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A study of the neutron irradiation effects on the susceptibility to embrittlement of A316L and T91 steels in lead–bismuth eutectic

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Abstract

The effects of neutron irradiation on the susceptibility to liquid metal embrittlement of two primary selected materials for MYRRHA project an accelerator driven system (ADS), was investigated by means of slow strain rate tests (SSRT). The latter were carried out at 200 °C in nitrogen and in liquid Pb–Bi at a strain rate of $5 \times 10^{-6}\ s^{-1}$. The small tensile specimens were irradiated at the BR-2 reactor in the MISTRAL irradiation rig at 200 °C for 3 reactor cycles to reach a dose of about 1.50 dpa. The SSR tests were carried out under poor and under dissolved oxygen conditions ($\sim 1.5 \times 10^{-12}$ wt% dissolved oxygen) which at this temperature will favour formation of iron and chromium oxides. Although both materials differ in structure (fcc for A316L against bcc for T91), their flow behaviour in contact with liquid lead bismuth eutectic before and after irradiation is very similar. Under these testing conditions none of them was found susceptible to liquid metal embrittlement (LME).

1. Introduction

Liquid lead–bismuth eutectic is selected as a coolant and spallation neutron source for multipurpose accelerator driven system (ADS) such as MYRRHA project. While it has excellent neutron-physical and thermal-hydraulic properties lead and especially bismuth can pose serious corrosion problems to the structural materials especially at high temperatures. Thus, the operating temperatures for the reactor have been limited to 450 °C. At this temperature the materials corrode at acceptable rates (e.g. 9Cr–1Mo modified martensitic steel corrodes at a rate of about 45 μm/year and austenitic stainless steel AISI 316L at 2 μm/year [1]). In addition, the use of LBE sets relatively benign stress requirements to the materials (50 MPa) thankful to its high boiling temperature (1670 °C). The commercial 9Cr–1Mo modified martensitic steel T91 and the austenitic steel AISI 316L have been selected as primary structural materials for the MYRHHA ADS. Beside the homogeneous corrosion another aspect of liquid metal corrosion can pose serious problems to the containment materials

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namely the process of liquid metal embrittlement (LME). LME is the early failure of metals exposed to liquid metals and subjected to stress in comparison with failure under gaseous, water or another inert environment. There are strong experimental evidences that under certain conditions steels might be susceptible to liquid metal embrittlement [2–4]. In all of the reported cases, the metallurgical conditions in terms of hardness have been modified. For instance, increasing the grain size of Armco iron rendered it susceptible to embrittlement by liquid lead [2]; welding simulations of F82H mod (8 Cr ferritic steel) made it susceptible to embrittlement by lead lithium eutectic (Pb–17Li) [3]; and also tempering under certain conditions leads to very high strength properties resulting in increased tendency to liquid metal embrittlement by lead, lead–bismuth eutectic of T91 steel [4]. Generally it is well established that harder materials are more susceptible to LME [5–7]. Under radiation, irradiation hardening would have an effect similar to the heat treatment hardening processes and hence affect the tendency of A316L steel and especially of T91 materials to liquid metal embrittlement. Therefore the main objective of this work is to investigate whether or not neutron irradiation increases the susceptibility of T91 and AISI 316L to embrittlement by liquid lead–bismuth eutectic.

2. Experimental details

2.1. Materials

Two materials have been investigated: austenitic stainless steel A316L and modified 9Cr–1Mo martensitic steel T91. The chemical composition of these materials is given in Table 1.

The materials are received in the following conditions: T91 was supplied by UGINE (France), heat 36224 normalized at 1040 °C for 60 min and tempered at 760 °C for 60 min. A316L: was supplied by SIDERO STAAL n.v. (Belgium), heat number 744060 in the shape of bars with diameter 6 mm and length 500 mm from which the specimens were manufactured. The material was solution annealed and 20% cold worked.

Sub-size tensile samples of length 27 mm with a gauge section 12 mm length and diameter 2.4 mm were used for the tensile tests. No additional treatment of the fabricated samples was done. Prior to testing they were degreased by ultrasonic in methanol bath.

Lead bismuth eutectic alloy (44.8% Pb, 55.2% Bi) was supplied by the Hetzel Metalle GmbH with reported minimum purity of Pb and Bi 99.985% and 99.99% respectively.

2.2. Tensile tests

Tensile tests are extensively utilized to study all aspects of environmentally assisted cracking (EAC). The tensile tests done within this study were carried out according to ASTM G 9.

