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Journal of Nuclear Materials 329–333 (2004) 1384–1387
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Corrosion behaviour of EUROFER in Pb–17Li at 500 °C

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Abstract

Corrosion resistance of the martensitic steel EUROFER 97 was examined in flowing Pb–17Li melt at the temperature of 500 °C for 2500 h. Changes of surface morphology as well as of specimen weight were observed. A noticeable loss of metal calculated from the specimen weight decrease was observed after 2500 h of testing. Concentration profiles of steel components near the steel surface were examined by EDX line-scan and point analyses.

1. Introduction

Liquid Pb–Li alloys are considered as potential coolants and tritium breeding fluids for a fusion reactor blanket concept. Reduced activation ferritic–martensitic (RAFM) steels with 8–10% Cr were developed and their compatibility with liquid metals was investigated. Corrosion behaviour of such types of steels like EUROFER and F82H were tested under static and dynamic conditions in flowing liquid metals at the temperature ranging from 400 to 600 °C. The main corrosion mechanism in Pb–17Li is dissolution of the steel components after some incubation period, which is affected by stability of original surface oxide layers, temperature and other parameters [1–3].

2. Experimental procedure

Seamless tubes ∅ 17 × 1.5 mm of reduced activation martensitic steel EUROFER 97 were normalised at the temperature of 975 °C for 15 min, cooled to RT in air and tempered at 740 °C for 45 min, cooled to RT in air. Tube surface finishing was performed by chemical pickling. The chemical composition is as follows: C 0.11; Mn 0.39; Si 0.05; Cr 8.82; V 0.19; W 1.09, Ta 0.15 wt%.

Nine tube specimens 100 × 14 × 1.5 mm were prepared by cutting delivered tubes in the longitudinal direction. Two surface specimen conditions were used for specimen testing: as-received, and after polishing. The polishing was carried out in a mixture of 5 ml HF, 85 ml H_2O_2, 10 ml H_2O, which should reduce the roughness of the original surface.

Specimens were tested in Pb–17Li melt at 500 °C, with exposure times of 500, 1000 and 2500 h. Chemical composition of the eutectic alloy contains Li 0.7; Bi 0.005; Ni 0.001; Ta 0.002; Sn 0.056; Na 0.027; Fe 0.003 wt%. Contents of other elements are lower than 0.0003 wt%. Residual lead layers on exposed specimens were removed in a sodium melt at 250 °C and in a solution of $CH_3COOH + H_2O_2 + H_2O$ for some specimens exposed 2500 h. EDX analyses were carried out on the cross section and surface of tube specimens. The weighing was carried out up to constant weights of cleaned specimens.

For EDX analyses, flat specimens 100 × 13 × 1.2 mm were also prepared by machining from EUROFER plate, thickness 14 mm. The plate chemical composition corresponds to the tube composition as given above. These specimens after surface grinding were exposed for 2000 h.

The experiments were conducted in a cylindrical device with a volume of 4.5 dm^3 consisting of a hot leg and a cold leg working as a cold trap. The specimens were placed in the hot section and were exposed at 500 °C in Pb–17Li under argon atmosphere. The temperature of the cold trap was 300 °C. The eutectic flow rate of 10 mm/s was controlled by a stirrer. Two holders, each with

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doi:10.1016/j.jnucmat.2004.04.202

three specimens, were exposed simultaneously in the vessel. The holders were replaced without the experiment interruption.

3. Results

3.1. Weight changes

The specimen weights after exposure were measured and calculated metal loss in μm are shown in Fig. 1 where the value of reduced activation ferritic–martensitic steels [2] tested under similar conditions is given for comparison. A small metal weight change was observed after 500 and 1000 h but a higher metal loss was observed after 2500 h. A weight loss of about 1.3 mg/cm^2 was measured after 2500 h exposure. There were no significant differences in weight changes between as-received and polished surface conditions.

