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Influence of temperature on the oxidation/corrosion process of F82Hmod. martensitic steel in lead–bismuth

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Abstract

A F82Hmod. martensitic steel has been tested in lead–bismuth under a gas atmosphere with a H_2/H_2O equilibrium of 0.3 to examine the influence of temperature on the oxidation/corrosion process. The temperature range studied was 535–550 °C, temperatures just below the temperature transformation of magnetite into wustite. The durations of the tests were 500 and 1000 h and the oxygen concentration in lead–bismuth was between 3×10^{-7} and 4×10^{-7} wt%. The results point out the existence of a threshold temperature, around 550 °C, above which corrosion occurs and the formation of a protective oxide layer is not possible. Two approaches have been considered to explain this behaviour: (a) a kinetic mechanism more than thermodynamic considerations as the driving force of the oxidation/corrosion in lead–bismuth under low oxygen potential, (b) the possible transformation of magnetite into wustite. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Lead–bismuth eutectic has been proposed as a coolant for accelerator driven subcritical systems as actinide burners due to its nuclear and physical–chemical properties. However, lead–bismuth presents a high aggressivity 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 [1]. 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 the necessary for the formation of oxide layers, the steels will experience an oxidation process [2]. Results obtained by Gorynin in flowing oxygen-containing lead for 3000 h at 550 °C point out that an oxidation process of steels (15–16 wt% Cr) occurs for oxygen contents in lead higher than 10^{-7} wt%. On the other hand, Yachmenyov [1] mentions that by maintaining the oxygen concentration in lead–bismuth in the range of 2×10^{-6}–5×10^{-7} wt%, the passivation of steel (12 wt% Cr) is stable for 12 000 h at 600 °C. Therefore, it is possible to passivate the surface of the structural steels in contact with lead alloys by maintaining the oxygen content higher than the necessary to form protective oxide layers. To prevent loop plugging, the oxygen concentration has to be lower than the equilibrium concentration to precipitate lead oxide. According to the Ellingham diagram for the formation of oxides as a temperature function, the oxygen partial pressure is around 10^{-25} atm, at 550 °C.

Using the equilibrium $H_2 + 1/2\,O_2 \leftrightarrows H_2O$ is possible to obtain the required oxygen potential at the temperature of interest for ADS systems. Most of the work dealing with the oxidation/corrosion process of

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structural materials in lead alloys identify M_3O_4 (M = Cr, Fe) as protective oxides [1]. However, Shumov observes a structural instability of oxide coating at 450–550 °C, due to a possible transformation of magnetite into wustite [3].

An experimental work has been carried out in order to gain some insight into the influence of temperature on the oxidation/corrosion process of a martensitic steel in lead–bismuth, in a range of temperature just below the transformation temperature of magnetite into wustite.

2. Experimental

F82Hmod. martensitic steel (7.75 wt% Cr, 2 wt% W) was tested in lead–bismuth eutectic under a controlled oxygen partial pressure. The steel was supplied in the normalised (1040 °C/37′) and tempered (750 °C/1 h/air cooled) condition. The experimental device consists of a furnace with a quartz tube in which several alumina crucibles can be placed (Fig. 1). Three tests were carried out in similar conditions. In the first and second tests, of 500 and 1000 h of duration respectively, three crucibles were placed in the furnace at temperatures ranging from 535 °C for the first crucible to 550 °C for the third. In the third test, of 500 h of duration, six crucibles placed in two parallel lines were used, with a similar range of temperatures. In all three tests, each crucible contained one steel specimen of approximately 30 mm × 6 mm × 6 mm and 40 g of lead–bismuth eutectic. Only two-third of the specimen was immersed in lead–bismuth during the tests.

A mixture of Ar and of Ar + 5%H_2 was continuously fed in order to get the required oxygen partial pressure. The impurities content of both gases are <2 ppm of oxygen and <3 ppm of water steam. A flow rate of 127 cm^3/min of Ar and 8.2 cm^3/min of Ar + 5%H_2 was passed through water at 7.4 °C in order to obtain a H_2/H_2O ratio of 0.3. According to the Ellingham diagram, for a H_2/H_2O ratio of 0.3 the oxygen partial pressure is 4.12×10^{-25} atm at 550 °C. For the tests temperatures, the oxygen concentrations in lead–bismuth were between 3×10^{-7} and 4×10^{-7} wt%.

Longitudinal sections of the specimens were prepared without removing the adhering lead–bismuth for optical microscopy and scanning electron microscopy examinations. Specimen analyses were performed by energy dispersive X-ray analysis (EDX). Auger spectroscopy was used to analyse the composition of particular areas in some of the samples. Oxide layers were analysed by X-ray diffraction (XRD) using a PHILIPS X'Pert-MPD system with the next following operating conditions: Cu-Kα radiation ($\lambda = 1.5405981$ Å), 45 kV, 40 mA; 2θ step 0.02° and counting time 2 s.

