Mechanical and corrosion behaviour of EUROFER 97 steel exposed to Pb–17Li

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Abstract

Corrosion and tensile samples of the EUROFER 97 steel were exposed to Pb–17Li in the LIFUS II loop at 480 °C. The specimens were extracted after 1500, 3000 and 4500 h exposure. After extraction, weight change measurements and metallurgical analysis were performed on the corrosion specimens, while tensile tests were performed at 480 °C. The results showed that EUROFER 97 underwent uniform corrosion and the mechanical properties seem to be unaffected or only slightly affected by the liquid metal. In this paper, the results are reported and discussed also with reference to previous similar work.

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1. Introduction

The eutectic lead–lithium containing 87 at.% of Pb and 17 at.% of Li (Pb–17Li) is considered in the water cooled lead lithium (WCLL) concept of a fusion reactor as the most suitable tritium breeding material [1]. The advantages of using Pb–17Li are due to the nuclear properties of the eutectic, since breeder and neutron multiplier are combined in the same material; and to the chemical properties, since the eutectic does not exhibit an explosive reaction when in contact with air and water [1,2]. On the other hand, one of the disadvantages that could be envisaged by choosing the liquid eutectic Pb–17Li as breeder is its compatibility with structural materials. A major candidate as structural material in the WCLL concept is one of a reduced activation ferritic martensitic (RAFM) steel. In recent years, much effort has been expended within the European Fusion Technology Programme in order to develop appropriate RAFM steels. The importance of this wide research programme is for example due to safety requirements, in

which it is mandatory to minimise problems associated with induced radioactivity in the structural materials. Several ferritic–martensitic steels, such as MANET, OPTIFER, F82H and so on, have been developed worldwide. In Europe, the progress of the research activities has resulted in the formulation of the RAFM steel named EUROFER 97. In normal use, a newly developed material needs general characterisation in terms of its mechanical and chemical properties, as well as characterisation for the specific application. A characterisation of concern in the WCLL concept is the compatibility of the newly developed steel in terms of corrosion and mechanical degradation in the liquid flowing Pb–17Li. A second type of test of great interest for the WCLL concept is the mechanical property degradation of the steel when exposed to the liquid metal, and under neutron irradiation. For this latter effect, few experimental results are available and ENEA, in collaboration with IPPE of Obninsk (RF), is planning an experimental campaign under the auspices of the ISTC in order to analyse thoroughly this phenomenon.

The aim of the activities conducted and herein presented were to evaluate the mechanical, and later the corrosion behaviour of the EUROFER 97 steel before and after exposure to the proposed breeder material. Both tensile and corrosion specimens were exposed to

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flowing Pb–17Li at a temperature of 480 °C. The results are compared with those reported in previous similar work performed on ferritic–martensitic steels.

2. Literature review

In the past, several corrosion tests were conducted on proposed structural materials in liquid Pb–17Li. The materials analysed were austenitic steels and ferritic–martensitic steels. Moreover, the tests were performed in both static and dynamic conditions. Hereafter the literature review refers only to the work performed in dynamic conditions and on ferritic–martensitic steels.

Type Fe–12Cr1MoVW steel, the composition of which is reported in Table 1, was exposed at 500 °C and at a liquid metal flow of 10^{-3} m/s [3]. Under these conditions, a corrosion rate of approximately 24 μm/y and a relatively uniform dissolution of the steel elements were observed. Further corrosion tests were performed on the three types of martensitic steels 1.4914, HT-9 and T91 [4]. The three steels, whose compositions are reported in Table 1, were exposed to a thermal convection loop at 450 °C. The flow of the alloy was estimated to be approximately 10^{-2} m/s and the measured corrosion rate

for the three steels was determined to be 30 μm/y. In this experiment, as in the previously cited one, homogeneous dissolution of the steels without the formation of a corrosion layer was observed. In 1986 the HT-9 steel and a 9Cr steel with composition close to the T91 steel were also tested in a forced circulation loop [5]. The loop parameters are reported in Table 2. Four corrosion test runs were performed at 371, 427, 454 and 482 °C, respectively. At the same time, tensile tests under controlled extension rates were performed on the HT-9. The corrosion rates obtained for the two types of steels were about 1 μm/y, at 371 °C, at 427 °C, the rate measured was between 6 and 8 μm/y while at 454 °C the rate increased to 9–10 μm/y. At least 482 °C the measured corrosion rate on the two types of steel was about 20 μm/y for the HT-9 steel and 9.0 μm/y for the 9Cr steel, these last two values being quoted after a run of 2000 h. It appears that there is a relevant discrepancy between the behaviour of the two steels which was not discussed by the authors. The metallographic examination performed on the HT-9 steel after the run at 482 °C showed uniform dissolution and preferential attack along grain boundaries and martensitic lath boundaries. The mechanical tests performed in the temperature range from 270 to 400 °C on the HT-9 steel showed that the