The tests were done in an autoclave in conjunction with a gas conditioning system at the irradiation temperature (200 °C) and strain rate $5 \times 10^{-6}\ s^{-1}$ following the following test sequence:

1. The sample was gripped into the sample holder and to avoid unscrewing small initial stress was applied.
2. The autoclave was closed and the liquid metal was subjected to pre-conditioning (reduction of the oxides) for 4 h by bubbling with $5\%H_2 + Ar$ gas. The gas flow is maintained at about 5 l/h.
3. Under the controlled atmosphere (i.e., with dissolved oxygen) the autoclave was preconditioned for 2 h by bubbling with gas containing water/steam at an appropriate ratio [8]. It is assumed that due to the small amount of liquid metal and the overlying cover-gas, the desired equilibrium dissolved oxygen concentration is achieved. However no direct measurement of the oxygen concentration was made as there is no oxygen sensor available by now that can work properly at this temperature (200 °C) [9].
4. After stabilization of the temperature inside the autoclave, the tensile tests was performed at predefined strain rate of $5 \times 10^{-6}\ s^{-1}$.

Table 1
Chemical composition (wt%) of AISI 316L and T91 steels

Material	Fe	Cr	Ni	Mo	Mn	V	Nb	S	Si	N	C	P
AISI 316L (1.4935)	Balance	16	10.1	2.1	1.58	–	–	0.016	0.51	–	0.022	0.029
T91 (1.4903)	Balance	8.3	0.13	0.95	0.4	0.2	0.08	–	0.4	0.02	0.11	–

5. After the sample was broken, it was removed from the hot autoclave and cleaned in hot tempering oil at 160–180 °C for about 5 min and degreased in a methanol bath by ultrasonic cleaning. For the irradiated samples ultrasonic cleaning equipment was not available. Therefore across the fracture surface of the irradiated samples beads of solidified eutectic could be still seen.

2.3. Irradiation

The irradiation was done in MISTRAL (Multipurpose Irradiation System for Testing of Reactor ALloys) in-pile sections (MIPS) for three reactor cycles. The samples holder of the MISTRAL irradiation rig can accommodate up to 91 tensile specimens (length 27 mm). They were positioned over 13 levels along the reactor axis. A heating element in shape of a rod with diameter of 9.4 mm and length of 855 mm was mounted in a double instrumentation (top/bottom) device, allowing easy replacement of the heating element in the reactor pool without disconnection of the instrumentation package. During the irradiation campaign the temperature was controlled by 14 thermocouples and maintained in the interval 200–204 °C.

The determination of damage effects versus neutron irradiation for ferritic steels is typically correlated with the fast neutron fluence (i.e., $E > 1$ MeV). In this experiment Fe dosimeters were used to determine the neutron fluence according to ASTM E 263-05. They were encapsulated in a stainless steel tube to prevent damage and corrosion. The dosimeters consist of wires with diameter 0.5 mm and different lengths. The neutron flux was calculated at reference power 56 MW using the ^{235}U spectrum and the spectral weighted neutron activation cross section for the reaction ^{54}Fe(n,p)^{54}Mn, $\langle\sigma\rangle = 81.7$ mbarn with effective threshold energy 2.80 MeV [10,11]. The fast neutron fluence ($E > 1$ MeV) was calculated from the saturation activity obtained from the experimentally measured activity of ^{54}Mn. The saturation activity was used to obtain the reaction rate which is used to calculate the neutron fluence rate. The latter was used to calculate the neutron fluence assuming the above mentioned reactor reference power and the periods during which the reactor operated at approximately constant power [11]. With the so calculated neutron fluence the dpa index for the irradiated materials was calculated. The irradiation damage in terms of displacements per atom for the investigated materials is given in Tables 2 and 3.

