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Corrosion behaviour of low activation steels in flowing Pb–17Li

H. Glasbrenner [*], J. Konys, Z. Voß

Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III, P.O. Box 3640, 76021 Karlsruhe, Germany

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Abstract

The aim of this work is focused on the understanding of the corrosion mechanism of potential structural materials with the eutectic Pb–17Li melt. Therefore, long-term exposure tests have been made on the steels MANET I, F82H-mod. and Optifer IVa in the forced convection Pb–17Li loop PICOLO up to 10 000 h. It was found that two processes are responsible for the corrosive attack: firstly, the dissolution of the oxide scale during the so-called incubation period, which is dependent on temperature and flow velocity of the melt. Secondly, the main corrosion attack consists of a strong depletion of Fe from the steel resulting in a porous low adherent layer on the surface of the steels in which Pb–17Li could penetrate easily. Unfortunately this layer has no capability of protecting the steel from further corrosion attack but is eroded away by the flowing eutectic melt. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The corrosion of structural materials is one of the issues to be investigated for the water-cooled liquid lead–lithium (WCLL) blanket concept. The eutectic melt with 83 at.% lead and 17 at.% lithium is considered as an attractive breeding material for future fusion reactors. Various studies were carried out exposing steel samples to Pb–17Li under static and dynamic conditions [1–5]. Two classes of steels were mainly investigated, austenitic and ferritic steels. The temperatures were varied between 400°C and 600°C. The composition of the eutectic was carefully controlled in most cases. Generally, no grain boundary attack by liquid lead and lead alloys was observed. It was found that austenitic steels have a poor resistance to Pb–17Li because of the high solubility of nickel in the melt [6,7]. For ferritic steels the corrosion, of after a more or less pronounced incubation period, is governed by uniform dissolution of iron and chromium at a rate that is distinctly less than that for nickel [2,5] as in the case of austenitic alloys. This behaviour suggests ferrites as the structural material in a liquid breeder blanket design. According to the requirements to use low-activation steels as structural materials ferritic 7–10% Cr alloys were developed for the application in fusion reactors [8]. Three of them, MANET I, Optifer IVa and F82H-mod., were exposed to the pumped Pb–17Li loop named PICOLO at 480°C.

2. Motivation

As published previously [9,10] it was found that two mechanisms are responsible for the corrosion process. Firstly, the dissolution of the passivating oxide layer happens on top of the steel surface. Secondly, the dissolution of the steel occurs whereby the elements with a high solubility in Pb–17Li, namely Fe and Cr, are partly leached out of the matrix. The remaining porous layer is enriched with steel elements which have a low solubility in Pb–17Li, e.g. W, V and Mo. Only small spots of such remaining layers were observed by energy dispersive line-scan analysis on the surface of samples exposed to Pb–17Li at 480°C for 1000 and 8000 h. The thickness of this layer increased with longer exposure time. Up to

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[*] Corresponding author. Delegated to Paul-Scherrer-Institut, 5232 Villigen PSI, Switzerland. Tel.: +41-7247 823 723; fax: +41-7247 823 956.

E-mail address: heike.glassbrenner@psi.ch (H. Glasbrenner).

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now in literature only the uniform dissolution of ferritic steels was mentioned.

The adherent Pb–17Li is normally removed from the surface of the specimens before the analysis. The question arose if the porous layer was always removed during the washing procedure and therefore was never detected in previous experiments or if this layer was only an intermediate product without any protecting character which was easily eroded by the flowing liquid alloy. In order to clarify these questions some of the exposed specimens were not cleaned after testing and were examined with the remaining Pb–17Li on the surface. The results are presented in this paper.

