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Short-term static corrosion tests in lead–bismuth

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Abstract

Martensitic steels have been proposed to be used as structural materials and as spallation target window in hybrid systems devoted to the transmutation of radioactive waste of long life and high activity. However, their compatibility with lead–bismuth in the operating conditions of these systems depends on the existence of a protective layer such as an oxide film. The feasibility of forming and maintaining an oxide layer or maintaining a pre-oxidised one has been studied. Martensitic steel F82Hmod. (8% Cr) has been tested in lead–bismuth under static and isothermal conditions at 400°C and 600°C. In order to study the first stages of the interaction between the steel and the eutectic, short-term tests (100 and 665 h) have been carried out. Pre-oxidised and as-received samples have been tested in atmospheres with different oxidant potential. For low oxygen concentration in lead–bismuth due to unexpected oxygen consumption in the experimental device, dissolution of as-received F82Hmod. occurs and pre-oxidation does not prevent the material dissolution. For high oxygen concentration, the pre-oxidation layer seems to improve the feasibility of protecting stainless steels controlling the oxygen potential of lead–bismuth with a gas phase. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Accelerator driven systems (ADS) are designed to transmute long life and high activity nuclear wastes. The physico-chemical and nuclear characteristics of lead–bismuth eutectic make this heavy liquid metal suitable to be used as spallation target and as coolant in a hybrid system [1]. However, heavy liquid metals, and particularly lead–bismuth, present a high corrosivity to most of the structural materials. Martensitic steels have been proposed to be used as structural materials and as spallation target window in a hybrid system [2]. Their compatibility with lead–bismuth in the operating conditions of these systems depends on the formation and maintenance of a protective layer such as an oxide film, according to the available experience, obtained in the former USSR [3]. The corrosion resistance is determined by the oxygen thermodynamic activity in the liquid metal. Oxygen contents lower than the equilibrium concentration suppress the spinel formation and promote material dissolution, and very high concentrations provoke lead–bismuth oxides. Therefore, the oxygen content should be between these two limits in order to be able to form a protective oxide on the steel surface [4]. The necessary oxygen content in the liquid metal may be obtained by gas injection, by lead oxide addition or using the H_2O/H_2 system [5].

Martensitic steel F82Hmod. (8% Cr) has been tested in lead–bismuth under static and isothermal conditions, at 400°C and 600°C in order to gain some insight into the first stages of the interaction between structural steel and the eutectic, and to study the feasibility of forming and maintaining an oxide layer as a means of protecting the structural materials.

2. Experimental

Pre-oxidised and as-received samples of F82Hmod., of approximately 20 × 14 × 4 mm^3, were tested in lead–bismuth, at 400°C and 600°C, for 100 and 665 h. Pre-oxidation of the samples was carried out in air, at 600°C, for 2 h with air cooing. To keep constant the oxidant potential of the lead–bismuth, a gas flow of 10 cm^3/min was injected into the liquid metal continuously. Argon

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with 10% hydrogen was used to maintain low oxidant potential in the lead–bismuth, and argon with a maximum oxygen content of 2 ppm was used with the objective of keeping on a higher oxidant potential in the eutectic. Assuming an oxygen content of 2 ppm in the gas, the oxygen concentration in lead–bismuth must be approximately 10^{-8} wt% after the first minutes of test. A scheme of the experimental device is shown in Fig. 1. Two specimens, one as-received and one pre-oxidised, were tested simultaneously in a porcelain crucible containing 350 g of eutectic. Most of the tests were performed using an austenitic steel tubing of 400 mm long and 1.75 mm internal diameter to inject the gas into the lead–bismuth (device 1). As alternative, a ceramic tubing (alumina, Al_2O_3) with the same dimensions was used in other tests (device 2).

The results obtained from the tests made using device 1 point out that the oxygen concentration that reached the samples was not high enough to form the protective oxide layer or to maintain the pre-oxidation layer on the steel surfaces at long times. In order to check if oxygen consumption occurs in the stainless steel tubing a new test was carried out in the experimental device 2, at 600°C, for 100 h in an argon atmosphere.

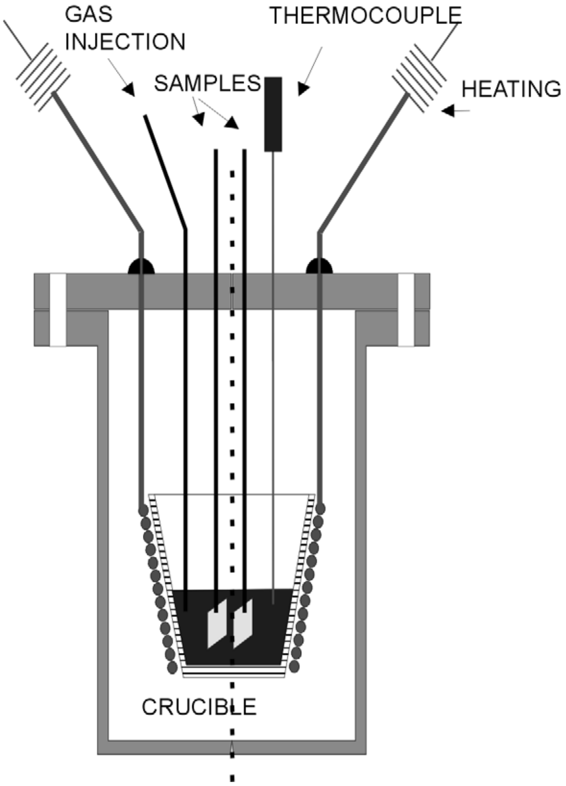

Fig. 1. Scheme of the experimental device.

