EUROfusion

WPBB-CPR(18) 20126

W Krauss et al.

Precipitation phenomena during corrosion testing in the forced-convection

Preprint of Paper to be submitted for publication in Proceeding of
30th Symposium on Fusion Technology (SOFT)

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Precipitation phenomena during corrosion testing in forced-convection Pb-15.7Li loop PICOLO

Wolfgang Krauss, Sven-Erik Wulf, Julia Lorenz, Jürgen Konys

Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz
76344 Eggenstein-Leopoldshafen, Germany

Several blanket concepts (e.g., HCLL, WCLL, DCLL) are based on the application of the liquid breeder Pb-15.7Li, which is in direct contact with the structural components. Compatibility testing has shown that the structural materials (e.g., Eurofer) always suffer from corrosion attack. The governing mechanism can be attributed to dissolution of the steel by the liquid breeder. A fusion device with blanket modules or also corrosion testing loops, e.g., the PICOLO loop of KIT, are non-isothermal systems. The components dissolved at higher temperature are transported with the breeder flow. At sections with cooler temperature oversaturation of the breeder will occur. Effects such as deposition, precipitate formation and transport of corrosion products will take place. Corrosion testing in PICOLO showed that such particles are formed and that they can seriously affect safe and reliable operation of Pb-15.7Li systems up to blocking of components. Thus, during maintenance work tubing sections and components were removed for analyzing the issue of corrosion product deposition. The operation conditions of the components and the loop are given in detail to assess the deposition scenarios together with the size and shape of the formed particles to support future loop design and purification measures.

Keywords: Pb-15.7Li corrosion; precipitations; particle shapes; particle transport; PICOLO loop

1. Introduction

Several breeding blanket designs are foreseen for fusion reactors beyond ITER, e.g. HCLL (helium-cooled lithium-lead), WCLL (water-cooled lithium-lead) or DCLL (dual-coolant lithium-lead) [1-3]. In all cases the liquid metal alloy Pb-15.7Li acts as breeding material. In the WCLL concept breeder and coolant are contained in two completely separate systems. The liquid breeder is circulating in a closed loop and is in direct contact with the structural materials of type Reduced Activation Ferritic Martensitic (RAFM) steel like Eurofer or CLAM-steel. Essential for reliable and safe operation of such a blanket system will be the compatibility of the breeder with the designated and specially developed 9%Cr steels. Analysing the behaviour of steels, e.g., austenitic (type 316) or martensitic-ferritic (type HT-9, 1.4914) ones [4-7], in contact with the Pb-15.7Li breeder is dating back at least to the 1980's. These tests performed in the medium temperature range of up to about 450°C (723 K) indicated that austenitic steels are more sensitive to corrosion attack due to their Ni amount. Due to the activation issue under fusion conditions more improved RAFM-steels were developed in the following years such as Manet I, F82H-mod. or Optifer IV and tested with respect to their stability in Pb15.7Li, e.g., in PICOLO loop at KIT [8]. Around the year 2000 the more innovative Eurofer steel entered into compatibility testing and testing temperatures increased towards 550°C (823 K) as a contribution to the meanwhile scheduled higher temperatures in a blanket system. Then changing the test conditions from 480°C (753 K) to 550°C the corrosion attack, equivalent to the mass loss, increased drastically from about 90 µm/year to roughly 400 µm/year at a flow velocity of 0.22 m/ [9]. Surely, the corrosion attack depends also on the flow velocity, however, only marginally on the composition of the RAFM-steel, e.g. Eurofer vs. CLAM-steel [10] or vs. ODS-Eurofer [11]. The mass loss at 0.1 m/s flow velocity found during testing in PICOLO loop is roughly half the value measured at 0.22 m/s. A rather good illustrative view for the corrosion attack of RAFM-steels in flowing Pb-15.7Li can be obtained using Sannier's correlation [12] as depicted in Fig.1.

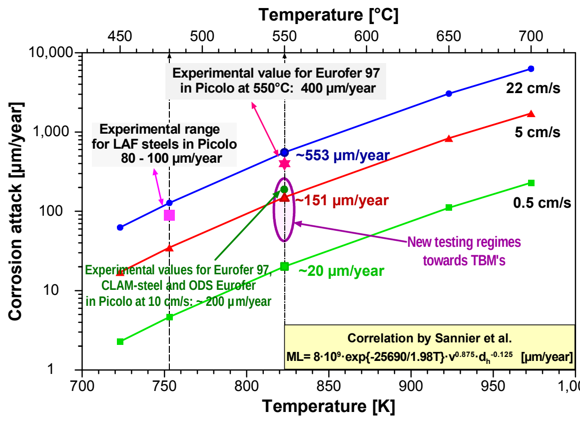

Fig. 1. Corrosion attack of RAFM-steels during corrosion testing in Picolo loop and predicted by Sannier's correlation.

