Investigation of Ferritic-martensitic Steels in Flowing Pb-17Li

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Technik und Umwelt

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Abstract

The aim of this work was focussed on trying to understand the corrosion mechanism of potential structural materials with the eutectic melt Pb-17Li. Long-term exposure tests have therefore been made on the steels MANET, 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 on flow velocity of the melt. Secondly, the main corrosion attack in which Fe is strongly depleted from the steel resulted in a porous low adherent layer on the surface of the steels in which Pb-17Li could penetrate easily. Unfortunately this layer has not the capability of protecting the steel for further corrosion attack but is eroded away by the flowing eutectic melt.

Korrosionsverhalten ferritisch-martensitischer Stähle in strömendem Pb-17Li

Kurzfassung

Der Einfluß des Brutmaterials Pb-17Li auf drei verschiedene ferritisch-martensitische Werkstoffe (MANET I, Optifer IVa und F82H-mod.) wurde bis zu Auslagerungszeiten von 10000 h bei 480 °C untersucht. Die Fließgeschwindigkeit des Flüssigmetalls Pb-17Li betrug 0,3 m/s in der Teststrecke des PICOLO-Kresilaufs. Ziel der Arbeit war es, den für die Metallauflösung verantwortlichen Korrosionsmechanismen aufzuklären.

Es wurden zwei unterschiedliche Prozesse gefunden, die den Korrosionsangriff bestimmen. Zuerst wird die Oxidschicht auf der Stahloberfläche aufgelöst. Dieser Vorgang ist abhängig von der Temperatur und der Fließgeschwindigkeit des Flüssigmetalls sowie von der Dicke der Oxidschicht. Anschließend erfolgt die Metallauflösung nach folgendem Mechanismus: Zuerst werden die Stahlhauptbestandteile Fe und Cr, die beide eine relativ gute Löslichkeit in Pb-17Li haben, herausgelöst. Die zurückbleibende sehr poröse Schicht besteht aus den in der Schmelze schlechter löslichen Stahlelementen wie W, Mo und V sowie aus Pb-17Li, das in die Schicht hinein diffundiert. Die Schicht schützt den Stahl nicht gegen weitere Korrosionsangriffe, da sie durch vorbeiströmendes Pb-17Li weg erodiert wird.

Content

1. Introduction

For the water-cooled liquid lead-lithium (WCLL) blanket concept, the corrosion of structural material is one of the issues to be investigated. The eutectic melt with 83 at% lead and 17 at% lithium is considered as an attractive breeding material for future fusion reactors.

Various studies have been carried out exposing steel samples to Pb-17Li under static and dynamic conditions [1-5]. Two classes of steels have been mainly investigated, austenitic and ferritic steels. The temperatures have been varied between 400 and 600 °C. The composition of the eutectic has been 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 in Pb-17Li because of the high solubility of nickel in the melt [6, 7]. For ferritic steels the corrosion 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 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. have been exposed in the pumped Pb-17Li loop named PICOLO at 480 °C.

2. Motivation

As published previously [9, 10] it was found that two mechanism are responsible for the corrosion process. Firstly, the dissolution of the passivating oxide layer on top of the steel surface happens. 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 EDX line scan analysis on the surface of samples exposed to Pb-17Li at 480 °C for 1000 and 8000 h, resp. With longer exposure time, the thickness of this layer increased as well. These observations made in our laboratory were never before described in the literature in which only the uniform dissolution of ferritic steels was mentioned.

Before the analysis started, the adherent Pb-17Li was removed from the surface of the specimens by washing in a mixture of CH_3COOH, H_2O_2 and C_2H_5OH (1:1:1). The question arised if this porous layer was always removed during the washing procedure and therefore

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never was 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 this fact some of the exposed specimens were not cleaned after testing and were examined with remaining Pb-17Li on the surface. The results will be presented in this paper.

3. Experiments

For corrosion measurements on structural materials in flowing Pb-17Li, the test loop PICOLO is used. 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 in length. Cylindrical corrosion test specimens had the dimensions of 8 mm in diameter and 25 mm in length. They had threads on both ends, thus they could be mounted to a stack of 16 pieces fixed in the central position of the test section tube. The length of the connected specimens was 400 mm in total. 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 °C ± 5 K, 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.

	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 1: Chemical composition of the investigated ferritic-martensitic steels in wt.%.

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.

	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 2: The conditions for hardening and tempering processes for the three steels.

