MYRRHA ADS-CANDIDATE MATERIALS COMPATIBILITY WITH LEAD BISMUTH BEFORE AND AFTER NEUTRON IRRADIATION

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Abstract

High chromium martensitic steels (9-12%Cr) are presently considered among the most promising candidates as structural materials for an Accelerator Driven Systems (ADS), on account of the severe expected service conditions, namely significant hardening and embrittlement caused by both neutron irradiation and contact with the lead-bismuth eutectic coolant. This work presents results obtained in the frame of the European 5th Framework program within the projects SPIRE and TECLA addressing the effects of neutron irradiation and liquid metal on basic in-service properties of three 9-12Cr ferritic martensitic steels as well as the austenitic steel 316L and the low activation steel F82H. The effect of irradiation was determined by post irradiation mechanical tests and comparison with non irradiated reference tests under the same conditions. The effect of liquid metal was examined by comparison with tests in inert environment (gas) on samples irradiated to the same dose.

Introduction

As part of the MYRRHA project research and development activities, a material research program has been started with the main objective of selecting structural materials for ADS MYRRHA. High chromium martensitic steels are among the most promising candidates due to their high resistance to irradiation damage (low swelling), thermal resistance and compatibility with liquid lead bismuth eutectic (LBE) at temperatures up to 550-600°C [0]. The effects of LBE on the materials properties are subject to many research activities worldwide. Beside the corrosion issue, the process of liquid metal embrittlement is of particular interest as this phenomenon may hinder the use of the selected material. Liquid metal embrittlement is the premature brittle failure of a normally ductile material when it is placed in contact with liquid metal [0]. Some authors add the prerequisite of stress to this definition, but failures due to exposure to liquid metals have been observed in the absence of external stresses as well. The main characteristics of LME are the very high crack propagation rate and the drastic reduction of strain to rupture (total elongation) [0]. Presently the phenomenon is considered to be without firm scientific foundations. Nevertheless, there are several empirical rules attempting to correlate and predict the occurrence and the severity of LME:

- Specificity – if the two interacting metals form a stable intermetallic compound with high melting temperature point, it is unlikely that they will form an embrittling couple

- Low mutual solubility – this rule can be argued as at high solubility the dissolution process may tend to blunt the crack tip (Joffe effect). On the other hand it is believed that a minute solubility is required to facilitate wetting. Nevertheless, totally immiscible metals exhibit LME.

- Intimate contact – the embrittling metal has to be present at the tip of the crack. The requirements for wetting are in conflict with these for low mutual solubility and absence of intermetallic compounds. At present it is recognized that wetting (or intimate contact) can be produced even with systems having negligible solubility [0]. In previous studies this controversy was argued by the existence of very low chemical affinity. The possibility that stress and lattice strain play a role in inducing chemisorptions in such systems has been mentioned as well [0]. The presence of oxygen can hinder the wetting process in the case of Pb-Bi eutectic.

However, all of them have exceptions and fail to cover all possible cases. It is generally believed that susceptibility to LME depends upon the thermal and mechanical history of the solid, as it alters its microstructure. Thus, the hardness and the deformation behaviour of the stressed solid metal can play a key role on its sensitivity to LME. Alloys in high strength conditions are usually more severely embrittled [0]. In summary, at least two necessary conditions have to be fulfilled in order to study the compatibility of a couple solid/liquid metals: i) a wetted and ii) a stressed solid merged in an infinite reservoir of non-oxidised liquid metal.

As for now, no experimental evidence about embrittlement of as-produced steels by liquid lead, or lead-bismuth has been reported. On the basis of the empirical rules for the occurrence of LME, the materials have been modified in order to promote or increase their susceptibility to LME. The easiest way is to subject the materials to various heat-treatments and to increase their hardness, thus changing the metallurgical conditions and hence the sensitivity to liquid metal embrittlement. Various tests have been carried in liquid lead [0], lead-lithium eutectic [0], and liquid lead bismuth eutectic [0] on steels (namely 9Cr-1Mo, T91) subjected to tempering, quenching and notching and subsequently tensile tested in liquid metal. These procedures resulted in brittle fracture behaviour, observed as reduction in total elongation and modification of the fracture surface morphology. These materials were driven far from any state representative of the real service conditions. Nevertheless such conditions would occur after very specific thermal treatments (e.g. welding). However it has been shown that the initial conditions can be successfully recovered after an appropriate post welding heat treatment [0]. Post irradiation hardening and embrittlement would have the same drastic effect, if not worse than the above mentioned heat treatment and it would be expected to promote embrittlement under exposure to liquid metals.