A thinning of a wall by a corrosion attack of 400 µm/year corresponds to a mass loss of roughly 4 kg/m*year of a steel surface. The removed steel components are transferred to the liquid metal. This feature is known since decades, e.g., as described in [13]. However, analyses of the formed corrosion products are scare. During maintenance work several sections of PICOLO loop were removed and analyzed with respect to

author's email: wolfgang.krauss@kit.edu

shape of the formed particles and the place of deposition. A sampling of Pb-15.7Li was performed at the expansion vessel to investigate the melt composition and the composition of formed surface scales.

2. PICOLO loop and operation conditions

2.1 Loop design

The actually operated configuration of the PICOLO loop is based on a loop design as proposed and realized in the 1980's by Borgstedt [6]. The PICOLO loop consists of a hot and a cold leg with a forced Pb-15.7Li flow. The flow velocity of the melt in the test section can be adjusted between 0.01 and 1 m/s by varying the pumping power. The highest temperature of the whole loop is in the test section, which is designed for testing at up to 550°C. The cold leg of the loop is operated at 350°C (623 K). The test samples are inserted into the test section via an expansion vessel with a free surface of the melt positioned in a glove box with purified Ar and monitored O_2 and H_2O levels in the range of 1 ppm.

The components electromagnetic flow meter, electromagnetic pump and magnetic trap are positioned in the cold leg together with a drain tank and an air cooler for reducing the melt temperature at very high flow velocities. All these parts are fabricated from 316 L steel and the operation temperature will not exceed 400°C. All components operated at higher temperatures are fabricated from steel 1.4914 which is similar to the tested RAFM-alloys.

Fig. 2 shows a sketch drawing of the PICOLO loop with the positions of the main components. The whole length of the tubing is approx. 12 m. One half of this is fabricated from CrNi-steel (cold leg) and about one third of the loop length is operated above ca. 450°C. All heaters are mounted at the outer surfaces of the components and the connecting lines of the components have 16 mm internal diameter.

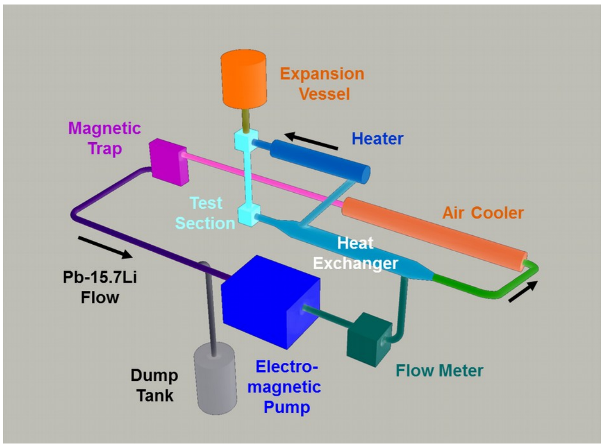

Fig. 2. Schematic view of the PICOLO loop.

The flow velocity in the test section with concentrically mounted test samples with a diameter of 8 mm is roughly 4 times the velocity value present in the pumping channel. The velocity in the heat exchanger, which consists of two concentrically arranged tubes, is rather similar for the upstream and downstream path and comparable with the value present in the pumping channel. The Pb-15.7Li has the smallest flow velocity in the heater with roughly 1/10 of the velocity in the test section. The flow regime in the test section of PICOLO under an operation with 0.1 m/s flow velocity is at the boundary between turbulent and mixed flow conditions. Laminar flow conditions may be (partly) present in the heater, which heats the Pb-15.7Li up to the desired testing temperature.

2.2 Corrosion testing and Pb-15.7Li conditions

The Pb-15.7Li inventory of PICOLO loop is roughly 15 liters and the pumping rate is about 55 l/h to obtain a flow velocity of 0.1 m/s in the test section. The corrosion attack of RAFM-steels is about 200 µm/year [11] at that flow velocity and at 550°C. The corrosion process will not be limited to the inserted stack of samples (diameter 8 mm and length 450 mm). The test section itself will also suffer similar attack. The samples inserted at top and bottom positions showed similar corrosion rates indicating that no downstream effects are present due to saturation of the Pb-15.7Li by dissolved impurities. This may imply that also some areas of the heat exchanger may corrode. The heater should not show significant corrosion attack due to the very low flow velocity. The sample stack will deliver about 2 g Fe and Cr corrosion products per year. On its own the test section exhibits the 5-fold surface area compared to the stack. Together with a part of the heat exchanger, the surface areas which deliver significantly corrosion products can be estimated to be 10 times the surface of samples. Thus, an amount of 20 g of corrosion products produced per year appears to be a realistic estimation.

