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Compatibility behavior of EUROFER steel in flowing Pb–17Li

J. Konys *, W. Krauss, J. Novotny, H. Steiner, Z. Voss, O. Wedemeyer

Foschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

ABSTRACT

Reduced activation ferritic-martensitic steels are considered for application in future fusion technology as structural materials. In the past, corrosion testing was performed at moderate temperatures of about 480 °C and showed acceptable homogeneous corrosion behavior. However, in the mean time the envisaged temperature limits increased to around 550 °C. Due to large uncertainties in extrapolations of the corrosion behavior from 480 to 550 °C, long-term tests were initiated which include also the development of modeling tools and analyzing for the first time in more detail transport and precipitation phenomenas. The tests performed at 550 °C and flow rate of 0.22 m/s revealed a corrosion rate of about 400 μm/year with emphasis to the long term exposed samples. The high amount of dissolved components formed precipitations at cooler loop positions which led to line blockages after short operation of about 3000 h. A comparison with global Pb–17Li data and 480 °C testing will be shown.

1. Introduction

In a future fusion system of the He-cooled liquid lead blanket type (HCLL), reduced activation ferritic-martensitic steels (RAFM) are considered as structural material, which are in direct contact with the breeding material Pb–17Li. At moderate temperatures of up to 480 °C various corrosion experiments in flowing Pb–17Li were performed in the past [1–4]. All examined RAFM steels (e.g. Manet, F82H-mod., Optifer and EUROFER 97) showed similar corrosion behavior concerning activation energies and mechanism [2,4]. These test series were mainly performed with respect to determine corrosion rates and mechanisms, only, and were neglecting other loop features like transportation phenomenas or precipitation effects. Extrapolations of these data to the newly envisaged 550 °C limit are problematic and exhibit large uncertainties due to missing models. Thus long-term tests at 550 °C including the development of modeling tools were initiated to build up a consistent data base for Pb–17Li corrosion and precipitation effects. These new activities are driven by the changes in TBM requirements and analyzing the knowledge on interacting loop effects with corrosion and safe loop operation like transportation of corrosion products and their precipitation at cooler loop sections.

2. Corrosion testing

The corrosion testing of bare EUROFER 97 samples was performed in flowing Pb–17Li with a flow velocity of 0.22 m/s in the PICOLO-loop. The highest temperature in the loop was present in the test section with 550 °C. The coolest sections were the electromagnetic pump and magnetic trap devices with roughly 350 °C. The fresh test samples had a diameter of 8.0 mm and were mounted concentrically in the test section with inner diameter of 16 mm. The flow velocity of 0.22 m/s is the calculated value for the fresh “un-coroded” configuration. The longest exposed sample was removed after nearly 12,000 h and the smallest exposure time was 500 h. Due to the high corrosion attack at 550 °C a high amount of precipitates was present in the loop which caused a first plugging after about 3000 h of operation. The blockage appeared in the mounted magnetic trap section which is installed to collect precipitates and prevent the electromagnetic pump from damages. Replaced fresh magnetic traps had in the following an average life time of around 3000 to 4000 h.

3. Corrosion attack

The corrosion testing of RAFM steels performed at 480 °C in PICOLO-loop in earlier test campaigns showed that dissolution of e.g. Fe, Cr out of the steel matrix is the acting corrosion mechanism which leads to a corrosion rate at 480 °C of roughly 90 μm/year at 0.22 m/s. The new tests performed at 550 °C delivered the same corrosion mechanisms and showed also a homogeneous attack of the surfaces at longer exposure times. In contrast to 480 °C testing the new corrosion testing showed rather small incubation periods below 500 h. The first sample removed in this campaign after 500 h exhibited only some small not attack surface fractions of about 5%. Measuring the step occurring between eroded and not attacked areas (Fig. 1) gave first hints that the corrosion attack is dramatically increased and indicated possible upper margins up to 700 μm/year. The whole testing program was running up to about

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* Corresponding author.
E-mail address: juergen.konys@imf.fzk.de (J. Konys).

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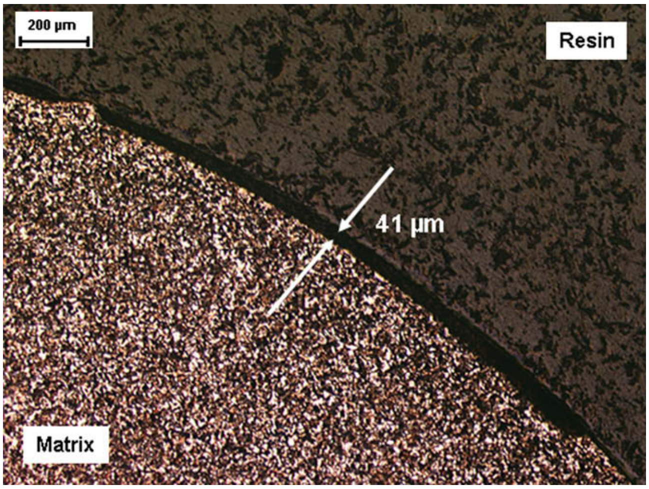

Fig. 1. Surface section of a sample removed after 500 h from PICOLO-loop testing at 550 °C.