3. Experiments

The test loop PICOLO is used for corrosion measurements on structural materials in flowing Pb–17Li. It consists of a 'figure-of-eight' type loop with a central recuperative heat-exchanger, a test section (hot leg) and a cold leg for corrosion product deposition and impurity removal with a pump, flow meter, cooler and magnetic trap. Heat exchanger, main heater, test section (hot leg) and the tubes of the hot section were fabricated of ferritic steel (DIN 1.4922) whereas in the cold section austenitic steel (DIN 1.4571) was used. The whole circuit was connected to a dry Ar 5.0 glove box on top of the expansion vessel. The glove box had a gas purification unit, which was capable to keep the oxygen concentration below 1 ppm. The Pb–17Li alloy was molten in the glove box and filled into the loop through the expansion vessel. A dump tank served for draining the liquid metal if necessary. The test section is a tube of 16-mm inner diameter and 440 mm length. Cylindrical corrosion test specimens had the dimensions of 8 mm in diameter and 35 mm length. They had threads on both ends, thus they could be mounted to a stack of 12 pieces fixed in the central position of the test section tube. The total length of the connected specimens was 400 mm. The pumping speed was 120 l/h, which corresponds to a flow velocity of 0.3 m/s. The temperature in the test section was maintained at (480 ± 5)°C, the coldest temperature before the magnetic trap was 350°C.

Three ferritic-martensitic steels have been selected for corrosion testing in Pb–17Li: MANET I, F82H-mod. and Optifer IVa. The chemical composition of these steels in wt% is given in Table 1. Hardening and tempering processes were carried out under vacuum (10^{-6} bar). The conditions chosen corresponded to the instruction given by the supplier and are summarised in Table 2. The corrosion testing on these steels is a repetition of tests published previously [9,10] in order to clarify the formation of the porous layer. Hence, the number of specimens and also the variation of exposure time are limited because of the time consuming tests.

Corrosion specimens were taken out of the liquid metal and replaced by fresh ones. The maximum exposure time was 10 000 h (F82H-mod.). The adherent Pb–17Li was removed from the specimens exposed for 2000 h by washing in a mixture of CH_3COOH, H_2O_2 and C_2H_5OH (1:1:1). Specimens exposed for 4000, 9000 and

Table 1
Chemical composition of the investigated steels in wt%, Fe – balance

Steel	Cr	C	Mn	V	W	Mo	Ni
MANET I	10.6	0.13	0.82	0.22	–	0.77	0.87
F82H-mod.	7.7	0.09	0.16	0.16	1.95	–	–
Optifer IVa	8.5	0.11	0.57	0.23	1.16	–	–

Table 2
The conditions for hardening and tempering processes of the three steels

Steel	Hardening process	Tempering process
MANET I	1075°C/30 min	750°C/2 h
F82H-mod.	1040°C/30 min	750°C/1 h
Optifer IVa	900°C/30 min	750°C/2 h

Table 3
Experimental conditions for the investigated ferritic-martensitic steels

Steel	2000 h exposure	4000 h exposure	9000 h exposure	10 000 h exposure
MANET I	Washed	–	Not washed	–
F82H-mod.	Washed	Not washed	–	Not washed
Optifer IVa	Washed	Not washed	–	–