The solubility limits of Fe and Cr in Pb-15.7Li are in the order of some (< 10) wppm [13,14] at 550°C and this indicates that at least 1 g of impurities can be dissolved in the melt. As a consequence 'deposition' processes of impurities have to take place at cooler loop sections due to oversaturation. This issue has already been reported by Borgstedt [13] and has been shown by modeling the corrosion/deposition phenomena for PICOLO [15]. Though, the 'deposition' does not form a coating of the surfaces inside the cold leg, i.e., the reversal process of homogeneous dissolution. In contrast the 'deposition' occurs by formation of precipitates which are embedded in the melt and mostly not fixed at a wall surface [16].

3 Results

3.1 Expansion vessel and Pb-15.7Li impurity levels

The expansion vessel is a component with free access to the Pb-15.7Li and is located directly above of the test section. It is also the position for filling the loop with fresh Pb-15.7Li which is melted in a separate furnace inside of the glove box. Usually, PICOLO loop is drained

author's email: wolfgang.krauss@kit.edu

and filled with fresh Pb-15.7Li when a new testing campaign is started to reduce the amount of precipitates inside of the loop. For monitoring purposes Pb-15.7Li is extracted periodically by access via the expansion vessel at a deep position directly at the entry to the test section. Tab. 1 shows the variation of the impurities determined by ICP-OES (atom emission spectrometry) in the melt versus duration of operation.

The drained loop was filled with fresh Pb-15.7Li delivered from Fa. GHM Stachow, Goslar, Germany, with an impurity of Fe < 5, Cr < 1 and Ni < 1 wppm, respectively. The table shows the measured impurities directly after filling with Fe in the range of 1 wppm. The loop was running for conditioning for 500 h at 480°C between filling and start (t=0) of the campaign after that extraction The Li concentration was rather constant over 12,000 h and the Ni level increased. The analyzed Fe and Cr concentrations seem to be not reasonable when considering the solubility limits indicated above. Especially the value of 30 wppm at 4000 h is very high and cannot be explained by only dissolved Fe. This may be an indication for the evidence of particles as the analytics cannot separate between dissolved Fe and Fe in form of particles.

In the component expansion vessel and connecting line stagnant flow conditions are present with a temperature gradient from 550 to 350°C at the free surface. A rough grey Pb-15.7Li infiltrated scale is formed at the cleaned surface within hours and is continuously increasing with time. Chemical analyses showed that significant amounts of Fe, Cr and Ni are present and that the Li concentration is increased (0.78 wt.%) compared to the melt. This may be explained by a Li reaction with O_2 / H_2O impurities present in the glove box atmosphere. By dissolution performed in a mixture of acetic acid / H_2O_2 / ethanol it was found that this surface scale contains solid Fe-Cr based particles.

Beyond analyzing the surface scale steel rods were immersed into the melt of the expansion vessel after cleaning the surface with the intention to 'coat' the rods by an adherent Pb-15.7Li layer. This layer was dissolved and the sediments were analyzed by SEM (scanning electron microscopy) techniques. Fig. 3 shows the observed particles which exhibited a gravel like structure in the range 5 to 50 µm and complex dendritically shaped species with size up to 200 µm and an Fe-concentration near 90 wt.%.. Some of the collected particles were oxide rich and other ones had a high Cr-amount of up to approx. 50 wt.%. Together with the melt analyzes from deep position it cannot be concluded that particles were all formed only in the expansion vessel.

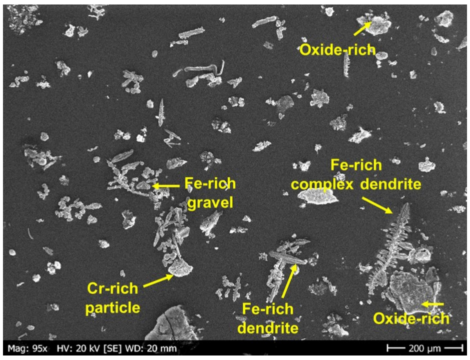

Fig. 3. Particles after Pb-15.7Li dissolution extracted from the expansion vessel by immersion of a rod.