3.2. Surface investigation

EUROFER 97 tubes have a martensitic microstructure and relatively higher roughness of the inner and outer surfaces (Fig. 2) in the as-received conditions. Polishing lowers the roughness of tube surface (Fig. 3). Specimen surfaces investigated after 500 and 1000 h of exposure in Pb–17Li show small changes in both as-received and polished conditions. The corrosive damage occurs locally and the major part of surface areas is not affected. The exposure after 2500 h evidences some visible decrease in the surface roughness for both surface conditions. The surface defects are more shallow and correspond to a weight decrease. The investigation of tube specimens reveals the preferential attack of grain boundaries and precipitates originated in the initial surface polishing as is shown in Fig. 4. This surface microstructure remained unaffected after the exposure in the melt.

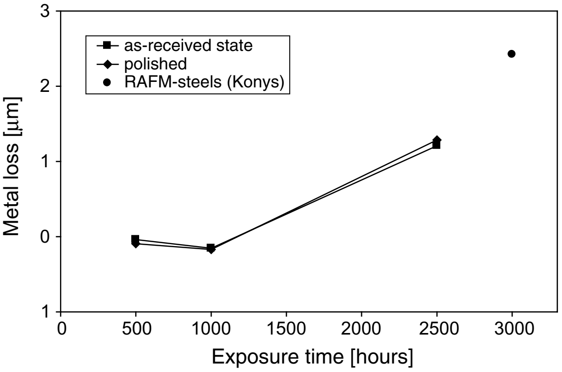

Fig. 1. Metal loss versus exposure time in forced Pb–17 at.% Li loop at 500 °C.

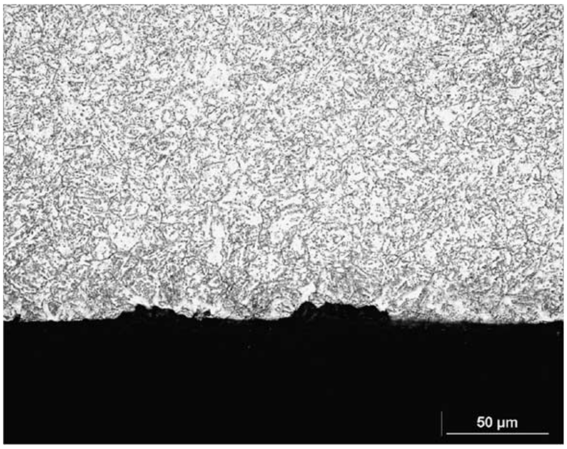

Fig. 2. Cross section of specimen inner surface in as-received condition, etched.

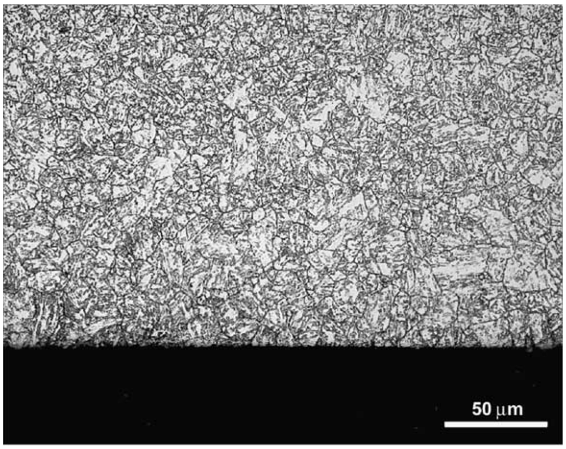

Fig. 3. Cross section of specimen inner surface after chemical polishing before testing, etched.

After 500 and 1000 h of exposure, surface layer spalling was observed (Fig. 5). The origin of this spalling is in the tube manufacturing. The effect of spalling probably influences the small weight increase of the specimens as a result of insufficient liquid lead removing from crevices.