This paper reports on whether irradiation hardening will result in a supplementary embrittlement of some selected steels by liquid metal. Several materials were irradiated at relatively low temperature which would lead to relatively high irradiation hardening. The requirement for intimate liquid metal/solid metal contact, as discussed above, was achieved during tensile tests. In fact, due to its higher hardness the surface oxide layer would break at a very early stage of deformation which will allow the freshly exposed bulk material to be in intimate contact, at an atomic scale, with LBE and therefore provide the necessary "wetting" conditions for LME to occur.

Experimental

Irradiation

The samples were irradiated in the BR-2 reactor in Mol. The irradiation was done in MISTRAL (Multipurpose Irradiation System for Testing of Reactor ALloys) in-pile sections (MIPS#1 and MIPS#2). The samples irradiated for the TECLA program were placed in the MIPS#1 irradiation rig and irradiated in channel B300 for three reactor cycles. The samples for the SPIRE program were irradiated in the MIP#2 irradiation rig and placed in channel C101 for 5 reactor cycles and in channel C259 for 8 reactor cycles. Both irradiation devices have similar construction. Figure 1 shows the sampler holder of the irradiation rig.

The main components of the in-pile section are the following:

4. A stainless steel force tube, having an outer diameter of 34 mm and whose main purpose is to resist the external pressure. The tube has variable thickness along its length, in order to provide uniform temperature on its internal surface;

5. A screen tube acting as a thermal insulation and is only used for irradiation temperatures above 270°C;

6. A sample holder that can accommodate up to 91 specimens of 27 mm length distributed on 13 levels; spring system is used for holding the samples in place. Place for 14 thermocouples is provided.

7. A heating element in shape of a rod with diameter 9.4 mm and length 855 mm;

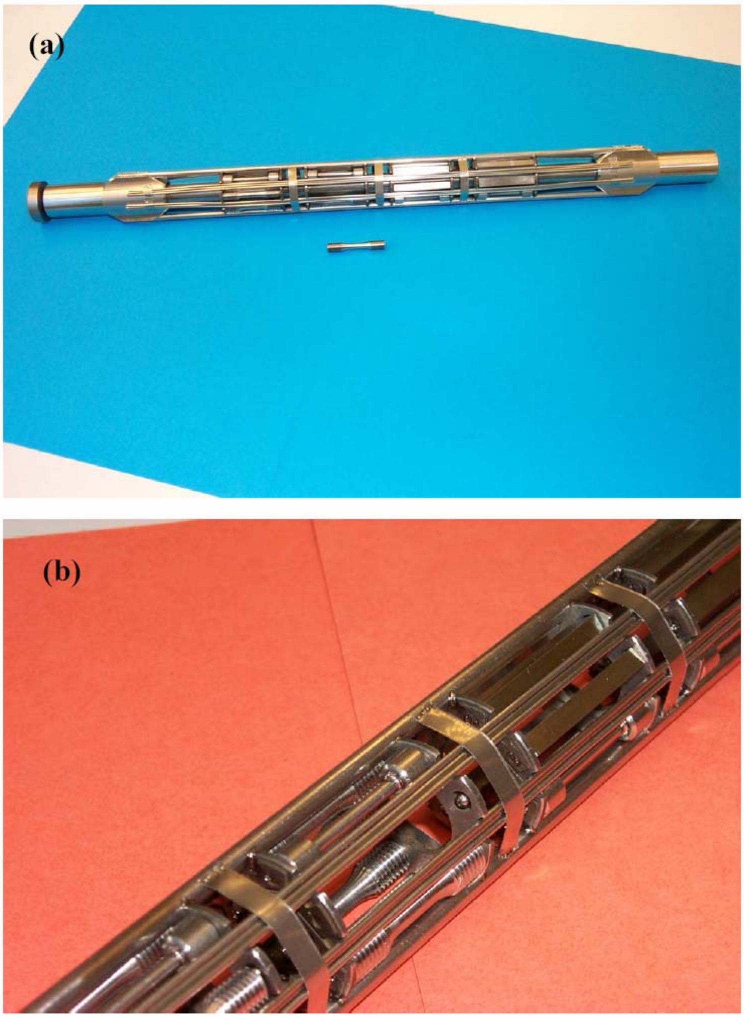
8. A double instrumentation (top/bottom), allowing easy replacement of the heating element in the reactor pool without necessary disconnecting the instrumentation package.

