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Post-irradiation examination on LiSoR 3 experiment

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Abstract

Liquid solid reaction (LiSoR) facility is a lead bismuth eutectic (LBE) loop which operates during irradiation with 72 MeV protons. In the LiSoR 3 experiment the beam current was set to 15 μA. Due to an erroneous signal of a leak detector in the beam line the experiment had to be stopped ahead of schedule after 264 h of irradiation. Nevertheless, the post-irradiation examinations (PIE) performed on the tensile specimen and the test tube by SIMS and SEM/EDX showed interesting results. No corrosion attack of LBE to the steel occurred, and no micro crack formed. An oxide layer consisting of a duplex structure was formed on the steel surfaces. The thickness of this layer is dependent on the position to the beam centre. The thickest layers were found directly in the irradiated zones both on the tube and on the specimen. Although the irradiation is still low, 0.2 dpa, the results are optimistic to MEGAPIE (1 megawatt pilot experiment) target.

1. Introduction

The liquid metal target MEGAPIE (1 megawatt pilot experiment) [1,2] will use lead bismuth eutectic (LBE) as spallation material due to its good physical properties, among others the extremely small neutron absorption cross section and a high yield of about 28 n per 1 GeV proton and only slight moderation of neutrons. Ferritic–martensitic steel T91 was selected as window material for the MEGAPIE target. During irradiation the steel will be directly in contact with LBE while the proton beam impinges onto it. The possible interactions between steel and liquid metal are liquid metal corrosion and liquid metal embrittlement.

It is well known that oxide layers on top of the steel surface protects the material against liquid metal corrosion attack as well as against liquid metal embrittlement (LME) by preventing intimate contact between liquid metal and solid metal [3,4]. The temperatures estimated to be reached during MEGAPIE irradiation are about 340 °C on the inner surface of the beam window being in contact with LBE. The overall irradiation time planned for MEGAPIE is around half a year. Hence, no corrosion attack is expected to happen to T91 by LBE for this temperature because the solubility of steel elements in LBE is extremely low below 400 °C.

Latest investigations performed on ferritic–martensitic steels (mainly T91) and LBE or lead revealed that this kind of steel can show LME under special conditions like hardening of the material or by inserting a stress concentrator [5–8]. The behaviour of steels in LBE or lead environment under

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irradiation is up to now a completely unexploited field and predictions are not possible. Hence, the liquid solid reaction (LiSoR) experiment, was launched to investigate the simultaneous influence of LBE and a proton beam on steel T91 [9]. The LiSoR set up is basically a LBE loop with a test section that is irradiated with a proton beam of 72 MeV. Test section no. 3 with a T91 specimen directly in the LBE flow was irradiated for 264 h [10]. After disconnecting the test section from the loop, transporting it into the Hotlab, dissembling and cutting the samples careful analyses were performed by secondary ion mass spectrometry (SIMS), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis. The results are presented in this paper.

2. Experimental

2.1. LiSoR loop with test section and specimen

The liquid metal loop LiSoR is a joint effort of PSI, Switzerland and SUBATECH, France with the support of CNRS, France. The LiSoR loop is connected to a beam line of PSI's cyclotron. More details concerning the loop are given in [9,11].

The test section was manufactured by SOTEREM, France. The tube with an ovoid cross section and a wall thickness of 1 mm was fabricated from standard heat-treated martensitic steel T91 which was delivered by Creusot Loire Industrie (France) and has a composition in wt% of 8.26 Cr, 0.13 Ni, 0.95 Mo, 0.43 Si, 0.38 Mn, 0.1 C, 0.2 V, 0.017 P, 0.065 Nb and with Fe in balance. After welding the test tube was re-worked mechanically by company Brehm, Switzerland to remove cracks which were formed during fabrication by EDM wire cutting. A special procedure was developed and tested before application to the test section [12]. At first an abrasive tool was used having a grain size of 240–320 μm to remove the cracked layer. The second step consisted in polishing with diamond paste of 16 μm for about 5 h resulting in a shiny surface after a total removal of about 40 and 50 μm.

