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Comparison of corrosion behavior of bare and hot-dip coated EUROFER steel in flowing Pb–17Li

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Abstract

In future fusion systems reduced activation ferritic–martensitic steels (RAFM) are considered as structural materials which are in contact with the cooling and breeding medium Pb–17Li. The most promising alloy to fit the requirements is the reference steel EUROFER 97. Due to the contact with Pb–17Li, the corrosion behavior will be of importance for the application, in addition to mechanical and neutronic properties. Corrosion testing of EUROFER 97 was performed at 480 and 550 °C at flow rates of 0.3 m/s. Both test series showed a homogeneous corrosion attack by dissolution mechanism, however, with a dramatic increase in rate from 90 to 700 μm/a. At least the 550 °C tests indicate that corrosion may cause a serious problem due to the high risk of blockage by precipitation. Thus corrosion resistant Al-coatings were developed and tested in Pb–17Li. The performed tests showed that the degree of protection depends strongly on properly reacted FeAl-scales.

1. Introduction

Reduced activation ferritic–martensitic (RAFM) steels are considered as candidate structural materials for a future fusion system of the water cooled liquid lead (WCLL) type. The new steel EUROFER 97, a 9%Cr W V Ta alloy, was developed and optimized on basis of the experience gained with older RAFM alloys of the OPTIFER, MANET and F82H-mod. type. Meanwhile, the thermal and mechanical behavior was examined [1] and first compatibility tests with the eutectic lead–lithium cooling and breeding medium of the composition Pb 87 at.% and Li 17 at.% were performed. In the PICOLO loop [2] cylindrical samples (diameter 8 mm, length 31 mm) were exposed to the corrosive liquid metal Pb–17Li at 480 °C for up to about 12000 h. The aim of these corrosion tests was to provide a database on EUROFER 97 corrosion in a fusion-relevant environment and to compare these results with the previously examined RAFM steels MANET I, Optifer IVa and F82H-mod [3]. Meanwhile, application conditions in a planned fusion system changed to higher temperature levels (helium cooled lithium lead concept). New tests were started at 550 °C for determining corrosion rates, mechanisms and studying transport effects. The first evaluation of the corrosion data indicates that corrosion rates are rather high (0.7 mm/a) and that dissolved material may cause problems in operation of fusion

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reactors. Thus, corrosion resistant scales may be required to guarantee proper working for long duration. Based on the HDA (hot-dip aluminization) process, developed for coating of MANET steel earlier [4], the first Al-coated EUROFER 97 samples were prepared and inserted into corrosion loop PICOLO for corrosion testing.

2. Experimental

The samples for the corrosion tests were fabricated by machining from plate material – produced by Böhler Edelstahl GmbH, Austria (thickness 14 mm, badge no. E 83698, plate no. 14, lot no. 249). The machining process was followed by fine grinding and all samples showed a bright metallic surface. The chemical composition of the EUROFER 97 master alloy together with the other above mentioned RAFM steels is given in [1]. The average roughness was measured to be about $R_a = 0.5$ μm, while the peak roughness values exceeded $R_z = 2.4$ μm (DIN standard). 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. No additional thermal treatment was performed after machining the bare uncoated samples. However, these values were used for conditioning the Al-dipped samples. The fabricated samples were cleaned in an ultrasonic bath (acetone) and dried before mounting into PICOLO loop or using in the HDA process. The performed Auger surface analyses showed that only a 10 nm thick O_2-scale was present on the bare samples. Detected contaminations were C, N, and O.

The Al coating was performed by dipping the EUROFER into an Al melt at 700 °C for 30 s in a glove box under purified Ar atmosphere and removing the excess Al from the surface. The process values – dipping into Al and subsequent heat treatment – were similar to the data given in [4] for aluminization of MANET steel.