During irradiation the temperature was measured by thermocouples placed into dummy cells and was maintained in the interval 200-204°C [0].

Dosimetry

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 these experiments, Fe dosimeters were used to determine the neutron fluence. They were encapsulated in a stainless steel tube to prevent damage and corrosion. The dosimeters were wires with diameter 0.5 mm and different lengths. Neutron flux was calculated at reference power 56.0 MW using the ^{235}U spectrum and the averaged cross section for the reaction $^{54}Fe(n,p)^{54}Mn$, $<\sigma>=81.7$ mbarn with effective threshold energy 2.80 MeV.

Figure 1. **An overall view of the MISTRAL irradiation device (a) and a close view (b) of the specimen holder.**



The fast neutron flux and fluence (E>1MeV) is obtained by multiplying the experimental equivalent fission flux and fluence by 0.87 i.e., the average ratio of the calculated fast flux to the equivalent fission flux [0]. The calculated doses are given in Table 1.

Table 1. **Irradiation doses and specimen designations of A316L and T91**

ID	Material	Dose	ID	Material	Dose	ID	Material	Dose, dpa
9E	T91	1.14	3B	A316L	1.46	IE	T91	2.93
9B	T91	1.15	3C	A316L	1.46	EC	T91	4.36
9C	T91	1.15	3A	A316L	1.57	CC	EM10	2.93
9D	T91	1.58	3D	A316L	1.72	AA	EM10	4.36
9A	T91	1.70				PI	HT9	2.53
						ME	HT9	4.36

Materials and test conditions

Two candidate materials for MYRRHA ADS have been investigated: the austenitic stainless steel A316L and the martensitic steel T91 irradiated up to 1.7 dpa. The mechanical properties of T91 have been compared with two other ferritic martensitic steels (EM10 and HT9) within the SPIRE program after irradiation to slightly higher doses (Table 1). The chemical composition of these materials is given in Table 2.

Table 2. **Chemical composition *(wt%)* of A316 L, T91, EM10, and HT9 materials tested in liquid Pb-Bi eutectic**

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	-
EM10	balance	8.97	0.07	1.06	0.49	0.013	<0.002	<0.003	0.46	0.014	0.099	0.013
HT9	balance	11.68	0.66	1.06	0.63	0.29	0.03	<0.003	0.45		0.204	0.020

The materials were received and tested in the following state:

- T91: supplied by UGINE, heat 36224 normalized at 1040 °C for 60´ and tempered at 760 °C for 60´.
- A316 L: supplied by SIDERO STAAL n.v., heat number 744060 in the shape of bars with diameter 6 mm and length 500 mm from which the specimens were manufactured. The material is solution annealed with some cold work.
- EM10: supplied by CEA, normalized at 990°C/50min, tempered at 750°C/60min.

The samples used are sub-size tensile samples with length = 27 mm, gage length = 12 mm and diameter = 2.4 mm. Lead bismuth eutectic alloy (44.8 % Pb, 55.2 % Bi) was supplied by Hetzel Metalle GmbH with reported purity: Pb 99.985% minimum and Bi 99.99% minimum. The tests were done in an autoclave in conjunction with gas conditioning system. The following test sequence was utilised:

- The sample is gripped into the sample holder and small initial stress was applied (to avoid unscrewing).

- The autoclave is closed and the liquid metal is subjected to pre-conditioning (reduction of the oxides) for 4 hours by bubbling with 5%H_2+Ar gas. The gas flow is maintained at about 5 l/h.

After the sample was broken, it was removed from the autoclave and cleaned in hot tempering oil at 160-180°C for about 5 min. Subsequently the adjacent oil was removed in methanol bath by ultrasonic cleaning. Post-test analyses comprised both visual and scanning electron microscopy observations of the fracture surface.