Therefore, there are two sets of results, one obtained in device 1 (non-inert device) and the other in device 2 (inert device). The behaviour of F82Hmod. was evaluated using weight losses to estimate the dissolution rate, optical microscopy to measure the depth attack, SEM/EDS to establish de attack morphology and the composition of oxide layers. Special attention has been devoted to the oxide layer characterisation by Auger spectroscopy.

Weight losses were determined after cleaning the samples in mercury to eliminate rests of lead–bismuth on the samples tested in device 1. The specimens were weighed before and after the experiment with a precision of 0.1 mg. The precision of the dimension measurement was of 1 μm.

Auger atomic concentrations were calculated according to [6,7] and were normalised to 100%. Sputtering depth profiling was performed using a 3.0 keV argon ion flux, the etching rate calibrations being achieved with a Ta_2O_5 thin film of known thickness.

3. Results

In general, as-received samples tested in device 1 suffer material dissolution whereas pre-oxidised samples show oxide decomposition. On the contrary, in the tests performed in device 2, oxide layers were formed on the as-received samples, and the pre-oxidation oxide layer was preserved on the pre-oxidised ones.

Fig. 2 shows the weight losses of the as-received and pre-oxidised samples tested at 400°C and 600°C for different times in argon and argon with hydrogen, in device 1. The meaning of the weight loss or dissolution rate is not the same for either type of samples. For the as-received samples weight loss means material dissolution, whereas for the pre-oxidised samples it means oxide decomposition plus material dissolution in some cases. On the other hand, these results have to be considered carefully since some rests of eutectic remain on the steel surface after the cleaning of the samples.

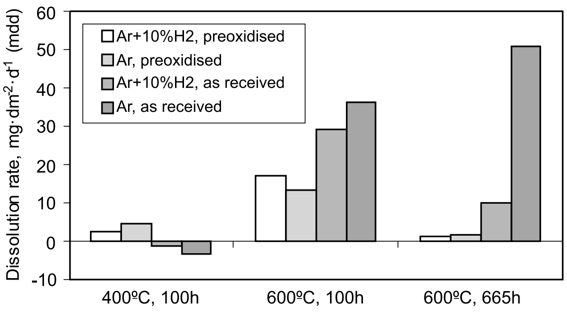

Fig. 2. Dissolution rate of the samples tested in device 1.

The first consideration is that, as it was expected, the samples tested at 600°C have a higher dissolution rate than those tested at 400°C, according with the higher solubility of the main elements constituents of the steel in lead–bismuth at high temperature. At 400°C, the dissolution rate is very low, and even a small weight gain was observed for as-received samples. This weight gain may be due to an oxide layer formed on the steel surface, to a lead–bismuth remaining on the steel or both.

At 600°C, a different behaviour as a function of time was observed between the as-received samples tested in argon and the rest of the samples. The first ones show an increase of the dissolution rate whereas the other samples show a decrease of the dissolution rate according with a parabolic law. At 600°C, the as-received samples dissolution rates measured in both tests, 100 and 665 h, point out that weight losses are higher in the environment with higher oxidant potential. On the other hand, at 600°C, for both atmospheres, the as-received samples present higher weight losses than the pre-oxidised ones.

Fig. 3 shows the morphology of the oxide layer formed on the reference pre-oxidised sample during the pre-oxidation process. Auger depth profile analyses performed in several spots show a homogeneous double oxide layer with a thickness of around 9 μm. The external oxide layer, of 6 μm thickness, is composed of iron and oxygen and the inner layer is formed by iron, chromium and oxygen.

The pre-oxidised samples tested at 400°C in device 1 in both atmospheres, show an almost intact oxide layer after 100 h. However, at 600°C, the sample tested in argon presents initiation of dissolution at small areas. The oxide layers morphology is more irregular in this case than in the case of the reference pre-oxidised sample. Some differences were observed in the composition depth profile analyses performed in different spots, Fig. 4. For example, in spot 3 the results point out that

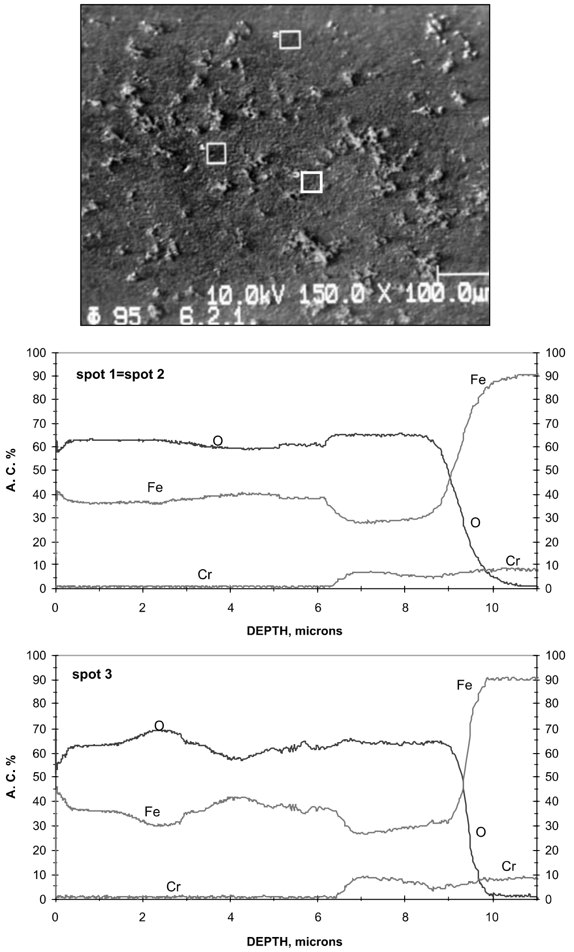

Fig. 3. Auger analysis of reference pre-oxidised F82H at 600°C for 2 h in air before testing in lead–bismuth.