The corrosion testing on these steels is a repetition in order to clarify some open points concerning the porous layer. Hence, the number of specimens and also the variation of exposure time is 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 h, 9000 h and 10,000 h were not cleaned in order to avoid the removing of the porous layer. The experimental conditions are summarised in table 3. The specimens corroded were cut and prepared for analytical investigation by optical microscopy, SEM/EDX and EDX line scan analysis.

	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	--	--

Table 3: Experimental conditions of the investigated ferritic-martensitic steels.

4. Results

The material loss has been previous discussed in detail [9, 10] and will not be presented in this paper. The corrosion behaviour of the three steels investigated was quite similar and no significant differences were observed. Hence, in the following the observations made were not subdivided for each steel but presented together.

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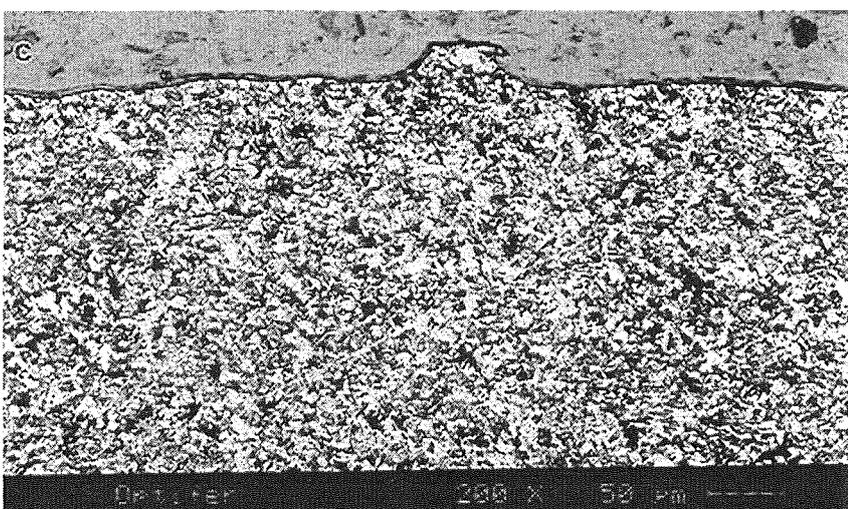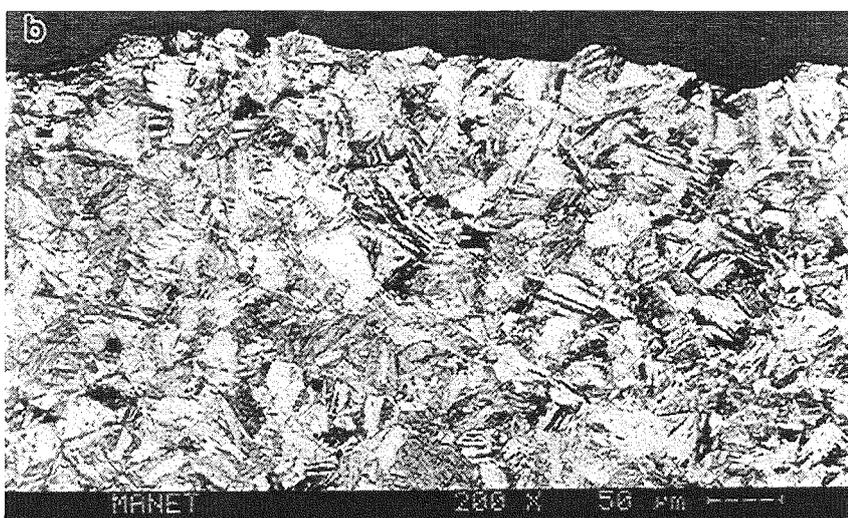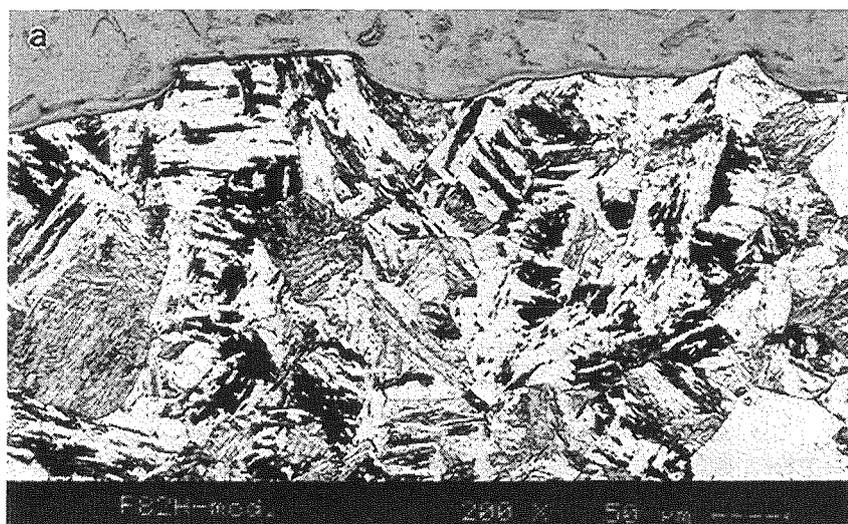
Fig. 1: Etched cross sections of a) F82H-mod., b) MANET I and c) Optifer IVa exposed for 2000 h in Pb-17Li at 480°C.