The material for fabricating the T91 test specimen was taken from the SPIRE (SPallation IRradiation Effects) program of EC FP5. The steel was produced by Ugine (France) and has a composition in wt% of 8.63 Cr, 0.23 Ni, 0.95 Mo, 0.31 Si, 0.43 Mn, 0.1 C, 0.21 V, 0.02 P, 0.09 Nb and with Fe as balance. The material was standard heat treated, namely normalized at 1040 °C for 1 h followed by air cooling, and then tempered at 760 °C for 1 h followed by air cooling. The surface of the specimen was mechanically polished up to abrasive papers of no. 2000. The exact dimensions of the specimen and the test tube are given in [9].

2.2. Experimental conditions

After successful leak test of the loop with the assembled test section the whole system was heated up before filling with 15 l of molten LBE from the storage vessel. The flow rate of the pump was 0.3 L/s, which corresponds to a flow velocity of about 1 m/s in the test section. The loop was operated about 24 h at a LBE temperature of 300 °C measured in the test section before irradiation was started. The proton beam parameters were the following: proton energy on target 72 MeV, beam current 15 μA, beam wobbling frequency 14.3 Hz in x and 1.19 Hz in y direction with a Gaussian beam profile of $\sigma_x = \sigma_y = 1.6$ mm. After 264 h of irradiation the leak detector located in the beam line recorded a leak and at once a software routine started automatically to end the experiment by stopping the beam, switching off the pump and draining the LBE. After this unintended termination of the experiment the proton fluence was 33.6 μA h/mm^2; the corresponding radiation damage in the tube is about 0.2 dpa, but 0.146 dpa in the inner tensile specimen. More details concerning the operation and the tests performed after the incident are given in [13].

2.3. Examination of irradiated samples

The disconnected test section of the loop was transported into the PSI hot cells. Several types of samples were cut from the LiSoR specimen and tube by means of an EDM (electric discharge machining) wire cutting device installed in a hot cell. A schematic of cutting samples out of the LiSoR samples is shown in Fig. 1. Additionally, the dose rates of the analysed samples are shown in Table 1.

SIMS analyses were performed at the PSI SIMS ATOMIKA4000, which is a fully shielded equipment. It allows determining the isotopic distribution by depth profiling or line scanning.

For all measurements carried out on the LiSoR samples $^{69}Ga^+$ as primary ions was used with an energy of 25 keV and an angle of 0° (normal incidence). The beam currents used were between 500 and 6000 pA. The pressure in the sputtering cham-

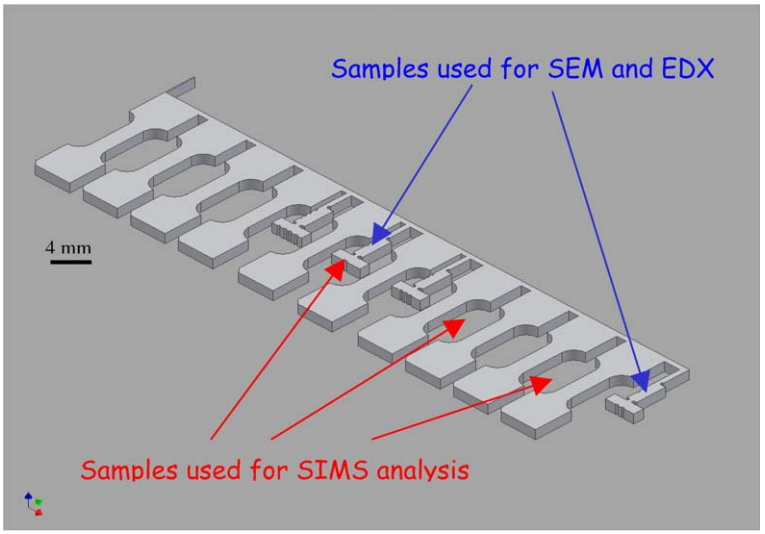

Fig. 1. LiSoR specimen was cut into small samples for examination as shown in this schematic.

Table 1
Dose rates and positions of the samples examined with SEM/EDX and SIMS

	Dose rate	
	μSv/h in 10 cm distance	μSv/h in contact
SEM/EDX examination		
Samples from the tensile specimen		
In the irradiated area	200	9000
Adjacent to irradiated area (29 mm)	<1	1
Samples from LiSoR tube		
In the irradiated area	200	6000
Adjacent to irradiated area (9 mm)	5	200
SIMS examination		
Sample from LiSoR specimens		
In the irradiated area	350	10000
Adjacent to irradiated area (13 mm)		30000
Adjacent to irradiated area (24 mm)	1	4
Samples from LiSoR tube		
In the irradiated area	500	10000
Adjacent to irradiated area (9 mm)	5	200

ber was 5.3×10^{-8} Pa. The size and the depths of the craters produced were measured by laser scan evaluation to determine subsequently the sputter rate which is needed for the depth calibration.