The test samples were screwed together in a stack of 12 pieces. Loading the stack into the test section of PICOLO loop was carried out in an Ar-glove box with a controlled O_2 level of below 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. Corrosion testing for bare EUROFER was performed at 480 ± 5 °C and for the new series at 550 °C. The testing of the Al coated samples was done only at 480 °C. The lowest temperature in the loop was about 350 °C for both test temperatures. Specimens were taken out of the loop in intervals of about 1500 h for 480 °C and 500 h for the 550 °C tests and replaced by fresh ones. The EUROFER 97 samples were analyzed 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.

3. Results of bare EUROFER 97

3.1. Low temperature testing at 480 °C

In the actual campaign EUROFER 97 samples were exposed to Pb–17Li at 480 °C with durations up to roughly 12 320 h. This is the longest time for all tested RAFM steels in the PICOLO loop at a flow rate 0.3 m/s and will thus increase the reliability in extrapolation of the corrosion behavior of the other RAFM steels to longer times. In general, samples were removed from PICOLO loop in intervals of about 1500 h and replaced by fresh ones. However, in this run one sample was additionally removed at 702 h for checking more precisely incubation time effects, which were detected in earlier tests and described in [2]. This sample clearly shows incomplete wetting and only some local corrosion attack. The sample removed at 1516 h exhibits complete wetting and corrosion attack over the whole surface. The performed metallographic examinations for exposure times over 1500 h showed a homogeneous corrosion attack and good contact of the adherent Pb–17Li layers to the samples after removal from the test loop. It was also seen that the contact zone – melt to base alloy – was smooth in general without any local attack in shape of grooves.

Additionally, line scans were performed with a local resolution of about 2–3 μm to examine the composition near the corrosion zone. Sharp changes in the Fe and Pb signals were always present at the interface of the liquid with EUROFER which indicates that no Pb diffusion into the matrix is present. The adherent Pb–17Li scale on top of the EUROFER can be divided in two subsections. The section which is in direct contact with the steel has a thickness of about 15–20 μm. The remaining Pb–17Li filled porous structure containing Fe and Cr is enriched in elements (e.g. W) with low solubility in the melt. Further away (20–80 μm) from the surface (Section 2) no significant enrichment of Fe, Cr or W compared to the melt composition could be detected. Based on these analyses, a dissolution mechanism is indicated as the mechanism for the corrosion attack. The time dependence of the attack is linear in the range 1500 to about 12 000 h. The corrosion rate was estimated to be about 90 μm/a for the 480 °C tests. These new tests up to 12 320 h confirmed the data reported earlier [2]. Below 1500 h an incubation period exists with incomplete wetting and only local attack which starts at about 700 h.

3.2. High temperature testing at 550 °C

A new test series was started at 550 °C after modification of the testing loop PICOLO as a result of the new blanket requirements (working temperature 550 °C) and technological tasks (precipitation and modeling). The first analyzed samples with exposure times up to 1000 h confirm the corrosion mechanisms found in the earlier 480 °C series. Micrographs of the samples removed after 500 h and 1025 h are shown in Fig. 1. The selected sections of the surfaces reveal an unwetted area with no adherent Pb–17Li and nearby surfaces with localized corrosion attack. In the regions with an adherent Pb–17Li layer, corrosion attack may have started shortly after inserting the samples into the test loop due to similar corrosion attack for the time spans 0–500 h and 500–1000 h. The micrographs illustrate that the incubation time is clearly shorter at 550 °C (half or less) compared to the 480 °C tests. They also show that corrosion attack proceeds linearly with exposure time. The evaluation of the corrosion depth, visible in the pictures as a step from the original surface to attacked area indicates rates of about 700 μm/a. This value is drastically increased (roughly by a factor 10) compared to the corrosion rates measured at 480 °C with about 90 μm/a. Line scans performed in the wetted areas of the sample exposed for 1025 h generally show a similar feature compared to analyses performed on samples tested at 480 °C. However, as can be seen in Fig. 2, the section of the adherent Pb–17Li scale with an increased amount of corrosion products has a width of about 40 μm compared to about 15 μm in the 480 °C tests. The profile of the Fe and Pb signals also indicate that no Pb diffusion into the EUROFER steel takes place. Dissolution appears to be the only corrosion mechanism at 550 °C also. This interpretation of the corrosion process is in agreement with results found by other groups [5] working in Pb–Li corrosion, albeit under different test conditions.