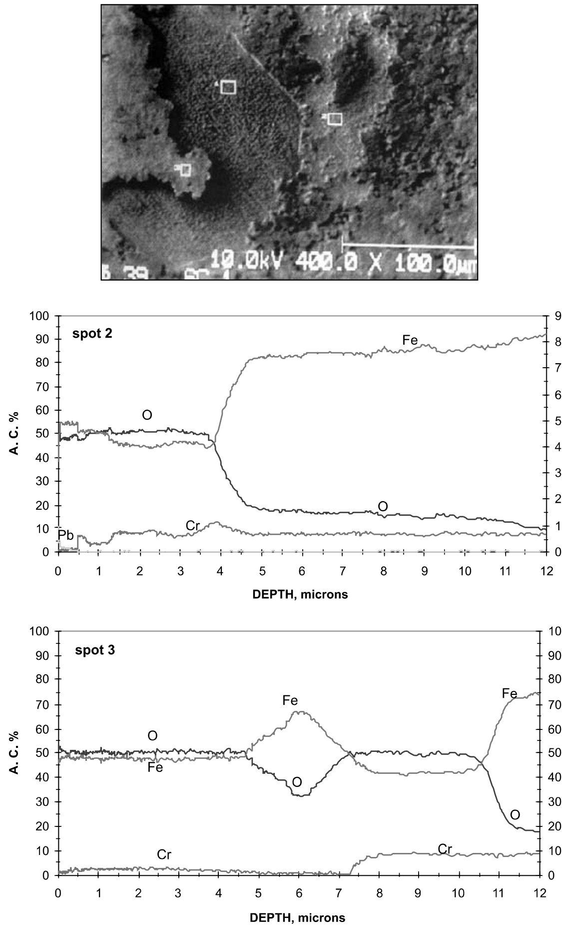

Fig. 4. Auger analysis of pre-oxidised F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in a non-inert device.

the oxide layer is a double layer of 11 μm of thickness with a similar composition that the reference one, except for a lower oxygen content. However, in spot 2 the external oxide layer was not detected and only a thinner layer of 4 μm of thickness formed by iron, chromium and oxygen was observed. The oxygen concentration of this layer is similar to the one measured in the thicker layer in the spot 3. In both cases, a certain oxygen content was detected in the analyses performed at 12 μm depth. The ratio O/Fe is lower than in the reference specimens. This lower ratio $O/Fe \sim 1$ point out the possibility of FeO instead of magnetite. The relative contents of iron, chromium and oxygen lead to consider the internal layer as a $(Fe_{1-x}, Cr_x)_2O_3$ spinel. In the case of the samples tested in argon with hydrogen, material dissolution has not been observed. However, no significant differences have been found either in the oxide layer thickness or in its composition.

At longer times, after 665 h, some differences in the behaviour of the pre-oxidised samples were observed depending on the environment. Samples tested in argon atmosphere show large areas with material dissolution, and some areas covered by a thin oxide layer. SEM examination show that the grain boundaries are revealed, Fig. 5. However, in the reductive environment, dissolution areas were not detected and the oxide layer was preserved in most of the surface. Fig. 6 presents Auger analysis of a sample tested in argon performed in both an oxide layer area and a dissolution area, spots 1 and 2, respectively. The oxide layer (spot 1) is a thin single layer of 0.4–0.6 μm formed by iron, chromium and oxygen with a Cr/Fe ratio of 1.6. In the dissolution area (spot 2) chromium depletion is observed up to more than 1 μm depth. Fig. 7 shows the appearance of the surface of the sample tested in argon with hydrogen and the Auger analyses. The oxide layer composition is similar to the one described above.

The metallographic examination of the pre-oxidised sample tested at 600°C for 100 h in argon atmosphere in the device with the ceramic tube (device 2) shows a homogeneous dark grey oxide layer of approximately 20 μm thickness. Underneath, a light grey layer appears with a thickness of 11 μm, which would correspond to a diffusion layer, Fig. 8. Composition depth profile ana-

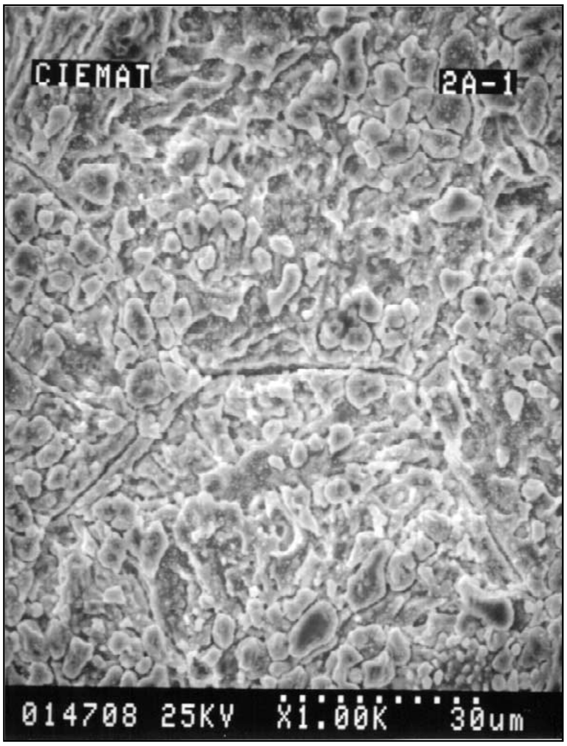

Fig. 5. SEM examination of pre-oxidised F82H tested in lead–bismuth at 600°C for 665 h in argon atmosphere in a non-inert device.

