# Comparison of Oxidation of Ferritic-Martensitic Steel EP-823 and Armco-Fe in Pb Melt Saturated by Oxygen

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## Abstract

The kinetic peculiarities of scale formation on the surface of ferritic-martensitic steel EP-823 and Armco-Fe in the Pb melt saturated by oxygen ($C_{O[Pb]} = 6 \cdot 10^{-3}$ wt %) at 650ºC were elucidated. It was determined that the corrosion rate measured as decreasing of thickness of specimens is similar for Armco-Fe and steel EP-823, however the scale formed on the steel is thicker then that one on the Armco-Fe. Scale on the steel surface has multiplayer morphology, consists of magnetite, totally penetrated by Pb and includes also the complex compounds $n\,PbO \cdot m\,Fe_2O_3$ – plumboferrites. The scale formed on the surface of Armco-Fe consists of thin outer magnetite layer followed by the thick inner wüstite one. Contrary to the steel the scale formed on the Armco-Fe is compact and contains neither Pb nor plumboferrites. The possible mechanisms of scales formation were discussed.

**Keywords:** Steel, Armco-Fe, Pb melt, Oxidation.

# 1. Introduction

Compatibility of structural materials and heavy liquid metals (Pb, Pb–Bi) proposed as candidate heat-transfers for fast reactors and accelerator driven systems is one of main problems of state-of-the-art reactor materials knowledge [1]. The physical-chemical interaction between lead melt and stainless steel depends on the concentration of oxygen impurity in the liquid metal. When oxygen concentration in lead melt is low ($C_{O[Pb]} < 10^{-7}$ wt%) the liquid medium is an aggressive dissolvent of main steel's components (Ni, Cr, Fe) and vice versa when concentration of oxygen is high ($10^{-7} < C_{O[Pb]} < 10^{-3}$ wt%) lead melt becomes strong oxidizing medium [2, 3]. Operation experience of the Pb–Bi eutectic as a heat-transfer in nuclear reactors of submarines testifies that the high corrosion aggressiveness of lead melt can be sufficiently suppressed by *in-situ* inhibition of liquid metal by oxygen impurity under restricted concentration diapason ($C_{O[Pb]} \approx 10^{-7}...10^{-6}$ wt %) [4]. It allows to form on the steels surface the $Me_3O_4$ protective oxide layer (Me: Fe, Cr) which inhibits the dissolution of steel's components into the melt [4]. The intensive experimental works are under performing in the leading research institutions of Russia, European Union, USA and Japan [1–13]. In spite of the heightened interest to the problem of compatibility of structural materials with the melts of heavy metals (Pb, Pb–Bi) the obtained results remain very scarce and therefore the nature of interaction in the complex system Fe[Cr,Ni,Si]/Pb[O] under various temperature – oxygen concentration conditions has not been elucidated yet. This paper is dedicated to the revealing of the peculiarities of oxidation of ferritic-martensitic steel EP-823 and model material – Armco-Fe in stagnant lead melt saturated by oxygen at 650°C.

# 2. Experimental Conditions

The specimens (10×5×1 mm) of steel EP-823 (wt. %: 0,17C; 2,04Si; 0,74Mn; 13,46Cr; 1,60Mo; 0,19W; 0,2V; 0,2Nb; 0,28Ni; 0,094N$_2$) and Armco-Fe were made of sheets. After thermal treatment (EP-823: vacuum annealing at 1050°C for 15 min + vacuum tempering at 750°C for 30 min; Armco-Fe: vacuum annealing at 700°C for 30 min) specimens were placed in the alumina crucibles then filled by lead at