Table 1
Chemical composition (wt%) of various ferritic–martensitic steels tested in flowing Pb–17Li (n.i.: not indicated)

	C	Cr	Mo	Ni	Mn	W	V	Si	Nb
EUROFER 97	0.1	8.8	0.003	–	0.44	1.15	0.2	0.05	0.002
Fe–12Cr1Mo	0.2	12	1	0.5	0.6	0.4	0.3	0.2	–
1.4914	0.13	10.6	0.77	0.87	0.82	–	0.22	–	0.16
HT-9	n.i.	11.8	0.99	0.48	0.5	–	0.29	–	–
T91	n.i.	9.0	1	0.09	0.42	–	0.3	–	0.3
9Cr	0.098	8.8	0.92	–	0.4	–	0.21	0.36	0.06
F82H	0.09	7.7	–	0.04	0.16	1.95	0.16	0.13	<0.01
Optifer IVa	0.11	8.5	–	–	0.57	1.16	0.23	–	–

Table 2
Corrosion rates evaluated on ferritic–martensitic steels and compared with the results the herein reported experiments

Steel	T_{max} (°C)	T_{min} (°C)	LM velocity (m/s)	Corrosion rate (μm/y)	Reference
1.4914	550	305	3×10^{-1}	370	[7]
Fe–12Cr1Mo	500	370	10^{-3}	24	[3]
HT-9	482	300	(Thermal convection)	20	[5]
9Cr				9	
MANET I, OPTIFER, F82H	480	350	3×10^{-1}	100	[8]
EUROFER 97	480	400	10^{-2}	40	This work
1.4914	475	415	8×10^{-2}	40	[6]
1.4914, HT-9, T91	450	390	10^{-2}	30	[4]
HT-9, 9Cr	454	300	(Thermal convection)	1	[5]
	427	300		6–8	
	371	300		9	

Pb–17Li environment had no effect on the tensile properties of the steel. The martensitic steel 1.4914 was tested also at 475 °C [6] in a thermal convection loop called TULIP and at 550 °C in a forced circulating loop called PICOLO [7]. The parameters used in both loops are reported in Table 2. The evaluated corrosion rates obtained on the 1.4914 steel were 40 μm/y in the TULIP loop conditions and 370 μm/y in the PICOLO loop conditions, with metallurgically uniform steel element dissolution observed in both cases. The interface of the sample tested at 475 °C was slightly indented to a depth of about 5–10 μm and no Cr depletion was observed. As expected for the corrosion rate of martensitic steels, by increasing the temperature and the flow velocity of the liquid metal, the corrosion rate increased. Recently three ferritic–martensitic steels, namely MA-NET I, F82H and Optifer IVa were exposed to flowing Pb–17Li at 480 °C and at a flow of 0.3 m/s [8]. In this experiment, the three steels, with compositions reported in Table 1, exhibited similar linear corrosion rates, estimated at about 100 μm/y. Moreover, from the metallographic analysis the authors indicated that preferred matrix dissolution occurred along the martensitic lath boundaries, and a porous corrosive layer even after cleaning the sample was observed. To have an overview of all the experiments cited, the corrosion rates and the testing parameters are summarised in Table 2. As can be seen in that table, a strong dependence occurs between the corrosion rate and the flow velocity, the temperature and the thermal-hydraulics conditions of the loop. In the past, attempts have been made to correlate these parameters to evaluate analytically the corrosion rate of martensitic steels [9].

The mechanical properties of the ferritic–martensitic steels when exposed to the liquid metal have been analysed on HT-9 steel as reported above [5] as well as on MANET steel [10]. In these experiments, the mechanical properties of the steels when exposed to the liquid metal were not affected.

3. Experimental

The EUROFER 97 samples were exposed to flowing Pb–17Li in the LIFUS II loop. The chemical composition of the EUROFER 97 steel, delivered by the Boehler Company (Germany), is reported in Table 1. LIFUS II is the experimental facility designed, installed and operated at the ENEA site of Brasimone. It consists of a 'figure-of-eight' shaped circuit (see Fig. 1), with the cold and hot parts crossing at the heat exchanger–economiser EX. The recirculation vessel S2, the mechanical pump P and the forced-air cooler C are the main components of the cold section. The liquid metal flow-rate required in the hot part of the loop, which contains the two test sections TS1 and TS2, is controlled via a regulation
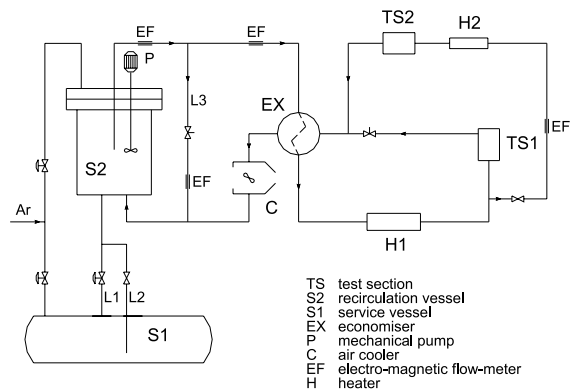