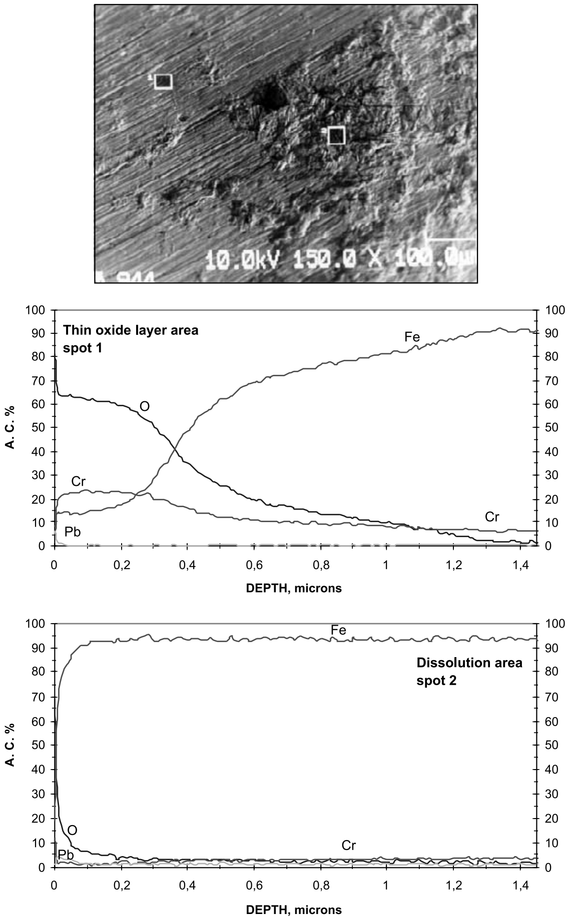

Fig. 6. Auger analysis of pre-oxidised F82H tested in lead–bismuth at 600°C for 665 h in argon atmosphere in a non-inert device.

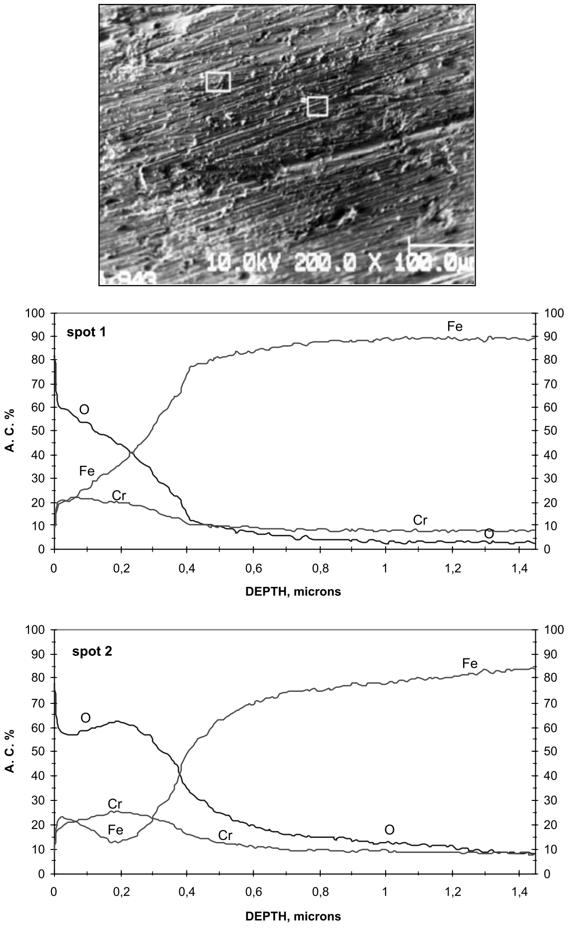

Fig. 7. Auger analysis of pre-oxidised F82H tested in lead–bismuth at 600°C for 665 h in argon with hydrogen atmosphere in a non-inert device.

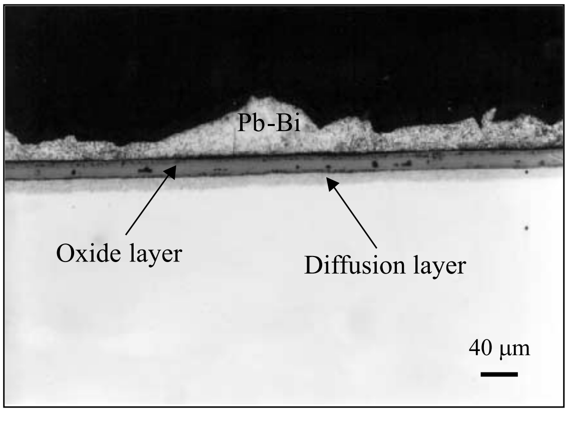

Fig. 8. Optical microscopy (×200) of pre-oxidised F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in an inert device.

lyses show a double oxide layer formed by an external layer composed of iron and oxygen, an internal layer with iron, chromium and oxygen, and underneath an oxygen diffusion zone of 10 µm thickness, Fig. 9. The internal layer composition seems to correspond to a $(Fe_{1-x}, Cr_x)_2O_3$ spinel.