3.2 Precipitates in the air cooler

The component air cooler is installed to cool down the melt flow passively or actively by an air stream depending on testing conditions. The temperature at the exit is set to be about 380°C for protecting the magnetic components from overheating. An inspection piece cut off there showed that particles are embedded in the Pb-15.7Li. The particles there exhibited a gravel like structure with dimensions between approx. 2 and 80 µm with a majority of particles in the lower µm range. Fig. 4 shows the cross section after etching by acetic acid mixture for 1 min. The particles exhibit a composition near the Fe/Cr ratio of Eurofer. The flow velocity in the tube was about 0.1 m/s.

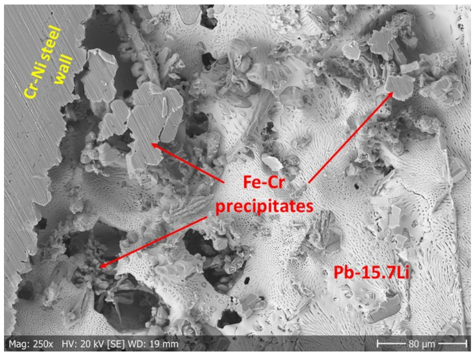

Fig. 4. Particles observed at the exit of the air cooler where no magnetic fields are present.

3.3 Deposits in the area of the magnetic trap

PICOLO loop is equipped with a magnetic trap for collecting ferromagnetic corrosion products. This trap is installed in the cold leg in front of the electromagnetic pump and the magnetically based flow meter. This trap

Table 1. Concentration of impurities and Li in Pb-15.7Li of PICOLO loop during one testing campaign

Time [h]	As filled	0	1000	4000	8000	10000	12000
Li [wt.%]	0.61	0.61	0.58	0.59	0.61	0.59	0.59
Fe [wppm]	1.2	35	5.6	30	6	<5	<5
Cr [wppm]	1.1	3	<1	14	<3	<3	<3
Ni [wppm]	6	14	11	32	34	60	71

author's email: wolfgang.krauss@kit.edu

consists of a permanent magnet and a square shaped flow channel of 20 mm width which is positioned between the magnetic poles. The field is perpendicularly orientated towards the flow direction. The operation temperature of the trap is 350°C and the amount of Pb-15.7Li inside is approx. 1.1 kg. The analyzed trap was removed after a power failure with flow breakdown and attempts to restart the flow again. Normal operation time with flow was about 15,000 h and 'annealing' without flow lasted for about 300 h. The trap was cooled down within half a day and cut off together with sections of the connecting lines (Fig. 5).

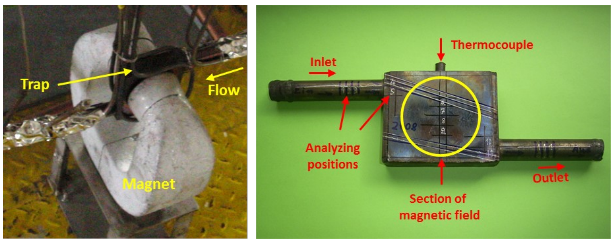

Fig. 5. Magnetic trap (AlNiCo permanent magnet poles) with flow path and analyzing positions.

As shown in Fig. 6 (etched cross section) a lot of precipitates were deposited or had grown in the contact zone melt to tube wall. An interesting feature is also that a significantly increased thickness of the layer is found at the top position of the tube. The Fe/Cr ratio of the precipitates is similar to the Eurofer composition and contains negligible Ni amounts from the corrosion of the stainless steel parts in the cold leg. The area with a significant amount of precipitates is about 600 µm thick at the bottom of the tube. At the top position the extension is up to 2.5 mm. SEM/EDX analyses indicate that the amount of the precipitates is in the range of 1-2 wt.% in this area.

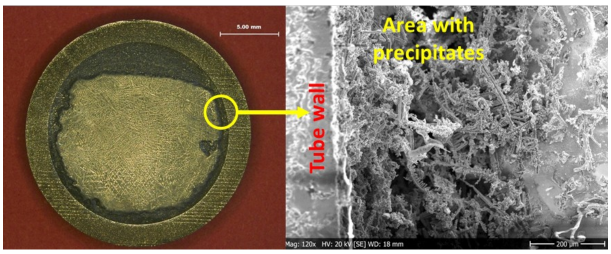

Fig. 6. Deposits inside of the tube (diameter 16 mm, flow velocity 0.1 m/s) in front of the trap together with SEM image of precipitates (mostly dendrites).