SEM analyses were carried out with a Zeiss DSM 962 having a hairpin cathode made of tungsten and operating at 30 kV. Additionally, the unit was equipped with two secondary electron detectors: Everhardt–Thornley for secondary electrons (SE) and Robinson for backscattering electrons (BSE). EDX analysis was performed with Noran System SIX with a pioneer detector and Norvar window. The operation distance during EDX analysis was 25 mm.

3. Results

3.1. SIMS results

SIMS analyses were performed on the surface of the samples without any additionally treatment, i.e. adherent LBE was not removed but LBE free areas were chosen for analyses. Both surfaces of each sample were examined.

3.1.1. Samples of the tensile specimen

The SIMS spectrum obtained on the sample located directly in the beam centre is shown in Fig. 2. The element ^{208}Pb was analysed in the most outer layers, whereas the element Bi was not detected. The species ^{72}(FeO) and ^{56}Fe were following the same trend: Their amount stayed constant up to a depth of approximately 400 nm, whereas ^{52}Cr was not detected in this area. With increasing depth a decrease of Fe and FeO took place and in parallel

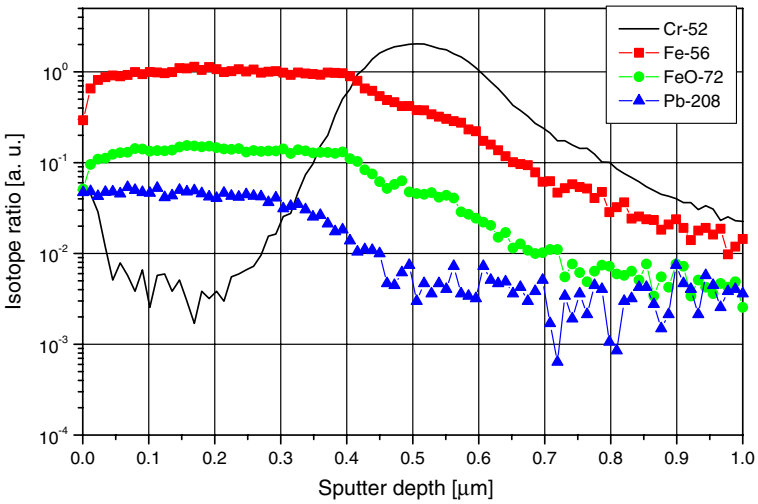

Fig. 2. SIMS spectra obtained on the sample located directly in the beam centre.

the amount of Cr increased from nearly zero, ran through a maximum and then decreased again. The maximum was in a depth of about 500 nm. The gradients of the Cr, Fe and FeO species achieved on the samples adjacent to the beam centre showed the same trend. In Fig. 3(a) Fe curves and in Fig. 3(b) Cr curves obtained on the three samples were put together for comparison. The thickness of the outer layer, constant amount of Fe and FeO without any Cr, was about 300 nm in a distance of 13 mm of the beam centre and approximately 250 nm in a distance of 24 mm. The peak maximum of Cr was approximately 400 nm (13 mm distance) and 350 nm (24 mm distance), respectively. It is well known that oxides formed on ferritic–martensitic steels consist of double structured oxides: the outer layer is the Cr-free magnetite Fe_3O_4, and the layer beneath is a $FeCr_2O_4$ spinel. This is in agreement with the SIMS results achieved on the three samples taken from the LiSoR specimen.

3.1.2. Samples of the tube

SIMS spectra measured on the two samples of the tube facing LBE during operation showed the species Fe and FeO on the outer surface and as well the element Pb was detected in this layer. In a depth of approximately 400 nm the amount of Fe and FeO decreased and Cr increased having its maximum at about 500 nm. The results achieved from the two samples are nearly the same which can be explained by the small distance of only 9 mm between them and hence they exposed more or less in the same environment.