The as-received samples tested, at 400°C, after 100 h, in device 1, show no attack in lead–bismuth in any of the atmospheres. At 600°C, after 100 h, material dissolution was observed in some areas of the samples surface in both environments. Slight dissolution the grain boundaries was observed in some areas at the samples tested in argon. However, Auger analyses show that the oxide layer found in some areas is a thin layer with a thickness between 0.7 and 1.5 µm, formed by iron, chromium and oxygen with a ratio $Cr/Fe \sim 1$, Fig. 10. Oxide layer characteristics are similar in both environments.

At 665 h and 600°C, as-received samples show material dissolution on most of the steel surface with revealed grain boundaries in both atmospheres. Depth attack has been measured in metallographic sections of the samples tested in both atmospheres, Fig. 11. The depth attack is up to 50 µm for the sample tested in argon whereas a shallower attack up to 10 µm was detected for the samples tested in the reductive atmosphere. In both cases, the attack tended to follow the grain boundaries, as can be seen in Fig. 12 for the sample tested in argon. Auger analyses of the as-received samples tested in argon show the existence of a very thin oxide layer (0.5 µm) with a high Cr/Fe ratio between 3.5

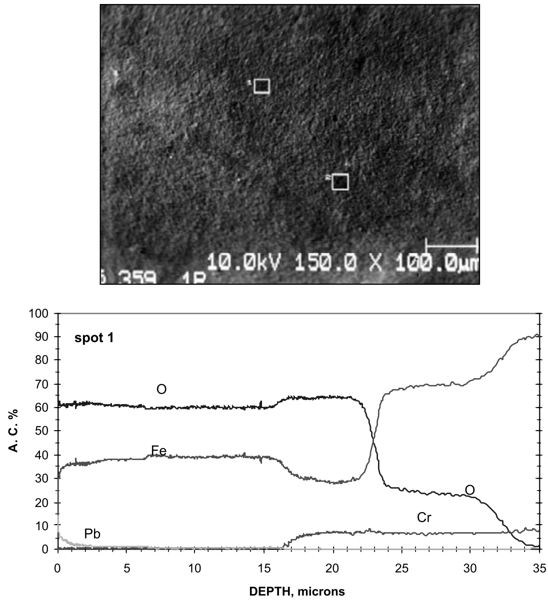

Fig. 9. Auger analysis of pre-oxidised F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in an inert device.

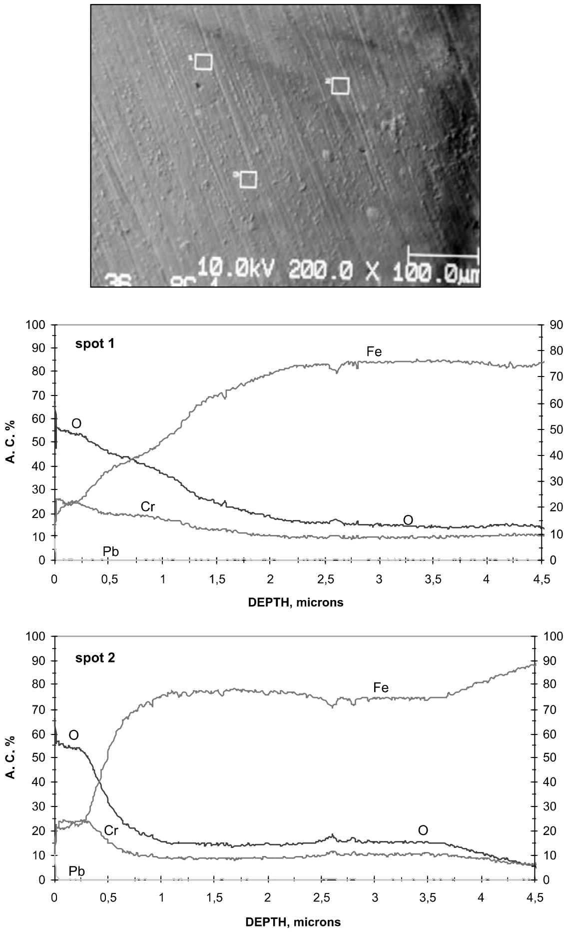

Fig. 10. Auger analysis of as-received F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in a non-inert device.

and 4 µm at the areas without attack (spot 1) and chromium depletion at the dissolution areas (spot 2), Fig. 13.

The metallographic examination of as-received samples tested at 600°C for 100 h in device 2 in argon atmosphere showed an irregular oxide layer, Fig. 14. In some zones, lead–bismuth was observed under the oxide layer. Auger analyses show a double layer, Fig. 15. The external layer (4 µm of thickness) was formed by iron and oxygen whereas the internal layer, with a thickness between 3 and 8 µm, had a high chromium concentration, placed at the oxide/metal interface, higher than the observed in the pre-oxidised sample tested in the same conditions. Lead–bismuth was incorporated into the external layer and into the internal layer.