350°C. The corrosion tests were carried out at 650°C. The liquid lead was saturated by oxygen since Pb-oxides were observed on the free surface of the melt. Accordingly to $\lg C_{O[Pb]max}=3,2-5000/T$ [3] the oxygen concentration in melt was $6 \cdot 10^{-3}$ wt %. After exposures samples were extracted from the melt quickly to save the high-temperature state of scale. The cross-sections were examined by optical (OM) to measure the thickness of scale and non-oxidized matrix. In order to estimate the direction of scale growing the initial interface between solid metal and liquid metal (X=0) was marked on the scheme obtained owing to microscope measuring (Fig. 1).
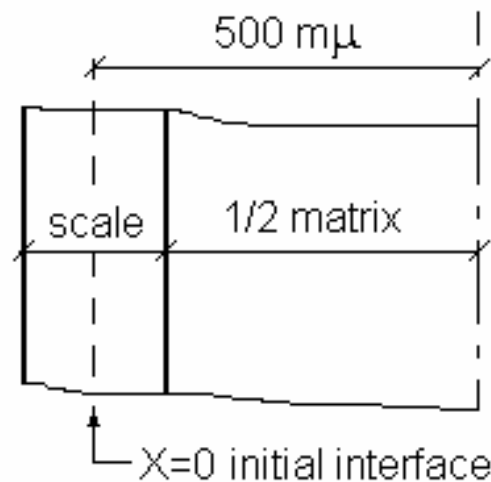


Figure 1. Scheme of determination of initial interface (X=0)
solid metal / Pb melt on the cross sections.

Scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction analysis (XRD) using Cu-K$\alpha$ radiation (0.05° 2$\Theta$ step) were used to determine the element and phase composition of scale. Microhardness was measured under the loads 20 and 50 g.

## 3. Results

Fig. 2 shows the oxidation kinetics of Armco-Fe and steel EP-823 at 650℃ in Pb melt saturated by oxygen. Under herein conditions of test, the scale formed on the surface of steel EP-823 is thicker then that one formed on the Armco-Fe while the decreasing of thickness of specimens is similar. The scales on the both materials grow in two directions with regard to the initial interface X=0: towards the melt

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and solid metal. The scale formed on the Armco–Fe has two equal outer and inner parts. Contrary to the Armco–Fe the outer part of the steel's scale is thicker then the inner one and this difference is being increased with time.
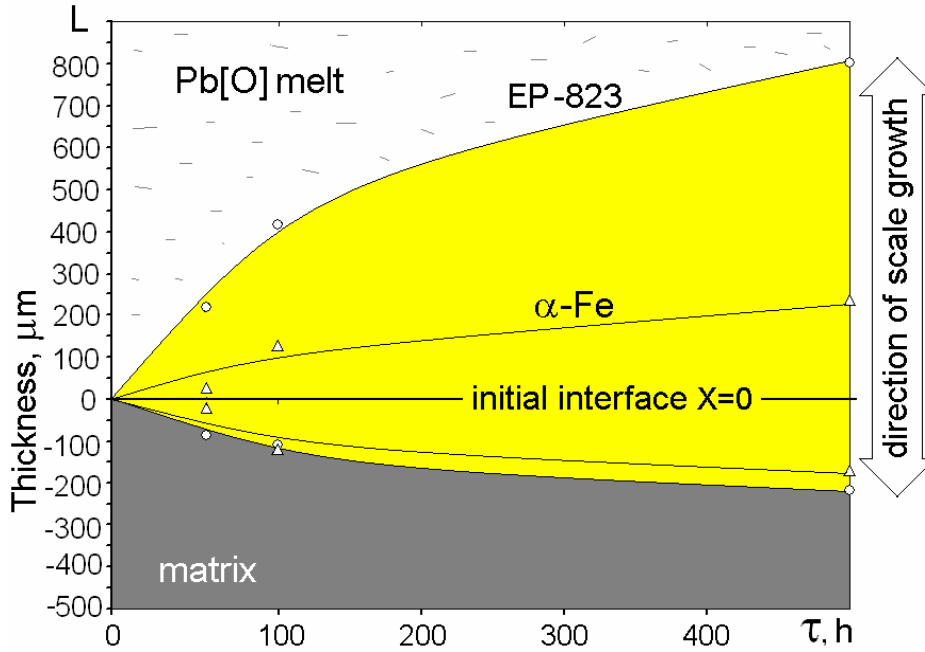


Figure 2. Oxidation kinetics of Armco–Fe and steel EP–823 in Pb melt saturated by oxygen at 650℃.