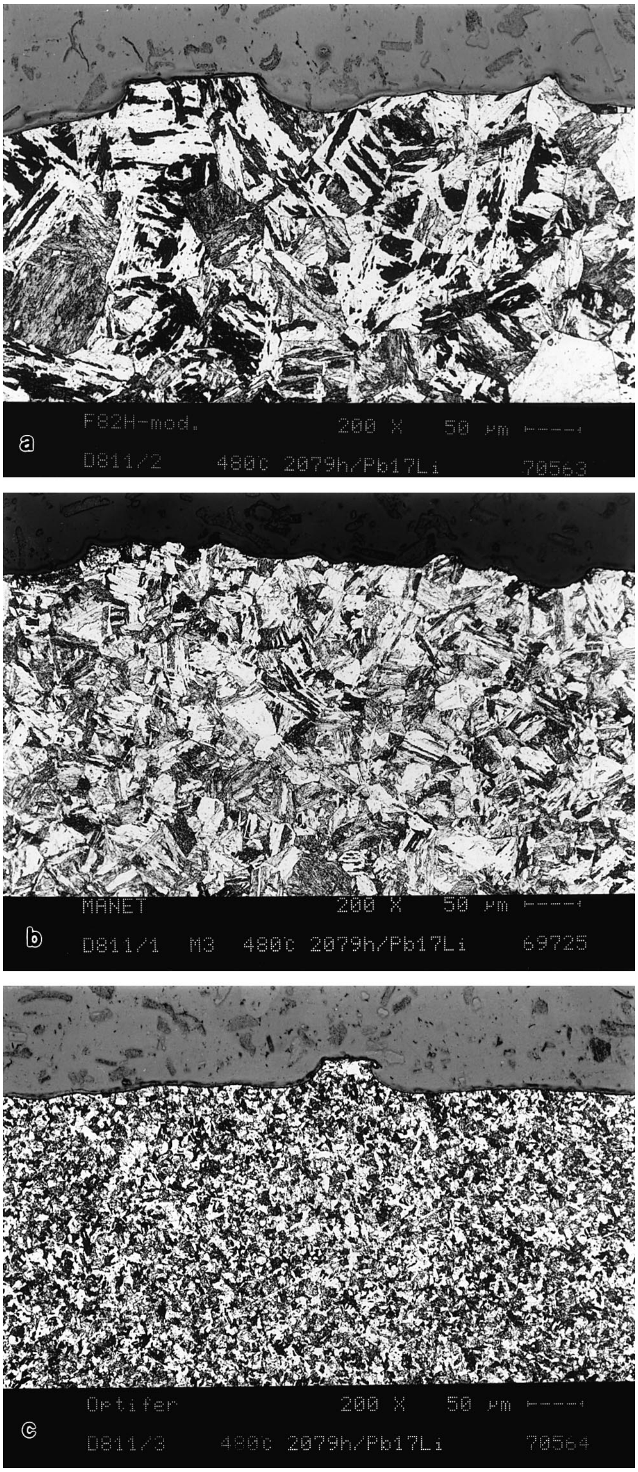

Fig. 1. Etched cross sections of (a) F82H-mod., (b) MANET I and (c) Optifer IVa exposed for 2000 h in Pb–17Li at 480°C.

10 000 h were not cleaned in order to avoid removing of the porous layer. The experimental conditions are summarised in Table 3. After exposure the specimens were cut and prepared for analytical investigations by optical microscopy, SEM/EDX mapping and EDX line-scan analysis.

4. Results

The corrosion behaviour of the three steels investigated was quite similar and no significant differences were observed. Hence, in the following the observations were not subdivided for each steel but presented together.

The etched cross-sections of the steel specimens exposed to Pb–17Li for 2000 h are shown in Fig. 1((a)–(c)). The beginning of the corrosive attack was found to be inhomogeneous. Unattacked areas, which still showed the original surface of the specimens and areas, which were already heavily attacked by the eutectic, are visible. This fact is due to the presence of passivating oxide scales on top of the steel surfaces [9,10], which might have a difference in thickness and composition. These scales consist of $MnCr_2O_4$ and $(Fe,Cr)_2O_3$ detected by means of XPS and AES analysis [11] and were formed during the heat treatment of the steels. The wetting of a passivated steel surface by Pb–17Li needs time (e.g. up to 3000 h of incubation time at 500°C [3]) before the samples fully interact with the flowing eutectic. This phenomenon is the so-called incubation period thereafter the corrosion proceeded distinctly faster by dissolution of iron and chromium.

The metallographic cross-sections of the specimens exposed for 4000, 9000 and 10 000 h looked quite similar. The sample surfaces were covered all over with solidified Pb–17Li because of avoiding the washing procedure. The oxide scale was already completely dissolved after 4000 h of exposure. The surface of the specimens was relatively smooth and showed a macroscopic wave-like contour as can be seen in Fig. 2(a) and (b). The microhardness values measured for all exposed specimens corresponded to the original values, hence the temperature had no influence on the microstructure of the bulk materials also after long-time exposure. Generally, intergranular attack and formation of a porous layer by leaching of alloying steel elements could not be detected on corroded specimens by means of metallographic examinations.