In contrary to this, SIMS results of the vacuum facing side of the two tube samples showed a difference between the sample located in the beam foot print and the adjacent sample. The gradient of the species Cr, Fe and FeO were following the same structure as it is expected for this kind of steels. The typical duplex structure of the oxide layer existed as well whereas the thickness was much less than on the steel surfaces being in contact with LBE during operation. The SIMS spectra are showing that the maximum of Cr in the sample located in the beam centre was around 180 nm and in the sample adjacent to the beam centre it was only about 70 nm. The magnetite layer in the beam foot print is thicker (about 90 nm) than in the adjacent sample (about 40 nm) (see Fig. 4(a) and (b)).

3.2. SEM/EDX results

SEM/EDX were carried out on embedded and polished cross section of the samples which were knowingly not cleaned to avoid removing LBE. Both sides of the samples were inspected carefully.

3.2.1. Samples of the tensile specimen

Two samples of the tensile specimen were examined by means of SEM/EDX. One was located directly in the irradiated zone the other was about 29 mm above the beam centre. Solidified LBE was detected on very few parts of both samples with a thickness of less than 3 µm as shown by the light areas on the sample adjacent to the beam centre in Fig. 5. EDX spot analyses were carried out in

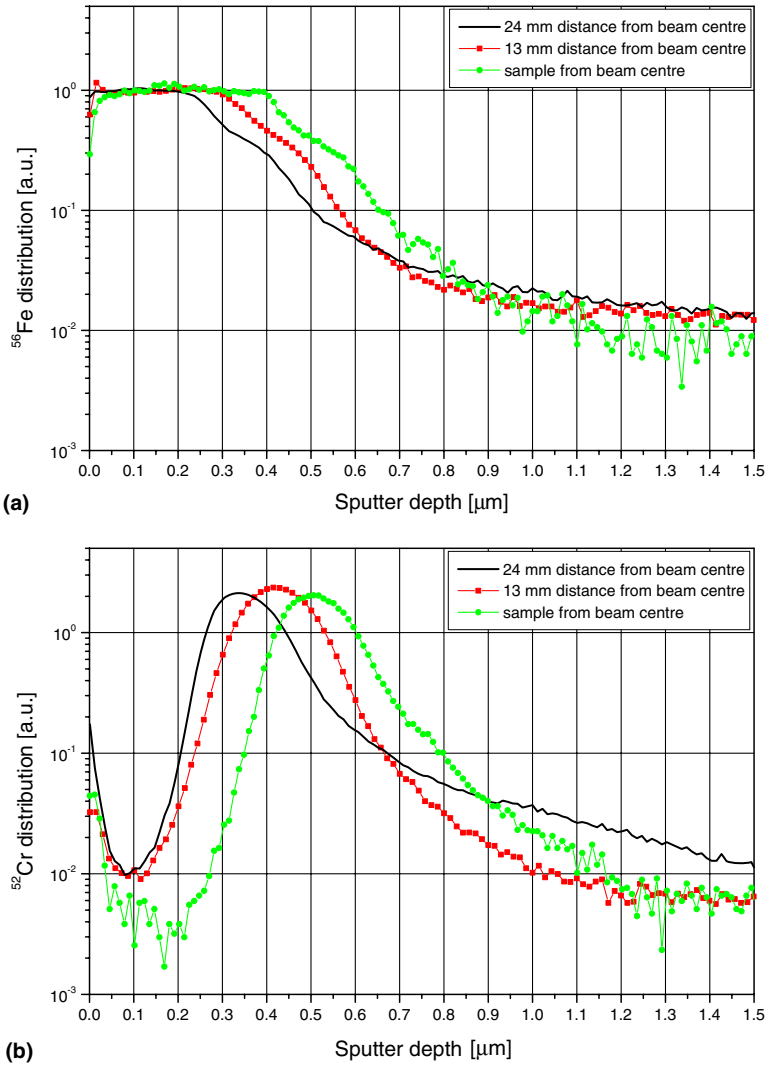

Fig. 3. Comparison of (a) Fe and (b) Cr distribution in LiSoR specimen dependent on their distance from the beam centre.

adherent LBE and on the steel surface nearby LBE. There was neither an enrichment of steel elements in LBE nor depletion of Fe or Cr out of the steel detected. The surface of the steel stayed unchanged and no change in structure indicated corrosion attack. The element distribution of Fe, Cr and O and the corresponding SE image of the sample cut out from the beam centre are shown in Fig. 6. A slight enrichment of oxygen in the surface layer is visible.