3. Results

After the corrosion tests in lead–bismuth eutectic at high temperature under controlled atmosphere, crucibles tested at different temperatures showed different appearances. In the crucibles tested at 550 °C, a black layer of magnetite covered lead–bismuth surface, whereas at 535 °C a more brilliant surface with small spots of yellowish–reddish oxides was observed. For each specimen, the areas immersed in lead–bismuth and the areas exposed to gas atmosphere were examined in detail, in order to identify the difference between the oxidation process in the gas phase and in liquid lead–bismuth, if any.

The specimen zones immersed in lead–bismuth with an oxygen concentration of 3×10^{-7} wt% at 535 °C present a heterogeneous double oxide layer. The different appearance of the oxide layer in the two corners of a sample tested at 535 °C for 500 h is shown in Fig. 2. In general, the external layer is porous and brittle whereas the inner layer shows a layered structure. Spalling of the most external layer was observed. Small particles of iron

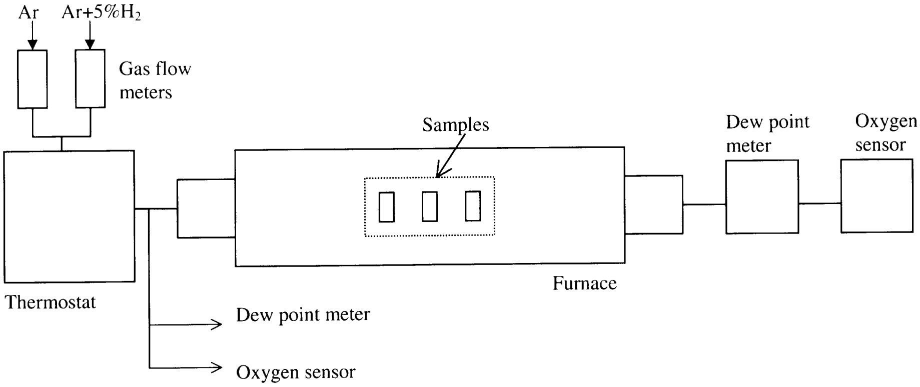


Fig. 1. Scheme of the experimental device.

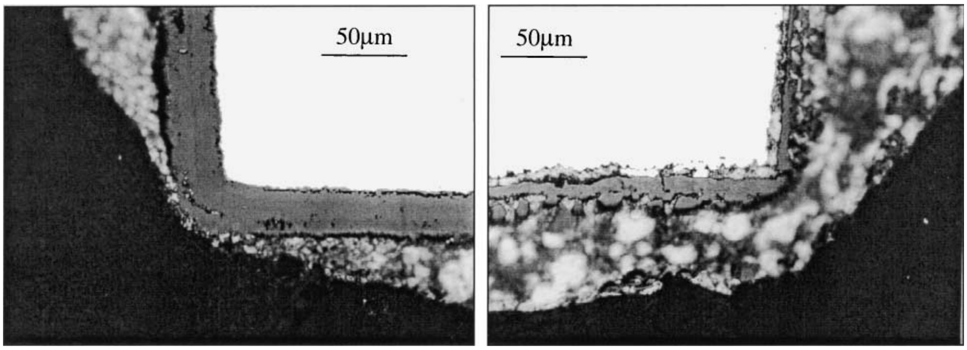


Fig. 2. Specimen tested in lead–bismuth with an oxygen concentration of 3×10^{-7} wt% at 535 °C for 500 h in lead–bismuth. Heterogeneous oxide scale.

oxide embedded in the eutectic were visible. Underneath the oxide/alloy interface an internal oxidation zone was observed. In this zone, cavities parallel to the specimen edges, apparently formed by the agglomeration of pores were detected (Fig. 3). In some areas the internal oxide layer was detached and lead–bismuth was observed between the oxide and the base metal. EDX composition of the oxide layers formed in lead–bismuth at the lower temperature for 500 h is shown in Fig. 4. The external oxide layer is mainly formed by iron, whereas iron and chromium enrichment was detected in the internal one. Besides, W was identified in this layer. Chromium enrichment was also detected in the internal oxidation zone. XRD points out that the external oxide layer is composed by magnetite whereas the internal one is formed by a spinel M_3O_4 ($M = Cr, Fe$). For longer tests, the composition of the oxide layers is similar to the one observed in the shorter tests but the thickness of both the oxide layer and the internal oxidation zone increases (Table 1).

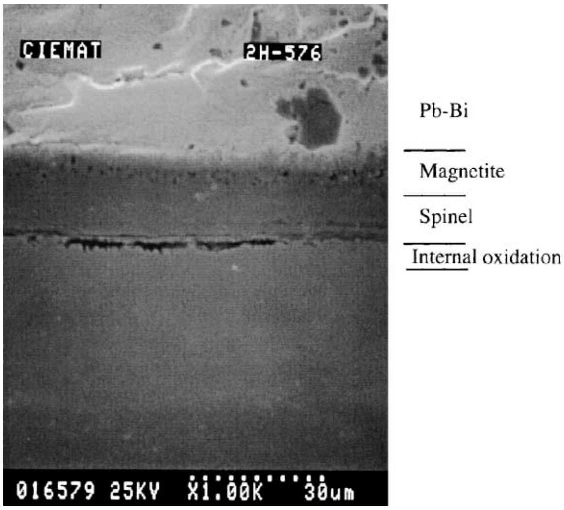


Fig. 3. Specimen tested in lead–bismuth with an oxygen concentration of 3×10^{-7} wt% at 535 °C for 500 h. Details of cavities in the diffusion zone and spalling of the magnetite layer.