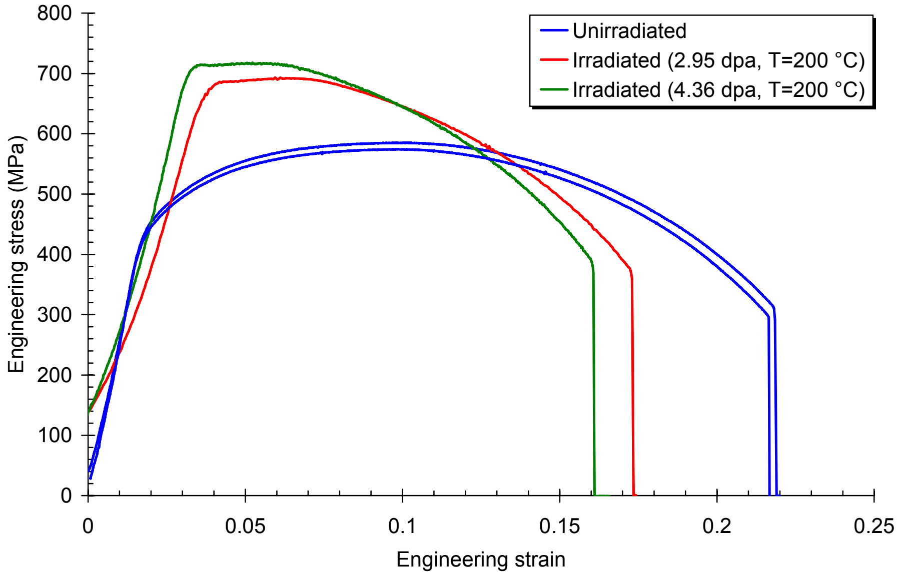
Results and Discussions

Mechanical testing in air before and after irradiation

Although the investigated materials have been characterized in terms of fracture toughness, impact and tensile tests, only the latter are described in this paper. They have been executed on unirradiated and irradiated samples in accordance with the ASTM E8M-01 and E21-92 (1998) standards. Crosshead displacement rate was 0.2 mm/min, corresponding to a strain rate of approximately 2.8×10^{-4} sec^{-1}; no extensometer was used.

Figure 2. **Engineering stress-strain curves of a) EM10 b) T91 and c) HT9 specimens tested at 200 °C in air.**

(a)



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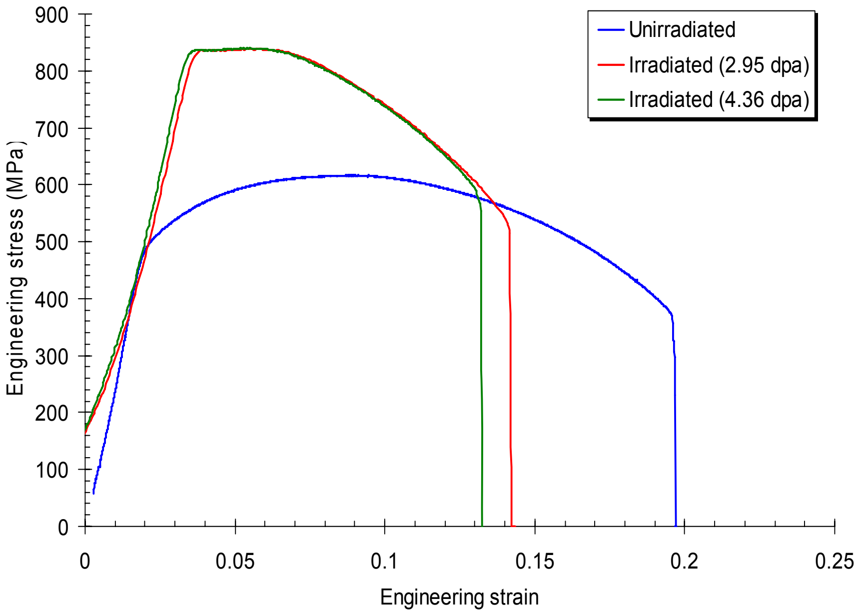

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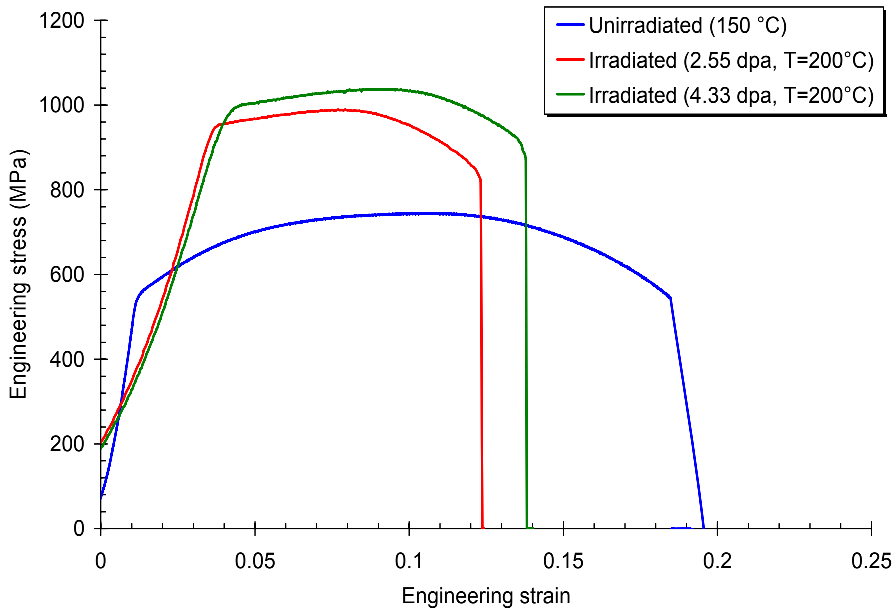


