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Corrosion of stainless steels in lead–bismuth eutectic up to 600 °C

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Abstract

An experimental program has been carried out to understand the differences in the corrosion behaviour between different stainless steels: the austenitic steels 304L and 316L, the martensitic steels F82Hmod, T91 and EM10, and the low alloy steel P22. The influence of oxygen level in Pb–Bi, temperature and exposure time is studied. At 600 °C, the martensitic steels and the P22 steel exhibit thick oxide scales that grow with time, following a linear law for the wet environment and a parabolic law for the dry one. The austenitic stainless steels show a better corrosion behaviour, especially AISI 304L. Under reducing conditions, the steels exhibit dissolution, more severe for the austenitic stainless steels. At 450 °C, all the materials show an acceptable behaviour provided a sufficient oxygen level in the Pb–Bi. At reducing conditions, the martensitic steels and the P22 steel have a good corrosion resistance, while the austenitic steels exhibit already dissolution at the longer exposures.

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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 nuclear and physical-chemical properties. Most of the work on heavy liquid metal coolants was performed in Russia over past four decades. It is accepted that austenitic steels may be used in contact with liquid lead–bismuth if the region of operating temperatures is not beyond 400 °C. For higher temperatures, martensitic steels are recommended [1]. However, long operation times leads to the dissolution of some elements of the steel (Ni, Cr and Fe, mainly) in the liquid metal and hence some method of protection is needed.

The control of oxygen activity in the liquid metals is a significant parameter for this protection. For oxygen concentrations 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 that necessary for the formation of oxide layers, the steels will experience an oxidation process.

An experimental work has been carried out to determine the influence of material composition, oxygen activity, temperature and time on the corrosion behaviour of structural materials in stagnant lead–bismuth in order to pre-select the most suitable steels and conditions to be used in ADS.

2. Experimental development

Static corrosion tests were performed on 25 × 12 × 4 mm samples of three martensitic steels (F82Hmod,

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Table 1
Experimental plan

	Oxidant atmospheres				Reductive atmospheres			
	Ar + 10% H_2 (wet)		Ar (saturation)		H_2/H_2O = 0.3		Ar + 10% H_2	
[O], wt%		4.7×10^{-4}	3.1×10^{-4}	2.0×10^{-3}	8.0×10^{-8} cal	1.1×10^{-8} mea 7.9×10^{-7} cal	1.3×10^{-10}	1.1×10^{-8}
T^e	450 °C	600 °C	450 °C	600 °C	450 °C	600 °C	450 °C	600 °C
Time (hours)								
100		X		X	X	X		
500		X	X	X			X	X
1500		X		X	X	X		X
2400							X	

EM10 and T91), a low alloy steel (P22) and two austenitic stainless steels (316L and 304L) in as-received state.

The experimental devices contain six crucibles of 40 mm diameter and 60 mm height. Each crucible contains one steel specimen and 350 g of lead–bismuth eutectic. The devices are equipped with thermocouples and with oxygen sensors developed by IQS to measure the content of oxygen introduced via the gas phase, in the molten lead–bismuth [2]. The gas flow rate is approximately 200 cm^3/min.

Table 1 shows the experimental conditions of the test performed. Every specimen is tested independently and they are threaded to a steel rod to be fixed in the crucibles. It is not necessary to interrupt long test for the withdrawal of the specimens exposed for the shorter periods, since they are independent experiments. In the cases in which the experimental value of oxygen concentrations is different from the calculated one, both values are indicated. In the experiments using the ratio $H_2/H_2O = 0.3$, the theoretical value is 8×10^{-7} wt% whereas the oxygen measurement is 1.1×10^{-8} wt%, similar to that obtained for Ar + 10% H_2. Therefore, in practice, these two atmospheres have the same oxygen content and they will be considered as one.

The behaviour of the different materials has been evaluated by optical and SEM/EDX microscopy and Auger spectroscopy in some specific cases.

3. Results

3.1. Oxidant atmospheres

The influence of Cr content on the thickness of the oxide layers formed on the steels tested under the two oxidising lead–bismuth environments at 600 °C for 100 and 1500 h is shown in Fig. 1. In both environments, oxide layers thickness decreases when the chromium concentration increases.