	Fe	Cr	W	Pb	Bi	
A	93.47	0.34		3.87	2.32	%at.
	80.01	0.27		12.29	7.43	%wt.
B	83.30	15.39	1.31			%at.
	81.71	14.05	4.24			%wt.
C	80.64	19.13	0.30			%at.
	81.28	17.95	0.77			%wt.
D	88.28	11.36	0.35			%at.
	88.26	10.58	1.16			%wt.
BM	91.62	7.48	0.89			%at.
	90.25	6.86	2.89			%wt.

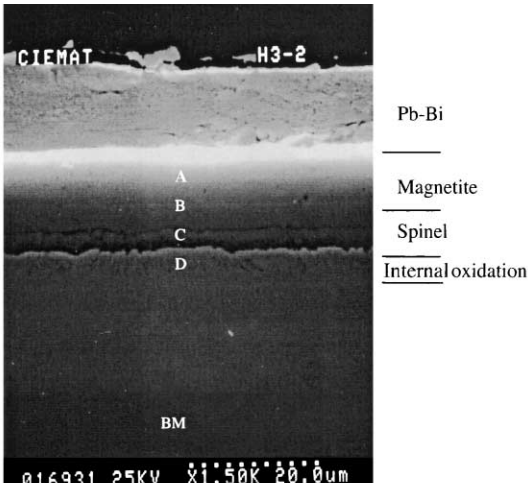


Fig. 4. Specimen tested in lead–bismuth with an oxygen concentration of 3×10^{-7} wt% at 535 °C for 500 h.

The oxide scales observed on the specimen zones exposed to the gas atmosphere, at 535 °C, are similar to the ones formed in lead–bismuth, except for the morphology of the outer part of the magnetite. In Figs. 5 and 6, the appearance of the specimens exposed to gas atmosphere for 500 and 1000 h are presented. In both cases, the outer layer of the magnetite has a columnar structure with a high porosity. This structure cannot be

Table 1
Oxides layer thickness formed on F82Hmod martensitic steel

	Oxide layer thickness (μm)					
	Lead–bismuth, 535 °C		Gas atmosphere, 535 °C		Gas atmosphere, 550 °C	
	500 h	1000 h	500 h	1000 h	500 h	1000 h
Magnetite	8	9	17	21	15	15
Spinel	7	11	7	13	10	12
Internal oxidation	4	5	4	5	7	7

	Fe	Cr	W	
A	98.76	1.24		%at.
	98.84	1.16		%wt.
B	81.54	17.88	0.58	%at.
	81.47	16.64	1.90	%wt.
C	77.71	21.74	0.55	%at.
	77.89	20.29	1.82	%wt.
D	87.89	11.81	0.30	%at.
	87.99	11.01	1.00	%wt.
BM	91.62	7.48	0.89	%at.
	90.25	6.86	2.89	%wt.

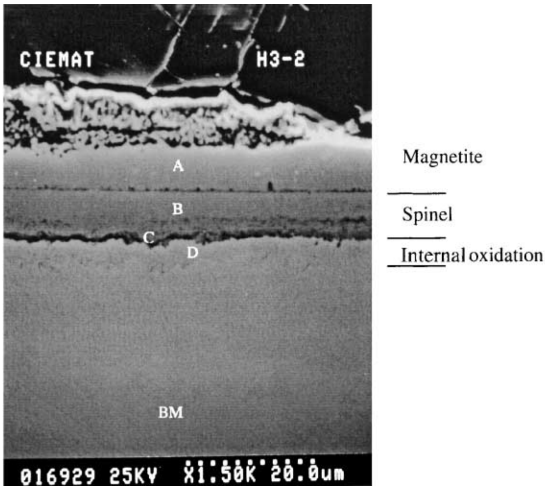


Fig. 5. Oxide scale formed at 535 °C for 500 h under gas atmosphere.

	Fe	Cr	W	
A	100.00			%at.
	100.00			%wt.
B	83.36	15.61	1.02	%at.
	82.32	14.35	3.32	%wt.
C	82.65	16.24	1.12	%at.
	81.48	14.90	3.62	%wt.
D	88.60	10.66	0.74	%at.
	87.75	9.83	2.42	%wt.
BM	91.62	7.48	0.89	%at.
	90.25	6.86	2.89	%wt.