Clear signs of irradiation hardening (increase of yield and ultimate tensile strengths and reduction of uniform and total elongation) are visible in all figures (Figure 2 a, b, and c). For EM10, considerable hardening is observed at 200 °C; the increase of yield strength with respect to the unirradiated data is 216.5 MPa (48%) at 2.95 dpa and 260.8 MPa (58%) at 4.36 dpa; the increase of σ_{UTS} is more moderate (113.5 MPa or 20% at 2.95 dpa and 138.1 MPa or 24% at 4.36 dpa). The hardening exponent, which is related to the capability of the material to harden with plasticity, decreases significantly, from n = 0.11 (baseline) to n = 0.037 (2.95 dpa) and n = 0.019 (4.36 dpa). In the case of ductility parameters (uniform and total elongation, reduction of area), we observe a decrease of 5-6% for the uniform elongation (consistent with the sharp decrease of the hardening exponent previously mentioned) and a similar decrease of 5-7% for the total elongation. As far as reduction of area is concerned, a sharp drop of 20% has been observed but only for the lower dose; for the higher dose, RA appears almost unchanged.

For T91, it can be observed that hardening is more significant than for EM10, with an increase at 200 °C of 69% (341 MPa - both doses) for the yield strength and 36% (222 MPa at 2.95 dpa and 224.3 MPa at 4.36 dpa) for the ultimate tensile strength. This is accompanied by a sharp decrease of the hardening exponent, which falls from 0.11 (baseline) to 0.014 (irradiated, both doses). Uniform elongation decreases by 4% (both doses) and total elongation by 7% (2.95 dpa) and 8% (4.36 dpa). Reduction of area increases by 7% (2.95 dpa) and decreases by 7% (4.36 dpa).

The irradiation hardening observed for HT9 at 200 °C is comparable, although slightly larger, to that measured on T91: yield and ultimate tensile strength increase respectively by 411.2 MPa (76%) and 257.3 MPa (35%) at 2.55 dpa and 441.7 MPa (82%) and 305.1 MPa (42%) at 4.33 dpa. On the other hand, the corresponding decrease of the hardening exponent is more similar to EM10, dropping from 0.125 (baseline) to 0.042 (2.55 dpa) and 0.050 (4.33 dpa).

The loss of ductility at 200 °C can be approximately quantified as a decrease of 5-6% for the uniform elongation, 8-9% for the total elongation and 26-27% for the reduction of area.

Table 3. **Summary of irradiation effects from tensile tests, quantifying the hardening and loss of ductility observed at 200 °C on EM10, T91 and HT9 as a consequence of neutron irradiation.**

Material	**Dose: 2.67-2.93 dpa**					**Dose: 4.10-4.36 dpa**				
	$\Delta\sigma_y$ (%)	$\Delta\sigma_m$ (%)	$\Delta\varepsilon_u$ (%)	$\Delta\varepsilon_t$ (%)	ΔZ (%)	$\Delta\sigma_y$ (%)	$\Delta\sigma_m$ (%)	$\Delta\varepsilon_u$ (%)	$\Delta\varepsilon_t$ (%)	ΔZ (%)
EM10	+48	+20	-6	-6	-21	+58	+24	-6	-7	-3
T91	+69	+36	-4	-7	+7	+69	+36	-4	-8	-7
HT9	+76	+35	-6	-9	-27	+82	+42	-5	-8	-26

LEGEND - σ_{p02} = yield strength; σ_{UTS} = ultimate tensile strength; ε_u = uniform elongation; ε_t = total elongation; Z = reduction of area.