EDX line-scan analysis was carried out on two different areas of each sample. In the following, the measured spectra are described in detail. No enrichment of any element could be observed in the surface near region of the MANET I specimens exposed to Pb–17Li for 2000 h. On the contrary, an enrichment of tungsten on the steel surfaces was stated on F82H-mod. (Fig. 3) and Optifer IVa (Fig. 4), both corroded for 2000 h. In the case of F82H-mod., the iron content decreased and the chromium content remained relatively unchanged compared to the steel composition in this tungsten rich region. In the case of Optifer IVa, the iron content decreased as well, but the chromium content seemed to increase like the tungsten content in this zone. The thickness of the enriched porous zones was of about 7 μm on the steel surface of both specimens.

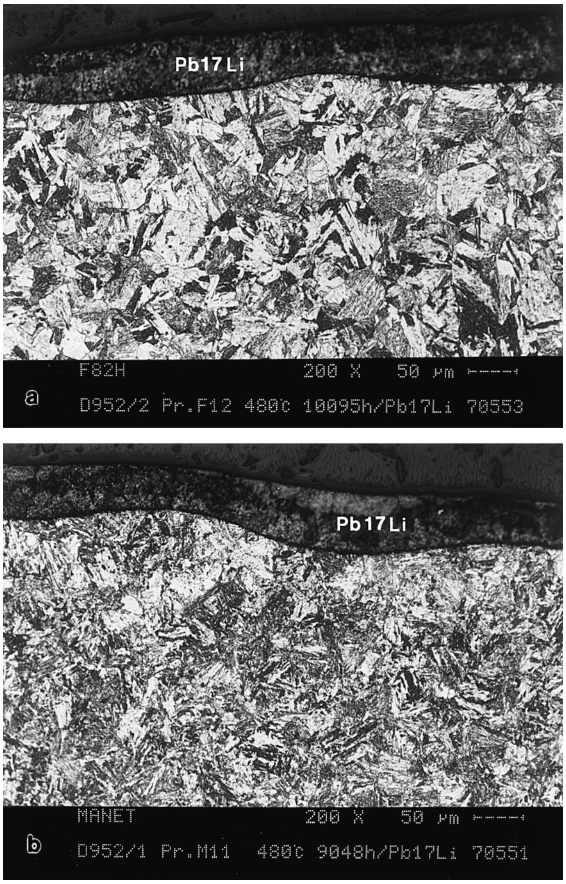

Fig. 2. Etched cross-sections of (a) F82H-mod. exposed for 10 000 h and (b) MANET I exposed for 9000 h in Pb–17Li at 480°C.

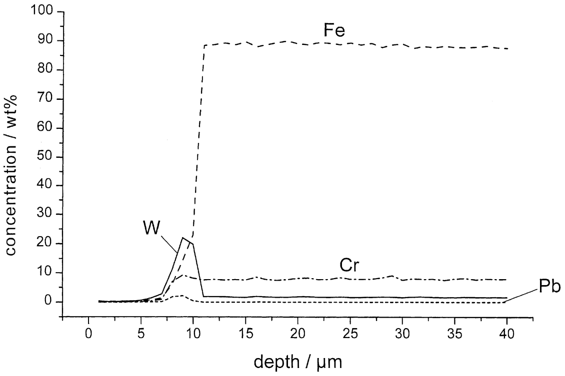

Fig. 3. EDX line scans across the cross-section of F82H-mod. after 2000 h of exposure to Pb–17Li at 480°C. Adherent Pb–17Li on the steel surface was washed off.