The scale formed on the surface of Armco–Fe is sufficiently compact, though the inner half of scale is porous (Fig. 3 a). In BE imaging the white contrast of Fe–matrix is changed by the grey color of scale upper part of which is taupe–colored. The microhardness of scale is averaged 4,5 GPa that corresponds to the hardness of wüstite and/or magnetite (4÷5.5 GPa). In spite of the general uniform growing of scale into the matrix the wüstite / matrix interface looks like fjord (has jagged form) (Fig. 3 b). Similarly to the pores the white islands of non–oxidized Fe are situated only in the inner half of scale growing towards the matrix (Fig. 3 b). In turn, the ellipse–shape oxide precipitates both big and small are observed in the matrix (Fig. 3 c). Such interosculation of phases, as well as the jagged form of the interface, provides the good scale's adhesion and mass exchange of reagents and, as a result, ensures the intensive growth of scale (~ 0,8 µm/h). It should be noticed that Pb does not penetrate into the scale, although it contains the pores. It testifies once more that scale is impervious to liquid metal.
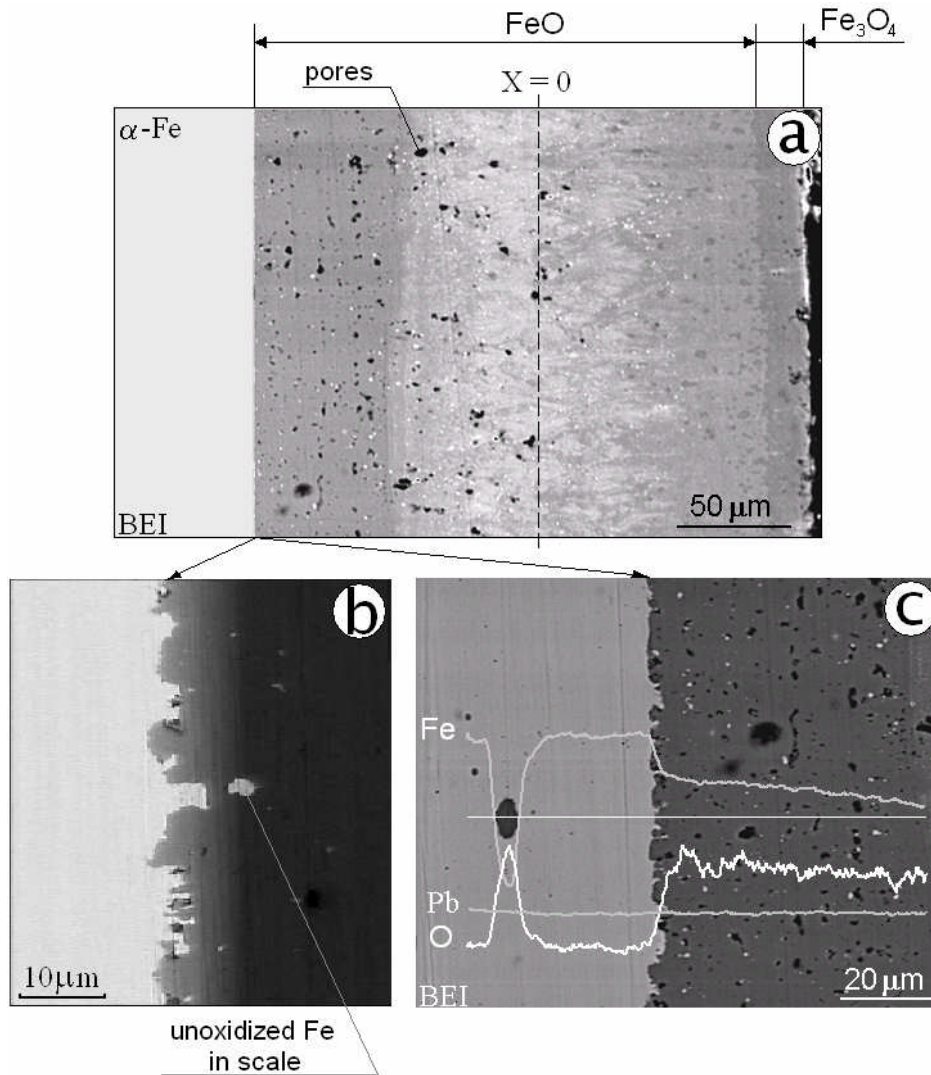
Figure 3. Scale microstructure (*a, b*) and elements distribution in the vicinity of interface "scale – matrix" (*c*) of Armco–Fe specimen after exposure to Pb melt saturated by oxygen at 650°C for 100 h.
X = 0 – initial interface "solid metal / melt".