Fig. 1. Schematic of the LIFUS II loop.

valve in the by-pass line L3, where TS1 is used for the testing of the EUROFER 97 steel. The entire cold section of the circuit, including the economiser EX, is made from austenitic steel AISI 316L. The structural material of the hot part of the loop is ferritic steel 2Cr1/4Mo, which gives a good compromise between mechanical behaviour and corrosion resistance in the presence of hot flowing lead alloys.

During the tests, the liquid metal flow velocity in the test section was about 10^{-2} m/s. This flow velocity approximately simulates the semi-stagnant conditions of the tritium breeding fluid. The temperature in the test section was maintained constant at 480 °C and the temperature difference between the hot and the cold parts of the loop was 80 °C. Both corrosion and tensile specimens were taken out every 1500 h, up to 4500 h. For each exposure time five tensile specimens and two corrosion specimens were planned. The tensile specimens were tested with the SYNTECH test machine at 480 °C and under Ar atmosphere without cleaning them of the Pb–17Li alloy, with the exception of the 4500 h tested specimens. The tensile tests were conducted under strain-controlled conditions with an extension rate of 2 mm/min which corresponds to an initial strain rate of 3×10^{-3} s^{-1}.

The corrosion rate was evaluated by means of weight measurement before and after exposure to the flowing liquid metal. One of the two-corrosion specimens was cleaned with a solution made by CH_3COOH, H_2O_2, C_2H_5OH in a ratio of 1:1:1, with the cleaning procedure performed until the weight of the specimen remained constant. The second corrosion specimen was used for metallurgical analysis and was not treated with the cleaning solution. The metallurgical analyses were performed with the aid of an optical microscope and an scanning electron microscope (SEM). The chemical compositions of the corroded layers were evaluated by means of energy dispersive X-ray spectroscopy (EDX) using ZAF correction.

4. Results and discussion

The metallographic observations on the corrosion samples tested have shown that the EUROFER 97 steel suffers from typical corrosive attack due to dissolution of the steel elements in the liquid metal. The samples extracted from the test section were all covered with the Pb–17Li alloy, indicating that at this temperature and after at least 1500 h the wetting of the surfaces occurred. In Fig. 2 the SEM micrograph obtained with the back scattered electron (BSE) detector on the cross-section of the 1500 h tested sample is reported. In this micrograph the Pb–17Li alloy is white coloured and is deposited on the steel surface which appears indented by the eutectic. In Figs. 3 and 4 the SEM micrographs obtained with the BSE detector on the cross-section of the 3000
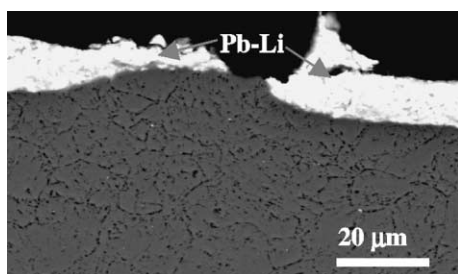
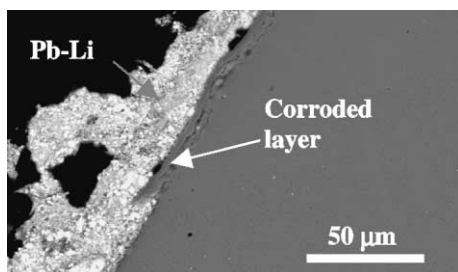Fig. 2. SEM-BSE micrograph of the cross-section of the 1500 h tested sample.

Fig. 3. SEM-BSE micrograph of the cross-section of the 3000 h tested sample.
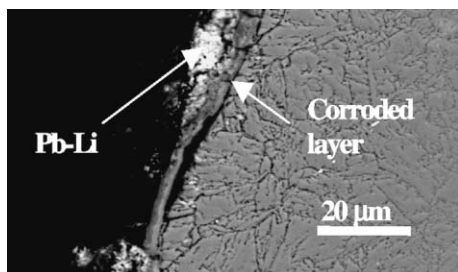

Fig. 4. SEM-BSE micrograph of the cross-section of the 4500 h tested sample.