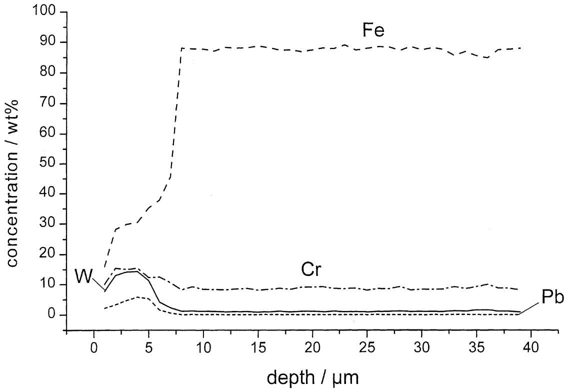

Fig. 4. EDX line scans across the cross-section of Optifer IVa after 2000 h of exposure to Pb–17Li at 480°C. Adherent Pb–17Li on the steel surface was washed off.

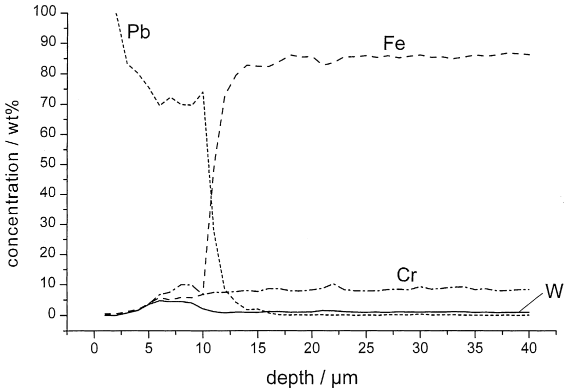

Fig. 5. EDX line scans across the cross-section of Optifer IVa after 4000 h of exposure to Pb–17Li at 480°C. Solidified Pb–17Li was not removed.

One has to bear in mind that all three specimens ($t = 2000$ h) were cleaned from adherent Pb–17Li. No or only a small amount of Pb was therefore found on the sample surfaces. Unfortunately the element Li cannot be measured by means of the EDX method. A slightly higher Pb content could be detected in the porous corrosion zones (Figs. 3 and 4). The EDX spectra of a F82H-mod. specimen exposed for 4000 h did not show any enrichment on the surface. There was a sharp transition from the steel surface to the adherent solidified Pb–17Li. The concentration of steel elements decreased within of around 2 µm from their original values down to zero. The EDX spectra on Optifer IVa corroded for 4000 h (Fig. 5) showed a slight enrichment on the surface of tungsten and chromium. In contrary to this, the iron content on the surface decreased by leaching of the steel matrix. A porous layer about 7 µm in thickness, therefore, remained into which Pb–17Li could have penetrated easily. The MANET I specimen exposed for 9000 h did not show any enrichment of molybdenum, only a thick layer of solidified Pb–17Li was found on the steel surface. A sharp transition of the element concentration from the steel surface to the adherent solidified eutectic Pb–17Li in the range of about 2 µm underlines this fact. The EDX spectra of F82H-mod. exposed to Pb–17Li up to 10 000 h is shown in Fig. 6. The transition from the steel composition to the adherent solidified Pb–17Li took place across circa 7 µm with a slight enrichment of tungsten and a decrease of iron and chromium.

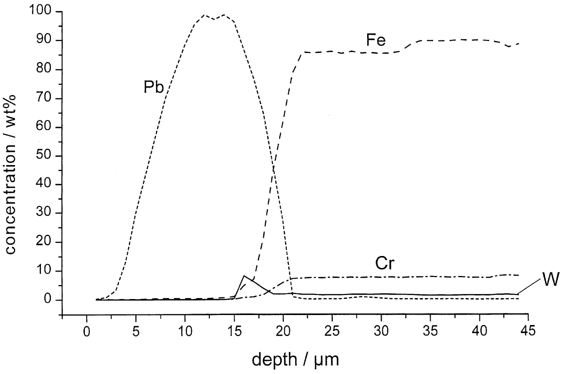

Fig. 6. EDX line scans across the cross-section of F82H-mod. after 10 000 h of exposure to Pb–17Li at 480°C. Solidified Pb–17Li was not removed.