Accordingly to XRD analysis the upper part of scale consists of magnetite ($Fe_3O_4$) (Fig. 4 a). The peaks of Pb are present in the XRD pattern because of residuals of solidified Pb on the scale surface. The scale was mechanically detached from the specimen surface to study the phase composition of inner part of scale by XRD. The inner part of scale consists of wüstite (FeO) (Fig. 4 b). Thus, the XRD result of inner and outer parts of scale correlates with the atomic contrast of scale (Fig. 3 a), which testifies that the ratio of wüstite and magnetite layers is 10:1. Haematite that is formed on pure iron under air oxidation is not detected in the composition of scale formed in liquid Pb. It could be seen from the image contrast that precipitates of magnetite are

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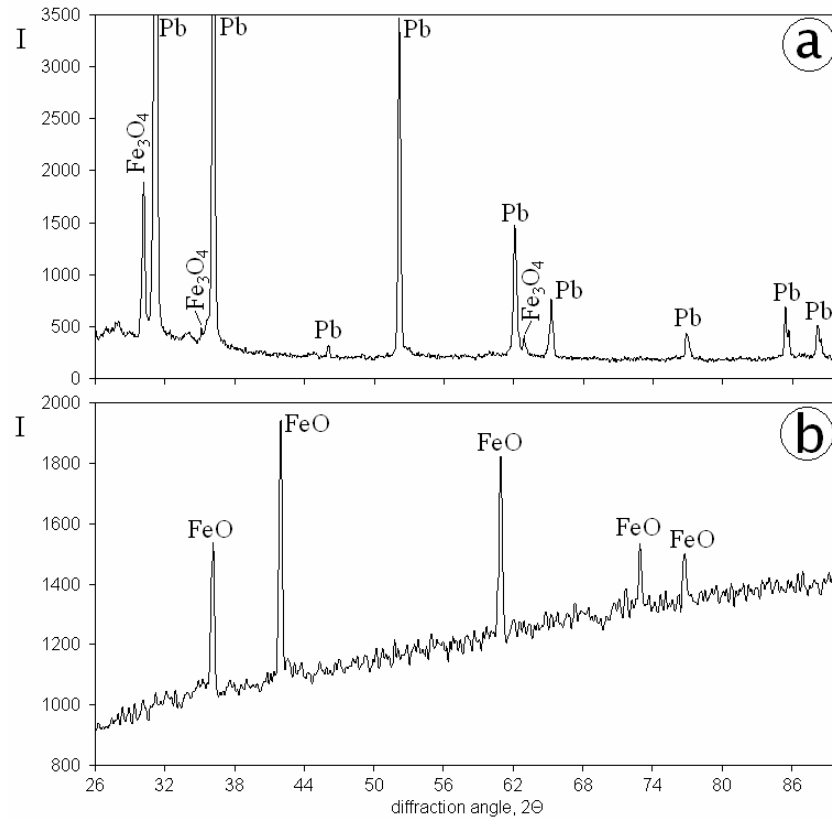situated in the bulk of wüstite close to the wüstite / magnetite interface.