and 4500 h tested samples are reported. As can be observed in those figures, a layer about 1 μm thick seems to detach from the surface of the steel. At the interface between the layer and the bulk material, voids could be observed, and the EDX analysis showed that the quasi-detached layer was Cr depleted. Moreover, the Pb–17Li penetrates along the interface between the corrosion layer and the matrix, enhancing detachment of the layer. The depletion of Cr is not justifiable on the basis of the solubility data since the solubility of Fe in the liquid Pb–17Li evaluated at 500 °C is 47 wppm [11] and that of the Cr evaluated at the same temperature is 10 wppm [12]. It seems that, as reported in a previous work [13], the depletion occurs due to the lower diffusivity of Fe in Pb–17Li with respect to Cr. In the work reported in Ref. [13], pure Fe, pure Cr as well as Fe–Cr steels were tested in capsules containing Pb–17Li at 500 °C. At this temperature, it was observed that the weight loss of pure Cr was higher than that of pure Fe despite the lower solubility of Cr with respect to Fe [13]. Moreover, on the Fe–Cr steels a similar corrosion layer as described for the EUROFER 97 steel was observed. The cross-section of the corroded samples were analysed even after cleaning and a loss of the Cr depleted corrosion layers could be observed, indicating that the layers were removed by the cleaning procedure. This loss could explain the absence of a corrosion layer in the metallographic experiments performed in the past on cleaned specimens. The corrosion mechanism that can be assumed as a consequence of the metallurgical analysis herein performed is the Cr depletion of a layer of few microns first and then the detachment of this layer with its complete dissolution into the liquid metal. Furthermore, the voids observed at the interface between the corrosive layer and the steel matrix could be a Kirkendall effects due to the preferential Cr diffusion in this layer. The weight measurements showed that a metal loss occurred after each exposure time. The weight loss increases linearly with time so that the constant corrosion rate could be determined, as reported in Table 2, to be about 40 μm/y under the given testing conditions. As shown in Table 2, the general corrosion trend of ferritic–martensitic steels has been confirmed in fact the testing parameters used in the LIFUS II loop and the corrosion rate estimated on the EUROFER 97 steel are comparable with those reported in Refs. [4,6]. On the other hand, as shown in Table 2, for a testing temperature of 480 °C and with a higher flow rate [8], the corrosion rate of ferritic–martensitic steels increases.

The tensile tests were performed at 480 °C under an Ar atmosphere. For each exposure to Pb–17Li a set of tensile specimens was tested: the yield strength, the maximum strength and the area reduction were evaluated, and finally the average values were calculated. In Fig. 5 these average values vs. exposure time in flowing Pb–17Li are plotted. At the zero point of the time axis of
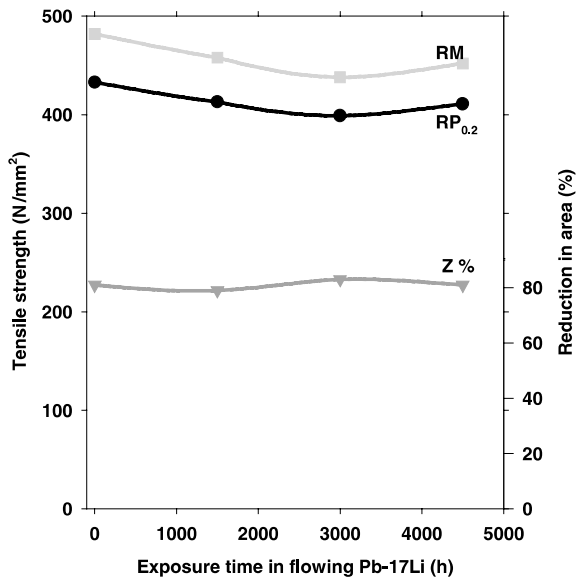
Fig. 5. Tensile properties obtained at 480 °C on the EURO-FER 97 steels exposed to Pb–17Li.

the plot, the average tensile properties of uncorroded samples obtained at 480 °C are reported. As can be observed in this plot, the exposure of the steel to the liquid metal did not affect its mechanical properties. The slight deviation of the average values from one exposure time to the next is within the standard deviation evaluated for each set of tests. Moreover, the trend of the area reduction showed that the EUROFER 97 steel did not suffer from mechanical degradation due to liquid metal attack. The observed tensile behaviour confirms the results obtained in the past, that the mechanical properties of the ferritic–martensitic steels are unaffected by flowing liquid Pb–17Li. However, no indications can be given about corrosion enhancement and liquid metal embrittlement under neutron irradiation.

5. Conclusions

The EUROFER 97 steel exposed to flowing liquid Pb–17Li at 480 °C up to 4500 h exhibited a linear trend

of weight loss with increasing exposure time. The corrosion rate evaluated in the given experimental conditions is 40 μm/y, which seems to be in accordance with the general trend of corrosion rates evaluated in the past. The tensile properties of the steels seem to be unaffected by exposure to the liquid metal. These results are very encouraging even if it is necessary to analyse corrosion enhancement and liquid metal embrittlement of the EUROFER 97 steel under neutron irradiation.

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