3.2.2. Samples of the tube

Both the vacuum and LBE facing sides of the two samples out of the test section tube have been examined. One sample was cut out of the beam centre; the other was from 9 mm away. On both samples the vacuum facing side did not show any changes by SEM/EDX analysis. The steel surfaces were not influenced by the beam during this short period of operation. The inner surface, i.e. LBE facing side was relatively rough as shown in Fig. 7. The re-working polishing process which was carried out on the already assembled test section has removed most of the micro cracks but the surface was not as smooth as expected. There was no difference observed between the two samples as a result of the little distance of each other. Solidified LBE was found on few areas which was only loosely attached on the steel surface. No interaction between steel and LBE was measured by EDX.

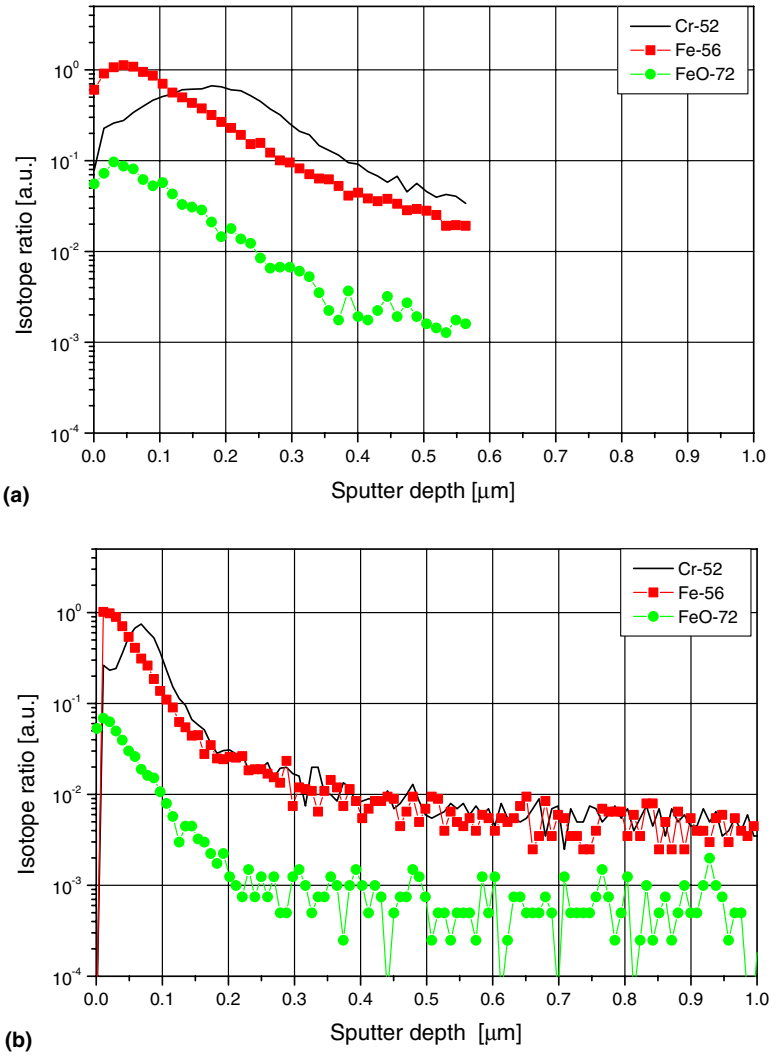

Fig. 4. The vacuum facing side of (a) sample located in the beam centre and (b) 9 mm above it.

An enrichment of oxygen, iron or chromium in the surface layer could not be detected due to the too low spatial resolution of EDX compared with that of SIMS.

4. Discussion and conclusions

LiSoR experiment was launched to investigate simultaneously the influence of flowing LBE and proton irradiation to steel T91 and it is world wide the first LBE loop that operates under irradiation. It was not expected to detect significant changes on the surfaces of the specimens and tube after the short period of irradiation (264 h). The maximum temperature calculated for the beam foot print was slightly above 330 °C on the inner surface of the tube (cooled by LBE) and 380 °C on the vacuum facing side. The temperature in the specimen was about 324 °C [14].

SEM/EDX analysis have shown no interaction between LBE and steel neither on the specimen nor on the tube. In some areas LBE was loosely attached onto the surface but wetting was not detected. During an operation time of 264 h at temperatures below 400 °C and in oxygen saturated LBE no corrosion attack is expected to happen. This is in agreement with the observations made by Aiello et al. [15] who has reported no corrosion attack up to 6000 h in oxygen saturated LBE at 400 °C but without irradiation.