3. Results

In general after the SSR test the lateral surface of the samples was clean and not wetted. Conversely, the fracture surface of all samples tested in liquid

Table 2
Results of the tensile tests on AISI 316L material tested in liquid Pb–Bi before and after irradiation

Environment	dpa	$\sigma_{0.2}$, MPa	ε_{tot}, %	ε_{plast}, %	ε_{unif}, %	σ_{UTS}, MPa	$\sigma_{fracture}$, MPa	RA, %
Air	0	501 ± 6%	22 ± 0.40%	20 ± 0.06%	9 ± 2%	555 ± 4%	361 ± 4%	83 ± 1%
Pb–Bi + 5%H_2 + Ar	0	499 ± 4%	22 ± 0.42%	20 ± 0.09%	9 ± 3%	579 ± 4%	364 ± 4%	73 ± 1%
Pb–Bi + oxygen	0	519 ± 4%	21 ± 0.42%	18 ± 0.11%	6 ± 4%	586 ± 4%	372 ± 4%	73 ± 1%
Air	1.30	748 ± 4%	14 ± 0.42%	12 ± 0.22%	0.00	748 ± 4%	491 ± 4%	63 ± 2%
Pb–Bi + 5%H_2 + Ar	1.30	733 ± 4%	14 ± 0.42%	12 ± 0.29%	0.00	741 ± 4%	477 ± 4%	56 ± 2%
Pb–Bi + 5%H_2 + Ar	1.53	735 ± 4%	15 ± 0.42%	12 ± 0.30%	0.00	737 ± 4%	477 ± 4%	59 ± 2%
Pb–Bi + oxygen	1.40	732 ± 4%	15 ± 0.42%	12 ± 0.32%	0.00	744 ± 4%	482 ± 4%	62 ± 2%

Table 3
Results of the tensile tests on T91 material tested in liquid Pb–Bi before and after irradiation

Environment	dpa	$\sigma_{0.2}$, MPa	ε_{tot}, %	ε_{plast}, %	ε_{unif}, %	σ_{UTS}, MPa	$\sigma_{fracture}$, MPa	RA, %
Air	0	483 ± 4%	22 ± 4.17%	20 ± 4.17%	7 ± 8%	609 ± 4%	322 ± 4%	75 ± 1%
Pb–Bi + 5%H_2 + Ar	0	500 ± 6%	22 ± 0.15%	19 ± 0.32%	5 ± 4%	601 ± 4%	314 ± 4%	77 ± 1%
Pb–Bi + oxygen	0	438 ± 4%	20 ± 4.17%	18 ± 4.17%	6 ± 9%	564 ± 4%	302 ± 4%	75 ± 1%
Air	1.00	815 ± 4%	16 ± 0.42%	14 ± 0.30%	4 ± 6%	839 ± 4%	511 ± 4%	68 ± 2%
Pb–Bi + 5%H_2 + Ar	1.37	811 ± 4%	14 ± 0.42%	11 ± 0.69%	4 ± 6%	834 ± 4%	627 ± 4%	42 ± 2%
Pb–Bi + 5%H_2 + Ar	1.00	800 ± 4%	15 ± 0.42%	12 ± 0.45%	2 ± 10%	823 ± 4%	528 ± 4%	61 ± 2%
Pb–Bi + 5%H_2 + Ar	1.48	792 ± 4%	16 ± 0.42%	13 ± 0.37%	3 ± 6%	827 ± 4%	531 ± 4%	63 ± 2%
Pb–Bi + oxygen	0.99	774 ± 5%	16 ± 0.42%	13 ± 0.26%	3 ± 7%	797 ± 4%	473 ± 4%	68 ± 2%

metal was completely covered with solidified lead–bismuth eutectic.

In the following the results will be present for each of the investigated materials.

3.1. A316L

In the as received conditions, liquid metal has no observable effect on the tensile properties of this material as it can be seen in Fig. 1 where the tensile curves of the tests are illustrated. Neither the total elongation, nor the stress to failure was modified due to the exposure to lead–bismuth eutectic. The absence of embrittlement under reducing conditions (i.e., purging the liquid metal with 5%H_2 + Ar gas) did not give us a chance to investigate any eventual effect of the dissolved oxygen. However, oxygen activity in the chromium region (i.e., favouring formation of iron oxides (magnetite), and chromium oxide) had no influence on the mechanical properties of the material under study. The fracture surface morphology consisted of small hemispheres, resembling dimples, characteristic for a ductile fracture mode (Fig. 2).

The irradiation resulted in significant hardening and plastic instability after the yield point. The uniform elongation is nearly zero. The stress–strain curves are identical after irradiation to 1.30, 1.40, and 1.53 dpa. Their shape does not depend much on the irradiation dose (Fig. 3). Irradiation hardening resulted in increase of the yield (σ_{02}) and tensile (σ_{UTS}) strengths with about 27 and 23% respectively. Liquid metal had no effect on the strength properties and the small differences in comparison with the test in air are within the experimental error.