Cross-section examination of the stainless steel tubing dipped into the lead–bismuth in tests with bubbling argon shows a totally different behaviour of the internal and external surfaces. The internal surface shows an heterogeneous thick oxide layer of around 30 µm and the external surface presents a layer with selective dissolution mainly of nickel and chromium, and no oxide layer at all, Fig. 16.

4. Discussion

Martensitic stainless steels suffer a dissolution process when exposed to lead–bismuth at high temperature. The driving force of the dissolution process is the temperature dependence of the solubility of the solid metal in the liquid eutectic, [8]. The solubility in lead–bismuth can be expressed as $\log S = A + B/T$. According to the data from IPPE reported by Li [9], the solubility values for iron, chromium and oxygen are 3.2×10^{-5}, 3.9×10^{-4}, and 1.4×10^{-4} wt% at 400°C, and 9.8×10^{-4}, 2.3×10^{-3}, and 2.0×10^{-3} wt% at 600°C, respectively. For short duration test, 100 h, as-received samples showed a better behaviour than at 600°C according with the solubility dependence on temperature. At this temperature during 100 h, the pre-oxidation layer was not disturbed. If the lead–bismuth oxygen concentration is high enough, a protective oxide layer will be formed on the steel surface preventing the material dissolution. The effect of oxygen concentration on the stainless steels corrosion resistance has been studied by Gorynin et al. [4]. These authors determined that for oxygen concentrations lower than 5×10^{-8} wt% austenitic steels in lead, at 550°C, undergo a dissolution process, whereas for higher concentrations an oxidation process occurs preventing the material dissolution. As-received samples tested in device 1 showed material dissolution whereas a similar sample tested in device 2, under the same experimental conditions, presented a double oxide layer formed by magnetite and iron/chromium oxide. These results point out an oxygen consumption in the experimental device 1. Examination of the stainless steel tubing used to inject argon into the lead–bismuth confirmed this hypothesis. The oxide layer detected on the internal surface of the stainless steel tubing in the tests performed with argon confirmed the oxygen consumption, and the layer with selective dissolution observed on the external surface supported that the oxygen concentration decreases to values lower than the necessary to form or maintain magnetite on the stainless steel.

According to Gorynin [4], in the dissolution range, thickness losses decrease when oxygen concentration increases. As-received samples tested in lead–bismuth in a reductive atmosphere, argon with 10% hydrogen, presented a lower dissolution rate than the samples tested in a nominally more oxidant environment, argon atmosphere. In addition, at 600°C, the dissolution rate in argon with 10% hydrogen decreased with time following a parabolic law whereas an increase of the dis-

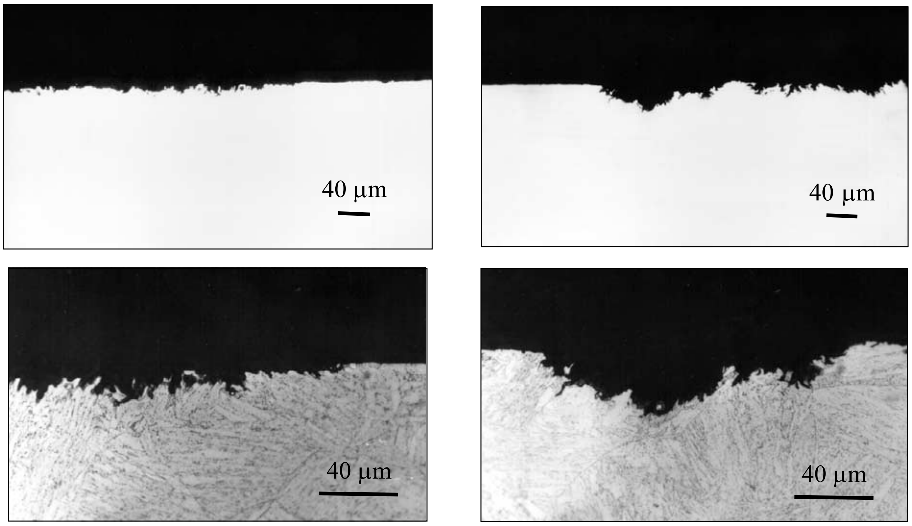

Fig. 11. Optical microscopy of as-received F82H tested in lead–bismuth at 600°C for 665 h in argon with hydrogen atmosphere (left photographs) and in argon atmosphere (right photographs), both in a non-inert device.

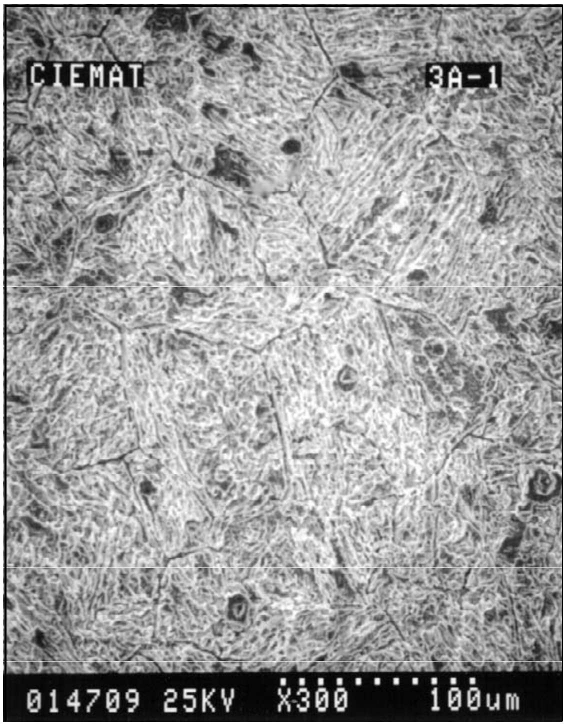

Fig. 12. SEM examination of as-received F82H tested in lead–bismuth at 600°C for 665 h in argon atmosphere in a non-inert device.

solution rate was observed in the samples tested in argon according with a linear law. On the other hand, contrary to the expected, pre-oxidised samples showed a slightly better behaviour in the nominally more reductive atmosphere. Taking into consideration Gorynin's results for low oxygen concentration in the range in which materials dissolution occurs, the oxygen dissolved in lead–bismuth in device 1 when argon is bubbled seems to be lower than when the gas used is argon with hydrogen.