Figure 4. XRD patterns of outer (a) and inner (b) surface of scale formed on the Armco-Fe specimen in the Pb melt saturated by oxygen at 650°C for 500 h (CuKα).

Contrary to the Armco-Fe the scale formed on the steel surface is totally penetrated by Pb (Fig. 5 a). The porous belts parallel to the interface are observed in the scale, especially in inner part at the scale / matrix interface. It was revealed by EPMA that scale consists of the repetitive layers: Fe-enriched oxide layers alternates with layer enriched by Cr, Si and Pb (Fig. 5 *b, c*). The redistribution of Cr is observed in the steel matrix only near the scale / matrix interface (Fig. 5 *c*). It should be noticed that Pb is observed in the scale but does not penetrate into the bulk of steel. Microhardness value of scale is 1 ÷ 3,5 GPa that does not correspond to the hardness of magnetite (~ 5 GPa) while the microhardness of steel matrix is not changed with time and averages ≈ 2,8 GPa. In spite of the fact that the scale is thick, multilayered and contained free Pb, it is holistic and adheres well to the steel surface.

Accordingly to the XRD analysis the scale consists of magnetite mainly (Fig. 6). The peaks of free Pb and its oxides and complex compounds $n$ PbO·$m$ Fe$_2$O$_3$ – plumboferrites are observed also in the XRD pattern.
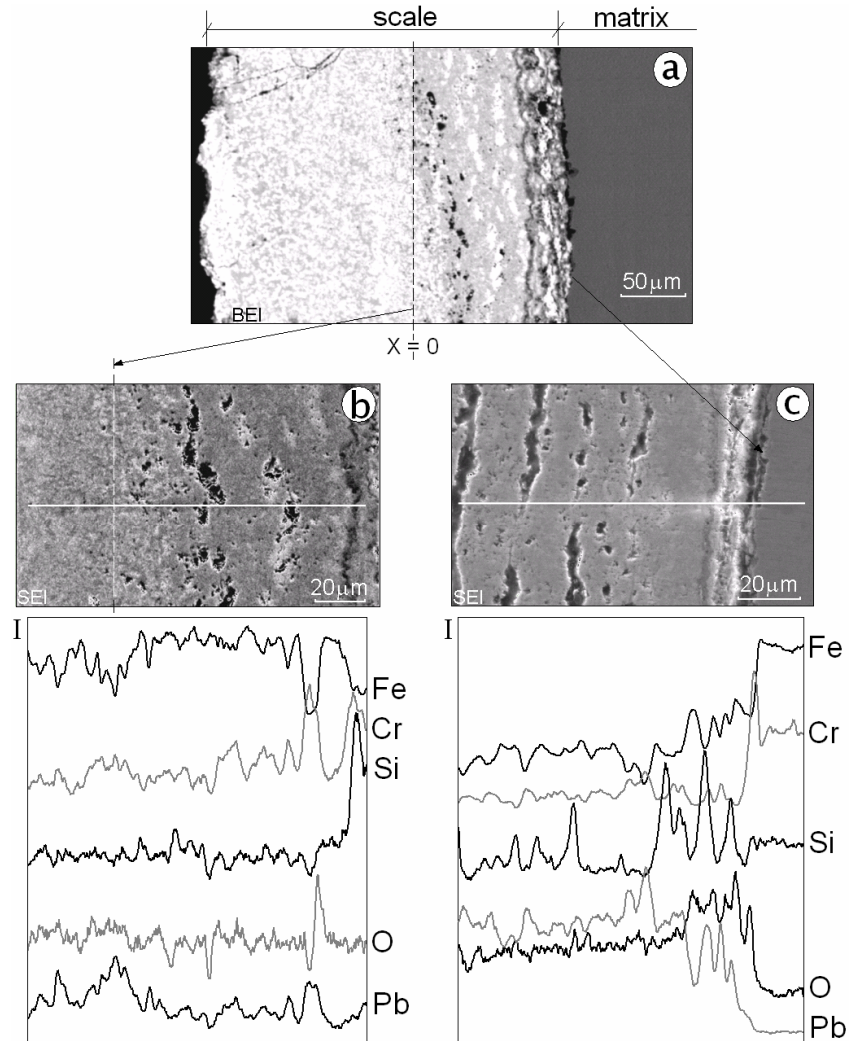


Figure 5. Microstructure (a) and elements distribution in the scale (b) and near "scale / matrix" interface (c) of steel EP–823 specimen after exposure to Pb melt saturated by oxygen at 650°C for 50 h.