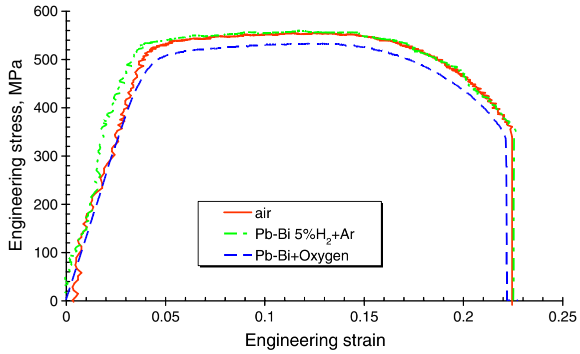

Fig. 1. Strain–stress curves of A316L material tested in liquid Pb–Bi at 200 °C and strain rate 5×10^{-6} s^{-1}.

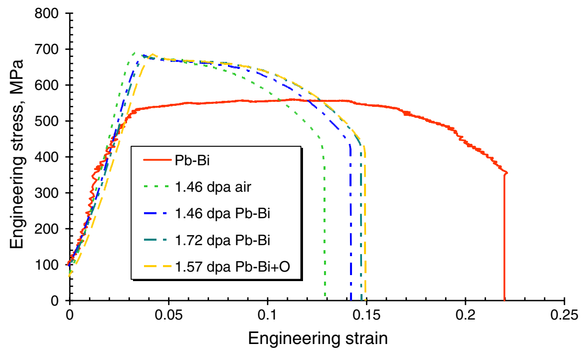

Fig. 3. Strain–stress curves of A316L material irradiated to different doses and tested in liquid Pb–Bi with and without dissolved oxygen at 200 °C and strain rate 5×10^{-6} s^{-1}.

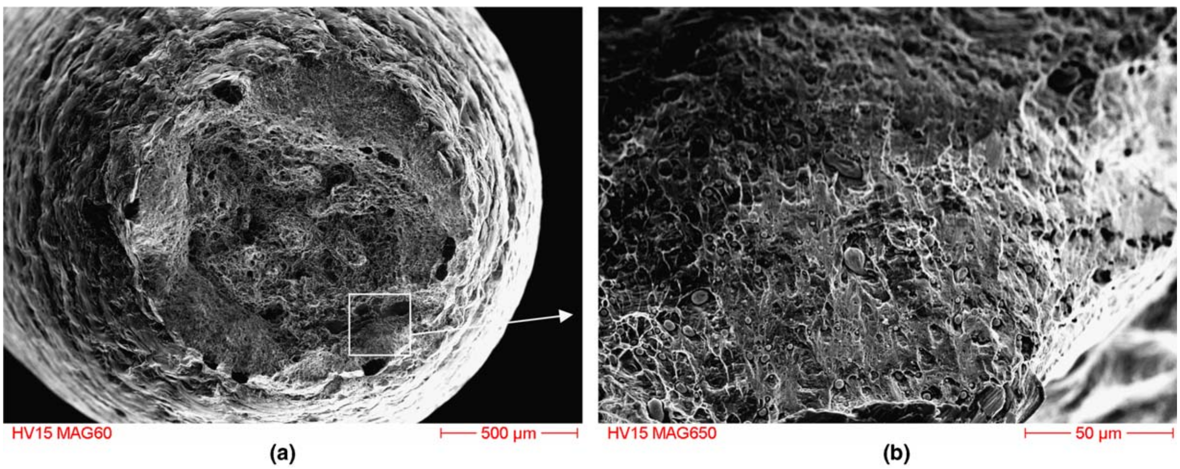

Fig. 2. Fracture surface overview of A316L sample tested in Pb–Bi at 200 °C under 5%H_2 + Ar gas (a), and magnification of the marked area from the sample tested in Pb–Bi under reducing conditions (b).

Regarding the strain to failure, the irradiation resulted in reduction of the total elongation with about 27%, which shows irradiation induced embrittlement. When tested in liquid metal the total elongation increased (irrespective to the irradiation dose) with 11–15% in comparison with the control test carried out in air (Fig. 3).

The fracture surface morphology of all samples is ductile irrespective to the testing environments as it can be seen in Fig. 4. The gauge surface of the specimens consists of rhomboidal tiles both when tested in air and in liquid metal. The fracture surface consists of dimples (in the centre) and stretched dimples at the peripheral area (Fig. 4), typical for a ductile fracture mode.