SIMS analyses have clearly shown that oxides were formed during irradiation on the tensile speci-

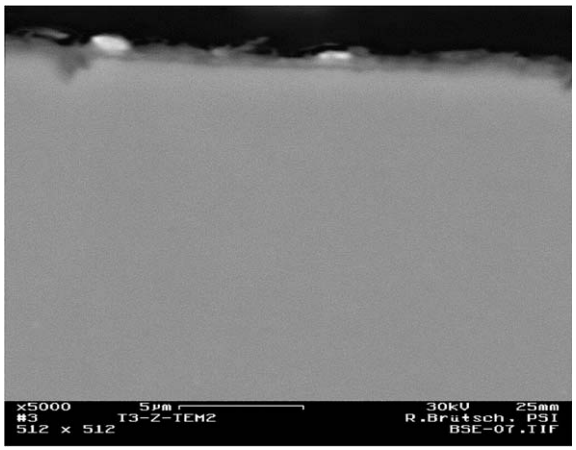

Fig. 5. BSE image of a sample of LiSoR specimen showing tiny amount of attached LBE on the steel surface.

men and on the tube (beam window). The oxides on tube and specimen exhibited a duplex structure. It is well known that ferritic–martensitic steels are forming double structured oxide layers: the outer layer consisting of magnetite and the inner layer of iron chromium spinel not only in air but also in lead [16,17] and LBE [18–21]. The thickest layer with around 400 nm of magnetite was revealed in the irradiated area and very close to it both on the specimen and on the tube. The thickness decreased with increasing distance of the beam centre. We believe that the increase in temperature induced by the beam is responsible for the formation of the oxide layers. It has to be mentioned that there was neither an oxygen control system nor an oxygen sensor installed to LiSoR loop system because in the conception phase of this facility no sensor worked reliable below 400 °C. Another unknown point is the life time of an oxygen sensor under irradiation. It is very likely that in our experiment LBE was oxygen saturated due to the lack of any reducing precautions and thus the oxygen content corresponds to about 5×10^{-5} wt% at 350 °C. The oxide layer formed on the vacuum facing side on the tube