Martensitic and P22 steels tested at 600 °C in lead–bismuth with an oxygen concentration of 4.7×10^{-4} wt%, wet atmosphere, present quite homogeneous and thick oxide layers, which grow with time following a linear law after an incubation period (Fig. 2). A double oxide layer was observed, the external layer formed by iron oxide and the inner layer by a spinel composed mainly of iron, chromium and oxygen. EM10 and T91 spinels show enrichment in chromium (20–30%) and molybdenum (6%). F82Hmod also shows chromium enrichment (25%) in the spinel oxide structure and the presence of tungsten. Low alloy steel P22 presents the thickest oxide layer, with high porosity that allows the penetration of lead–bismuth in the external iron oxide layer. It also shows a slight chromium and molybdenum enrichment in the spinel.

The evolution of the oxide scale on these materials tested at 600 °C in lead–bismuth with an oxygen concentration of 2.0×10^{-3} wt%, dry atmosphere, is presented in Fig. 3. The oxide layers formed on the steels also grow with time, following a parabolic law. The structure of the oxide layers presents no remarkable differences with those formed under the wet atmosphere. However, under the dry oxidant atmosphere, the oxide layers are

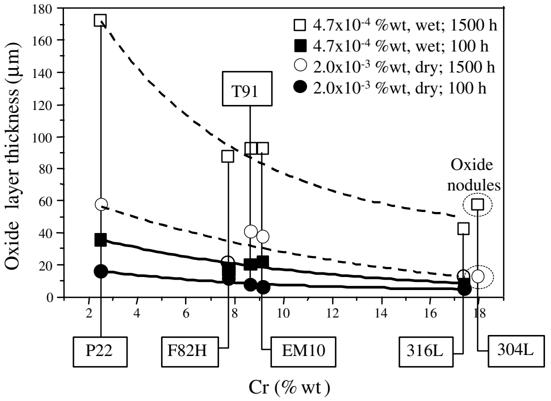

Fig. 1. Influence of the chromium content on the oxide layer thicknesses formed on stainless steels tested in the oxidising lead–bismuth at 600 °C for 100 and 1500 h.

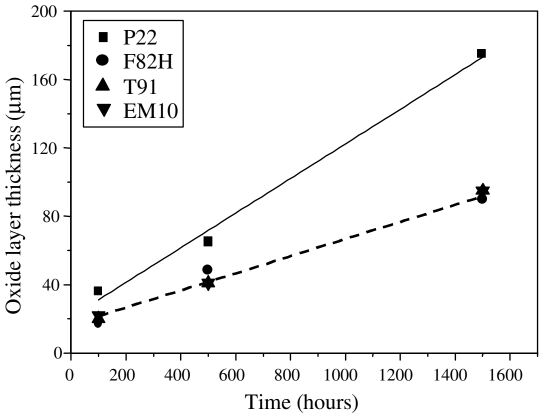

Fig. 2. Measurement of the oxide layer thickness on the martensitic steels T91, EM10 and F82Hmod, and the low alloy steel P22 tested at 600 °C in lead–bismuth with an oxygen concentration of 4.7×10^{-4} wt% (wet environment) in dependence of the exposure time.

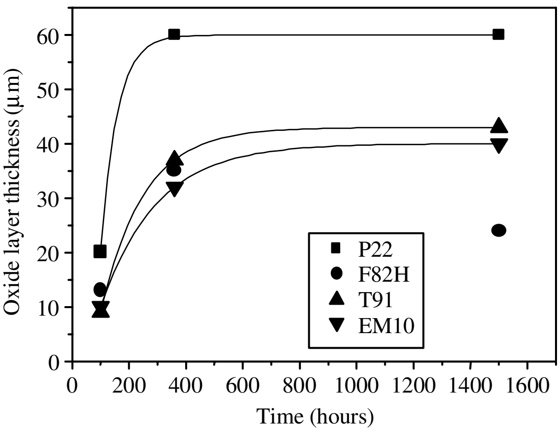

Fig. 3. Measurement of the oxide layer thickness on the martensitic steels T91, EM10 and F82Hmod, and the low alloy steel P22 tested at 600 °C in lead–bismuth with an oxygen concentration of 2.0×10^{-3} wt% (dry environment) in dependence of the exposure time.

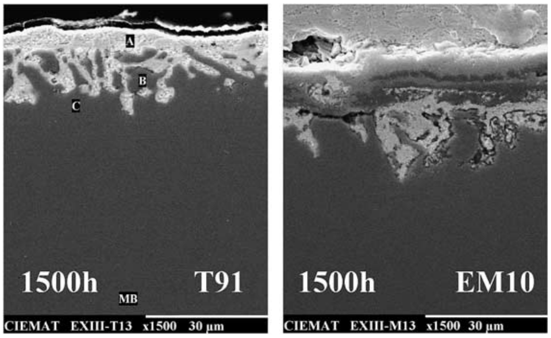

Fig. 4. SEM photos of the cross-sections of the martensitic steels T91 (left) and EM10 (right) tested in lead–bismuth with an oxygen concentration of 2×10^{-3} wt% (dry environment), at 600 °C for 1500 h. Deterioration of the oxide layers and initiation of dissolution.

thinner, less stable and suffer deterioration with time. Fig. 4 shows the general aspect of T91 and EM10 steels after 1500 h. After this time, the oxide layers are very thick and there are probably compressive stresses that provoke cracks, Pb–Bi penetration and, finally, the spalling of the oxide layer in some areas.