The mechanical parameters of all stainless steel samples tested before and after irradiation are given in Table 2.

3.2. T91

Lead–bismuth eutectic did not have measurable effect on the mechanical properties of the martensitic steel T91 in its standard conditions. The tensile curves are not modified due to the contact with the liquid metal (Fig. 5). The minute differences are assigned to materials imperfections and fall within the experimental error. The fracture surface of the unirradiated T91 material consists of small dimples (about 5 times smaller than these of unirradiated 316L) distinctive for ductile fracture mode (Fig. 6).

Irradiation of T91 steel resulted in a decrease of ductility (reduction of strain to failure) with 23% at 1.00 dpa. When tested in liquid lead–bismuth, the total elongation decreased with about 8%. The only exception was the sample irradiated to 1.37 dpa, for which the total elongation in comparison with the test in air decreased with 18%. The latter is assigned to the higher irradiation dose relative to the reference test on a sample tested in air which was irradiated to 1.00 dpa and used to evaluate the effect of the liquid metal. The reduction in area depends very little on the irradiation dose and tends to be constant at doses higher than 1.00 dpa (Fig. 7). The sample irradiated to 1.37 dpa is of particular interest. It has a lower strain to failure and reduction in area linking to possible effect of the liquid metal. It is logical that at a higher dose (1.48 dpa) the embrittlement effect (whether due to the irradiation or the liquid metal) will be greater (in terms of increased hardness and reduced ductility). However, this was not the case (Fig. 7). The ductility of the sample irradiated to 1.7 dpa is higher than the ductility of all the irradiated and tested in

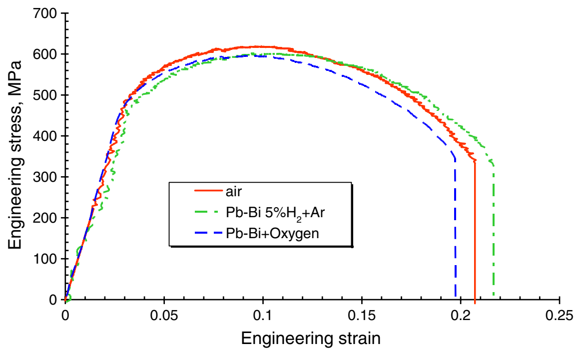

Fig. 5. Strain–stress curves of T91 material tested in liquid Pb–Bi at 200 °C and strain rate 5×10^{-6} s^{-1}.

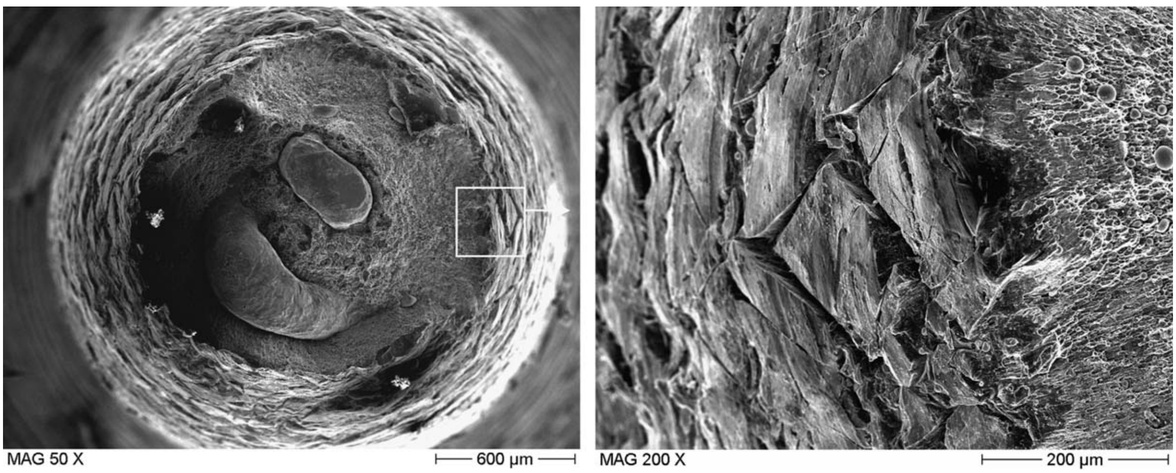

Fig. 4. Fracture surface overview of A316L sample 3D irradiated to 1.53 dpa and tested in Pb–Bi.