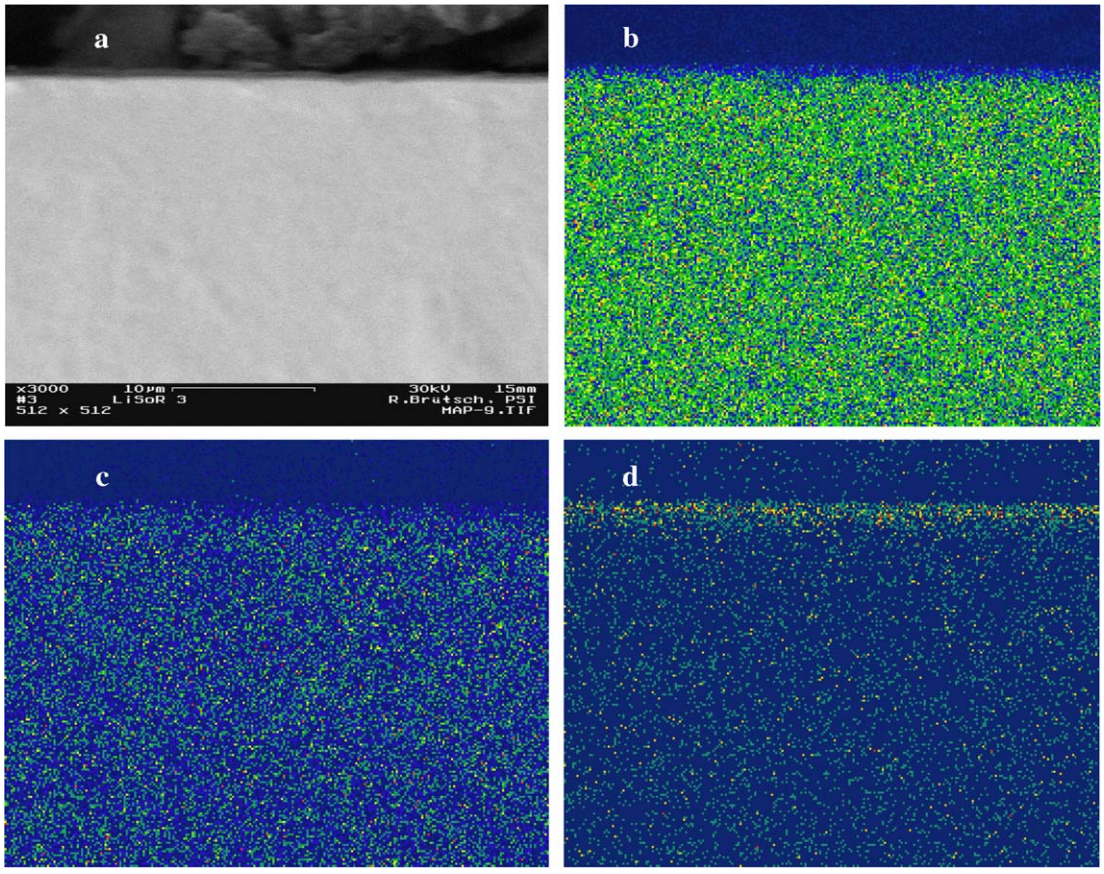

Fig. 6. (a) BSE image of a sample located in the beam centre with corresponding element distribution maps: (b) iron, (c) chromium and (d) oxygen.

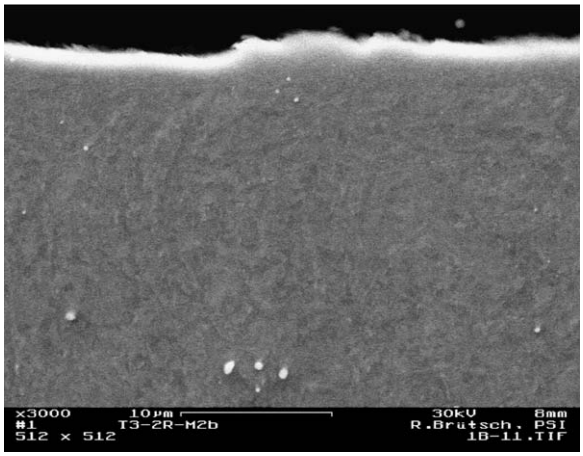

Fig. 7. The roughness of the inner surface of the tube is a consequence of re-working procedure and not of corrosion attack.

is much thinner although the temperature is with 380 °C (calculated value) higher than on the inner surface due to the absence of LBE cooling. The magnetite layer in the beam foot print (vacuum facing side) is thicker (about 90 nm) than in the adjacent sample (about 40 nm). Although the oxide layers of the vacuum facing side are very thin in both samples the duplex structure is in both cases developed. Oxidation behaviour of steel T91 below 400 °C was up to now not treated in the literature and hence no oxidation rates exist. The formation of a duplex structured oxide layer on T91 in oxygen saturated LBE ($C_{O_2} = 10^{-5}$–10^{-6} wt%) at 400 °C is reported in [15] whereby a 3 μm thick layer was formed after 3000 h of exposure and a 6 μm thick layer after 6000 h. The oxidation behaviour of T91 at 400 °C corresponds quite well with our results: oxide layer of around 800 nm after 264 h of exposure at a temperature below 400 °C.

The formation of oxide layers is of great advantage:

- Oxide layers protect the structural materials (in our case T91) against corrosion attack of LBE.
- Oxide layers behave as protecting barrier between LBE and steel and prohibit any intense contact, which is a necessity for the incidence of LME.

The behaviour of T91 in LBE during long term irradiation experiments and under reducing environment is of great interest and is still an open issue.

Lillard et al. [22] have performed as well an irradiation experiment in the presence of LBE. Pre-oxidised HT9 samples with an oxide scale in the order of 3 μm thickness were irradiated with pulsed protons in the LANSCE WNR facility. The energy of the particle beam was 800 MeV and the current of the protons was approximately 63 nA. Impedance spectroscopy on each sample was performed before irradiation, during (30 min) and after irradiation. The results achieved on HT9 pre-oxidised samples during different stages of the experiment diverge strongly among each other. It is reported that the oxide layer is destroyed during irradiation or kept stable but a growth of the oxide layer was never detected. These results are controversy to our results. Further experiments are needed to understand fully the measured values and it has to be critically proven if impedance spectroscopy is an appropriate method to assess the corrosion rate in real time during irradiation.

