Corrosion behavior of EUROFER steel in flowing eutectic Pb–17Li alloy

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Abstract

Reduced-activation-ferritic-martensitic (RAFM) steels are considered for application in fusion technology as structural materials. The alloy EUROFER 97 was developed on the basis of the experience gained with steels of the OPTIFER, MANET and F82H-mod. type. These alloys will be in contact with the liquid breeder Pb–17Li and their corrosion behavior is of significance for their successful application. Corrosion tests of EUROFER 97 in flowing Pb–17Li at 480 °C were performed up to about 12 000 h to evaluate the kinetics of the dissolution attack. The exposed samples were analysed by metallography and scanning electron microscopy (SEM) with EDX. The results show that EUROFER 97 is attacked by flowing liquid Pb–17Li with a flow velocity of about 0.3 m/s similar to the earlier examined steels and that the typical steel elements are dissolved. The observed attack is of uniform type with values of about 90 μm/year. The corrosion rate is a somewhat smaller for EUROFER compared to the other RAFM steels but with equal activation energy.
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1. Introduction

In a future fusion system of the water cooled liquid lead (HCLL) type, RAFM-steels are considered as structural materials. The new alloy EUROFER 97, a 9 Cr–W–V–Ta alloy, was developed from a base of experience with RAFM alloys e.g. Optifer type [1]. The thermal and mechanical behaviour have been examined [2]. The compatibility with the eutectic lead–lithium cooling and breeding medium (Pb-17 at.% Li) is outstanding. In the PICOLO loop [3] cylindrical samples (diameter 8 mm, length 31 mm) made from EUROFER 97 were exposed to Pb–17Li. The aim of these corrosion tests was to provide a data base on EUROFER 97 corrosion in a fusion relevant liquid metal, Pb–17Li, and to compare these results with the previously examined FM alloys: MANET I, Optifer IVa and F82H-mod [4].

2. Experimental

The samples for the corrosion tests were fabricated from plate material – alloy produced by Böhler Edelstahl GmbH, Austria (thickness 14 mm, charge no. E83698, plate no. 14, lot no. 249). The vacuum arc melting processing is described in [5]. The shaping process was followed by fine grinding. All samples showed a bright metallic surface. The average roughness was measured to be about $R_a = 0.5$ μm, maximal peak values in roughness exceeded $R_z = 2.4$ μm. The austenitization conditions of the bar materials were 980 °C, 27 min and cooling in air. Tempering was done at 760 °C for 90 min with subsequent air cooling. The fabricated samples were cleaned in an ultrasonic bath (acetone) and dried before mounting into the hot leg of PICOLO loop. Loading and unloading of the test samples, which were screwed together to a stack of 12 pieces, was carried out in an Ar-glove box connected on top of the loop. The atmosphere of the glove box is purified to guarantee an O_2 level of 1 vppm. The inner diameter of the test section is 16 mm, thus the concentrically mounted samples are surrounded by a Pb–17Li flow of 4 mm in thickness. The chemical composition of the used EUROFER 97 master

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alloy together with the above mentioned other FM steels is given in [2,4]. Specimens were taken out of the loop about every 1500 h and replaced by fresh ones. The test temperature in the hot leg was about 480 ± 5 °C and the lowest one in the loop 350 °C. The EUROFER 97 samples were analysed by standard metallographic techniques and by applying SEM and EDX methods. Additionally diameter measurements on fresh and corroded samples were carried out to determine corrosion rates.

The Pb–17Li alloy was delivered by Metaux Speciaux, France, with an average Li content of 0.68 wt% and Sb, Ag, Zn, Cd, Fe, Cu and Ni below 10 wppm.

3. Results of EUROFER 97 attack

3.1. Optical microscopy

The metallographic pictures didn't show remaining unaffected surface fractions at any sample. All test pieces were covered by a Pb–17Li skin which were in good contact with the base alloy. It is concluded from these analyses that wetting of the complete sample was finished at least after a test of 1516 h, when the first sample was removed. Two changes in surface structure are evident in comparison to the unexposed reference sample. First, an increase in surface roughness is visible with dimensions in the 1 μm range for depth and periodicity and second, at some positions, a concave feature of the surface with a depth up to about 10 μm can be detected with long periodicity (some 100 μm). The different erosion depths may be correlated to the start of corrosion at a different timescale due to delayed wetting or corrosion attack. The microstructure found after etching suggests

that the corrosion attack seems to be stronger at formerly austenitic grain boundaries and at positions with a high density of grain boundaries. However, this observation needs further study as it was not the goal of this first corrosion campaign on EUROFER 97. In general the surface structure of all analysed samples did not change much in roughness and global appearance.

