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Bending tests on T91 steel in Pb–Bi eutectic, Bi and Pb–Li eutectic

H. Glasbrenner *, F. Gröschel

Spallation Neutron Source Division, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Abstract

The influence of specific liquid metals on the behaviour of the ferritic/martensitic steel T91 are investigated to understand better the processes taking place at the metal surface. Of special interest is particularly if there is a penetration of selected elements out of the melt along grain boundaries. Metallurgical investigation, SEM and EDX analyses analysis were performed on bent T91 specimens exposed to static LBE, Bi and Pb–17Li at 300 °C for 1000 h. Steel T91 was used in the standard and specially annealed conditions. It is shown that the heat treatment of the steel has a strong influence on the corrosion resistance. Additionally the strain affected on the component is responsible for the occurrence of LME.

1. Introduction

There are many advanced and innovative technologies under development dealing with liquid metals due to their excellent and unique properties. For example in a future ADS (accelerator driven system) reactor it is foreseen to use lead or lead–bismuth eutectic (LBE) as coolant and neutron spallation target [1].

When a solid metal is exposed to a liquid-metal environment, various physico-chemical processes may take place as for example liquid metal corrosion [2–4] and liquid metal embrittlement (LME) [5–8]. LME can lead to a severe and very fast usually brittle inter granular failure of the ductile structural material. There exist several theories e.g. described in the review paper [6] trying to explain the phenomenological features of LME but up to now it is not possible to forecast the behaviour of different liquid metal–solid metal combinations. The interaction of lead to steel has been already intensively investigated. For example Nicolas et al. [9] have published that armco iron and different mild alloy steels are embrittled by lead. Nicaise et al. [10] have reported that lead can induce severe LME if the ferritic/martensitic steel T91 is hardened by heat-treatment. In contrast to it liquid metal embrittlement tests performed in Pb [10] and Pb–17Li [11] have shown no influence on the mechanical behaviour of normal heat-treated martensitic steels. Data on the influence of pure bismuth on the mechanical properties of steel are scare and controversial. Rädecker et al. [12] did not observe an embrittling effect by performing tensile tests on a mild steel (St 35) in liquid bismuth at 300 °C whereas Tanaka and Funkunga [13] revealed a significant decrease in the reduction area of mild steel stressed at 350 and 460 °C with a recovery temperature of 550 °C.

Recently, Guerin et al. [14] have shown that an embrittling influence of LBE to T91 steel in normal metallurgical state is dependent on the liquid and gas phase contact i.e. the absence of a stable oxide film on

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* Corresponding author. Tel.: +41 56 310 4712; fax: +41 56 310 2199/3131.
E-mail address: heike.glasbrenner@psi.ch (H. Glasbrenner).

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the steel surface seems to promote LME. This is in agreement with the results published by Fazio et al. [15] who reported that the tensile properties of T91 after exposure to LBE having a low oxygen activity at 400 °C for 1500 h revealed a mixed brittle-ductile fracture morphology and a decrease of the area reduction factor compared to a non-corroded specimen was observed whereas the tensile properties of 316L stayed unaffected. Some papers were already published addressing the interaction between different kind of steels and their mechanical properties in lead, bismuth and LBE but a complete perspective on the mechanical behaviour under the proposed conditions is up to now not available.

The aim of this experimental work is to determine the influence of different environments (bismuth, LBE and Pb–17Li) on the behaviour of ferritic steel trying to understand the processes taken place. Therefore bending tests were performed on the T91 steel specimens which were set up under standard and special annealed conditions as well. The specimens were exposed to static LBE, Bi and Pb–17Li at 300 °C for 1000 h. Of special interest is if there is a favoured penetration of one element along grain boundaries which may then be responsible for the liquid metal embrittlement.

2. Experimental

2.1. Materials

The as received T91 steel (produced by USINOR, Le Creusot, France; Heat no. 504/3) was heat treated at PSI in two different ways: the standard heat treatment (1050 °C for 30 min, air quenching and tempering at 750 °C for 1 h: denoted in the following as T91) and a special heat treatment (1050 °C for 30 min, air quenching and tempering at 500 °C for 1 h: marked as T91*) in order to produce a hardened material. The Vicker micro hardness achieved for T91 is about 240 HV0.05, for T91* around 420 HV0.05.

It is reported in the literature that hardened material is generally more severely embrittled [10,16,17]. The chemical composition of T91 used is listed in Table 1.