The pre-oxidation layer composition changes with time in lead–bismuth, at 600°C. After 100 h, oxygen content decreased and the heterogeneous decomposition of the layer started. After 665 h the pre-oxidation layer disappeared and a new oxide layer similar to the formed on the as-received samples was detected on small areas of the samples surface. This new layer was a thin layer very rich in chromium with a high ratio Cr/Fe, higher in the as-received samples than in the pre-oxidised ones. Oxygen concentration in lead–bismuth was not enough to form magnetite. Iron/chromium oxide with a lower free energy of formation than magnetite were formed, [10]. The lower the oxygen concentration the higher the ratio Cr/Fe in the oxide layer formed on F82Hmod. in lead–bismuth at high temperature. Decomposition of the pre-oxidation oxide seemed to contribute to the oxygen concentration in lead–bismuth.

At the dissolution areas, the attack seemed to start at the grain boundaries due to a preferential dissolution. When the dissolution was advanced, the grain boundaries were revealed. The beginning and evolution of the attack was the same for the as-received and for the pre-oxidised sample. Pre-oxidation delayed but did not prevent material dissolution in lead–bismuth with low oxygen concentration.

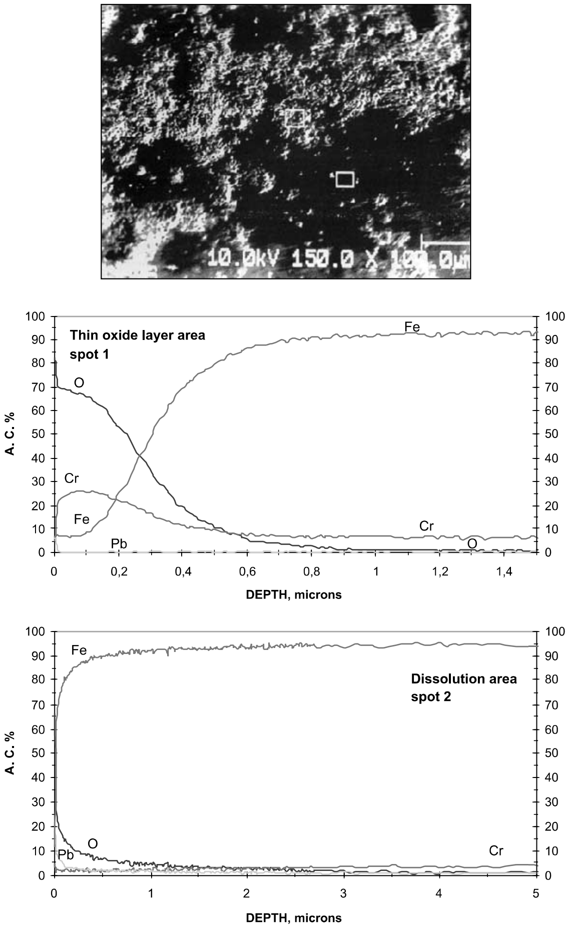

Fig. 13. Auger analysis of as-received F82H tested in lead–bismuth at 600°C for 665 h in argon atmosphere in a non-inert device.

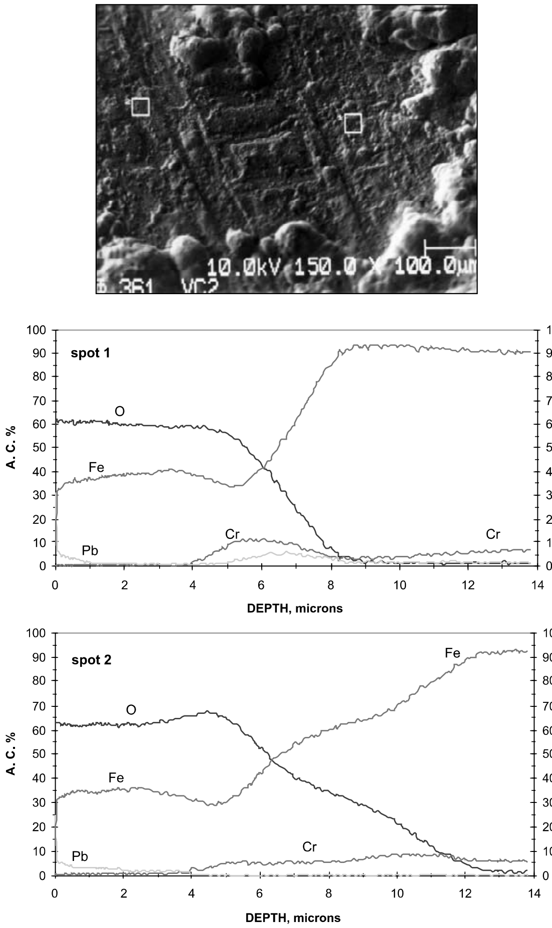

Fig. 15. Auger analysis of as-received F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in an inert device.