The thickness of the specimens of both investigated materials are decreased substantially as a result of intensive oxidation. The corrosion rates are almost the same: 3.0 and 3.82 mm / year for Armco–Fe and steel EP–823 correspondingly.

Distinction in kind of oxidation of specimen's edges of Armco–Fe and steel EP–823 was observed (Fig. 7). The specimen's edges of Armco–Fe are covered completely by scale, whereas the edges on the steel specimens are uncovered. Such configuration of the scale on the specimen's edges can be as evidence that the formation of scales on

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the Armco-Fe and steel EP-823 in liquid Pb saturated by oxygen differs substantially.
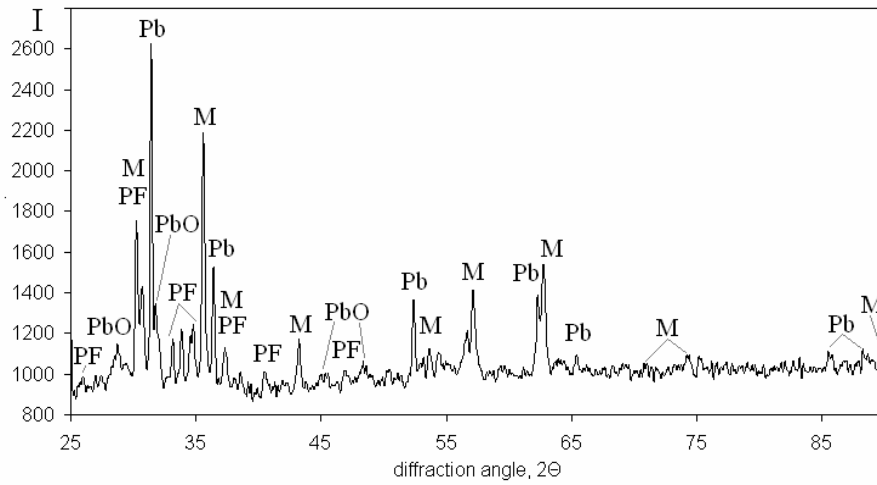


Figure 6. XRD pattern of scale formed on the steel EP-823 specimen in the Pb melt saturated by oxygen at 650°C for 500 h.
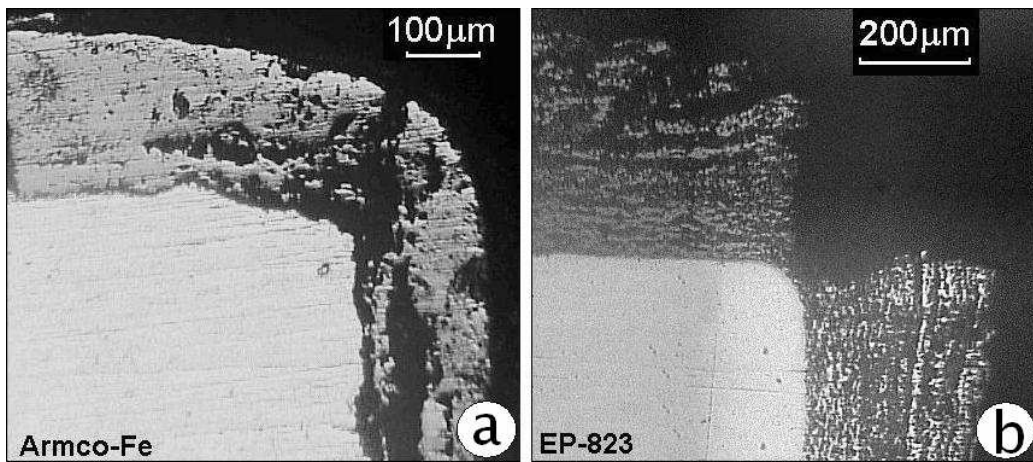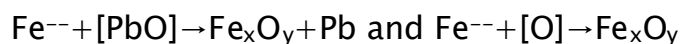M – magnetite, PF – plumboferrite (CuKα).