In fig. 1 a-c, the etched cross sections of the steel specimens exposed to Pb-17Li for 2000 h are shown. 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 consisted of $MnCr_2O_4$ and $(Fe,Cr)_2O_3$ which are known to be unstable in Pb-17Li, thus they got dissolved slower than the steel matrix. This phenomena was the so-called incubation period thereafter the corrosion proceeded distinctly faster by dissolution of iron and chromium.
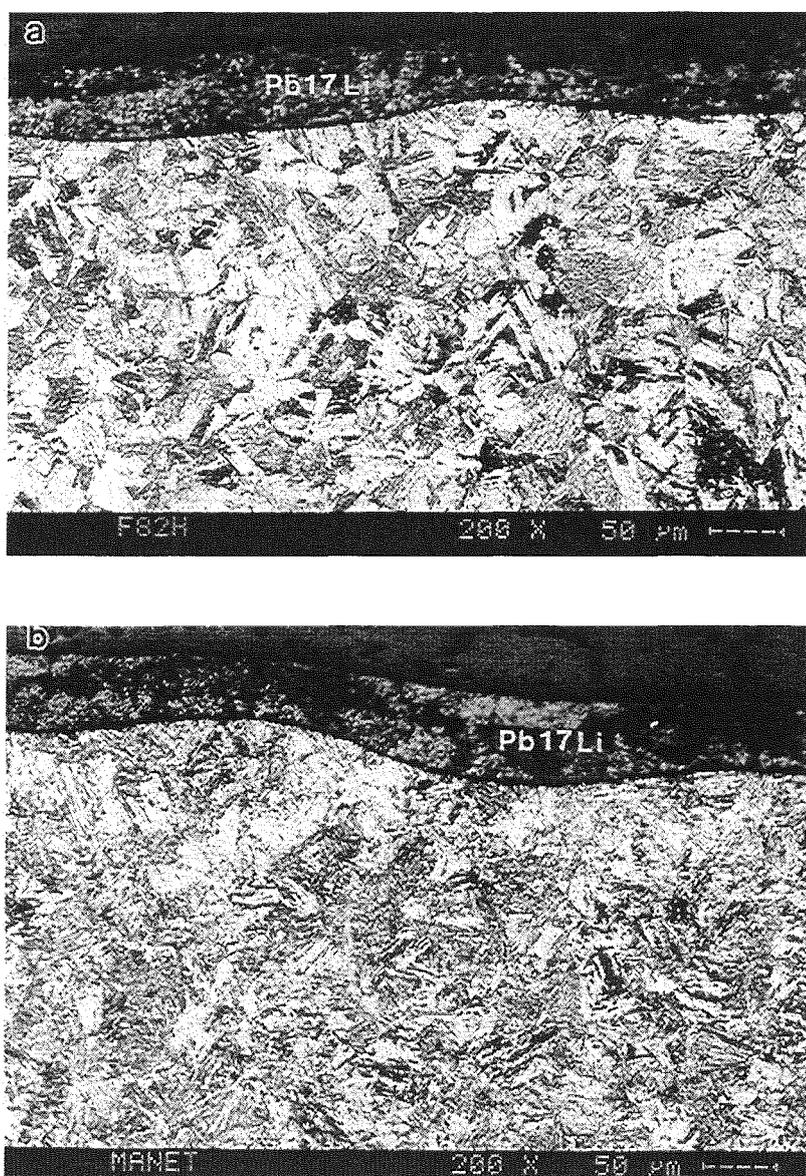
Fig. 2: Etched cross sections of a) F82H-mod. exposed for 10,000 h and b) MANET I exposed for 9000 h in Pb-17Li at 480°C.