For austenitic steels, longer tests would be necessary to determine if the oxide layers growth follows a linear or parabolic law. On one hand, AISI 316L austenitic steel presents, in general, homogeneous and compact oxide layers, thinner than the one observed on the martensitic steels, with a very high chromium content (≅40%) and molybdenum enrichment (6–11%) in the spinel. Nickel does not participate in the oxide structure, but a high enrichment (24%) of this element is present just below the oxide layer. On the other hand, AISI 304L austenitic steel samples tested for 100 h did not show oxide layers visible by SEM, but a very thin chromium oxide layer, approximately 0.5 µm thickness, was detected by Auger analysis. After 500 and 1500 h, a similar oxide layer was detected by SEM and Auger (Fig. 5), except for some isolated oxide nodules. After testing at 600 °C for 1500 h, AISI 304L steel presents carbide precipitation at grain boundaries, numerous at the sample edges, whereas 316L does not present these changes in the microstructure.

At 450 °C, martensitic steels and the low alloy steel P22 tested for 500 h under argon atmosphere present an oxide layer covering the entire surface, but it is much thinner than that formed at 600 °C. There is chromium enrichment in the spinel, specially for T91 steel. However, neither oxide layer nor dissolution has been detected by SEM for both the austenitic stainless steels, AISI 316L and AISI 304L.

3.2. Reducing atmospheres

After 500 h at 600 °C, martensitic steels present a thin oxide layer, whereas austenitic steels suffer slight dissolution, greater for AISI 316L steel. After 1500 h, no oxide layer is observed and dissolution occurs. The dissolution is slight for EM10, F82Hmod and P22 steels, but becomes important for T91 steel, with an attack of 13 µm depth. Chromium depletion is observed below the dissolution zones. Austenitic steels present a quite severe dissolution after 1500 h, with an attack of 63 µm depth for AISI 316L and of 83 µm for AISI 304L. A very important nickel depletion is observed in the dissolution zone. The dissolution depth of the different materials

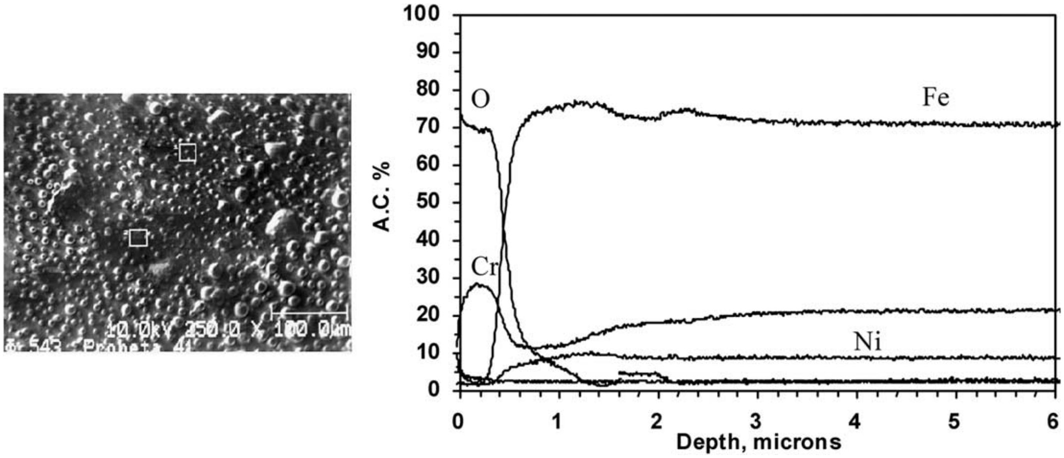

Fig. 5. SEM image (left) and Auger depth composition profile of the oxide layer formed on the AISI 304L steel after 500 h of exposure at 600 °C in Pb–Bi with an oxygen concentration of 4.7×10^{-4} wt% (wet environment).

