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Corrosion of ferritic–martensitic steels in the eutectic Pb–17Li

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Abstract

Three different ferritic–martensitic steels were exposed to Pb–17Li under dynamic conditions at 480°C up to 8000 h. On the surface of all 7–10% Cr reduced-activation steels, a two-layer oxide scale consisting of $MnCr_2O_4$ spinel and $(Fe,Cr)_2O_3$ formed during the heat treatment. This was detected by means of XPS and AES analysis. It was found that the corrosive attack started with the dissolution of $MnCr_2O_4$ spinel and $(Fe,Cr)_2O_3$. When the oxide scale was dissolved by the liquid metal the corrosive attack continued into the steel matrix. Investigations of the corrosion mechanism have revealed that the steel elements Fe and Cr were strongly dissolved. Those steel elements, which have a low solubility in Pb–17Li, like W, Mo, V, remained in the matrix and were enriched in the surface near layer. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The use of Pb–17Li alloy as a tritium breeder for fusion reactors requires an assessment of its compatibility with the structural materials. In the past, many corrosion investigations were carried out to examine the corrosion rate and the corrosion mechanism of several austenitic and ferritic steels and vanadium alloys [1–7]. In particular, the corrosion mechanisms of austenitic steel exposed to Pb–17Li were intensively investigated. For the ferritic–martensitic 8–12% Cr steels several authors have presented corrosion rate data, but only a small amount of information on the corrosion mechanism of these steels is known. The 7–10% Cr reduced-activation steels were developed for application in a fusion reactor [8]. Three of them, MANET I, Optifer IVa and F82H-mod have been exposed to Pb–17Li under dynamic conditions at 480°C up to 8000 h.

2. Experiment

The corrosion tests have been carried out in a figure-of-eight type loop (details are described in [4]) named PICOLO. The pumping speed of the liquid melt 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. Corrosion specimens were taken out of the liquid metal about every 1000 h and replaced with fresh ones. The maximum exposure time was 8000 h. The adherent Pb–17Li was removed from the specimen surface by washing in a mixture of CH_3COOH, H_2O_2 and C_2H_5OH (1:1:1). The clean specimens were cut and prepared for analytical investigation by optical microscopy, SEM/EDX and EPMA.

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 is given in Table 1. Hardening and tempering processes were carried out under vacuum (10^{-6} bar). The conditions chosen corresponded to the instructions given by the supplier and are summarised in Table 2. For a better understanding of the corrosion mechanism, the surfaces of the original specimens were characterised by means of XPS and AES analysis.

3. Results

After the vacuum heat treatment before exposure to Pb–17Li, the specimens still showed a bright metallic surface. Only chromium, manganese and oxygen could

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Table 1
Chemical composition of the investigated ferritic–martensitic steels

	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 for the three steels

	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

be detected in the outer surface of the steels by XPS and AES analysis, and the iron content could be neglected by means of XPS. The concentrations measured for each element corresponded to the compound $MnCr_2O_4$ spinel. The AES depth profiles also revealed an iron–chromium oxide with a thickness of about 5 nm.

After exposure to Pb–17Li, cross-sectional investigations revealed that the corrosive attack occurred locally, and even after longer exposure times there were still areas without any attack. A typical corrosion pattern of the investigated steels is shown in Fig. 1.

AES investigations revealed that, for areas where no attack occurred, a few nm thick $(Fe,Cr)_2O_3$ layer still protected the material. This layer was dissolved during long-term exposure to the liquid metal. $MnCr_2O_4$ spinel could not be detected even after 1000 h of exposure. This is due to the fact that $MnCr_2O_4$ is a less protective oxide than $(Fe,Cr)_2O_3$ [10].

Taking unattacked areas as a zero line, the metal-loss could be determined on the cross-sectional cuts using optical and electron microscopy. Results of metal-loss measurements are indicated in Fig. 2. The graph reveals that the corrosion rate of all steels investigated was similar. Specimens exposed to Pb–17Li longer than 6000 h had no more unattacked areas, which could be used as a zero line. Unfortunately, no additional marker was set on the sample surface of the original materials before exposure. Therefore, the metal-loss values measured on the 8000 h specimens are probably too low and were not added to the diagram.