The metallographical cross sections of the specimens exposed for 4000 h, 9000 h and 10,000 h, resp. looked quite similar. The sample surfaces were covered all over with solidified Pb-17Li because of avoiding the washing procedure. The oxide scale is already completely dissolved after 4000 h of exposure. The surface of the specimens was relatively smooth and shows a macroscopic wavelike contour as can be seen in fig. 2 a and b. The micro hardness values measured for all exposed specimens corresponded to the origin values, hence the temperature had no influence to the micro structure of the bulk materials also after long time.

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 metallographical examinations.

EDX line scan analysis were carried out on two different areas of each sample. In the following the spectra measured will be described in details. On the surface of the MANET specimens exposed for 2000 h to Pb-17Li no enrichment of any element could be observed (see fig. 3). On the contrary to this an enrichment of W on top of the steel surfaces was revealed on F82H-mod. (fig. 4) and Optifer IVa (fig. 5), both corroded for 2000 h. In the case of F82H-mod. the iron content decreased and the chromium content stayed relatively unchanged compared to the steel composition in this W rich region.
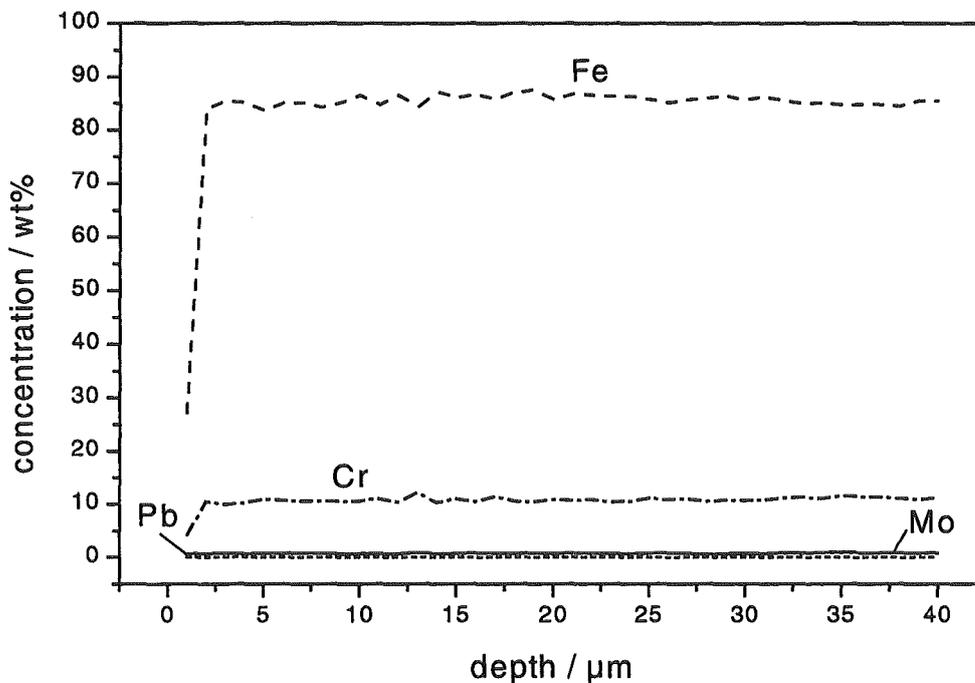
Fig. 3: EDX line scans across the cross section of MANET after 2000 h of exposure to Pb-17Li at 480°C. Adherent Pb-17Li on the steel surface was washed off.