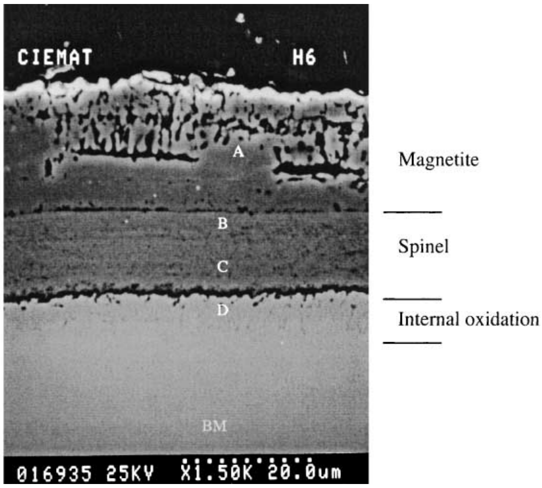


Fig. 6. Oxide scale formed at 535 °C for 1000 h under gas atmosphere.

observed on the magnetite external layer of the specimens tested in lead–bismuth. Thickness of these oxide layers is higher than the one formed in lead–bismuth, as can be seen in Table 1. In both environments, the total thickness of the oxide scale increases with time.

Oxide scale formed in gas atmosphere, at 550 °C, consists also of a double oxide layer similar in appearance and composition to the one formed at lower temperature (Fig. 7). The columnar outer layer of magnetite observed at lower temperature was not detected at this temperature. Thicknesses of the different oxide layers are included in Table 1.

At 550 °C, the specimens immersed in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% underwent a corrosion process instead of the oxidation process foreseen according to thermodynamic considerations. A heterogeneous behaviour among the specimens tested at this temperature was observed. Some of them showed dissolution with chromium depletion (Fig. 8) whereas in others non-protective oxide layers and dissolution areas with significant chromium enrichment and iron depletion were detected (Figs. 9 and 10). In these figures, the degradations found in the specimens tested for 500 and 1000 h, respectively, are presented.

The behaviour observed in the gas atmosphere/lead–bismuth transition areas is of special interest. In Fig. 11, the appearance of the interface gas atmosphere/lead–bismuth area of one specimen tested for 500 h is shown. The magnetite layer formed in gas atmosphere

	Fe	Cr	W	V	
A	99.22	0.78			%at.
	99.27	0.73			%wt.
B	79.39	17.54	3.07		%at.
	75.01	15.43	9.56		%wt.
C	77.64	20.86	1.13	0.38	%at.
	76.78	19.20	3.67	0.34	%wt.
D	87.15	12.42	0.44		%at.
	87.02	11.54	1.43		%wt.
BM	91.62	7.48	0.89		%at.
	90.25	6.86	2.89		%wt.

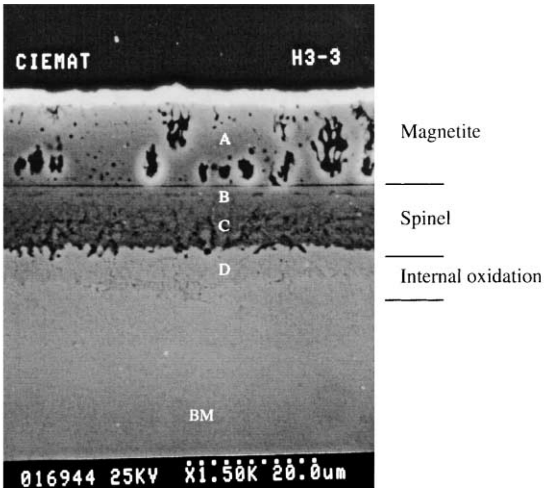


Fig. 7. Oxide scale formed at 550 °C for 500 h under gas atmosphere.

	Fe	Cr	W	Pb	Bi	
A	97.35	2.65				%at.
	97.53	2.47				%wt.
B	91.69	6.55		0.43	1.34	%at.
	87.84	5.84		1.54	4.79	%wt.
C	91.84	5.67	1.06	0.91	0.52	%at.
	89.82	5.05		3.24	1.88	%wt.
D	93.04	6.69	0.26			%at.
	92.91	6.22	0.87			%wt.

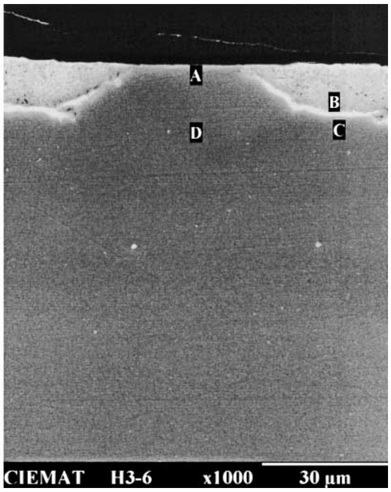


Fig. 8. Specimen tested in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% at 550 °C for 500 h.

	Fe	Cr	W	Pb	Bi	
A	88.31	3.41		7.14	1.15	%at.
	72.23	2.60		21.67	3.50	%wt.
B	80.55	18.54	0.91			%at.
	79.91	17.13	2.96			%wt.
C	92.41	7.32	0.27			%at.
	92.30	6.80	0.90			%wt.
D	31.41	6.10		8.85	53.64	%at.
	11.61	2.10		12.13	74.17	%wt.
E	94.14	5.49	0.37			%at.
	93.71	5.09	1.21			%wt.
BM	91.62	7.48	0.89			%at.
	90.25	6.86	2.89			%wt.