12,000 h and showed always a good wetting of the surfaces and a homogeneous corrosion attack as can be seen for example in the micrograph shown in Fig. 2a. Compared to 480 °C (Fig. 2b) only insignificant changes in the surface structure may be present. No evidence was found in metallographic analyses for leaching or cracking off of complete martensitic needles in shape of particles. Line scan analyses showed that a sharp boundary is existing between matrix and Pb–17Li melt as can be seen in Fig. 3 by the concentration signal for e.g. Fe which drops within the resolution distance (~3 µm) from roughly 90% to 0%. This behavior excludes deep grain boundary infiltration effects by Pb–17Li. The enrichment of the adherent Pb–17Li scale by e.g. Fe or W corrosion products indicate that in surface near regions a reduced mixing is present and diffusion controlled transport may be pronounced near surfaces.

The material take off was measured optically in dependence of the exposure time using the metallurgical cuts and all samples showed a symmetrical spherical attack within the resolution limits of about 5 µm. The determined corrosion attack during Pb–17Li exposure is given in Fig. 4. Extrapolations done by samples removed after short times (500–1500 h) deliver rather high corrosion values of about 700 µm/year. This high rate seems to be an overestimation of the yearly loss due to error bars in diameter determination and short exposure times. For long exposure times (2500–12,000 h) smaller rates were evaluated. Fig. 4 depicts the measured values without and with corrections for flow velocity changes. Due to diameter changes by corrosion in the test section the flow velocity of $\upsilon(t = 0) = 0.22$ m/s was reduced to nearby 0.18 m/s after about 12,000 h roughly 80% of the originally selected velocity. Thus depicted measured corrosion values in Fig. 4 are too small and show a too optimistic behavior. At least the reduced flow has to be considered and a correction has been performed for

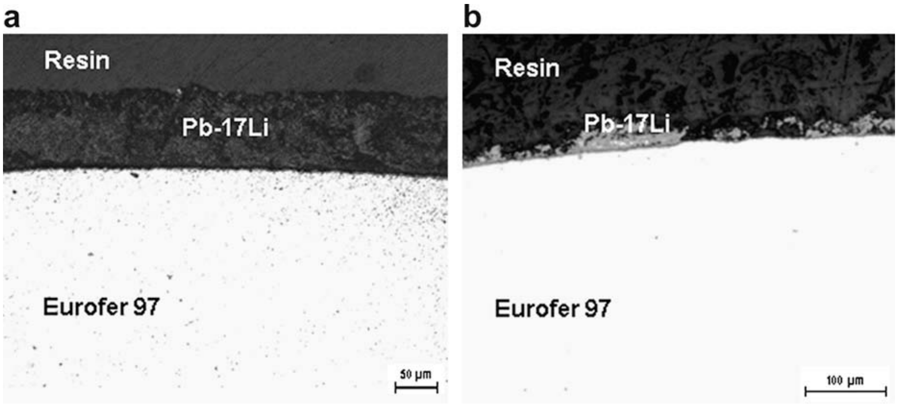

Fig. 2. EUROFER 97 exposed for about 10,006 h at 550 °C (a) and for about 12,320 h at 480 °C (b) to Pb–17Li in PICOLO-loop. Both samples were cleaned from adherent excess Pb–17Li melt after removal.

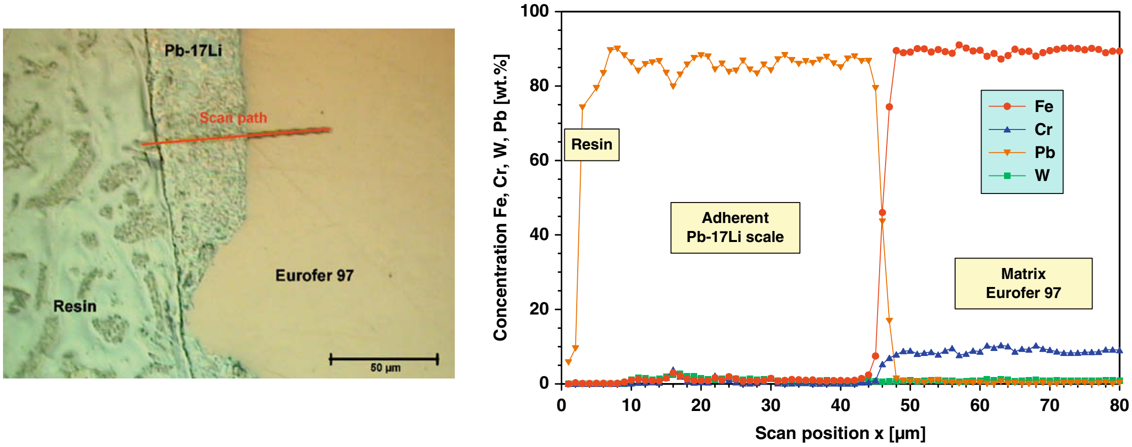

Fig. 3. Line scan path of a sample (SEM, C-coated) exposed 1025 h to Pb–17Li in PICOLO-loop and corresponding concentration profile.