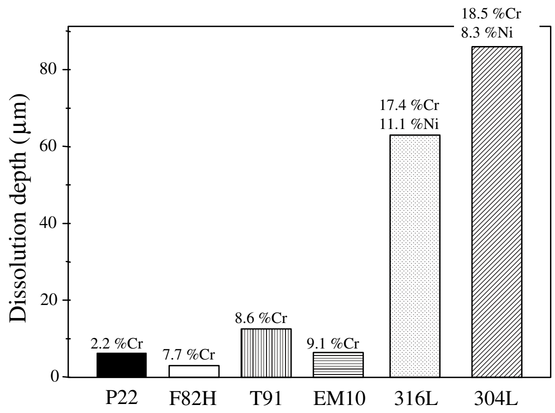

Fig. 6. Dissolution depth occurred to the steels tested for 1500 h at 600 °C in lead–bismuth with an oxygen content of 1.1×10^{-8} wt%.

tested for 1500 h at 600 °C in lead–bismuth with an oxygen content of 1.1×10^{-8} wt% is shown in Fig. 6.

Steels tested at 450 °C under reducing atmosphere remain intact after 500 h. After 2400 h, no signs of corrosion are observed for the martensitic steels, but the austenitic stainless steels show minor signs of dissolution, milder for AISI 304L than AISI 316L.

4. Discussion

Under the oxidising atmospheres, the austenitic stainless steels tested at 600 °C show a good corrosion behaviour. The oxide layers formed on these steels are thin and adherent, thus apparently protective, especially in the case of AISI 304L steel. Others have tested the AISI 316L steel in similar conditions. Ricci et al. [3] obtained similar results. Benamati et al. [4] found that, after 1500 h at 550 °C, the steels presented in few areas a thin oxide scale on the surface, mostly with a spongy appearance. After 3000 h, this spongy layer shows Pb–Bi penetration beneath it. AISI 316L steel showed a dissolution process at this temperature. This result is different from ours, although in our case, tests were carried out at 600 °C but only for 1500 h.

Müller et al. [5] tested AISI 316L steel for 2000 h at 420, 550 and 600 °C in flowing liquid Pb–Bi with an oxygen content up to 1×10^{-6} wt%. At the lowest temperatures, specimens developed partly thick oxide layers. However, at 600 °C, deep liquid metal penetration and massive ablation of material by erosion is observed. This result is different from ours, but it is necessary to point out that Müller tests are performed in flowing conditions with a much lower oxygen content.

It is important to point out the difference in behaviour between the two austenitic stainless steels, AISI 316L and AISI 304L. The AISI 304L steel develops a very thin (0.5 µm) chromium oxide layer, whereas the AISI 316L steel forms a double oxide layer of 45 µm thickness. This different behaviour between the two austenitic stainless steels was unexpected. A possible explanation is given based on the differences in composition and the difference in the evolution of microstructure.

On one hand, the AISI 316L steel tested under oxidising lead–bismuth environment exhibits a double oxide layer, with Mo enrichment in the spinel. The only significant difference in composition with the 304L steel is the presence of molybdenum in the AISI 316L steel. Noteworthy, Mo seemingly promotes the formation of duplex magnetite/spinel scales, where the Mo is retained in the inner spinel layer [6].

On the other hand, the 304L steel tested under oxidising lead–bismuth environment exhibits a very thin and protective chromium oxide layer. In this material, a high content of chromium at the oxide/steel interface, which would contribute to the chromium oxide formation, seems to be promoted by the disordered structure of the cold work layer observed at the steel surface, that favours a more rapid Cr diffusion, as well as by the presence of chromium carbide precipitation at the grain boundaries in the bulk material and, preferentially, at the cold worked layer. The presence of areas with chromium depletion associated to chromium carbides can be considered negligible due to the long duration of the tests.

Martensitic steels tested under the oxidising atmosphere with a 2.0×10^{-3} wt% oxygen content in the lead–bismuth (saturation conditions), results in thick oxide layers, which grow with time following a parabolic law. However, these layers are not protective, since deterioration of the oxide layer and dissolution was detected after 1500 h of exposure.

Other authors have also studied the corrosion behaviour of the martensitic steels under oxidising atmospheres [3]. They found that a thick and compact double oxide layer is formed at 600 °C for 1000 h of exposure. F82Hmod martensitic steel was investigated by Benamati et al. in oxygen-saturated molten lead at 520 °C [7]. After 3700 h, the corrosion products formed on the steel consist of two morphologically different sublayers. The external one is composed of Fe_3O_4 and the internal of Me_3O_4, being Me iron and chromium. Also, lead was detected in the outer sublayers. Müller et al. [8], found three distinct oxidation zones on the martensitic steel (9% Cr) surface tested in lead with 8×10^{-6} at.% oxygen at 550 °C: an outer magnetite scale, a spinel layer beneath the original surface and, below it, an oxygen diffusion zone. They concluded that these oxide layers could effectively prevent the steel from selective dissolution of the alloy elements in the liquid lead.