Figure 7. Cross section of edges of Armco-Fe (a) and steel EP-823 (b) specimens exposed to oxygen-saturated Pb melt at 650°C for 100 h.

## 4. Discussion

When thermodynamic activity of oxygen in the liquid Pb $a_O \rightarrow 1$ the clusters [Pb-O] appear in the melt [14]. These clusters on a par with the solute [O]-atoms can deposit on the surface of oxidized metal (Fe-Armco or steel). The following chemical reaction between growing oxide and adsorbed components depends on the activity of Fe-cations ($a_{Fe}$) at the oxide / melt interface. If $a_{Fe}$ is high enough the next reactions take place mainly:

$$Fe^{--}+[PbO] \rightarrow Fe_xO_y+Pb \text{ and } Fe^{--}+[O] \rightarrow Fe_xO_y$$

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Thus, magnetite (or wüstite–magnetite) scale grows during oxidation. The lack of Fe-cations ($a_{Fe} \rightarrow 0$) provokes reaction between [Pb–O]–clusters and Fe-oxides:

$$Fe_xO_y + [Pb–O] \rightarrow Fe_xPb_yO_z$$
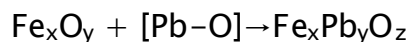
Thus the plumboferrite layer appears.

Plumboferrites were detected in the composition of the scale formed on the steel EP-823. Contrary to the steel the scale formed on the Armco-Fe does not contain plumboferrites and is impervious to the liquid metal. The similar result was observed after exposure of pure Fe to oxygen-saturated Pb-Bi eutectic ($C_{O[Pb-Bi]} = 1.2 \cdot 10^{-3}$ mass %) at 550°C for 500 h [8]. As it can be seen from the micrograph presented in [8] the scale (~ 70 μm) is free from Pb and Bi and possesses by good adhesion to matrix. Authors do not give a composition of the scale, though it is reasonably to suppose that the scale consists of magnetite.

Symmetrical growing of scale with regard to the initial interface X=0, arrangement of pores and non-oxidized incorporations of iron in the inner part of scale mainly allow to suppose that structural defects are of primary importance in the diffusion processes of scale growing. The role of structure defects becomes more evident under taking into account the next considerations: the bulk diffusion of oxygen is impossible because of low oxygen solubility in the iron lattice; both magnetite and wüstite are *p*-type oxides where Fe-cations diffuse preferentially.

Flow of *Fe*-cations towards the melt causes the growth of scale over the initial interface X=0. Here well-known cation mechanism of scale growth like in gas medium is realized. As a result, the opposite flow of *Fe*-vacancies towards the matrix is initiated. It should be emphasized that besides of cation flow for scale growth the additional flow of *Fe*-atoms towards the melt is necessary in order to support the equilibrium state between the liquid metal and surface of oxidizing metal. That means that opposite flow of cation vacancy towards the matrix becomes stronger as well in comparison with oxidation in gas medium. The non-equilibrium vacancies deposit at the structural defects (grain boundaries, sub-boundaries etc.) and coalesce. In such manner the network of micro-pores allowing the non-regular oxygen diffusion into the matrix is formed. Formation of pores under the

oxide / matrix interface causes the dissociation of outer oxide and diffusion of oxygen along micro-channels. In this way the scale grows towards the melt and matrix simultaneously. Owing to high activity of iron ($a_{Fe}$) the [Pb–O]–clusters are being reduced permanently on the scale surface. As a result the scale does not contain Pb.