3.2. SEM EDX analyses

The SEM/EDX analyses were performed with the samples prepared for optical microscopy. The surfaces were freshly polished with diamond additives down to 1 μm under flowing water for a short time. This procedure was chosen to minimize Pb contaminations on the steel surfaces coming from the adherent Pb–17Li scale and to achieve mostly flat surfaces because edge rounding can affect EDX counting rates by shadowing. Fig. 1 shows the EDX measurements together with the corresponding SEM picture of a sample exposed for 3011 h to the flowing liquid metal. The adherent Pb–17Li scale shows a not uniform brightness in the SEM picture. The dark positions can be correlated to low emissive positions e.g. coming from voids or embedded particles with low Z (steel additives). The boundary steel to Pb–17Li is similarly shaped as the boundary Pb–17Li to embedding material in contrast. This may be a hint, that diffusion of Pb into steel is not present. Also by SEM analyses, no diffusion of lead into the steel was detected.

The path for performing the element analyses is marked by crosses ranging from the embedding resin to the steel. Under investigations were the elements Fe, Cr, Mn, W (the main steel components) as well as Pb and O. Within the EUROFER alloy, concentrations of these elements were constant. Small concentrations of the steel
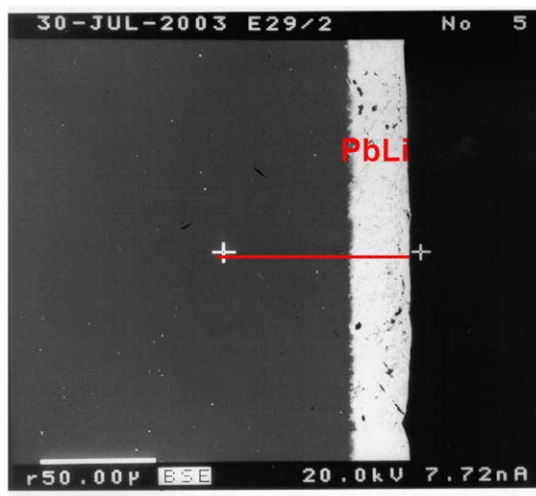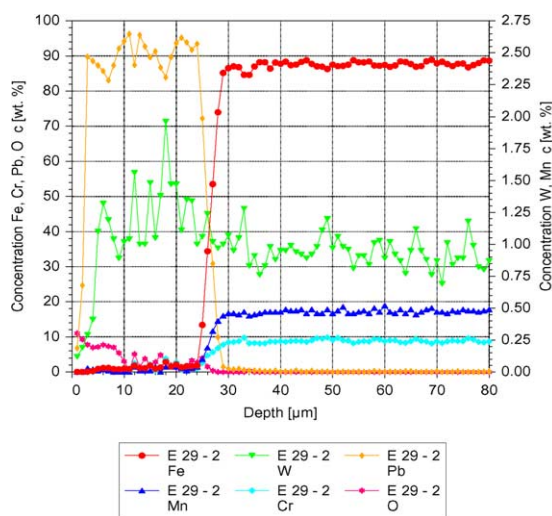

Fig. 1. SEM and EDX analyses of EUROFER 97 exposed for 3011 h to Pb–17Li at 480 °C.

components Fe, Cr, Mn and W were detected in the adherent Pb–17Li-scale. The measured values were about 2% for Fe and Cr, 1% for W and 0.1% for Mn. However, the signal was not constant in this scale. This result suggests that particles are embedded because the measured values are above the solubility limits for these elements in Pb–17Li [7]. Furthermore, it can be concluded, that an adherent, stagnant layer covers the samples during the tests.

The micrograph and EDX analyses of a sample exposed for about 12 000 h are shown in Fig. 2. The EDX scan shows a similar concentration profile compared to the analyses performed at shorter exposure times. No depletion effects in Fe and Cr or Pb infiltration into the matrix can be detected within the resolution limits. Both EDX and metallographic analyses underline the mechanism of a mostly uniform corrosion attack in flowing Pb–17Li also deducible from the smooth corrosion front with low roughness. At some positions – at least some 1–2% of the total cylindrical surface – reduced corrosion attack was observed. Different explanations e.g. presence of ferritic phase, Ta enrichment etc., are under evaluation. At the moment, delayed wetting is assumed to be the as most probable explanation. All the metallographic tests indicate that the corrosion mechanism can be attributed to the leaching out of steel elements under formation of a non protective porous corrosion zone.