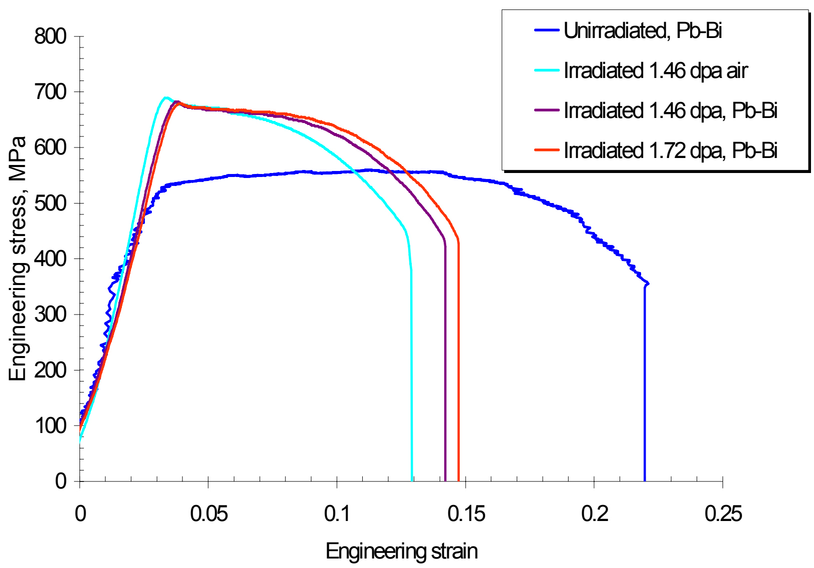
As expected, F/M steels with 12%Cr are more irradiation-sensitive than 9%Cr steels (EM10 and T91), mainly owing to the formation of α phase. On the other hand, as already mentioned, EM10 and T91 differ mainly on the basis of their V and N nominal content. V is a carbide nitride former, which promotes the formation of small carbides in much higher number for T91 than for EM10. This circumstance facilitates the increase of yield and ultimate tensile stresses; after irradiation, this effect becomes even more significant as defect accumulation is promoted by the presence of small carbides.

Mutual effects of LBE and irradiation

Comparison of A316L and T91 after irradiation to 1.7 dpa

Figure 3. **Strain stress curves of irradiated and unirradiated a) A316 L and b) T91 material tested in liquid Pb-Bi at 200°C and strain rate 5.10^{-6} s^{-1}. (red. stays for reducing cover gas atmosphere, i. e. 5%H_2+Ar)**

a)



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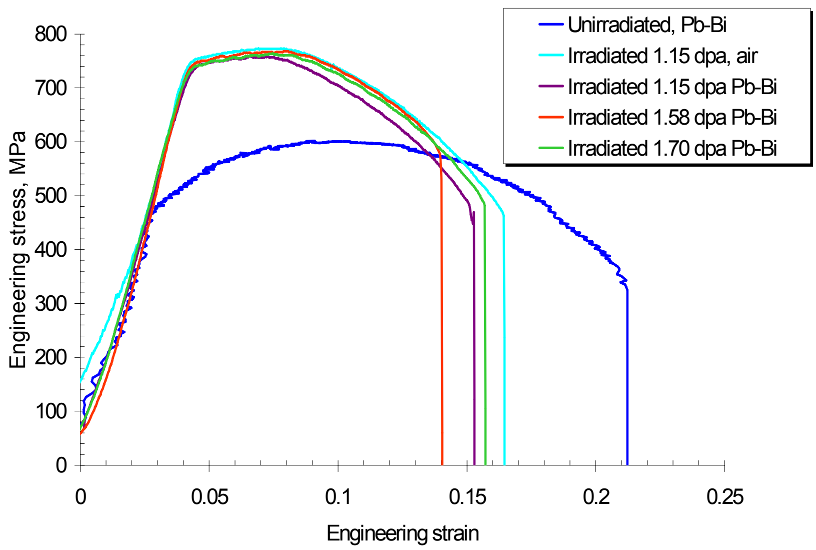
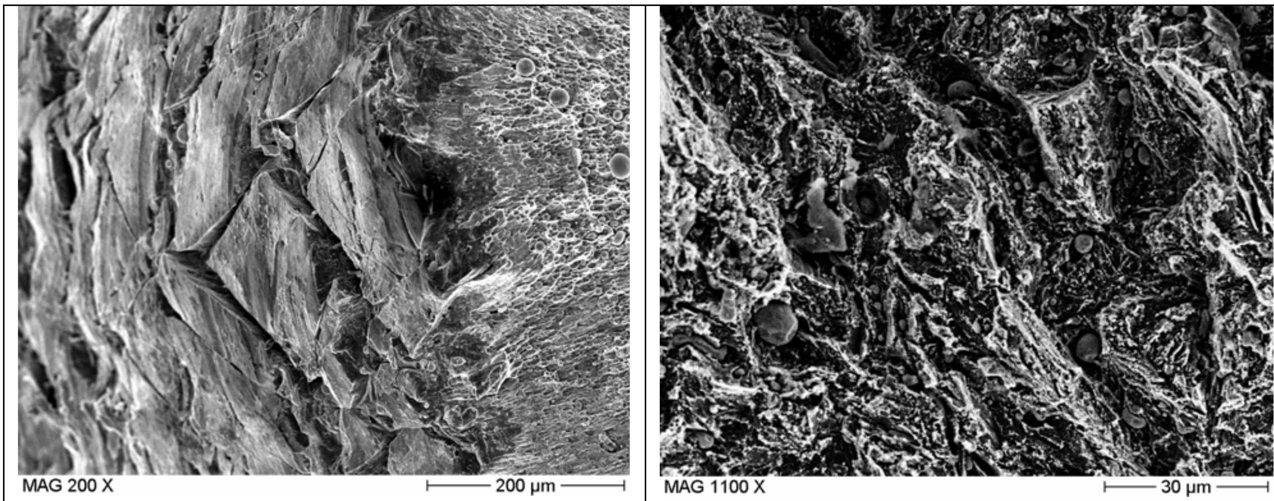