The estimated rates for both temperature conditions can be compared with predictions from correlations established empirically by Sannier et al. [6] on the basis of corrosion data coming from different Pb corrosion tests. Using Sannier's correlation, corrosion rates were estimated for different flow rates and temperatures. Fig. 3 shows the dependence of metal loss for the flow rate of 0.3 m/s, the test velocity in PICOLO loop, and two lower flow rates of 0.05 m/s and 0.005 m/s. The last one represents nearly stagnant conditions. The PICOLO results (480 and 550 °C) are inserted into this diagram of predicted corrosion rates. These measured rates are in rather good agreement with the correlation. However, this equation will not replace more accurate future modeling work that includes the precipitation effect on corrosion loop behavior. The observed high corrosion rate of 700 μm/a in the PICOLO tests at 550 °C have to be confirmed in the ongoing test program up to longer exposure

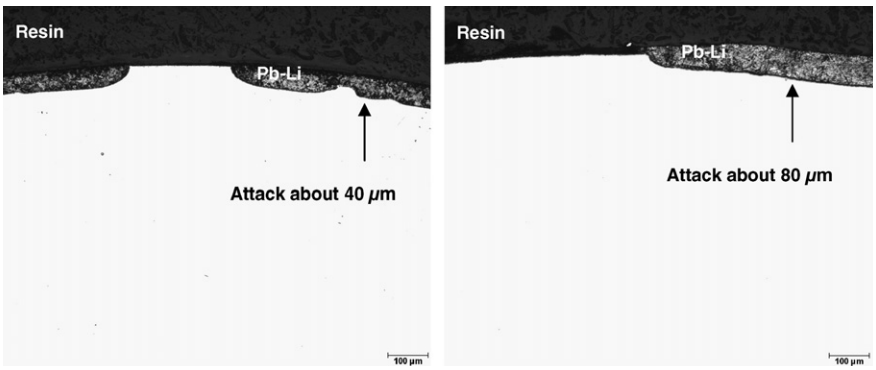

Fig. 1. Microstructure of corrosion zones near a small unattacked area after 500 h (left) and 1025 h (right).

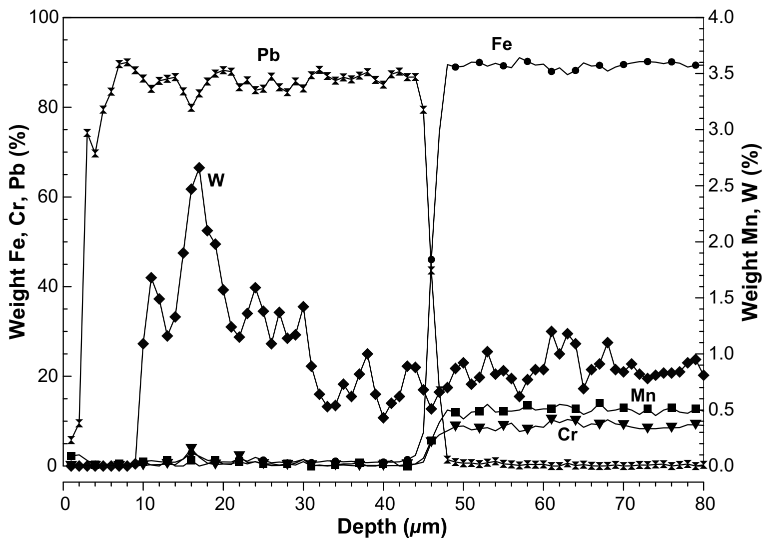

Fig. 2. Line scan across corrosion zone of EUROFER sample exposed to Pb–17Li for 1025 h at 550 °C.