Bi was delivered as pellets by Hetzel Metalle Berlin GmbH, Germany having a purity of 99.9%. Impag AG (Switzerland) supplied the eutectic Pb–55.5Bi (44.8 wt% Pb and 55.2 wt% Bi) alloy which contained a few ppm of impurities: Ag 11.4, Fe 0.78, Ni 0.42, Sn 13.3, Cd 2.89, Al 0.3, Cu 9.8, Zn 0.2. The eutectic Pb–17Li was provided by ENEA from Nuova Samim (Italy) and had a Li content of 0.70 wt% (17.4 at.% Li).

2.2. Bending test conditions

U-bend specimens were cut parallel to the direction of rolling; hence the relative orientation for the bending is longitudinal. The maximum deformation calculated for the tension face is around 25%. The intention was the generation of as many gliding planes as possible because they could be responsible for LME and interact as starting point. After the specimens were bent into the right shape the position was fixed by bolt and nuts to avoid relaxation of the tensile elastic strain. For exposure the ferritic specimens were placed in ferritic crucibles. Molten Bi and lead alloys were filled into the crucibles in a glove box under He atmosphere. The crucibles were closed gas tight by using copper seals. The oxygen content was not controlled during the experiment due to the fact that an oxygen sensor does not work at 300 °C. In total six crucibles were filled with the U-bend specimens and the according liquid metal or alloy. The crucibles were placed in a furnace at 300 °C. After 1000 h each crucible was opened and the specimens were removed for detailed examination. The surfaces of the melts were covered with oxide. Hence the tests were performed under oxygen saturated conditions. In Table 2 the tests performed up to now are summarised.

Table 1
Actual composition in wt% of T91; Fe in balance

Steel	C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Al	Co	Nb
T91	0.088	0.0006	0.019	0.317	0.597	0.099	8.76	0.862	0.186	0.054	0.021	0.019	0.073

Table 2
Test conditions for the exposure of U-bend specimens under static conditions

Steel	Bi	LBE	Pb–17Li
T91 Standard state (T91)	300 °C, 1000 h	300 °C, 1000 h	300 °C, 1000 h
T91 Hardened state (T91*)	300 °C, 1000 h	300 °C, 1000 h	300 °C, 1000 h

After exposure polished cross sections were made of the exposed specimens without removing the adherent solidified melt. Subsequently metallurgical examination, SEM and EDX analyses were carried out.

3. Results

3.1. Metallurgical examination

The cross sections of the specimens were examined both on the bent and on the straight parts in order to compare the influence between the stressed and non-stressed area concerning corrosion resistance. The straight part of the specimens (areas without any stress) shows generally less corrosion attack compared to the bent part, but on some regions a penetration of liquid metal/alloy into the steel surface is clearly visible.

As next the results obtained for the specimens in the bent area are presented: T91 and T91* exposed to LBE at 300 °C gave the same results and only little attack is revealed in the bent area like in the straight part. The T91 specimen exposed to Pb–17Li (Fig. 1(a)) shows tiny cracks which seem to be filled with solidified alloy. A strong corrosion attack was revealed on the T91* specimen. The penetration of Pb–17Li into the steel matrix and the formation of cracks are obvious (see Fig. 1(b)). The same observation was made on the T91 (Fig. 2(a)) and T91* (Fig. 2(b)) specimens exposed to Bi.

3.2. Analysis of the cross sections by SEM and EDX

The interface between the solidified melt and steel was investigated in detail in order to understand the reactions happened.

3.2.1. Inspection of T91* after exposure to LBE

There were no cracks found neither on the bent area nor on the straight part of the T91* specimen. An oxide layer on the surface is detectable which separates the

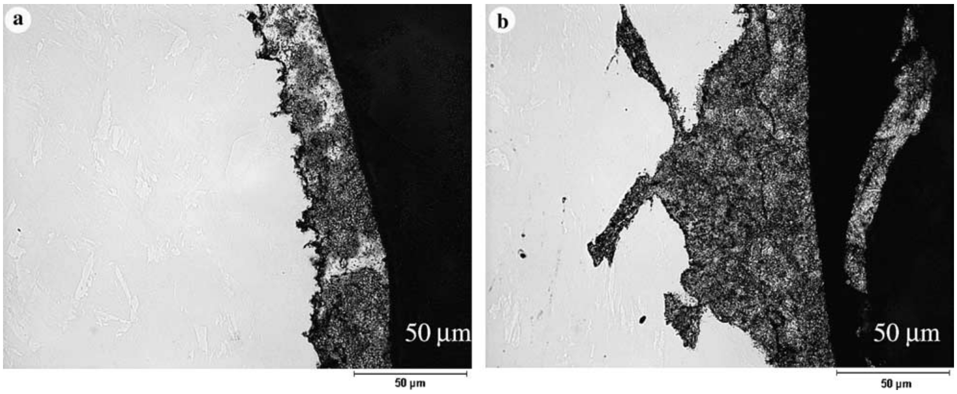

Fig. 1. Bent part of the T91 (a) and T91* (b) specimens after exposure to Pb–17Li.