Chemical analyses revealed that the Fe concentration in the magnetic trap varies between ca 1 % (near inlet and outlet position) and 5 % at the central position. Dominating are particles with dendritic structures. Precipitates were forming network-like configurations especially in the center of the trap. These filigree structures can easily grow in length up to some 100 µm as illustrated in Fig. 7. Precipitates were also found in the outlet tube of the magnetic trap. However, the observed 'deposits' contained more particles with gravel like structure beyond dendrites. The dimensions of these

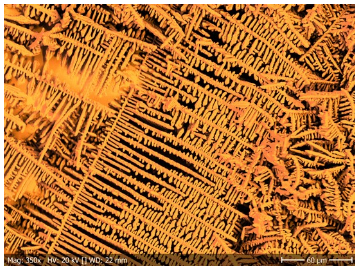

Fig. 7. Dendritic-like structure of precipitates in the center of the trap, the orientation of the microcut is parallel to the magnetic field (colored SEM image).

particles (Fig. 8) were in the range of some µm to 50 µm, roughly. Two options may exist for the enrichment by gravel like particles compared to the inlet – (a) changed growth conditions or (b) low retention of small particles by the trap. The discrimination of (a) or (b) is not possible.

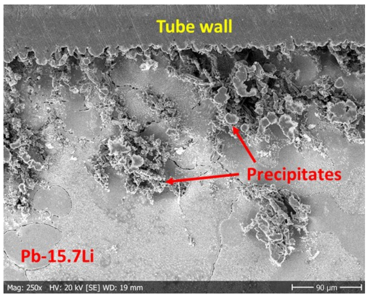

Fig. 8. Gravel and dendrite like structures of particles found in the outlet tube of the trap.

3.4 Deposits in the electro-magnetic pump

The forced flow of the breeder is generated by a moving electro-magnetic field which propels the Pb-15.7Li in a duct fabricated from 316 L steel with a sectional area of about 4 x 130 mm. The inspected pumping channel was removed after loop draining during revision works due to deformations in the central part (6 mm height) and cut off for analyses. This channel was used for roughly 3 years. After draining the channel was still filled with 'sediments. Fig. 9 shows a broken out part (approx.. 6 mm in height) and the corresponding SEM image of prepared cross section. Filigree shaped Fe/Cr precipitates could be observed which are infiltrated by Pb-15.7Li. The precipitate concentration is low (1 % level) but it led to plugging of the pumping channel.

3.5 Other precipitate affected loop components

During revision works particles were also found in the magnetic flow meter (T=350°C) and in the tubes of the warmer components of the heat exchanger and surprisingly also in the heater at temperatures of 500 to

author's email: wolfgang.krauss@kit.edu

550°C. Growing of particles locally in the heater may be doubtful due to the high temperature. The other source for finding deposits there may result from transport of the particles with the breeder flow into the heater. Such circulating particles would well fit to the chemical analyses of the melt at the entrance of the test section with Fe values above of the solubility limits.

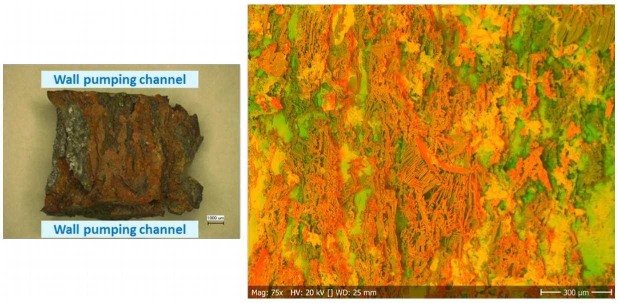

Fig. 9. Precipitates in the electro-magnetic pump. Red colored = Fe particles with main orientation parallel to the magnetic field lines.

4 Conclusions

The test samples and the components of PICOLO loop showed significant corrosion attack in the hot leg of the loop indicating that the Pb-15.7Li is not saturated when entering the test section. No (clear visible) reduced corrosion attack of samples by downstream effects was observed in the test section. The dominating corrosion mechanism is dissolution of the steel. A wall thickness of about 200 µm/year was dissolved during this test campaign and provided the source for forming of precipitates at cooler loop sections due to occurring oversaturation of the Pb-15.7Li at low temperatures.