constant flow velocity 0.22 m/s to see more realistic corrosion values. Assuming that Sannier's correlation [5] is valid at least for constant temperature and small changes in flow velocity a correction should be possible with high reliability. Sannier's correlation predicts material loss (ML) in the given form of dissolution depth per year by:

$$\mathrm{ML} = 8 \times 10^{8} \times \exp[-25,690/1.98\mathrm{T}] \times v^{0.875} \times d_{\mathrm{h}}^{-0.125} [\mu\mathrm{m/a}]$$

Thus, the correction has to consider only the parameters v (velocity) and d_h (hydraulic diameter) to find out relative changes. Calculating the changes of $\mathrm{F}(v * d_h)$ and comparing to the start value F_0 for $v_0 = 0.22$ m/s and $d_{h0} = 4.0$ mm predicts the impact of flow velocity changes on corrosion attack.

For a material loss of about 0.48 mm as determined for exposure time 12,000 h a reduced corrosion attack by about 19% is predicted if constant loop parameters would be used. Assuming that the correction factor F(0)/F(t) changes linearly all observed rates have to be increased e.g. for 12,000 h by about 9.5%. Some other parameters will also affect and reduce corrosion attack during testing. For example a reduced mass flow (90 – 100% level of nominal value due to delayed adjusting by control devices for about 10% of testing time) will cause an additional correction by 2%. This type of corrections was performed for some long term exposed samples to generate corrosion attack values at constant 0.22 m/s Pb–17Li flow velocity. These corrected values are given by separate symbols in Fig. 4. The linear interpolation of the corrected values leads to a corrosion rate of about 400 μm/year with more emphasis to the values evaluated for the long term exposed samples.

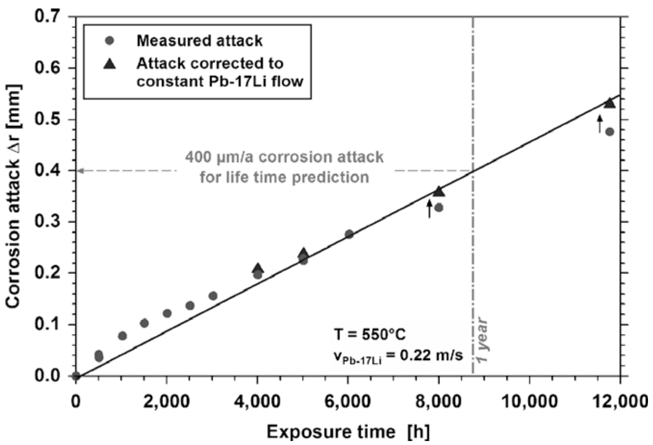

Fig. 4. Corrosion attack of EUROFER 97 at 550 °C in PICOLO-loop. Depicted are the measured values without correction for reduction in flow velocity due to gap widening.

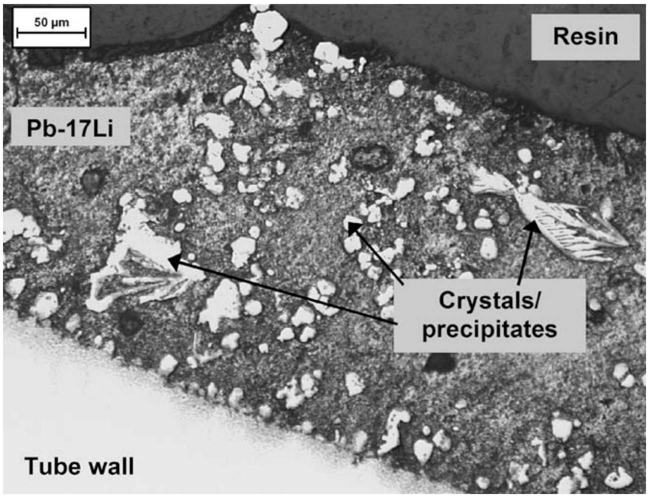

Fig. 5. Drained tube section with adherent Pb-Li scale and precipitates included.