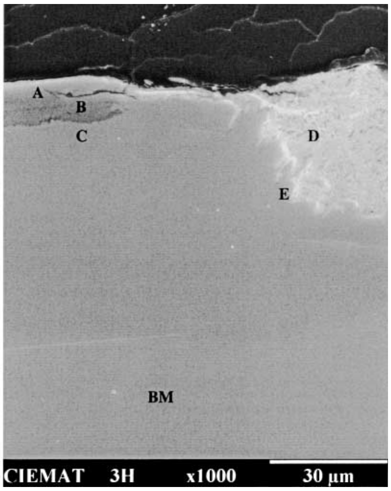


Fig. 9. Specimen tested in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% at 550 °C for 500 h.

	Fe	Cr	W	Pb	Bi	
A	22.57	44.93	0.91	15.37	12.22	%at.
	12.98	26.20	1.72	32.80	26.29	%wt.
B	22.60	56.13	0.62	13.75	6.89	%at.
	14.70	34.00	1.33	33.19	16.77	%wt.
C	89.88	8.44	0.62		1.05	%at.
	86.67	7.58	1.97		3.78	%wt.
D	89.47	9.73	0.15		0.64	%at.
	88.22	8.93	0.48		2.36	%wt.
E	87.22	11.87	0.91			%at.
	86.13	10.91	2.96			%wt.
BM	91.62	7.48	0.89			%at.
	90.25	6.86	2.89			%wt.

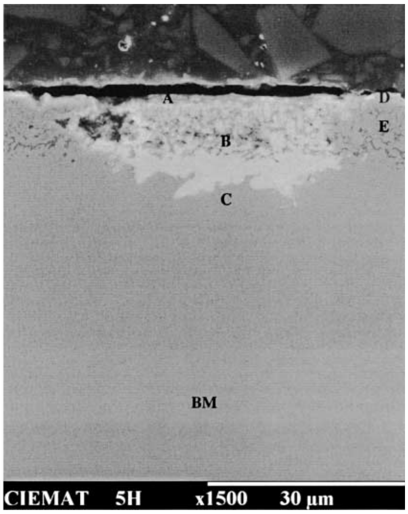


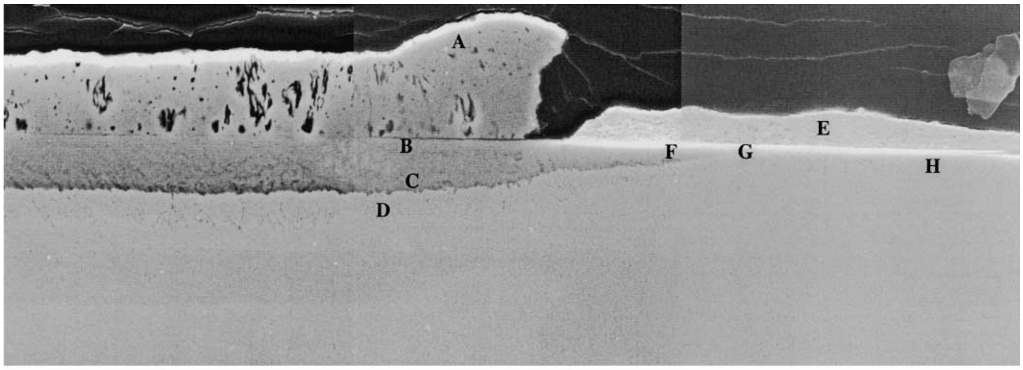
Fig. 10. Specimen tested in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% at 550 °C for 1000 h.

disappears sharply and the thickness of the spinel layer decreases considerably at the interface zone until disappearing totally into the lead–bismuth. Spinel under lead–bismuth presents chromium concentration as high as 30 wt%. An area below the interface of the specimen tested for 1000 h is present in Fig. 12. In this area, some oxide films rich in chromium above a porous zone next to a dissolution area were observed. EDX analyses point out that this oxide film is formed by iron with a high chromium concentration, whereas the porous area underneath it has some chromium depletion. Preferential iron dissolution occurred in the dissolution area. Auger analyses performed in an area of this specimen with apparent dissolution are shown in Fig. 13. A thin oxide film rich in chromium with lead–bismuth incorporated to it (indicated as lead in the figure) and an oxygen diffusion zone of 10 µm were detected.

4. Discussion

The results of all three tests are consistent, confirming that under the tested conditions martensitic steel F82Hmod. in lead–bismuth undergoes an oxidation or corrosion process depending on the temperature. The results point out the existence of a threshold temperature, above which corrosion occurs and the formation of protective oxide layers is not possible.