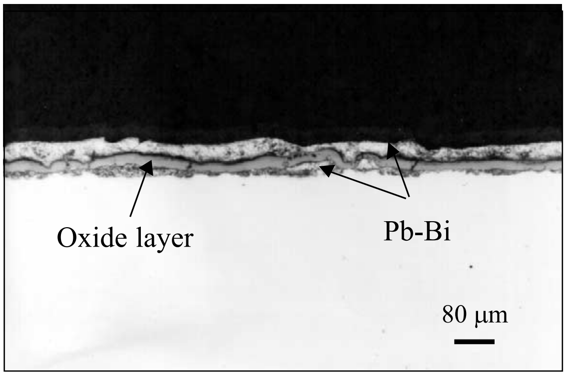

Fig. 14. Optical microscopy (×100) of as-received F82H tested in lead–bismuth at 600°C for 100 h in argon atmosphere in an inert device.

When the oxygen concentration in lead–bismuth was high enough for an oxidation process to occur, higher that 10^{-8} wt% as in the test performed in device 2, the pre-oxidised sample presented a homogeneous double oxide layer thicker than the pre-oxidation layer but with similar composition, except in the presence of a diffusion layer not detected in the pre-oxidised sample. The as-received sample tested in the same conditions showed a non-homogeneous double oxide layer thinner than the previous one with similar composition. The oxide layer formed on the as-received sample was non-protective, permeable to lead–bismuth, contrary to the observed in the pre-oxidised sample. Martensitic steel F82Hmod. was investigated by Benamati et al. [11] in oxygen-saturated molten lead by immersion tests at 520°C. After 3700 h, the products formed on the steel consisted 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. Chromium depletion was found in

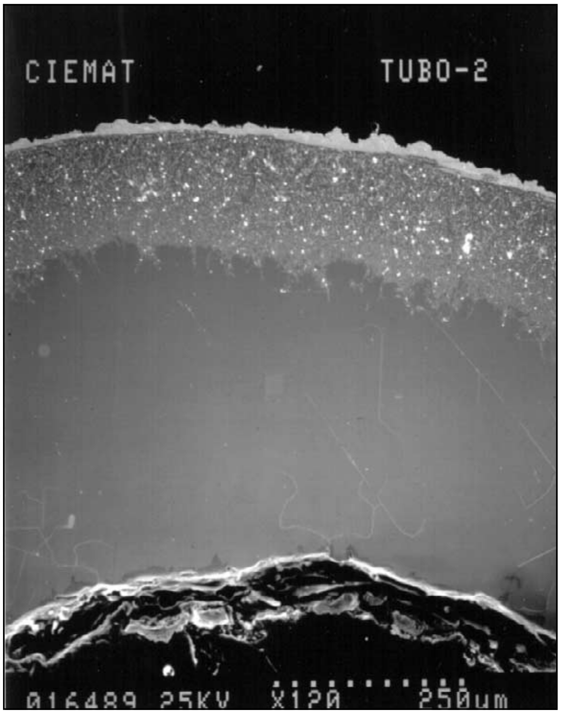

Fig. 16. Metallographic cross-section of the stainless steel tubing used in argon test.

the steel reaction products interface. Lead was detected in the outer sublayers of all the product layers. According to Müller et al. [12] three distinct oxidation zones were developed at martensitic steel (9% Cr) surface tested in lead with 8×10^{-6} at.%, at 550°C, an outer magnetite scale, a spinel layer placed beneath the original surface and below this one, and an oxygen diffusion zone. These authors concluded that oxide layers on steel can effectively prevent the steel from selective dissolution of the alloy elements in liquid lead. Fedirko et al. [13], pointed out that the protective characteristics of oxide layer depend on the oxygen concentration in the liquid metal. For oxygen concentration 10^{-3} wt% on the surface of Fe–Cr–Al alloys, these authors observed the formation of non-protective multiphase layers based on iron, chromium and lead oxides, whereas for lower oxygen concentrations 10^{-5} wt% they observed the formation of protective, non-permeable to lead, subsurface oxide films with structure of spinel, with the composition of Fe_3O_4–$FeCr_2O_4$ solid solution. The characteristics of the oxide layer formed on the pre-oxidised sample point out that pre-oxidation seems to provide the growth of homogeneous, adherent and non-permeable to lead–bismuth oxide layers.

5. Conclusions

The different behaviour of martensitic steel F82Hmod. observed in both devices, non-inert and inert devices, point out the relevance of the experimental device to obtain reproducible and significant results on the corrosion resistance of the materials in lead–bismuth. Stainless steel tubing used to inject argon into the lead–bismuth consumed almost totally the argon oxygen content changing the system conditions from an oxidation to a dissolution regime.

In oxidation conditions, pre-oxidised samples show a better behaviour than the as-received one. The oxide layer observed in the pre-oxidised sample was very homogeneous, non-permeable to lead–bismuth whereas the oxide layer formed on the as-received sample was heterogenous and permeable to lead–bismuth. Pre-oxidation of martensitic steel F82Hmod. seems to improve the feasibility of protecting stainless steels controlling the oxygen potential of liquid lead–bismuth with a gas phase. However, long time tests in static and in flowing lead–bismuth are necessary to confirm the trend pointed out by the results of this experimental work.

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