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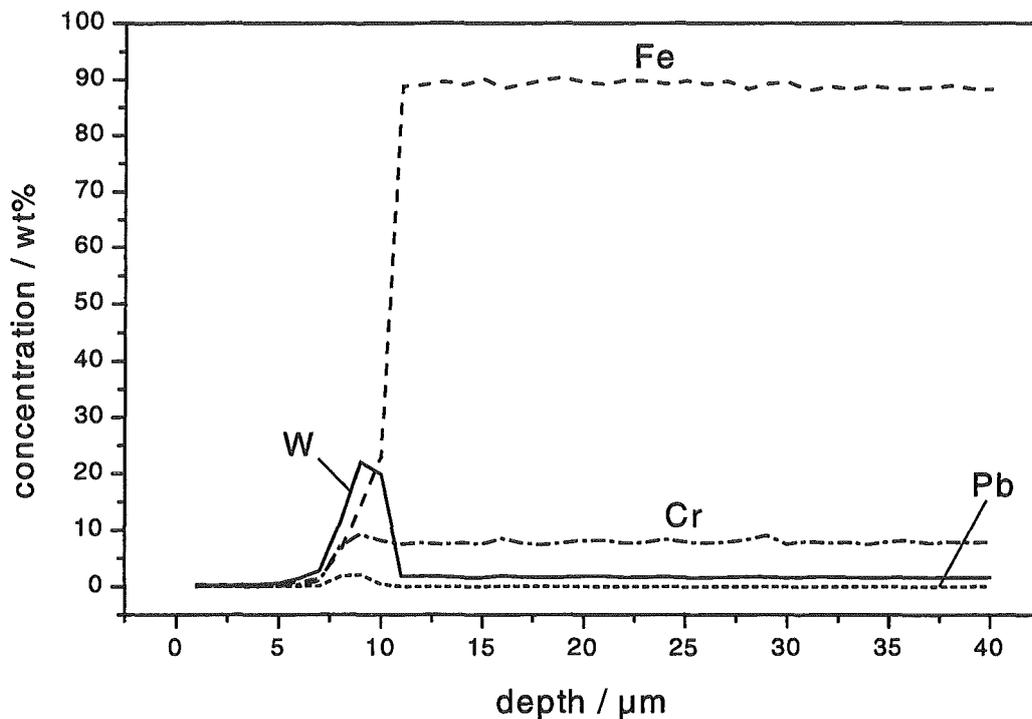
Fig. 4: EDX line scans across the cross section of F82H-mod. after 2000 h of exposure to Pb-17Li at 480°C. Adherent Pb-17Li on the steel surface was washed off.
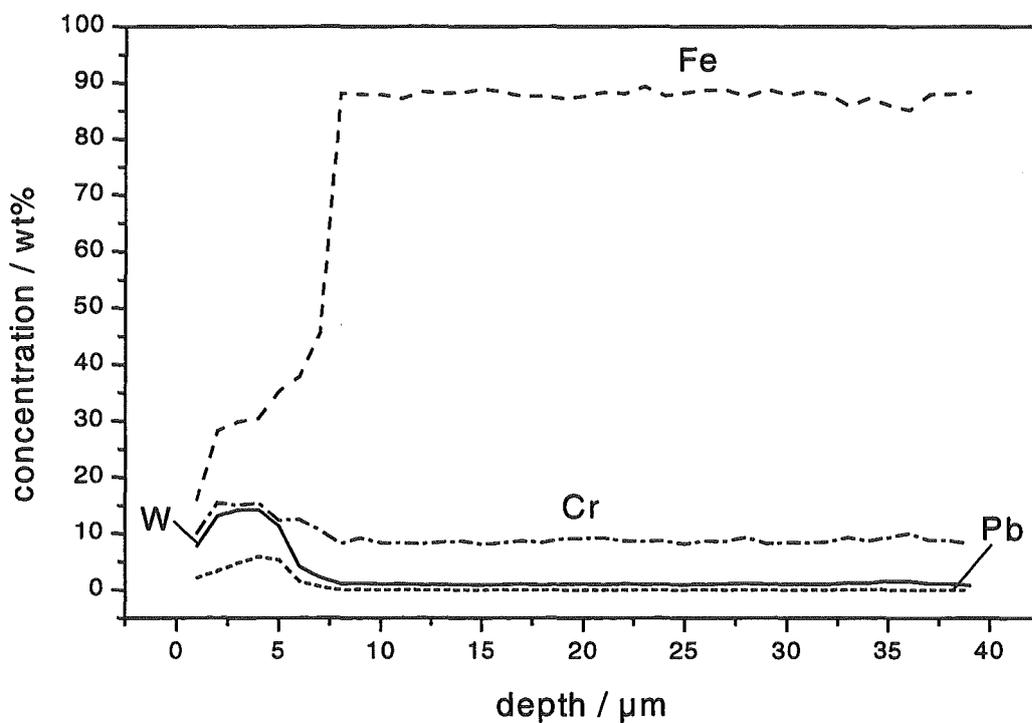
Fig. 5: EDX line scans across the cross section of Optifer IVa after 2000 h of exposure to Pb-17Li at 480°C. Adherent Pb-17Li on the steel surface was washed off.

In the case of Optifer IVa the iron content decreased as well, but the chromium content seemed to increase like the W content. One has to bear in mind that all three specimens were cleaned from adherent Pb-17Li, no or only a small amount of Pb was therefore found on the sample surfaces.