Locally, parts of a porous but still adherent layer were observed on the attacked steel surface at higher magnifications. This finding was somewhat surprising since those layers have never been mentioned in the literature before. EPMA line scan analyses have been carried out across this layer on specimens exposed to Pb–17Li for 1000 and 8000 h. It was found that the Fe and Cr content of this porous surface layer decreased with longer exposure times, leaving a scale which was enriched by the elements which are known to have a very low solubility in Pb–17Li. In the case of Optifer IVa and F82H-mod the layer was enriched in constituents W and V; in the case of MANET I the concentration of the elements Mo and V were increased in this porous layer compared to the bulk material. The line scans measured on F82H-mod after exposure times of 1000 and 8000 h are shown in Figs. 3(a) and (b).

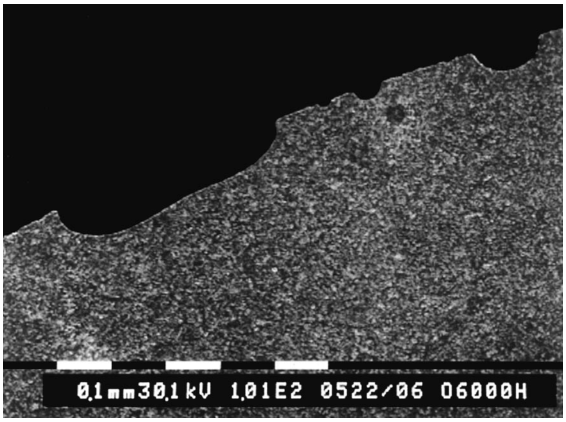

Fig. 1. Cross-section of Optifer IVa (etched), exposed for 6000 h in Pb–17Li at 480°C.

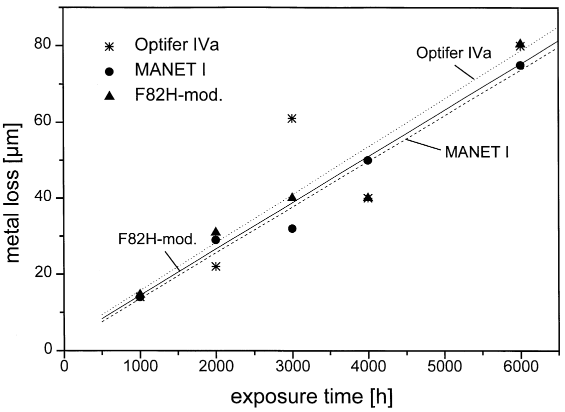

Fig. 2. Metal loss vs exposure time for MANET I, F82H-mod and Optifer IVa.

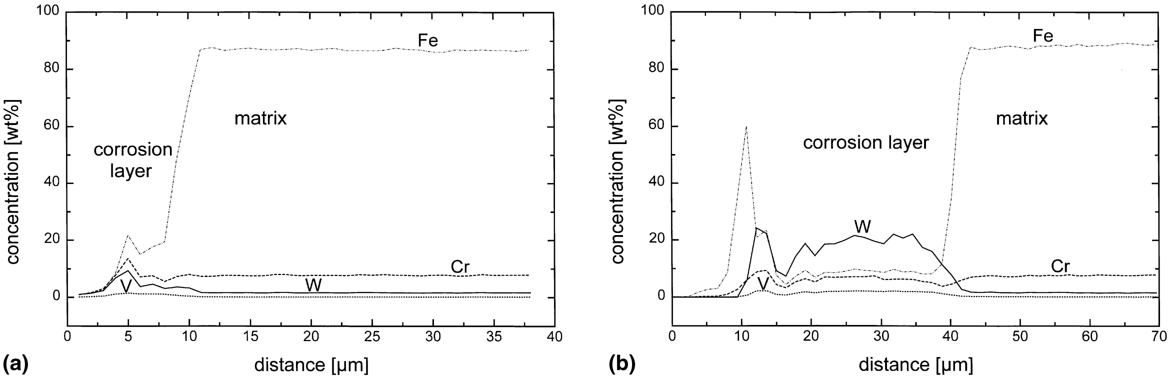

Fig. 3. EPMA line scans across the cross-section of F82H-mod after: (a) 1000 h; (b) 8000 h exposure to Pb–17Li at 480°C.