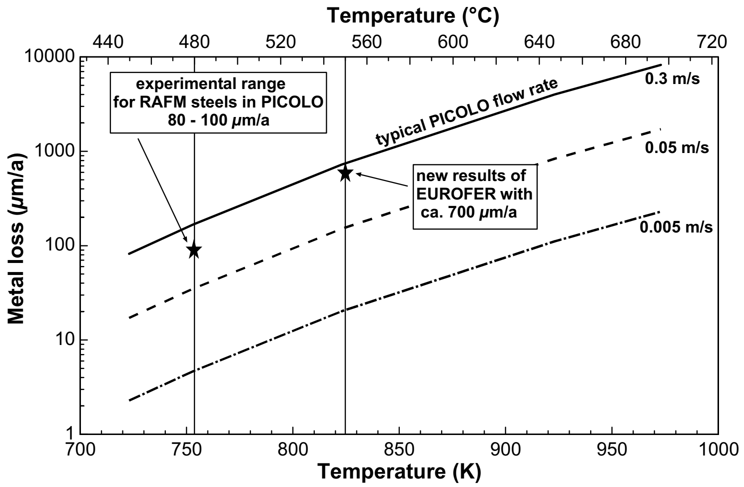

Fig. 3. Calculated (6) and measured corrosion rates of RAFM steels as a function of temperature and flow rate.

times to increase reliability of the data. Nevertheless, the first corrosion results indicate that this high corrosion rate will significantly influence design for long application times and may lead to precipitation effects which may be difficult to manage in the cooler areas of the loop or in a fusion system.

4. Aluminization of RAFM steels EUROFER and MANET

Corrosion testing in the PICOLO loop showed that corrosion rates increase dramatically with temperature. Of course, a reduction in flow rate may help. However, the dissolved and transported amount of corrosion products and their precipitation behavior will nevertheless remain a serious problem in system operation. One possible option may be the coating of EUROFER by Al and subsequent forming of corrosion resistant scales. In a previous program, a hot-dip aluminization process was developed for coating. MANET or F82H mod. steels [4] with the intention of reducing tritium permeation and achieving corrosion resistant scales. It was shown that a complex procedure for dipping into the Al melt and subsequent heat treatment was necessary to form the corrosion resistant Al_2O_3 and

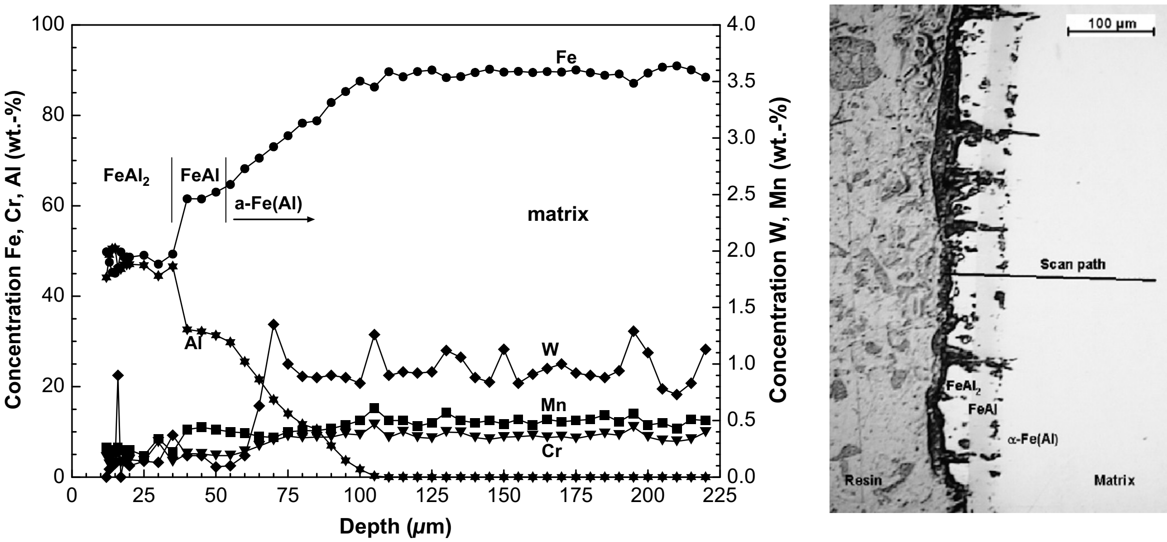

Fig. 4. Line scan (left) and scan path (right) of EUROFER sample tested for 6292 h at 480 °C in PICOLO loop.