5. Discussion

The studies carried out have been mainly focused to understand the corrosion mechanism of potential structural materials by Pb–17Li and to compare them with the results obtained previously [3,9,10]. The three materials investigated correspond to the same class of steels, i.e. they are similar in composition and structure. Thus, the observed behaviour of the steels in Pb–17Li was quite similar. The corrosive attack was found to be a two-step process: firstly, the dissolution of the passivating oxides occurs during the so-called incubation period, and secondly the dissolution of the steel matrix is followed. Already after 2000 h of exposure, only little parts of the original surface were still visible, after 4000 h the oxides disappeared completely. These observations are in full agreement with results published earlier by Borgstedt et al. [3] for MANET I steel, who found an incubation period of about 3000 h at 500°C and 2700 h at 550°C. These corrosion examinations were carried out in the same test facility, the PICOLO loop, in which the flow velocity of the liquid melt was aboutd 0.3 m/s in the test section.

Contrary to these results, the measured incubation period required longer times (> 6000 h) in the tests presented in [9,10] for all investigated ferritic-martensitic steels. One reason for this difference could be the change in flow velocity of the liquid melt. During the operation of PICOLO, the amount of precipitations increased in the magnetic trap and in the cold sections of the loop. This precipitation was dissolved from the specimens as well as from the structural parts of the loop in the hot section. Results presented in [9,10] were obtained on specimens which have been corroded in the PICOLO loop as well, but the loop was nearly completely plugged at the end of the test. The claim was to reach the required exposure times (8000 h) before stopping the loop to remove these particles to reach again the required flow rate of 0.3 m/s. As a result the flow velocity decreased continuously from 0.3 m/s down to around 0.1 m/s. The incubation period is therefore not only dependent on temperature [3] but also on flow velocity. With increasing flow rate, the incubation period decreased due to the influence of erosion.

A second effect of the low flow velocity in the former test was the presence of porous areas of about 7 μm in maximum thickness on top of the steel surfaces which were not eroded. The elements W, Mo and V with a low solubility in Pb–17Li were enriched in this porous area. The concentration of the steel elements Fe and Cr decreased compared to the concentration in the matrix.

In contrary to this, no porous areas or layers could be observed by means of metallography on specimens corroded in Pb–17Li with a flow rate of 0.3 m/s. The results obtained by EDX can be interpreted as follows. An enrichment of W was found on nearly all F82H-mod. and Optifer IVa specimens independent of exposure time and post treatments. The thickness of the enriched porous zone was about 5 μm and the layers were characterised by a strong Fe depletion and by Pb and Li penetration into the porous area. Pb could also be analysed in the porous layers on specimens, which went through the washing procedure. This fact underlines the porous character of the reaction zone. On MANET I steel sheets, no enrichment of Mo or V was observed independent of the exposure time of the specimens (2000 h and 9000 h). A possible reason for this observation might be the content of W, which is much higher in F82H-mod. and Optifer IVa than that of Mo in MANET I.

The constant flow velocity of 0.3 m/s seems to be responsible for the decrease of incubation time from over 6000 h to less than 4000 h. The porous layer formed is easily eroded by the flowing melt and no thick layer can be formed as described in the previous tests [9,10]. The protecting character of this low adherent layer can be neglected.

6. Conclusions

The corrosion of three ferritic-martensitic steels by Pb–17Li was examined. Two different processes are responsible for the corrosive attack. Firstly, the passivating oxide layer on the steel surface is dissolved. This so-called incubation period is dependent on temperature and on the flow velocity of the melt. The second step is the dissolution of the steel matrix which is characterised by a strong depletion of the steel element Fe. The remaining porous zone shows a low adherence to the steel matrix and can be easily eroded from the surface by the flowing melt. The thickness did not exceed 5 μm. Hence, no protecting character can be ascribed to the W enriched and Pb–17Li penetrated layer.

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