The use of a gas atmosphere with a H_2/H_2O ratio of 0.3 guarantees an oxygen partial pressure, 3.46×10^{-25}



	Fe	Cr	W	Pb	Bi	
A	100.00					%at.
	100.00					%wt.
B	80.12	19.56	0.31			%at.
	80.63	18.33	1.04			%wt.
C	75.66	21.64	2.70			%at.
	72.27	19.25	8.49			%wt.
D	88.93	11.02	0.04			%at.
	89.53	10.33	0.14			%wt.
E	9.76			50.57	39.67	%at.
	2.82			54.25	42.93	%wt.
F	59.17	37.71		2.04	1.07	%at.
	55.89	33.16		7.15	3.79	%wt.
G	87.25	10.28	0.47			%at.
	87.04	11.41	1.55			%wt.
H	81.78	14.52		2.58	1.11	%at.
	75.00	12.40		8.79	3.81	%wt.
BM	97.62	7.48	0.89			%at.
	90.25	6.86	2.89			%wt.

Fig. 11. Interface gas atmosphere/lead–bismuth for the specimen tested at 550 °C for 500 h with an oxygen concentration of 4×10^{-7} wt%.

atm at 550 °C, higher than the oxygen equilibrium pressure for the magnetite formation at both temperature 535 and 550 °C, according to the Ellingham diagram [4].

The oxidation of martensitic steel F82Hmod. observed at 535 °C in lead–bismuth agrees with the thermodynamic considerations. A double oxide layer similar to the one formed in the gas atmosphere was detected. The oxide scale formed in lead–bismuth was heterogeneous in thickness. Spalling of the most outer layer and detaching in the interface oxide/alloy was observed (Fig. 2). Besides, cavities were detected underneath the interface oxide/alloy. All these oxide features agree with the description of Evans [5] for the scale thickening in gas atmosphere and with the process of growth of oxide films in lead described by Ferdiko et al. [6]. Scale growth occurs through the diffusion of metallic atoms from the metal into the oxide as ions, leaving vacancies at the interface. Vacancies accumulated at the matrix–oxide interface coalesce to form cavities that can promote oxide detaching. Vacancies can diffuse through metal as well as through oxide, joining one to another to form brittle and porous oxides. Simultaneously with the cation diffusion, anion diffusion occurs.

Oxide layers formed in gas atmosphere at 535 °C were thicker than the ones observed in lead–bismuth. A similar trend was observed by Mueller et al. [7]. These authors report that the growth rate of the magnetite scale is 2–3 times higher in gas atmosphere than in lead containing 8×10^{-6} at.% oxygen at 550 °C. On the other hand, they point out that the differences between oxide layers formed in atmosphere and in lead is just the growth rate of the magnetite scale and spinel zone, whereas the structures of both are similar. On the contrary, Gorynin et al. found that the oxide thickness is one order of magnitude lower in air than in lead with an oxygen concentration of 1×10^{-5}–1×10^{-6} wt%, at 550 °C [2].

At 550 °C, a thick double oxide layer also covered the specimens zones exposed to gas atmosphere. The composition of the oxide layers formed at both temperatures, 535 and 550 °C, is very similar. However, the scale

	Fe	Cr	Pb	Bi	
A			29.12 28.95	70.88 71.05	%at. %wt.
B	48.99 33.23	32.74 20.67	12.80 32.22	5.47 13.88	%at.. %wt.
C	62.36 66.53	26.38 30.23	11.26 3.24		%at.. %wt.
D	88.30 89.02	11.70 10.98			%at.. %wt.
E	92.51 89.48	6.08 5.47	1.41 5.04		%at.. %wt.
F	89.70 84.79	7.96 7.01	2.34 8.21		%at.. %wt
G	90.38 90.98	9.62 9.02			%at.. %wt
H	16.39 7.00	33.53 13.34	29.12 46.15	20.96 33.51	%at.. %wt
I	14.71 6.45	37.27 15.21	31.47 51.18	16.56 27.16	%at.. %wt
J	14.33 5.14	19.62 6.56	38.56 51.49	27.40 36.81	%at.. %wt
K	66.42 39.43	8.35 4.61	5.58 12.30	19.65 43.66	%at.. %wt
L	90.52 91.12	9.48 8.88			%at.. %wt.

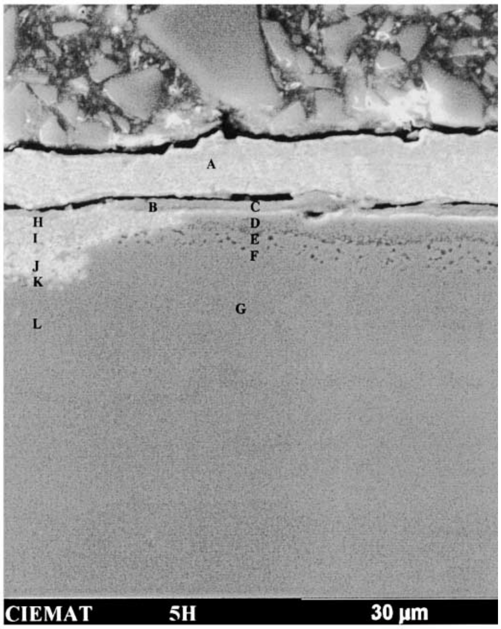


Fig. 12. Specimen tested in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% at 550 °C for 1000 h. Appearance of oxide layer just below the interface gas atmosphere/lead–bismuth.