EDX line-scan analyses on cross sections were performed in two ranges: up to 40 and up to 10 μm from the surface. To keep the exposed surface unchanged the specimens were washed only in sodium melt. The specimen surface did not show changes in the concentration profiles of Cr, Fe, W, Mn and V after 500 and 1000 h of exposure. After 2000 and 2500 h of exposure, a local decrease of Cr and Fe content was observed near the

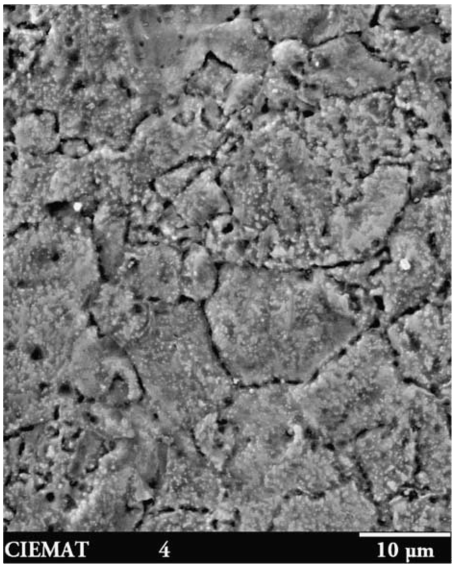

Fig. 4. Microstructure of specimen attacked surface, exposed for 2500 h in Pb–17Li at 500 °C.

surface (Fig. 6) which corresponds to the assessment obtained in [3]. The thickness of depleted layers was around a few microns as was evaluated from the EDX line scan in the 10 µm range.

EDX point analyses of tube surfaces allowed changes in the content of Cr, W and Fe on the tube surface to be investigated. The relative ratio defined as the surface element content (Cr_{sur}) to its content in the material matrix (Cr_{matr}) was evaluated (see Table 1). As an example of the EDX point analysis, the data measured on the specimen surface after 2500 h are presented in Table 2.

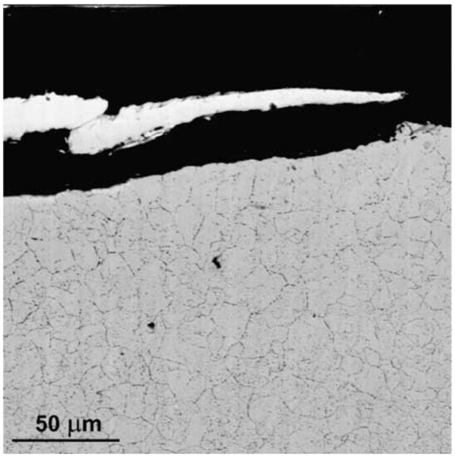

Fig. 5. Surface layer spalling after 2500 h exposure in Pb–17Li at 500 °C, specimen cross section.

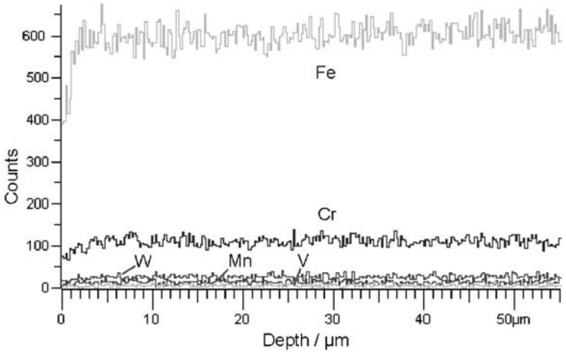

Fig. 6. EDX line scan of specimen cross section after 2000 h exposure in Pb–17Li at 500 °C.

Table 1
Ratio of the element surface content (Cr_{sur}) to its content in the material matrix (Cr_{matr}) after exposure in Pb–17Li at 500 °C

Elemental com position surface/ matrix ratio	Exposure time	
	500 h	2500 h
Cr_{surf}/Cr_{matr}	1.04	0.97
W_{surf}/W_{matr}	1.01	1.22
Fe_{surf}/Fe_{matr}	0.99	0.98

4. Discussion

In flowing Pb–17Li at 500 °C the EUROFER 97 tube specimens show corrosive attack which manifest itself by changes of surface morphology and by weight decrease due to dissolution of soluble components of the steel after some exposure time. The investigation reveals a non-uniform corrosion during an incubation time.