Al–Fe scales. During these processes, the temporarily formed brittle Fe_2Al_5-phase is transformed into more ductile FeAl and α-Fe(Al) equilibrium phases. Corrosion testing in the PICOLO loop showed that this phase sequence with a total thickness of about 150 μm withstands the Pb–17Li at 480 °C without visible attack [4]. Similar to these process steps, EUROFER samples were Al-coated and annealed to form the required phases. The coated EUROFER samples were annealed at 980 °C/for 0.5 h and 760 °C/for1.5 h, to recover the FM structure in the bulk and to form the surface scales. Fig. 4 shows the surface of an EUROFER sample exposed to Pb–17Li for 6292 h and the line scan performed along the marked path in the SEM picture. The highest Al level is about 50 wt% in the near surface region which was in contact with the Pb–17Li melt and belongs to the phase $FeAl_2$ with a thickness of about 20 μm. The $FeAl_2$ field is followed by the next stable phase FeAl. Between FeAl and the EUROFER matrix, a continual Al decrease in the α-Fe is visible. The Al reacted zone is roughly 120 μm thick. The three Al phases detected in the line scan can be correlated to the different grey colors in the SEM picture shown on the left. The microstructure indicates that the Al-rich phase $FeAl_2$ is strongly attacked and partially removed as can be seen in the lower part of the picture. It seems that the corrosion attack was delayed or stopped after reaching the FeAl phase. However, compared to the good results obtained in HDA and corrosion testing of MANET steel, the transformation of Al-rich phases (e.g. $FeAl_2$) into FeAl was not finished for EUROFER. Thus, an optimization of the heat treatment parameters has to be done in the future to increase and guarantee corrosion resistance.

5. Conclusions

The corrosion behavior of EUROFER 97 was examined in flowing Pb–17Li using the PICOLO loop. The detected corrosion rates per year were of the order of about 90 μm at 480 °C and roughly 700 μm at 550 °C. At both test temperatures uniform and homogeneous corrosion attack was observed. The time dependence was found to be linear neglecting possible incubation effects during the beginning of the tests. Dissolution of Fe, Cr, etc. out of the RAFM-steel is the major corrosion mechanism. The corrosion tests with EUROFER 97 ran to about 12000 h at 480 °C, twice the duration of earlier tests with other RAFM-steels. The reliability of all corrosion rates of tested RAFM-steels and their extrapolations to longer exposure times is increased by this new data. Comparing the RAFM steels exposed to Pb–17Li in PICOLO loop, EUROFER showed the most uniform and smallest corrosion attack of all steels tested at 480 °C. The slopes (activation energies) of the mass loss curves vs. time are rather similar; however, EUROFER showed the longest incubation times at 480 °C.

The new test series started at 550 °C showed a significant increase in corrosion attack with temperature at constant flow rate. The detected rates are in agreement with extrapolation performed by using empirical correlations. However, development of modeling tools which describe transport and precipitation as well as dissolution is necessary. The rapid corrosion at 550 °C and the large amount of corrosion products in the loop may cause serious problems in handling such an advanced system. Due to this fact, development and application of corrosion barriers will be necessary at least in the hot regions to guarantee a proper functioning. The developed HDA process for Al coating of RAFM-steels shows good potential concerning corrosion resistance of aluminized steels in general. The tests indicated that Al rich phases (e.g. $FeAl_2$) are less stable in Pb–17Li. The performed tests with EUROFER 97 showed that the heat treatment has to be adapted to guarantee a complete transformation of the Al rich scales similar to the results obtained with coated MANET which showed good corrosion resistance in Pb–17Li over more than 10000 h.

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