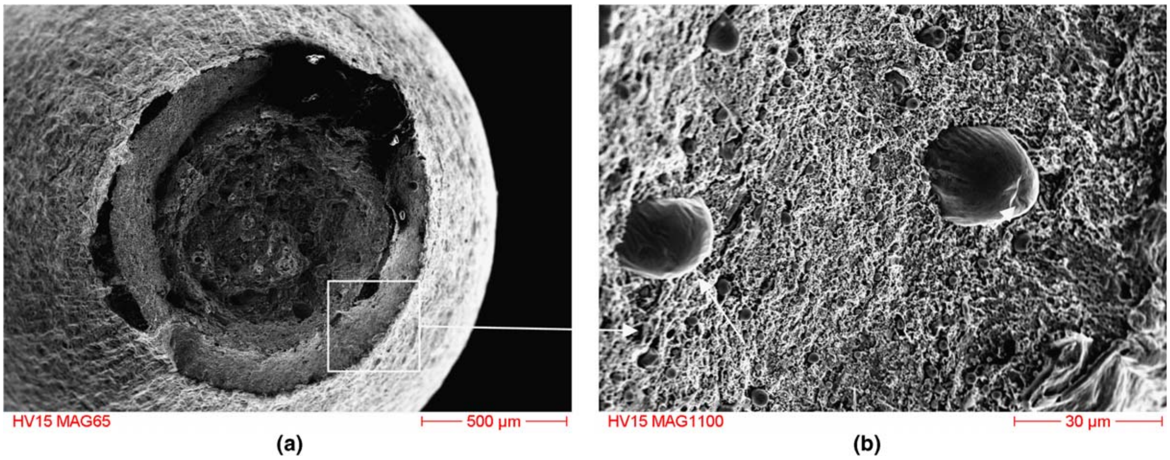

Fig. 6. Fracture surface overview of T91 sample tested in Pb–Bi at 200 °C under 5%H_2 + Ar gas (a). Fibrous fracture surface appearance characteristic for a ductile fracture mode (b).

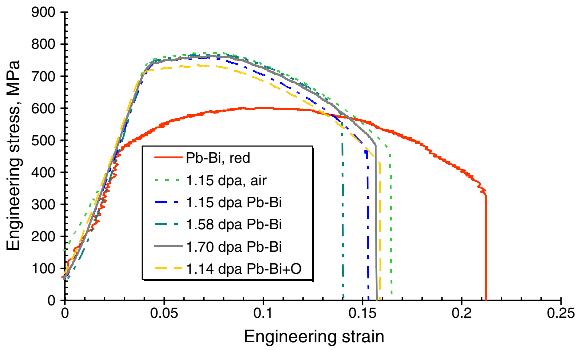

Fig. 7. Strain–stress curves of T91 material irradiated to different doses and tested in liquid Pb–Bi with and without dissolved oxygen at 200 °C and strain rate 5×10^{-6} s^{-1}.

liquid metal samples except for the sample irradiated at 1.00 dpa and tested in LBE with dissolved oxygen (Fig. 7). Analyses of the fracture surface showed that all of the irradiated samples have a peculiar morphology of the lateral (gauge) surface, similar to these of the stainless steel consisting of rhomboidal tiles (Fig. 8).

The test results of the T91 samples are present in Table 3.

4. Discussion

The evaluation of the combined effect of irradiation and liquid metal on the mechanical behaviour