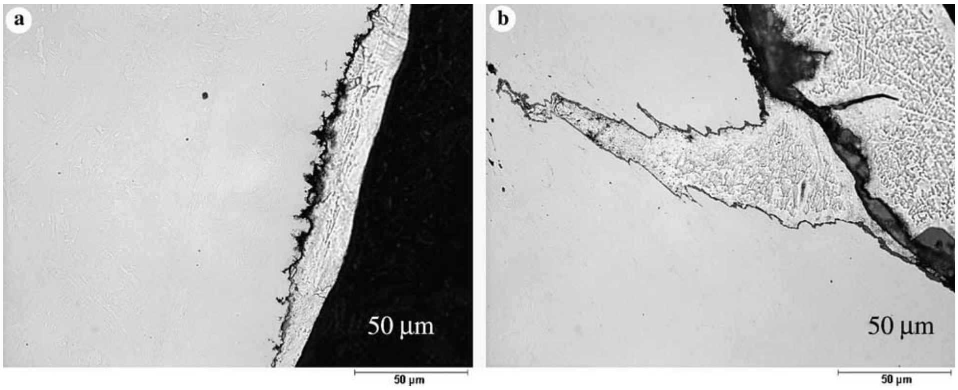

Fig. 2. Bent part of the T91 (a) and T91* (b) specimens after exposure to Bi.

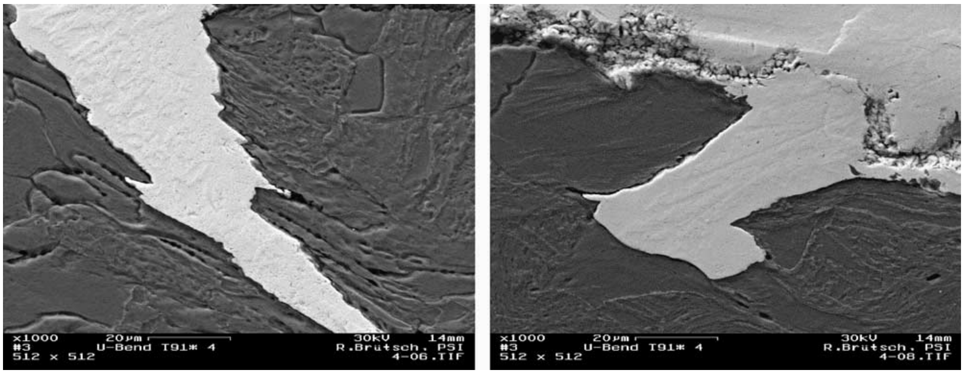

Fig. 3. Liquid metal embrittlement and liquid metal corrosion have taken place in T91* exposed to liquid bismuth.

adherent LBE from the steel. This could be the reason that no liquid metal embrittlement has occurred. The EDX analyses made on the steel and on its oxide layer revealed more or less the ratio of the steel as Fe/Cr = 10. Additionally in the oxide layer the elements Pb and Bi were detected having a ratio of Pb/Bi of about 3 (LBE has a ratio of Pb/Bi = 0.8). The higher amount of Pb could be ascribed by the larger affinity to oxygen of Pb compared to Bi. In the boundary layer of the solidified melt the amount of Bi is enriched which is the result of the preferred depletion of Pb (Pb/Bi = 0.25). The steel elements were analysed as well in this boundary layer. The content of Cr is proportionally higher than in the steel matrix (steel Fe/Cr = 10; solidified Pb–Bi Fe/Cr = 2.5) which is explainable with the higher solubility of Cr compared to Fe in lead bismuth [18,19]. To summarise the observations made one can say that the oxide layer on the steel surface is still intact but the dissolution of it has already started.