On etched specimens it was found that preferred matrix dissolution along martensitic lath boundaries occurred. It was interesting to note that this effect was greater for MANET I than for Optifer IVa and F82H-mod.

4. Discussion

The corrosion rate was found to be similar for all investigated steels. Up to about 6000 h exposure time, a linear corrosion rate was found on the basis of metal-loss measurements. For longer exposure times, the metal-loss could not be exactly determined due to the absence of a zero line.

The corrosive attack of the investigated ferritic–martensitic steels in Pb–17Li was found to be inhomogeneous. This observation is in contrast to those of some other authors [5,7]. The inhomogeneous attack resulted from the existence of a two-layered scale, which was formed during the vacuum heat treatment after specimen machining. This system consisted of an inner layer of $(Fe,Cr)_2O_3$ and an outer layer of $MnCr_2O_4$ spinel. The formation of $MnCr_2O_4$ spinel on iron–chromium alloys was due to the fact that MnO is thermodynamically more stable than Cr_2O_3 and Fe_xO_y, and more importantly that manganese has a higher diffusivity than chromium at elevated temperature in these alloys [9–11]. Similar enrichment of Mn in the outer regions had been detected previously. It has been reported, that only a few tenths of a percent of Mn leads to the formation of $MnCr_2O_4$ when added to a binary Fe–Cr alloy [10,11].

After the dissolution of the in Pb–17Li unstable mixed oxides, corrosion of the steel matrix began. The corrosion mechanism can be explained by means of EPMA line scan analyses. Despite intensive specimen cleaning before metallographic sample preparation, a porous and still adherent surface layer was observed on all steels investigated. Specimen cleaning after exposure in liquid metal was a routine procedure in previous studies. But unfortunately in this case, not only the adherent film of solidified Pb–17Li was removed but apparently also most of the porous corrosion layer. Parts of the layer could still be found on some cleaned specimens. EPMA line scan analyses clearly revealed that after 1000 h exposure time those layers contained a high concentration of Fe and a lower concentration of Cr, W, Mo and V. However, after longer exposure time (8000 h), the Fe concentration was reduced significantly and the concentration of those elements which have a low solubility in Pb–17Li was relatively high. This observation of leaching of one or more alloy constituents from the surface of the alloy because of selective dissolution is typical of liquid metal corrosion [13].

The observation of preferred corrosive attack along martensitic lath boundaries was published in an earlier paper [1]. The present investigation has shown that this behaviour was more pronounced for MANET I than for the other steels. A possible explanation might be that MANET I formed more $M_{23}C_6$ (M = Cr, Fe, Mo, W, V) precipitates on martensitic lath boundaries than the other steels investigated [12]. The formation of $M_{23}C_6$ precipitates caused a depletion of Cr, Mo, W and V in the vicinity of the martensitic lath boundaries, making matrix dissolution easier in these areas.

5. Conclusion

Two different corrosion mechanisms were responsible for the corrosive attack of ferritic–martensitic steels by Pb–17Li. The first step of corrosion was the dissolution of the two-layer oxide scale formed during the vacuum heat treatment on the surface of each steel. Secondly, the steel matrix was attacked by Pb–17Li. Steel elements, which have a high solubility in Pb–17Li were partly leached out of the matrix. Elements which have a low solubility in Pb–17Li (e.g., Mo, W, V) remained in the matrix enriching the surface compared to the bulk steel composition.

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