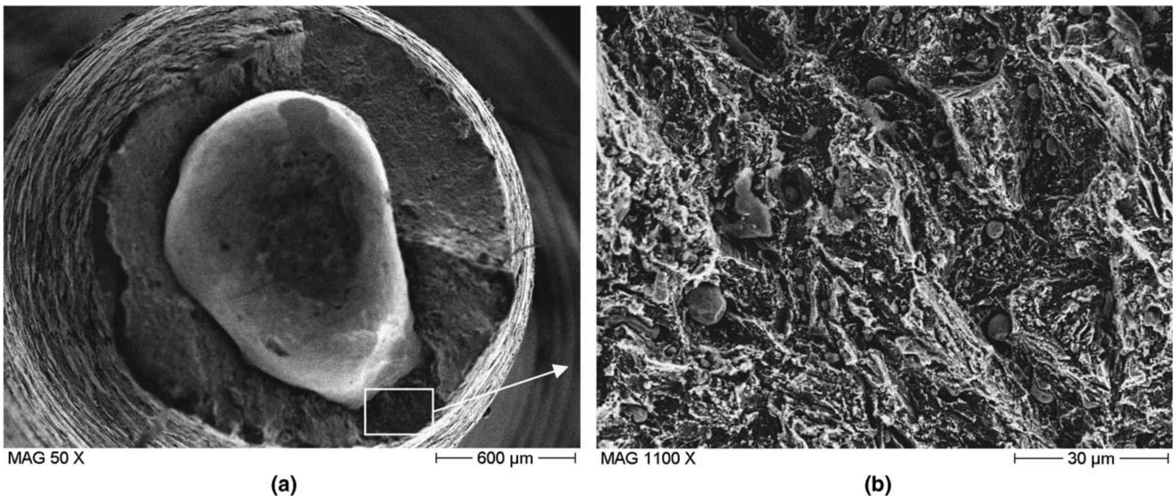

Fig. 8. Fracture surface overview of sample 9D irradiated to 1.37 dpa tested in Pb–Bi, overview (a), and (b) magnification of the mark area from (a).

of SS316 and T91 steels was done by comparison between tests performed in a controlled chemistry PbBi environment with tests carried out in inert gas environment known not to affect the mechanical properties of the investigated materials [12] using the exactly same experimental setup. The control (reference) tests were carried out after irradiation to 1.30 and 1.00 dpa for AISI 316L and T91 materials respectively. Former irradiation of the same kind of materials [13,14], have demonstrated that the irradiation induced hardening does not change drastically between 1 and 2 dpa, therefore we can use samples irradiated at slightly different doses but within experimental variation for comparison and estimation of the effects of irradiation and liquid lead bismuth eutectic. Thus, we will not be considering the effect of accumulated dose at this stage.

The effect of the dissolved oxygen at the test temperature (200 °C) cannot be observed due to the immunity of the tested material to LME and because of the very slow kinetics of oxidation.

What concerns the T91 sample irradiated to 1.37 dpa, at this point we can state that the observed effect is mainly due to irradiation than to any possible embrittlement by liquid lead–bismuth eutectic. The visible crystalline feature on the fracture surface morphology (Fig. 8) has facets consisting of dimples rather than the flat surfaces typical for intercrystalline fracture (intergranular ductile fracture [15]). Further, it is known that low temperature irradiation of 9Cr–1Mo martensitic steel results in considerable hardening caused by radiation induced dislocation loops and precipitates and occurs at temperatures up to 425–450 °C. In addition irradiation hardening and embrittlement reaches saturation at $\sim$10 dpa at these temperatures [14,13]. Therefore at 1.53 dpa the observed effect should be even greater but this was not the case. The fracture surface of the sample irradiated at 1.53 dpa lacks crystalline or brittle features. Therefore the observed embrittlement of the sample irradiated to 1.37 dpa and tested in liquid lead bismuth eutectic is assigned to radiation effects.

The irradiation hardening at these temperatures resulted in yield strength increase $\Delta\sigma_{02}$ equal to 155 MPa for the austenitic steel A316L and 260 MPa for the martensitic steel T91. However, increasing the hardness alone did not lead to embrittlement of the T91 material [4]. The material was embrittled after additional stress concentrator (notch) was introduced. This hardening is far below the hardening recently reported (more than 500 MPa increase) to increase the tendency of the latter material to embrittlement by liquid lead [4]. In the latter work the increase in the yield strength is considerably higher than the hardening resulting from neutron irradiation and hardening after irradiation under neutron–proton mixed spectrum [16]. The effect of the stress concentrators is recognized in the literature of LME [5,6]. Recent work showed that brittle crack can also propagate from sharp surface crack resulting from electric discharge machining (EDM). After short term exposure to liquid metal the surface crack were filled with liquid lead–bismuth and after some plastic deformation during tensile testing resulted in brittle fracture [17].

Neutron irradiation did not alter the behaviour of A316L material when tested in liquid LBE. The conditions for embrittlement of this material (if they exist) are still to be determined. It is possible due to its high nickel content, that any surface crack will be blunted by crack apex dissolution and cease further crack propagation.

5. Conclusions

The susceptibility of AISI 316L and T91 materials to stress corrosion in liquid lead bismuth eutectic was investigated before and after irradiation at 200 °C. No observable effects were found due to the contact with the liquid metal in both unirradiated and irradiated conditions. The post irradiation hardening did not affect the susceptibility of these materials to liquid metal embrittlement and the materials retained their mechanical properties independent on the test environment.

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