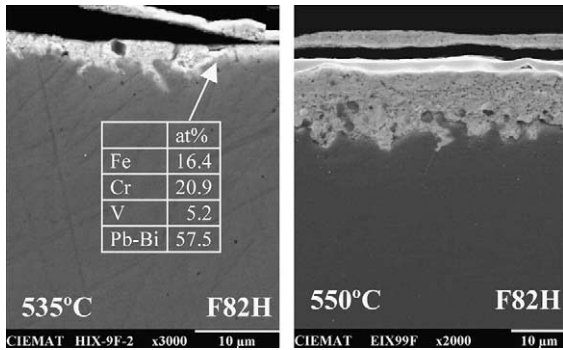


Fig. 4. Martensitic steel F82H tested in lead–bismuth under an atmosphere with a H_2/H_2O ratio of 0.3, at 535 and 550 °C for 3000 h.

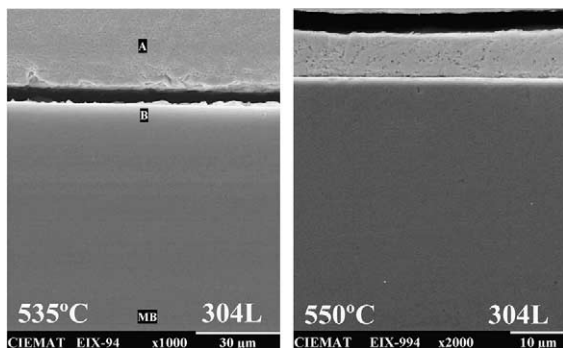


Fig. 5. Austenitic steel AISI 304L tested in lead–bismuth under an atmosphere with a H_2/H_2O ratio of 0.3, at 535 and 550 °C for 3000 h.

excellent behaviour even after 3000 h for both temperatures and oxygen concentrations (Fig. 5).

4. Discussion

In a previous paper [3], tests carried out on F82Hmod steel in lead–bismuth eutectic under gas atmosphere with H_2/H_2O ratio of 0.3 pointed to the existence of a threshold temperature between 535 and 550 °C. This result was unexpected since the difference in temperature, only 15 °C, was too small to justify

the difference in behaviour, oxidation at 535 °C and dissolution at 550 °C. As a possible explanation the transformation of magnetite into wustite, that takes place in this temperature range, was considered, although wustite was not identified with the techniques used. In this sense, Shumov et al. [5] indicate that a possible transformation of magnetite into wustite could contribute to make that the protective oxide layers formed at a certain temperature, becomes not protective at temperatures slightly higher.

This apparent threshold temperature depends on the oxygen concentration in lead–bismuth. For F82Hmod steel tested in similar conditions but in Pb–Bi with a higher oxygen concentration, a $H_2/H_2O = 0.03$ gas atmosphere, the apparent threshold temperature seems to shift to a higher range, between 550 and 600 °C. The same behaviour was observed for EM10 and T91 martensitic steels.

According to Yachmenyov et al. [6], an oxygen concentration in lead–bismuth higher than a critical value is necessary for the formation of protective oxide layers. If the oxygen concentration is higher than the equilibrium concentration for magnetite formation but lower than this critical value, material corrosion occurs. In this case, a kinetic mechanism more than thermodynamic conditions would be the driving force for the corrosion observed between 550 and 600 °C. The oxygen critical concentration depends on the temperature, the composition and surface state of steel, the tests duration and, in the case of loops, the temperature gradient.

The results obtained after 500 h show that at 550 °C, only at the higher oxygen concentration, $H_2/H_2O = 0.03$, this critical oxygen concentration seems to be reached, since oxide layers on the steel surface are observed. However, at 600 °C, all the martensitic steels show dissolution for all the times and oxygen concentrations tested, which seems to indicate that the critical oxygen concentration should be higher at this temperature. For longer times, 3000 h, all the martensitic steels tested suffer dissolution even at 535 °C and both oxygen atmospheres. Fig. 6 shows a possible explanation. At short times, oxide layers are formed, apparently adherent and stable, but the evolution with time seems to be dependent of oxygen. These oxide layers grow with time, taking place compressive stresses that provoke cracks, Pb–Bi penetration and, finally, the spalling of the oxide

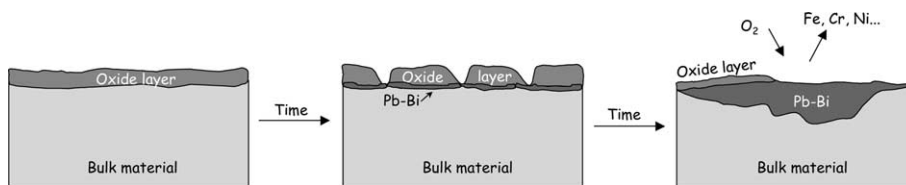


Fig. 6. Evolution with time of oxide layer formed on the steels surface. Competition between rehealing and dissolution.

layer in some areas. Therefore, at long times, there is a competition between the heterogeneous dissolution of metallic elements and the formation of a new oxide layers. However, the rehealing rate seems to be lower than the dissolution rate and, consequently, material dissolution occurs. Longer tests would be necessary to check if the rehealing of the steel surfaces is possible.

Fedirko et al. [7] studied the influence of oxygen containing (6×10^{-3} wt% O) lead on the corrosion of Armco iron, Fe–16Cr and Fe–16Cr–1Al alloys at 650 °C under static conditions. They propose a process of propagation of the corrosion similar to ours, but under their conditions, with very high oxygen content in lead, the rehealing process takes place.

Muller et al. [8] tested martensitic and austenitic stainless steels in flowing liquid lead–bismuth eutectic with an oxygen concentration of 10^{-6} wt% at 550 °C for 4000 and 7200 h. The steels suffer dissolution or oxide spall off with LBE infiltrated into the spinel zone after 4000 h. But, after 7200 h of exposure, a new oxide layer was formed, in some cases underneath the LBE infiltration zone.

AISI 316L austenitic steel presents a similar behaviour to martensitic steels, oxidation at 535 and 550 °C at short times under the $H_2/H_2O = 0.03$ but dissolution at 600 °C. At long times, dissolution is observed. However, AISI 304L austenitic steel present a completely different behaviour, since it presents an excellent behaviour for all the conditions tested. This difference between the two austenitic steels was unexpected, since the only significant difference in composition is the presence of Mo in AISI 316L. Soler et al. [9] found similar differences in the behaviour of the two austenitic steels, even with higher oxygen concentrations.

5. Conclusions

In stagnant conditions, there seems to exist a threshold temperature at short times of testing above which corrosion occurs and the formation of protective oxide layers is not possible. This threshold temperature depends on time, materials composition and, mainly, oxy-

gen content in lead–bismuth. According to the results obtained, it is between 535 and 550 °C for F82Hmod. steel tested for 1000 h under a gas atmosphere with a H_2/H_2O ratio of 0.3, which corresponds to a calculated oxygen content of 3×10^{-7} wt %. It shifts to the range 550–600 °C for F82Hmod, EM10, T91 and AISI 316L steels tested for 500 h under a gas atmosphere with a H_2/H_2O ratio of 0.03, which corresponds to a calculated oxygen content of $3\text{--}8 \times 10^{-6}$ wt %. For AISI 304L steel, it is above 600 °C, since no dissolution has been detected for this steel.

However, the oxide layer disappear with time and, after 3000 h all the materials, except AISI 304L, suffer dissolution, more severe for the martensitic steels and the highest temperatures tested. Longer tests would be necessary to check if the rehealing of the steel surfaces is possible.

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