Precipitates were found in all inspected parts removed from the cooler loop sections. The observed dissolution / deposition scenario is in good agreement with predictions concerning the reduction of oversaturation by deposit formation [15]. The analyses showed that different types and shapes of particles were found depending on local conditions. Surely, the intended purification by the installed magnetic trap was not appropriate. Essential is that particles were found in front of the trap. The benefit of the perhaps ‘insufficiently’ acting trap was that the reduction of oversaturation by precipitate formation could be clearly verified in adjacent components. The shown pictures show the risk of line plugging by precipitates through local growth and transport as well the enhanced deposition in components exposed to magnetic fields

Acknowledgments

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

author’s email: wolfgang.krauss@kit.edu

References

[1] L. A. El-Guebaly, L.V. Boccaccini, R.J. Kurtz L.M. Waganer: Technology-related challenges facing fusion power plants, in Fusion Energy and Power 1-69 (2015) New York, Nova Science Publishers Inc.

[2] G. Aiello, G. de Dinechin, L. Forest, F. Gabriel, A. Li Puma, G. Rampal, E. Rigal, J.F. Salavy and H. Simon: ‘HCLL TBM design status and development’, Fusion Engineering and Design 86 (2011), 2129–2134

[3] J. Aubert, G. Aiello, N. Jonquères, A. Li Puma, A. Morin and G. Rampal: ‘Development of the water cooled lithium lead blanket for DEMO’, Fusion Engineering and Design, 2014, 89, 1386–1391

[4] V. Coen, P. Fenici, H.‘Kolbe, L. Orecchia, T. Sasaki Compatibility of AISI 316 L stainless steel with the $Li_{17}Pb_{83}$ eutectic, Journal of Nuclear Materials 110 (1982) 108- 114

[5] O.K. Chopra, D.L. Smith, Compatibility of ferrous alloys in a forced circulation Pb-17Li system, Journal of Nuclear Materials 141-143 (1986) 566-570

[6] H.U. Borgstedt, G. Frees, G. Drechsler, Corrosion of stainless steel in flowing PbLi eutectic, Journal of Nuclear Materials 141-143 (1986), 561-565

[7] O.K. Chopra, D.L. Smith, Corrosion of ferrous alloys in eutectic lead-lithium envioremeent, Journal of Nuclear Materials 122-123 (1984) 1219-1224

[8] H. Glasbrenner, J. Konys, Z. Voß, Corrosion behaviour of low activation steels in flowing Pb-17Li, Journal of Nuclear Materials 281 (2000) 225-230

[9] J. Konys, W. Krauss, H. Steiner, J. Novotny, A. Skrypnik, Flow rate dependent corrosion behavior of Eurofer steel in Pb–15.7Li, Journal of Nuclear Materials 417 (2011) 1191-1194

[10] J. Konys, W. Krauss, Z. Zhu, Q. Huang, Comparison of corrosion behavior of EUROFER and CLAM steels in flowing Pb–15.7Li, Journal of Nuclear Materials 455 (2014) 491-495

[11] W. Krauss, S.-E. Wulf, J. Konys, Long-term corrosion behavior of ODS-Eurofer in flowing Pb-15.7Li at 550°C, Nuclear Materials and Energy 9 (2016) 512-518

[12] J. Sannier, T. Flament, A. Terlain, Corrosion of martensitic steels in flowing Pb–17Li, in: Proc. 16th Symp. Fus. Tech., 3–7 Sept., London, UK, (1990) 901

[13] H.U. Borgstedt, G. Drechsler, G. Frees, Z. Peric, Corrosion testing of steel X 18 CrMoVNb 12 1 (1.4914) in a Pb-17Li pumped loop,, Journal of Nuclear Materials 155-157 (1988) 728 -731

[14] I.E. Lyublinski, V.A. Evtikhin V.Yu. Pankratov, V.P. Krasin, Numerical and experimental determination of metallic solubilities in liquid lithium, lithium-containing nonmetallic impurities, lead and lead-lithium'eutectic, Journal of Nuclear Materials 224 (1995) 288-292

[15] H. Steiner, W. Krauss, J. Konys, Calculation of dissolution/ deposition rates in flowing eutectic Pb–17Li with the MATLIM code, Journal of Nuclear Materials 386–388 (2009) 675–677

[16] J. Konys, W. Krauss, J. Novotny, H. Steiner, Z. Voss, O. Wedemeyer, Compatibility behavior of Eurofer steel in flowing Pb-17Li, Journal of Nuclear Materials 386–388 (2009) 678–681

author's email: wolfgang.krauss@kit.edu