Fig. 6 shows the EDX spectra of a F82H-mod. specimen exposed for 4000 h. On top of the surface no enrichment of any element could be detected. There was a sharp transition from the steel surface to the adherent solidified Pb-17Li. The steel elements decreased within of around 2 μm from their steel values down to zero.
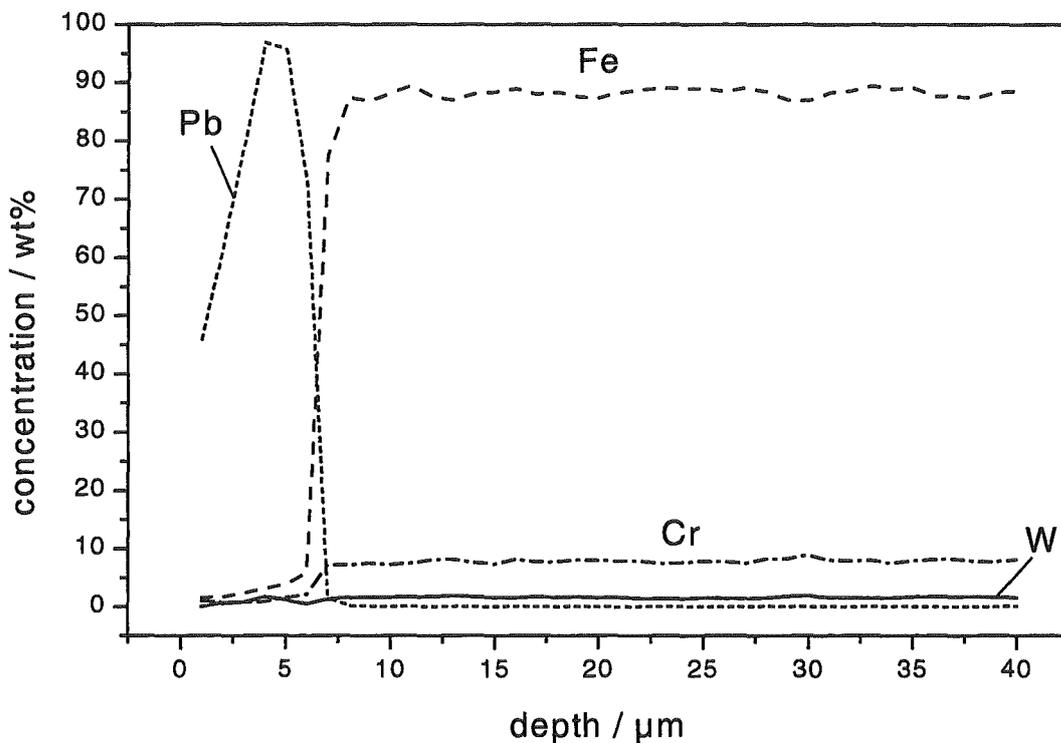
Fig. 6: EDX line scans across the cross section of F82H-mod. after 4000 h of exposure to Pb-17Li at 480°C. Solidified Pb-17Li was not removed.

In the spectra of Optifer IVa corroded for 4000 h (fig. 7) a slight enrichment of W and Cr was observed on the surface. In contrary to this the iron content decreased by leaching of the steel matrix. An extreme porous layer, therefore, remained in which Pb-17Li could have penetrated easily in.