morphologies show some differences. At 550 °C, the magnetite layer seems to have a higher density of cavities and pores than the one formed at 535 °C. However, the most outer layer of magnetite with a columnar structure observed in the specimens tested at 535 °C was not detected at 550 °C. The internal spinel layer has a similar chromium enrichment at both temperatures but the tungsten concentration is higher in the specimens tested at 550 °C. Besides, the layered structure of the most internal part of the spinel was better defined in the samples tested at this temperature. Finally, the depth of the internal oxidation at high temperature was almost double that the one observed at low temperature, whereas the composition was similar.

According to the equations given by Li [8], oxygen activity in lead–bismuth during the experiment at 550 °C was 40 times the minimum thermodynamic activity for magnetite formation. However, contrary to the observed at 535 °C, oxidation was scarcely observed and material corrosion occurred. Apparently, a competition between oxidation and corrosion processes takes place, being the last faster. According to Yachmenyov [1] a certain oxygen concentration in lead–bismuth higher than a critical value is necessary for the formation of oxide protective 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, kinetic mechanism more than thermodynamic conditions would be the driving force for the corrosion observed at 550 °C. The oxygen critical concentration depends on the temperature, the temperature gradient in the case of a loop, the composition and surface state of steel and the tests duration. Therefore, it does not seem probable that a temperature difference of 15 °C is the only factor explaining the corrosion observed in lead–bismuth at 550 °C. A possible additional factor could be the formation of an unstable and non-protective oxide in lead–bismuth.

Shumov et al. [3] reported that oxide coating formed on ferrite martensitic steels (12 wt% Cr) formed in lead–bismuth with an oxygen activity of 10^{-3}–10^{-4} wt% at 600 °C presents a different behaviour depending on the temperature. This phenomenon was named by the authors “temperature instability of the threshold type”. The oxide coating maintains its stability at temperatures below 450–500 °C. For higher temperatures, oxide is subjected to amorphisation, identified by XRD scanning, as a result of structural defects. The authors suppose that the amorphisation is caused by the formation of wustite. Apparently, the wustite is distributed throughout the bulk of the oxide in the form of fine particles. Wustite formation can be due to the interaction of a thick spinel film and steel at temperatures above that of spinel–wustite transformation. Wustite is a p-type conductor with a high concentration of lattice defects. The defects consist of vacant cations sites and an equivalent number of electron defects represented chemically by Fe^{3+} ions. Wustite has worse protective

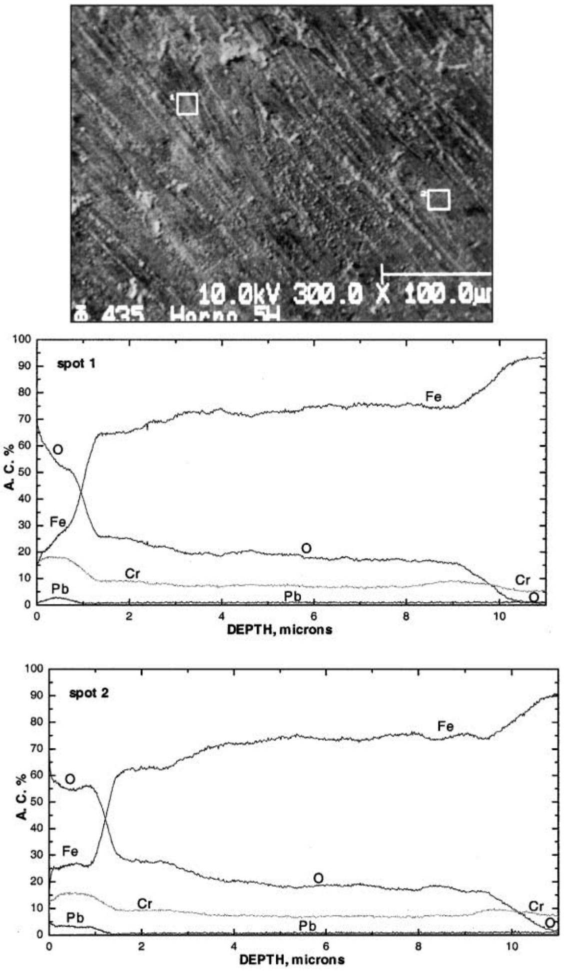


Fig. 13. Auger analysis of the specimen tested in lead–bismuth with an oxygen concentration of 4×10^{-7} wt% at 550 °C for 1000 h.

properties due to the higher mobility of cations in its lattice. Mobility of iron ions in wustite is about 3 orders of magnitude greater than in magnetite at a given temperature [9].