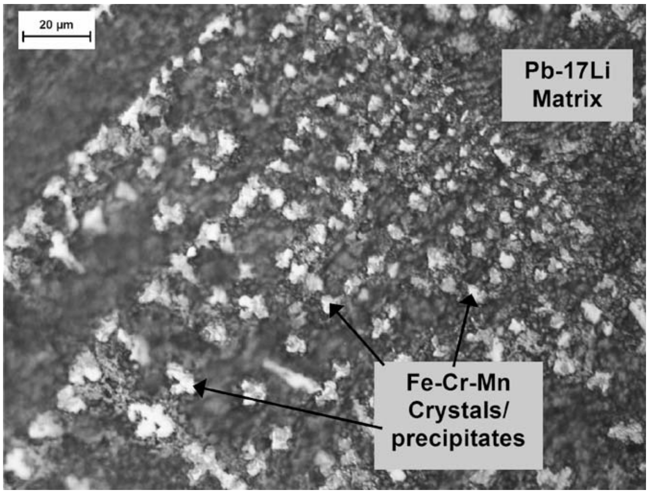

Fig. 6. Precipitations in the centre of the magnetic trap.

Sannier's correlation is also a possible method to compare empirically the Pb–17Li corrosion regimes in general. Both determined corrosion rates for 480 °C with about 90 μm/year and for 550 °C with roughly 400 μm/year fit very well into these correlation. This means that the newly performed 550 °C testing series deliver realistic values. New modeling tools were developed in parallel for analyzing the PICOLO testing campaigns and the results will be found in [6]. The most reasonable result will be that small changes in temperature of 70 K lead to drastically increased corrosion rates by a factor of 5 and those remarkable amounts of corrosion products are present and transported by Pb–17Li in the loop.

4. Precipitations

The corrosion products dissolved in warm loop regions will form precipitations in cooler sections. First metallographic analyses, performed at some tube segments operated at 350 °C, confirmed not the expected homogeneous coating of the inner surfaces by deposition as opposite process of dissolution. The analyzed cuts of drained loop sections showed a lot of nicely grown crystals up to 100 μm in size embedded in the adherent Pb–17Li melt as given in Fig. 5. The dimensions of the crystals indicate that they were formed over longer time intervals, however, not necessarily at the position of detection. A higher amount of such precipitates (Fig. 6) was collected in the mounted magnetic trap device with their main axis oriented parallel to the magnetic field. The chemical analyses detected a Fe concentration of about 4.3 wt.% in Pb–17Li. The Pb–17Li flow was heavily suppressed by these particles after an operation time of about 3000 h at 550 °C in the test section. This behavior represents clearly the risk of line plugging by precipitations in a loop due to dramatically increased corrosion at hot temperature positions and the transportation/nucleation effects.

5. Conclusions

For the first time corrosion testing of EUROFER 97 was successfully performed under 550 °C conditions at a flow rate of 0.22 m/s and exposure times up to about 12,000 h. The newly started corrosion testing and modeling activities showed that a dramatically increase in corrosion rates takes place at a small increase of operation temperature from 480 to 550 °C by a factor of 5. The observed dissolution/corrosion mechanisms in the testing zone are the same as detected at lower temperatures in the past and are in agreement with results reported earlier [2–4]. The loop operation and corrosion testing pointed out the high risk of loop blockages by forming precipitates within short operation times of roughly 3000 h. The performed first analyses indicate that the precipitates are freely transportable in the melt and may be deposited/collected at positions with low flow velocity or special magnetic field conditions. The modeling tools developed in parallel confirm the evaluated corrosion mechanisms and rates as well as the observed precipitation behavior. Both, experimental and analytical analyses indicate that safe operation of Pb–17Li systems without the risk of line plugging may need corrosion resistant coatings to bring down corrosion and precipitation behavior at high operation temperatures to a manageable level also at small flow velocities.

Acknowledgements

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References

[1] H.U. Borgstedt, G. Drechsler, G. Frees, Z. Peric, J. Nucl. Mater. 155–157 (1988) 728.
[2] H. Glasbrenner, J. Konys, H.D. Röhrig, K. Stein-Fechner, Z. Voss, J. Nucl. Mater. 283–287 (2000) 1332.
[3] G. Benamati, C. Fazio, I. Ricapito, J. Nucl. Mater. 307–311 (2002) 1391.
[4] J. Konys, W. Krauss, Z. Voss, O. Wedemeyer, J. Nuc. Mater. 329–333 (2) (2004) 1379.
[5] J. Sannier, T. Flament, A. Terlain, Corrosion of martensitic steels in flowing Pb–17Li, Proc. 16th Symp. Fusion Technology, 3–7 September, 1990, London, UK, 901.
[6] H. Steiner, W. Krauss, J. Konys, Calculation of Dissolution/Precipitation Rates in Flowing Eutectic Pb–17Li with the MATLIM code, ICFRM-13, Nice, France, December 10–14, 2007.