3.3. Corrosion rate determined from diameter reduction

Corrosion rate as a function of exposure time was determined by evaluation of diameter changes. For this analysis all samples were mechanically measured before inserting into PICOLO loop with accuracy of ±2 μm. The diameters of removed samples were determined from the metallurgical cuts by optical microscopy. In general, no characteristic deviations from the cylindrical shape could be found by diameter determinations performed crosswise to each other. The obtained maxima of radii reductions by corrosion are given in Fig. 3. The graph shows a linear correlation of corrosion rate and time with a slope of about 90 μm/yr. The obtained dependency underlines the expected corrosion mechanism of corrosion by dissolution – a linear phenomena – and the existence of effects responsible for delayed corrosion attack in the short term behaviour triggered
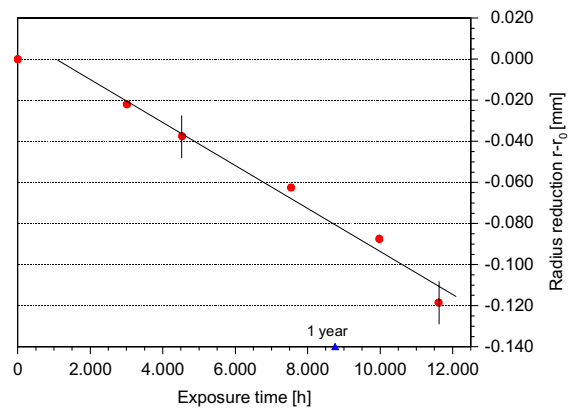

Fig. 3. Radius reduction as a function of exposure of EUROFER 97 rods to flowing Pb–17Li.
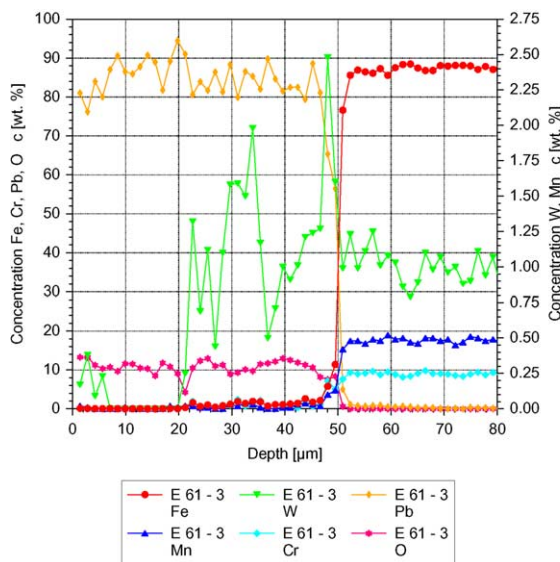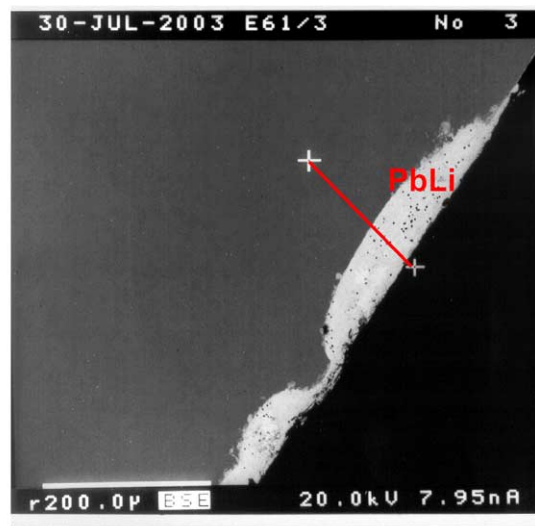

Fig. 2. Microstructure of EUROFER 97 exposed for 11 618 h to Pb–17Li at 480 °C.

by delayed wetting or slow dissolution of passivating oxide scales. The performed tests with durations of up to about 1.5 yr – about twice the time of tests performed with the previously examined FM-alloys – improve the reliability of describing the corrosion of FM-steels as linear phenomena. The duration for delayed corrosion attack, the so called incubation time, can be estimated to be about 1000 h.