Fedirko et al. [9] pointed out that the protective characteristics of oxide layers depend on the oxygen concentration in the liquid metal. For Fe–Cr–Al alloys, at oxygen concentration of 10^{-3} wt% in the liquid metal, they observed the formation of non-protective multiphase layers based on iron, chromium and lead oxides. For lower oxygen concentrations, 10^{-5} wt%, they observed the formation of protective, non-permeable to lead, subsurface oxide films with the structure of the spinel, of composition Fe_3O_4–$FeCr_2O_4$ solid solution. Their results are in accordance with ours, although the steels tested are different in composition.

The martensitic steels tested under the oxidising atmosphere with a similar oxygen concentration in lead–bismuth, 4.7×10^{-4} wt%, but with a certain water content, show a different corrosion behaviour. They also show thick oxide layers, which grow with time, but following a linear law instead of a parabolic law. The layers are thicker than those formed under the dry oxidising atmosphere and seem to be more protective.

No reports have been found in the literature on the effect of water vapour in lead–bismuth. However, some authors have studied this effect in gas atmospheres.

Nickel et al. [10] have studied the effect of the O_2 and H_2O content on the oxidation behaviour of the 9% Cr steel P91 in the 600–800 °C temperature range. They obtained an extremely low oxidation rate close to parabolic in a N_2–1%O_2 gas at 650 °C. In wet environments of N_2–1%O_2–xH_2O gas composition, a linear rate is obtained, depending on the H_2O content as well as the H_2O/O_2 ratio, but a incubation period was always observed. Besides, the oxide layers formed in the wet atmospheres are thicker than those formed in the dry atmosphere.

Abuluwefa et al. [11] describes rates of oxidation of low carbon steels in different gas atmospheres in the temperature range of 800–1150 °C. They mention that for samples oxidised in O_2 containing gases, scales become detached at the early stages of oxidation. However, detachment is not observed for the samples oxidised in H_2O atmospheres.

Under reducing atmospheres, having 1.1×10^{-8} wt% oxygen content in the lead–bismuth, the austenitic stainless steels (AISI 316L and AISI 304L) undergo a slight dissolution after 2400 h at 450 °C but a severe dissolution after only 1500 h of exposure at 600 °C. This dissolution attack is mainly due to the high nickel content of the steels. As said before, Ni is highly soluble in lead–bismuth. Martensitic steels present a better corrosion behaviour. They suffer only a slight dissolution at 600 °C at the prolonged exposures. Weeks and Klamut [12] emphasised that the driving force for the dissolution is the temperature dependence of the solubility of the solid metal in the liquid eutectic. Gorynin et al. [1] determined that, for oxygen concentrations lower than 5×10^{-8} wt%, the austenitic stainless steels undergo in lead at 550 °C a dissolution process, whereas at higher oxygen concentrations oxidation occurs preventing dissolution.

5. Conclusions

The results obtained point out that, at 600 °C, under the two oxidising Pb–Bi environments, 2.0×10^{-3} and 4.7×10^{-4} wt% oxygen contents, the austenitic stainless steels exhibit a good corrosion behaviour, as these steel form thin, adherent and apparently stable oxide layers, especially AISI 304L, probably due to a particular surface state. Martensitic steels show very thick oxide layers that grow with time, following a linear law in the wet atmosphere and a parabolic law in the dry atmosphere. However, these layers seems to be not protective.

Under reducing environments, at 600 °C, oxide layers were formed at short times but they disappear after prolonged exposures and dissolution occurs, which increases with time. The austenitic stainless steels exhibit severe dissolution, much stronger than the martensitic steels, mainly due to the high solubility of nickel in lead–bismuth.

At 450 °C, all the materials show a good corrosion behaviour in presence of Pb–Bi containing oxygen, especially the austenitic stainless steels. Under the reducing atmospheres, the martensitic steels have an acceptable corrosion behaviour, while the austenitic stainless steels show an initiation of dissolution after 2400 h of testing.

The results obtained under reducing environments, even at low temperatures, indicate that a precise control of the oxygen activity in the lead–bismuth eutectic is necessary. Under the oxidising conditions tested, all the steels could be used at 450 °C, but only the austenitic stainless steels exhibit an acceptable behaviour at 600 °C. However, longer tests in flowing Pb–Bi are needed to confirm these results.

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