3.2.2. Inspection of T91 after exposure to Bi*

Two BSE images of T91* are shown in Fig. 3 after corrosion testing in Bi. It is obvious that two types of corrosion attack have occurred: liquid metal embrittlement (responsible for the crack) and liquid metal corrosion (formation of a diffusion layer between steel surface and bismuth consisting of steel elements and Bi); additionally no oxide layer can be detected on the steel surface. Bi was not found in the steel matrix by EDX analysis. In contrast to this Fe and Cr was analysed in Bi: the ratio Fe/Cr near the crack tip is about 3.2, in the middle of the crack about 2.5 and on the steel surface there are still steel elements measurable. The higher solubility of the steel element Cr compared to Fe in liquid Bismuth is responsible for the larger amount of Cr compared to the ratio in the steel (Fe/Cr = 10). The diffusion layer consists mainly of Bi including the steel elements Fe and Cr with a ratio of about 13. The reason for the higher iron content in this layer could be brought up by dissolution of the oxide layer of the steel surface because the oxide is mainly formed of Fe_3O_4 and $FeCr_2O_4$ i.e. the iron content on the steel surface is higher than in the bulk if there is an oxide layer present.

3.2.3. Inspection of T91 after exposure to Pb–17Li*

The oxygen solubility in Pb–17Li is very low [20] and one can say that the experiment was performed under reducing conditions. This assumption is in agreement with the inspection of the T91* surface by means of EDX using 10 and 20 KeV accelerator energy where no oxide layer was present after exposure. The absence of the oxide film could also be the reason for LME. Analyses performed on the solidified Pb–17Li in the crack showed the steel elements Fe and Cr in a ratio of 7.5. Near the crack tip in the steel matrix, a tiny amount of lead was detected. A diffusion layer as it was observed on the T91* with Bismuth could not be detected neither on the bent nor on the straight part of the steel specimen.

4. Discussion and conclusions

T91 U-bend specimens which were heat treated under standard conditions and exposed to LBE, Bi and Pb–17Li respectively at 300 °C for 1000 h did not show any LME neither in the straight nor in the bent part. There is no corrosion attack on these specimens visible. Exposure time is too short and/or temperature is not high enough for initiating this kind of process on T91 in standard state under the given conditions.

T91* exposed to LBE shows a protective oxide layer on the steel surface all over the probe. This seems to be the reason that no corrosion attack or LME took place on this steel sheet. The presence of an oxide layer on T91* staying in contact with LBE seems to be sufficient to protect the steel of LME. This possible influence of an oxide film on the steel surfaces to the inhibition of LME was lately discussed [14,15]. Anyway, the dissolution of the oxide film started already indicated by lead and bismuth diffusion into the layer. It is only a question of time, when LME will happen on T91* exposed to LME.

T91* U-bend specimens immersed into Pb–17Li and Bi showed the following results: Corrosion attack on the straight part of the T91* U-bend specimens and LME on the bent part is visible due to the absence of any protecting oxide layer on top of the steel surface. The stress in the U-bend specimen is not uniform because there is a stress gradient through the thickness varying from a maximum tension on the outer surface to a maximum compression on the inner surface, the stress varies from zero at the ends of the specimen to a maximum at the centre of the bend, and the stress may vary across the width of the bend. Hence LME is expected to happen at the centre of the bend or near by which was observed in our experiments.

The precise analysis of T91* (tempering at 500 °C instead of 750 °C for 1 h) does not induce any modification in prior austenite grain size, the transformation concerns only the nature and the distribution of the precipitates. It is believed to be associated with critical carbide morphology present when Fe_3C is firstly formed. It may be caused by film-like carbides precipitated on grain boundaries and subboundaries [10,20]. This phenomenon is called 'embrittlement during tempering' which results in an increase of the steel hardness. It seems that the precipitates have sensitised the steel for liquid metal embrittlement which is absolutely thinkable because the cracks formed by LME are often inter granular. Further analysis with TEM is foreseen to gain more information on the nature of the precipitates formed. In the case of T91* specimen exposed to Bi and Pb–17Li the oxide scale on top of the steel surfaces was already dissolved and thus LME could occur. In the case of T91* exposed to LBE, an oxide layer is still present this protected the steel for LME. We believe that the oxide scale is dissolved by time and LME is expected to be happen as well.

The following list summarises the treatments/conditions that seem to have an effect on the interaction of steel T91 and liquid metal/alloy:

- the temperature used for tempering T91 after quench hardening;
- the status of the surface of the steel (i.e. presence of oxide layer);
- the impact of stress influences the interaction of T91 steel with the liquid melt/alloy.

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