Similar corrosion tests, however at a rather low flow velocity of about 10^{-2} m/s (only 3% of PICOLO loop flow rate), were performed in the LIFUS II loop of ENEA [6]. A linear corrosion rate of about 40 μm/yr was reported. The lower corrosion rate is due to the dependency on flow rate and thereby the two test series are consistent and complementary. In contrast to PICOLO loop tests, the presence of an adherent but detached defect rich steel scale of about 1 μm with a lower Cr content was observed. This observation as well as the shifted Cr/Fe ratio, can be explained by the less abrasive lower flow rate.

4. Comparison to other RAFM alloys

Ferritic-martensitic steels (MANET I, Optifer IVa, F82H-mod. and EUROFER 97) were investigated in the PICOLO loop under similar conditions for durations up to about 12 000 h. All the steel tests agree, that corrosion occurs at long exposure times by dissolution of alloying elements. The steel components (not completely dissolved particles coming from the corrosion zone) could be detected in a Pb–17Li stabilized surface scale of about 20 μm at a flow rate of 0.3 m/s. In none of the tests Pb-diffusion into the matrix was found. The microstructural analyses showed that corrosion attack is of uniform nature for EUROFER 97 as well as for the other FM steels. Effects which can cause strong inhomogeneous attack due to passivating scales during short term exposure, as mentioned in results of MANET I tests [3], were not detected. For all FM steels, areas with visible corrosion attack have a similar appearance. Of all tested alloys, EUROFER 97 has the smallest grain size of previously formed austenite. A summary of maximal corrosion attack results are given in Fig. 4. The lines for each alloy type were inserted by optical fitting and help to illustrate the time dependency. Corrosion of the four alloys can be described by a linear time correlation and the fitted lines are nearly parallel. The EUROFER 97 line indicates an existing incubation period.

The corrosion line for EUROFER 97 is clearly positioned below the curves for the earlier examined alloys. The advantage for EUROFER 97 in corrosion rate is in the range of 10–20%. The reduced corrosion rate of EUROFER 97 compared to the other FM-steels can not be explained by chemical composition of the main alloy elements, because they are quite similar for
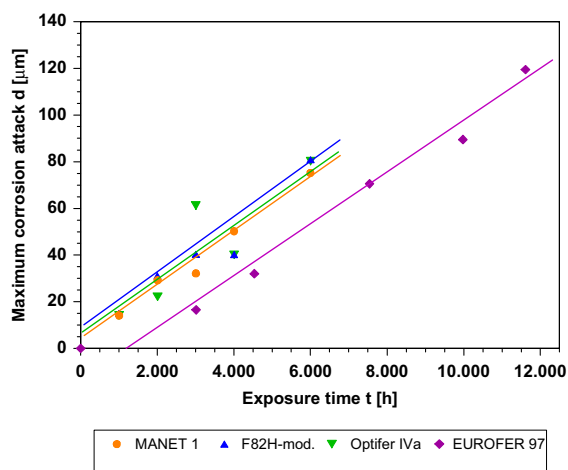

Fig. 4. Comparison of corrosion rates of FM-steels.

all tested steels. It is proposed at the moment that minor elements e.g. Ta, N or lower impurity levels and thus grain boundary effects may be responsible for the differences. However this topic lies far a head of the planned work program for this campaign and will need additional tests.

5. Conclusions

The corrosion behaviour of EUROFER 97 was examined in flowing Pb–17Li using the PICOLO loop up to ca. 12 000 h. The detected corrosion rate per year is of the order of about 90 μm at 480 °C. The time dependency can be said to be linear neglecting possible initial incubation effects. The corrosion attack appears to be a little bit more pronounced at positions with a high density of martensitic grain boundaries and also at locations of former austenitic ones. However, these features as well as the presence of ferritic grains and incubation effects needs more detailed experiments and evaluation. Overall, EUROFER 97 shows uniform corrosion behaviour and smaller corrosion rates than the other FM steels. The reduced corrosion attack of EUROFER 97 compared to the other FM-steels may be due to its finer grain size and microstructure or the higher Ta content similar to the arguments given for it's better ageing resistance. Additional benefit may come from lower impurity levels and thus smaller amounts of precipitates on the grain boundaries or higher N concentrations which are known to reduce diffusion.

Acknowledgements

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