Comparing the results of LiSoR 2 and 3 showed that because of the larger beam size and smaller current, the maximum temperatures (localized and oscillated with the wobbling beam) in the irradiation areas of both the tube and the tensile specimen were much lower than that in LiSoR 2. The temperature gradient in the irradiation area of the tube induced a maximum shear stress of about 25 MPa and a compression stress of about 150 MPa which are essentially no danger to the material. Therefore, the crack observed in the tube of LiSoR 2 [23] was not formed in LiSoR 3. Moreover, no micro cracks were detected in the irradiation areas of both the tube and the tensile specimen even if the later was stressed at 200 MPa. Although the irradiation dose is only about 0.2 dpa of LiSoR 3, it is already twice of LiSoR 2 (0.1 dpa) and the outcome shown here are optimistic to MEGAPIE because the LiSoR results were achieved under MEGAPIE relevant conditions. In the beginning of the MEGAPIE experiment LBE will be saturated with oxygen and in the early stage of irradiation an oxide scale might be formed on the T91 beam entrance window. An oxide scale has a positive influence on the life time of the beam window by avoiding wetting which is known to be the initial reaction for LME and corrosion attack.

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Boutellier dissembling the test section and H. Schweikert performing the EDM wire cutting of the samples using manipulators in hot cells has to be acknowledged.

References

[1] F. Gröschel et al., J. Nucl. Mater. 335 (2004) 156.
[2] G.S. Bauer, M. Salvatores, G. Heusener, J. Nucl. Mater. 296 (2001) 17.
[3] M.H. Kamdar, Treat. Mater. Sci. Tech. 25 (1983) 361.
[4] M.G. Nicholas, C.F. Old, J. Mater. Sci. 14 (1979) 1.
[5] J.-B. Vogt, A. Verleene, I. Serre, A. Legris, J. Nucl. Mater. 335 (2004) 222.
[6] T. Auger, G. Lorang, S. Guérin, J.-L. Pastol, D. Gorse, J. Nucl. Mater. 335 (2004) 227.
[7] G. Nicaise, A. Legris, J.B. Vogt, J. Foct, J. Nucl. Mater. 296 (2001) 256.
[8] D. Kalkhof, M. Grosse, J. Nucl. Mater. 318 (2003) 143.
[9] T. Kirchner et al., J. Nucl. Mater. 318 (2003) 70.
[10] H. Glasbrenner, Y. Dai, F. Gröschel, J. Nucl. Mater. 343 (2005) 267.
[11] S. Dementjev, H. Glasbrenner, T. Kirchner, F. Heinrich, I. Bucenieks, E. Platacis, A. Pozdnjaks, G. Kirshtein, Magnetohydrodynamics 37 (2001) 386.
[12] H. Glasbrenner, R. Brütsch, F. Gröschel, T. Rebac, PSI-Report TM-34-03-02, 2003.
[13] H. Glasbrenner, V. Boutellier, Y. Dai, S. Dementjev, F. Gröschel, D. Viol, PSI-Report TM 34-02-09, 2003.
[14] K. Samec, PSI Technical Report, TM-34-05-02, 2005.
[15] A. Aiello, M. Azzati, G. Benamati, A. Gessi, B. Long, G. Scaddozzo, J. Nucl. Mater. 335 (2004) 169.
[16] H. Glasbrenner, J. Konys, G. Müller, A. Rusanov, J. Nucl. Mater. 296 (2001) 237.
[17] C. Fazio, G. Benamati, C. Martini, G. Palombarini, J. Nucl. Mater. 296 (2001) 243.
[18] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.
[19] G. Müller et al., J. Nucl. Mater. 335 (2004) 163.
[20] F. Barbier, A. Rusanov, J. Nucl. Mater. 296 (2001) 231.
[21] D. Gomes Briceno, F.J. Martin Munoz, L. Soler Crespo, F. Estefan, C. Torres, J. Nucl. Mater. 296 (2001) 265.
[22] R.S. Lillard, M. Paciotti, V. Tcharnotskaia, J. Nucl. Mater. 335 (2004) 487.
[23] Y. Dai, H. Glasbrenner, V. Boutellier, R. Bruetsch, X. Jia, F. Groeschel, J. Nucl. Mater. 335 (2004) 232.