The tensile curves of A316L and T91 tested in air and in LBE before and after irradiation are plotted in. Both materials show significant hardening and radiation embrittlement (i.e., reduction in ductility due to irradiation) in comparison with the unirradiated conditions. The irradiation of the austenitic material resulted in plastic instability after the yield point and absence of uniform deformation even at doses as low as 1.46 dpa. On the other hand, T91 retains its plasticity after irradiation up to 1.7 dpa, and deforms uniformly as well. Both materials show little difference in their tensile behaviour with the dose increase. The mechanical parameters are approaching saturation already at doses equal to 1.7 dpa.

The effect of liquid metal exposure is assessed relative to reference tests carried out in control environment (air) for which we know that both materials are inert to environmentally assisted cracking (EAC). The control tests have been performed on samples irradiated to 1.46 dpa and 1.15 dpa of A316L and T91 materials respectively. This could introduce difficulties when estimating the effect of liquid metal at higher irradiation doses (e.g., 1.7 dpa), but both materials remained immune to liquid metal embrittlement after irradiation up to 1.7 dpa. The tensile curves are following the same pattern and do not differ from the control test in air. Fracture surface analyses done on these samples showed only dimple fracture morphology characteristic of ductile fracture mode (Figure 4 a and b). Possibly the induced irradiation hardening is under the threshold value for LME on these materials if they are susceptible. Nevertheless, the saturation of the strength and ductility parameters with the irradiation dose would probably not render the materials sensitive to LME even after irradiation to higher doses.

Figure 4. **Fracture surface morphology of a) A316 L and b) T91 irradiated to 1.72 and 1.58 dpa respectively and tested in liquid Pb-Bi eutectic.**



a) b)

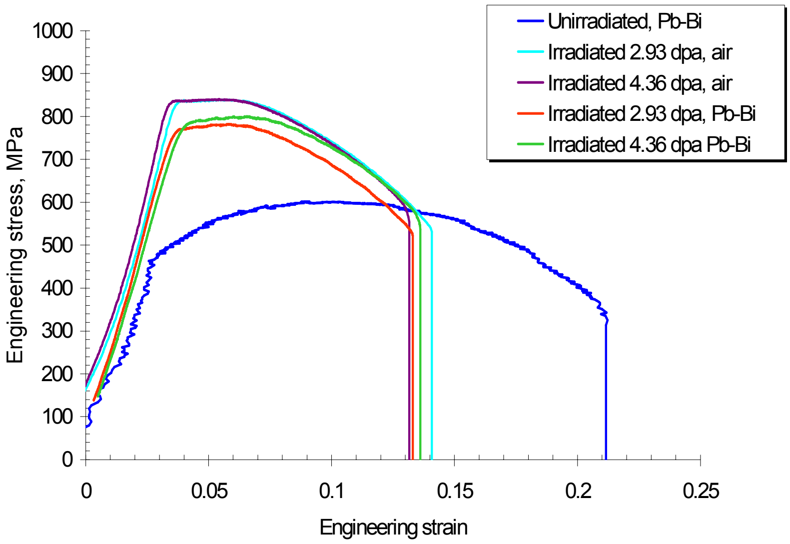
Comparison among three F/M steels tested in Pb-Bi after neutron irradiation

The stress-strain curves of T91, EM10, and HT9 irradiated to 2.93 and 4.36 dpa are given in Figure 5. To assess the effect of the environment, specimens irradiated up to similar doses have been tested both in air and LBE. As it can be seen in Figure 5, the differences in terms of yield and ultimate tensile stresses resulting from tests performed in air and LBE are within the typical experimental uncertainties for this type of test (±10%). No significant effect can be observed on uniform and total elongation either. Such slight differences cannot be attributed to an environmental effect but mainly to data scatter.