Therefore, in spite of the thermodynamics the kinetic factor is primary of significance. Permanent moving of cations prevents the formation of plumboferrites ($Fe_xPb_yO_z$) and the scale impervious for liquid metal grows on the surface of Armco iron (Fig. 2).

With respect to steel EP–823 it was reported [9–11, 13] that under lower temperatures and oxygen concentrations in the melt the scale formed on the steel surface consists of outer – $Fe_3O_4$ and inner $(Fe, Cr)_3O_4$ oxide layers and inner oxidation zone where Cr and / or Si are oxidized selectively. Moreover it should be noticed that outer and inner oxides look like mirror image of each other that testifies about their interdependent growing [15].

Under herein test conditions the scale formed on the EP–823 consists of repetitive layers. It seems this layer has the sub-layers enriched by Fe alternating with areas enriched by Cr, Si and Pb (Fig. 5) and reminds the double oxide layer reported in [9–11, 13]. Therefore, it is reasonably to suppose that behavior of steel EP–823 in Pb melt look like cyclic corrosion in gaseous medium. During each cycle the thin double oxide layer grows accordingly to the cation–vacancy mechanism described above for Armco–Fe. Due to active alloying elements (Si, Cr), high temperature and oxygen activity in the melt ($T = 650°C$, $a_O = 1$) The protective double oxide layer could be formed very quickly. Formation of inner spinel $(Fe, Cr)_3O_4$ enriched by Si hampers effectively the iron diffusion towards the melt ($a_{Fe}=0$). Thus the clusters [Pb–O] absorbed on the oxidizing steel's surface become more active and can react with outer magnetite as well as with inner spinel according to state diagram [16]. Because of transformation of spinel layer into plumboferrite the moving of Fe-cations towards the melt renewals and the process of inner spinel and outer magnetite formation repeats. In turn, the increasing of Fe activity in the scale leads to the dissociation of plumboferrite and appearance of free Pb in the scale.

Future investigation should be carried out in order to specify the mechanism of interaction. Especially the questions: why the scale on the steel's surface keeps integrity at high temperature in spite of free Pb in its structure and why the scale does not cover the edges of steel specimen (Fig. 7) should be answered.

Very intensive oxidation of cladding candidate material for fast reactors – ferritic-martensitic steel EP-823 in Pb melt saturated by oxygen underline once more the necessity of keeping of the oxygen content in the melt in the narrow concentration range ($C_{O[Pb]} \approx 10^{-7}...10^{-6}$ wt %) to suppress on the one hand the steel's components dissolution and from the other hand to prevent their intensive oxidation and loop contamination by PbO oxides [4, 13].

## 5. Conclusions

The kinetic peculiarities of scale formation on the surface of ferritic-martensitic steel EP-823 and Armco-Fe in the Pb melt saturated by oxygen ($C_{O[Pb]} = 6 \cdot 10^{-3}$ wt %) at 650°C were elucidated.

- The corrosion of Armco-Fe and steel EP-823 as a function of decreasing of specimens thickness is almost similar, while the scale formed on steel is thicker in comparison with that on the Armco-Fe;

- The phase composition and morphology of scales formed on the investigated materials differ entirely. The spongy scale consisting of magnetite and plumboferrites, totally penetrated by Pb is formed on the steel surface. Contrary to the steel the scale formed on the Armco-Fe is compact, consists of magnetite and wüstite and contains neither Pb nor plumboferrites. Pb does not penetrate into the matrix of investigated materials and was observed only in the scale formed on the steel;

- The cation-vacancy model of scale growing on the Armco-Fe and steel EP-823 in Pb[O] melt taking into account the participation of defects (cation vacancies) in diffusion processes, dissociation of Fe-oxides at the "scale/matrix" interface, existence of the [Pb-O] clusters in the Pb melt and its adsorption on the oxidizing surface of solid metal is discussed.

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