The MANET specimens exposed for 9000 h did not show any enrichment of Mo, only a thick layer of solidified Pb-17Li was revealed on the steel surface (fig. 8).
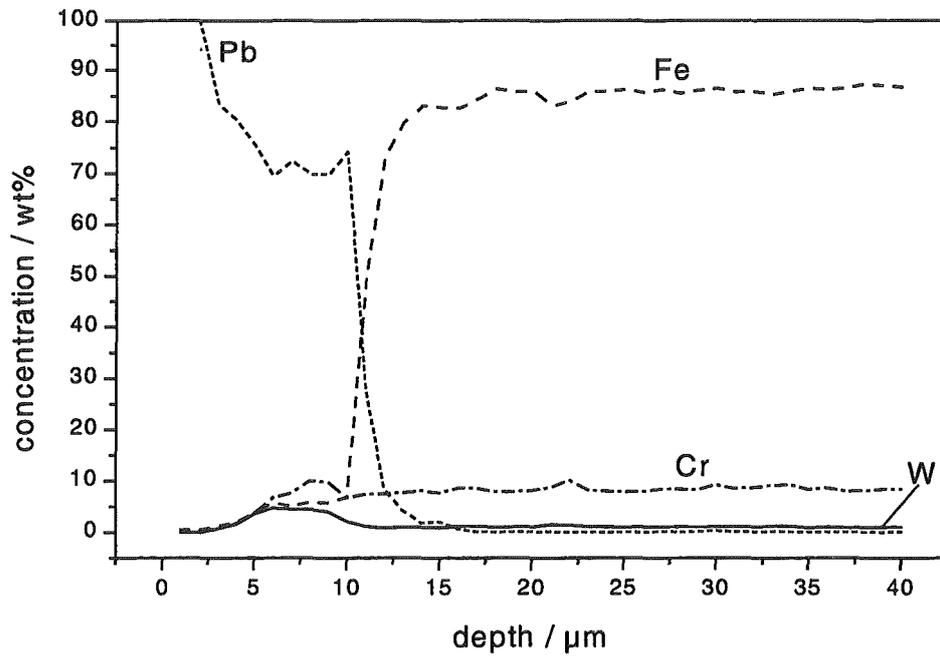
Fig. 7: EDX line scans across the cross section of Optifer IVa after 4000 h of exposure to Pb-17Li at 480°C. Solidified Pb-17Li was not removed.
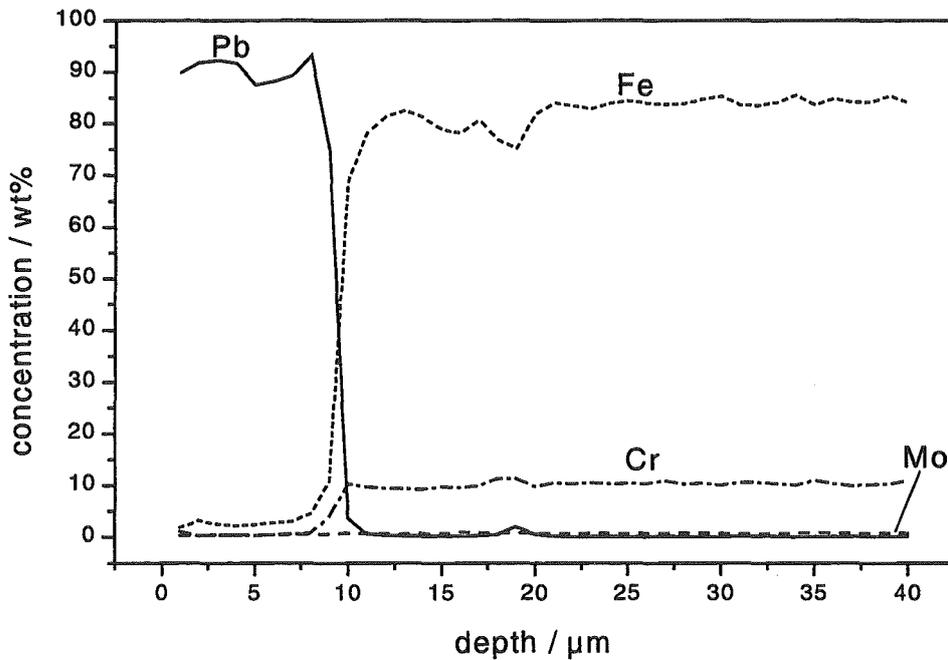
Fig. 8: EDX line scans across the cross section of MANET after 9000 h of exposure to Pb-17Li at 480°C. Solidified Pb-17Li was not removed.