The temperature of the transformation of magnetite into wustite in pure iron, is not well documented but generally reported between 556 and 570 °C [10]. According to Gemma [11], the formation of metastable wustite is possible at temperatures below the transformation temperature of Fe_3O_4/FeO. Under a certain oxygen pressure this metastable FeO may be oxidised to unstable Fe_3O_4. However, the transformation temperature can be shifted to higher values by alloying the iron with Mo, Cr, Ni and V and to lower values with Mn additions [12]. Influence of W, identified in the oxide scales formed on F82Hmod., is not known. In chromium alloys, Cr is present in the oxide scales at the oxide/metal phase boundary as a component of the spinel layer. Chromium interferes with iron cations diffusion lowering the oxidation rate. At high temperature, wustite can form an intermediate layer between the spinel and the magnetite layers [12], but chromium produces a decrease in wustite composition range [9].

If the transformation of magnetite into wustite takes place, the effective partial pressure of oxygen will be defined by the oxygen partial pressure of the magnetite decomposition. The actual oxygen activity in lead–bismuth will be lower than the calculated. The available results do not allow us to confirm or reject this transformation as the cause of the corrosion observed at 550 °C. However, the following observations support the plausibility of this hypothesis. Magnetite formed in gas atmosphere disappears sharply at the interface gas/lead–bismuth at 550 °C (Fig. 11) whereas the thickness of the internal spinel layer decreases gradually into the lead–bismuth at the same time that the chromium concentration increase up to 30 wt%. Oxide film rich in chromium was also detected at the interface zone of the specimen tested for 1000 h, at the same temperature (Fig. 12).

Available information on iron–chromium oxide stability in lead–bismuth is very scarce. Mueller et al. [7] found that, after corrosion tests in lead at 550 °C containing 8×10^{-6} at.% oxygen under controlled H_2/H_2O gas atmosphere, the OPTIFER martensitic steel shows the typical corrosion attack with three different zones. The zone at the top consists of brittle magnetite without appreciable Cr concentration. The layer in the middle contains Cr–Fe spinel and in the interior an oxygen diffusion zone exists. Spinel layer is missing in some places of the specimen. On the other hand, Benamati et al. [13] point out that the oxide layers formed on F82Hmod. in oxygen-saturated lead, at 520 °C, are not protective against oxidation. The possible formation of the spinel FeO–Cr_2O_3 was taken into account by these authors, although finally the formation of a spinel-type $(Fe,Cr)_3O_4$ was preferred. From another point of view, Shumov et al. [3] in the paper quoted above mention that the hydrogen might have a strong influence on the phase properties in the system Fe–Pb–O. Hydrogen can modify the concentrations of mobile vacancies and the diffusion of cations. Equilibrium diagram of Fe–Pb–O–H is needed for the understanding of the possible hydrogen effect on the stability of oxide layers formed in lead–bismuth with low oxygen potential, using H_2/H_2O ratio.

Regarding dissolution process, two types of processes have been observed. One of these proceeds with chromium dissolution according to the dissolution mechanism in liquid lead–bismuth without oxygen observed in previous tests [14]. The other one, observed in the dissolution areas found in the specimens that present some oxidation in lead–bismuth, takes place with iron preferential dissolution. The dissolution area presents a high porosity. According to the physico-mathematical model of iron corrosion in liquid lead developed by Matychak [15] the atoms of oxygen are adsorbed on the surface of iron until the surface concentration increases up to a value which corresponds to conditions of equilibrium with the medium. If oxygen is insufficient for the formation of stable chemical compounds, the oxygen can dissolve in iron following the diffusion law. Simultaneously, iron dissolves in lead. As a result of the outflow of iron cations from the metal, new non-equilibrium vacancies are formed in the diffusion zone promoting the formation of a porous zone. The oxygen diffusion zone detected by Auger analyses (Fig. 13) and the porous zone observed in several specimens tested at 550 °C agree with the previous description in spite of the existence of chromium in the martensitic steel that has a higher solubility than iron in lead–bismuth [16].

5. Conclusions

Corrosion tests of F82Hmod. in lead–bismuth under a gas atmosphere with a H_2/H_2O ratio of 0.3 point out a strong influence of the temperature on the behaviour of martensitic steel F82Hmod. Post-test examinations support the existence of a temperature threshold around 550 °C. At 550 °C, the formation of non-protective oxide layers and dissolution of the material have been observed whereas an oxidation process with the formation of protective oxide layers has been detected at 535 °C.

Two approaches have been considered to explain the F82Hmod. corrosion in lead–bismuth observed at 550 °C. The first one considers that a kinetic mechanism more than thermodynamic considerations is the driving force of the oxidation/corrosion in lead–bismuth with low oxygen potential. The other one is based on the possible transformation of magnetite into wustite and on the influence of lead–bismuth in this transformation and on the stability of the oxide layers.

The relevance of these results for the use of martensitic steels in ADS systems calls for further testing to confirm the viability of protection of martensitic steels using the equilibrium H_2/H_2O. Special attention must be paid to the identification of the oxide layer composition and the characterisation of its protective properties.

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