Therefore, the effects of LBE on the tensile properties of these materials are very similar, in that none of them was found susceptible to liquid metal embrittlement.

Figure 5. **Stress-Strain curves of unirradiated and irradiated a) T91, b) EM10 and c) HT9 tested in liquid Pb-Bi at 200°C and strain rate 5.10^{-6} s^{-1} (Pb-Bi) and 3.10^{-4} s^{-1} (air)**.

(a)



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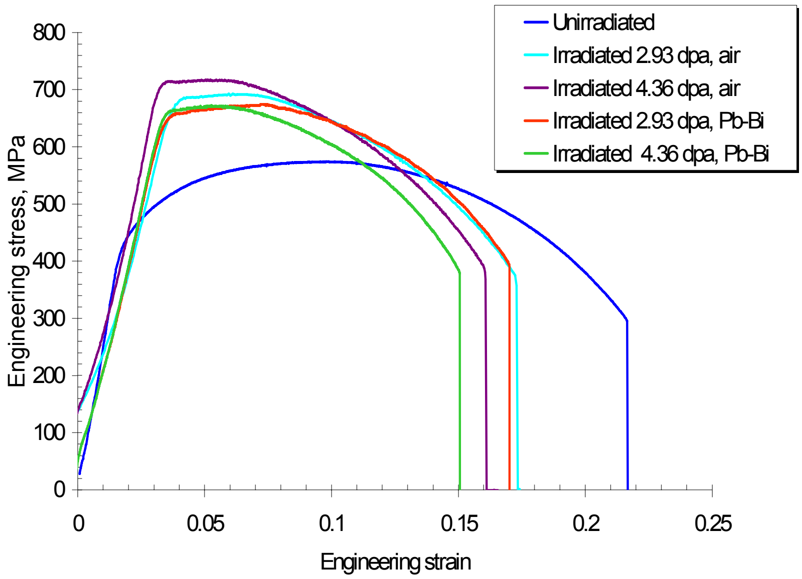

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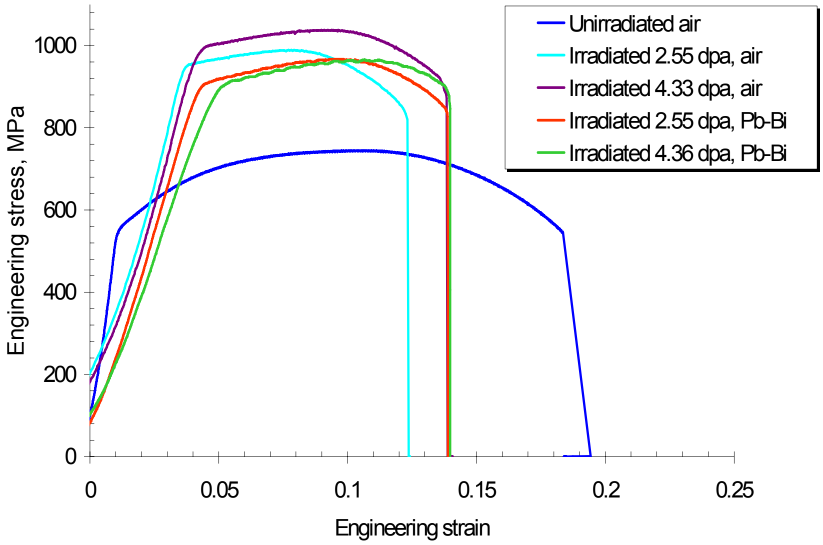

Conclusions

The effects of neutron irradiation and liquid metal have been assessed by tensile tests on one austenitic and three martensitic steels. Subsequently, comparison has been made between the effects of irradiation and liquid metal on the austenitic and martensitic steels and between the same on three ferritic martensitic steels.

The austenitic steel has poor irradiation resistance in comparison with the martensitic structures. However, both types of materials were immune to liquid metal embrittlement after neutron irradiation up to 1.7 dpa under the above tests conditions.

When tested in liquid metal, none of the three F/M steels was found susceptible to LME.

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