The EDX spectra of F82H-mod. exposed to Pb-17Li up to 10,000 h is shown in fig. 9. The transition from the steel composition to the adherent solidified Pb-17Li took place over around 8 μm. A slight enrichment of W could be observed as well.
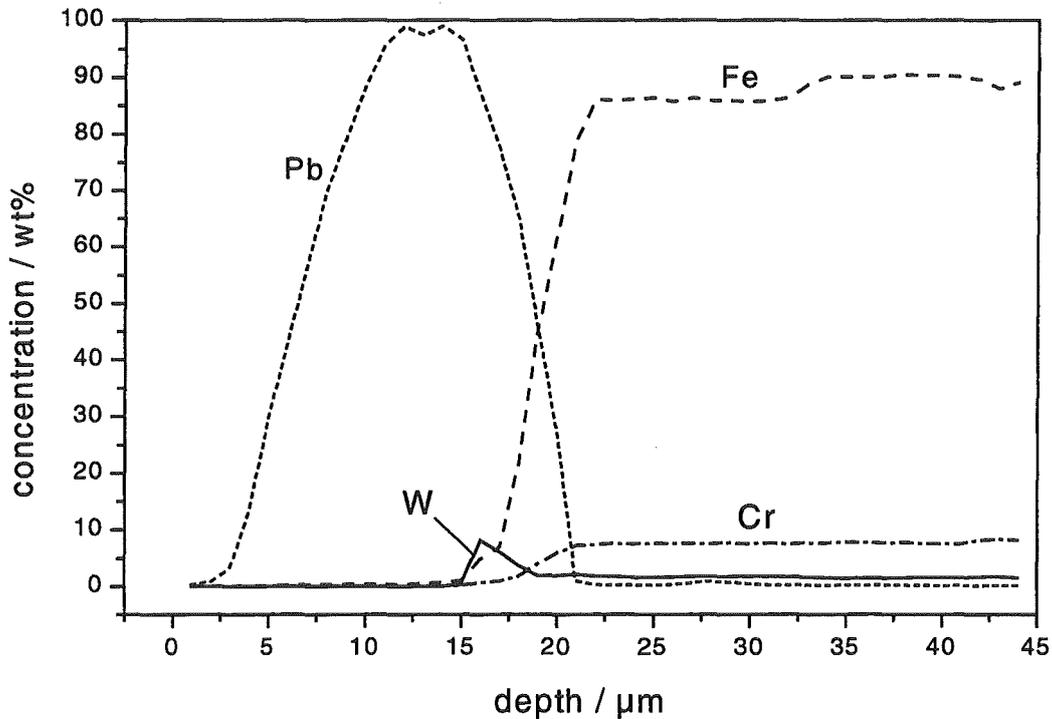
Fig. 9: EDX line scans across the cross section of F82H-mod. after 10,000 h of exposure to Pb-17Li at 480°C. Solidified Pb-17Li was not removed.

5. Discussion

The studies carried out have been mainly focussed on trying to understand the corrosion mechanism of potential structural materials by Pb-17Li and to compare the results revealed before [3, 9, 10]. The three materials investigated correspond to the same class of steel, i.e. similarity in composition and structure. Thus the behaviour found of the steels in Pb-17Li was quite similar.

As published previously [3, 8, 9] the corrosive attack was found to be a two step process: firstly, the dissolution of the passivating oxides occurs, the so-called incubation period, and secondly the dissolution of the steel matrix. Already after 2000 h of exposure, only little parts of the original surface were still visible, after 4000 h the oxides have disappeared completely. These observations are in full agreement with results published earlier by Borgstedt et al. [3]

who found an incubation period of around 3000 h at 500 °C and around 2700 h at 550 °C for MANET steel. These corrosion examinations have been carried out in the same test facility, the PICOLO loop, in which the flow velocity of the liquid melt was around 0.3 m/s in the test section.

In 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 of the 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 got dissolved in the hot section of the loop of the specimens as well as of the structural parts of the loop. Therefore the corrosion tests had to be interrupted after several thousand hours to remove these particles to reach again the required flow rate of 0.3 m/s.

Results presented in [9, 10] were obtained on specimens which have been corroded in 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. As a result the flow velocity had decreased from 0.3 m/s continuously 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 fact of erosion.

As mentioned already above, another phenomena was observed on these specimens exposed to Pb-17Li by low flow velocity. Porous areas on top of the steel surface could be identified whereby the elements with a low solubility in Pb-17Li (i.e. W, Mo and V) were enriched. The content of the steel elements Fe and Cr had decreased compared to the content in the matrix. No porous areas or layers could be observed on specimens corroded in Pb-17Li with a flow rate of 0.3 m/s by means of metallograpy. The results obtained by EDX can be interpreted as follows. Generally, there is no systematic difference observed whether Pb-17Li was washed away from the specimens or not.

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 around 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 were undergoing the washing procedure. This fact underlines the porous character of the reaction zone. On MANET steel sheets, no enrichment of Mo or V was observed independent how long the specimens were exposed (2000 h and 9000 h). A possible reason

for this can be that the content of W is much higher in F82H-mod. and Optifer IVa than Mo in MANET.

The constant flow velocity of 0.3 m/s seemed to be responsible for the different results revealed before [9, 10]. The porous layer formed is easily eroded by the flowing melt and no thick layer can be formed. The protecting character of this layer showing a low adherence can be neglected.

6. Conclusions

The corrosion mechanism 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 as well on flow velocity of the liquid melt. The second step is the dissolution to 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 never exceed 5 μm. Hence no protecting character can be ascribed to the layer in which the element W is enriched and Pb-17Li penetrates simply in.

7. References

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