After 500 and 1000 h exposures, corrosion attack is non-uniform. Both unaffected and affected areas of the specimen surfaces were observed. This is probably due to the presence of protective layers with different behaviour in melt and also successive wetting of the specimen surface. After 2500 h exposition, corrosive attack took place practically along the whole surface and protective layers did not prevent dissolution. Dissolution of metal led to smoothing of surface irregularities and a decrease of surface roughness. A noticeable weight decrease and calculated loss of metal were observed after 2500 h of testing. The weight decrease of approximately 1 mg/cm^2 after 2500 h is in relatively good correlation with the value of about 4 mg/cm^2 evaluated from data of Fe–12Cr–1MoVW steel after 3000 h under similar test conditions with the flow rate of 25 mm/s [4]. Lower values of both metal loss and weight decrease compared with ones presented in [2,4] can be explained by a longer incubation time needed for initiation of metal dissolution under our experimental conditions.

Table 2
Normalised chemical composition of specimen surface after exposure 2500 h in Pb–17Li at 500 °C (wt%), EDX point analysis

Spectrum	V	Cr	Mn	Fe	Ni	W	Total
Spectrum 1	0.28	9.59	0.00	87.26	0.96	1.91	100.00
Spectrum 2	0.49	8.68	0.02	88.52	0.62	1.67	100.00
Spectrum 3	0.30	8.53	0.15	88.55	0.27	2.20	100.00
Spectrum 4	0.25	9.87	0.25	87.12	0.41	2.10	100.00
Spectrum 5	0.27	9.74	0.42	86.13	0.66	2.78	100.00
Spectrum 6	0.29	10.11	0.17	87.26	0.04	2.13	100.00
Spectrum 7	0.22	9.50	−0.08	87.14	0.90	2.32	100.00
Mean	0.30	9.43	0.13	87.43	0.55	2.16	100.00
Standard deviation	0.09	0.60	0.17	0.85	0.33	0.35	

The 500 and 1000 h exposures have no evident effect on the surface composition, as shown by EDX line-scan and point analyses. After 2000 and 2500 h, a slight decrease of Cr and Fe could be observed in a few microns layers [3]. The content of W and V near the surface does not decrease, on the contrary, there is an increase of the W content compared to the matrix composition (Table 1). The increased W content corresponds to EDX results [1] for similar F82H steel tested for 2000 h at 480 °C.

Thus, the main mechanism of corrosive attack is dissolution of steel which takes place after some incubation period needed for removing the surface protective layers. These layers inhibit the contact between the liquid metal and the steel surface. The attack results in the dissolution of Cr and Fe as components with higher solubility in Pb–Li as well as an increase in the relative content of less soluble W [5]. The interaction of the melt with grain boundaries did not result in excessive intergranular attack and depth of such interaction was not possible to evaluate.

5. Conclusion

Corrosive behaviour of martensitic steel EUROFER 97 was examined in Pb–17Li for 2500 h. Melt interaction with steel results in its dissolution which is demonstrated by changes in surface morphology and specimen weight losses. A noticeable specimen weight decrease was observed after 2500 h. The experiments have shown that the surface corrosive attack is revealed only after a certain incubation period. During this period, the surface layers do not enable a direct attack of the surface by the melt. At longer exposure times, those layers are not more resistant and do not prevent dissolutions of steel components. Concentration profiles of steel components near the steel surface were examined by EDX line-scan and point analyses. Under these experimental conditions, the slight decrease of Cr and Fe, as higher soluble steel components in Pb–17Li, was found. The increase of W content, as a component with lower solubility in liquid metals, was observed near the steel surface.

Acknowledgements

The authors wish to thank to Mrs A.M. Lancha from CIEMAT, Spain, Mr M. Svoboda from Institute of Physics of Materials of the Czech Academy of Sciences, and Mr T. Chráska and J. Matejicek from Institute of Plasma Physics of the Czech Academy of Sciences and Ms E. Keilová from Nuclear Research Institute for the specimen investigations and analysis. This work has been supported by the European Commission within the European Fusion Technology Programme.

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