Influence of Zn as a spallation product on the behaviour of martensitic steel T91 and austenitic steel 316L in liquid Pb–Bi

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Abstract

The liquid Pb–Bi alloy is proposed as material for the spallation target in hybrid systems. During the spallation process, several chemical elements are produced in the target which could generate specific liquid metal embrittlement phenomena. Among these species, zinc is known as an element which can promote LME (liquid metal embrittlement). Corrosion tests were carried out in liquid Pb–Bi in isothermal static conditions without and with 80 wppm of zinc at 150 °C, 350 °C and 600 °C up to 6000 h. No modification of the corrosion kinetics of T91 martensitic and 316L austenitic steels was observed for either unstressed or U-bend specimens with zinc in Pb–Bi. Moreover, no sign of embrittlement was observed for any of the samples with and without zinc.
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1. Introduction

Liquid eutectic lead–bismuth alloy (Pb–Bi) is considered as a candidate material for the spallation target dedicated to produce the neutrons for the transmutation of long-lived nuclear wastes. During operation, the spallation reactions in Pb–Bi due to the proton impingement will lead to the formation of many elements (all the elements with an atomic number lower than those of the target atoms). The concentrations of these generated elements depend on the target running conditions.

From calculations, mercury and thallium are expected to be among the main spallation products but although zinc should be produced at a very low concentration, it is known to be a weakening element. As no data exist on the behaviour of steels in contact with liquid Pb–Bi alloy with traces of such elements, tests have been performed to characterise the behaviour of 316L and T91 steels as unstressed and U-bend specimens in contact with isothermal static liquid Pb–Bi containing some traces of Zn. The results are reported and discussed hereafter.

2. Experimental

The experimental conditions of the tests are given in Table 1.

The tests have been carried out in COLIMESTA device which allows to immerse some specimens in pots containing about 7l of Pb–Bi under a controlled atmosphere in a glove box. Oxygen concentration in Pb–Bi was continuously recorded by means of an oxygen sensor. The mean oxygen concentration throughout the test was around 10^{-14} wt% in the presence of zinc.

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Table 1
Immersion conditions of the 316L and T91 steel specimens in static isothermal liquid Pb–Bi

Temperature (°C)	Specimen	Maximum deformation	Zn content wt ppm	C_{O_2} in Pb–Bi wt%	Duration (h)	Materials
150	Unstressed and bent after test	0% and after test 12.5%[a]	80	$\approx 10^{-14}$	3000	316L, T91
	U-bend	12.5%[a]	80	$\approx 10^{-14}$	3000	316L, T91
			0	$\approx 7 \times 10^{-8}$	6000	316L, T91
350	Unstressed	0%	80	$\approx 10^{-14}$	3000	
	U-bend	12.5%[a]	0	$\approx 7 \times 10^{-8}$		316L, T91
			80	$\approx 10^{-14}$	3000	
	U-bend	33%[b]	0	$\approx 8 \times 10^{-10}$	3000	316L
			80	$\approx 10^{-14}$		
600	Unstressed and bent after test	0% and after test 12.5%[a]	0	$\approx 8 \times 10^{-10}$	3000	316L, T91
	U-bend	12.5%[a]	0	$\approx 8 \times 10^{-10}$	3000	316L, T91

[a] 12.5% of deformation corresponds to 25% of UTS for 316L and 62.5% for T91.
[b] 33% of deformation corresponds to 66% of UTS for 316L.

The specimens, fixed at a holder, were introduced in the liquid Pb–Bi without and with approximately 80–100 wppm of Zn under the glove box purified argon atmosphere. Before insertion of zinc, the Pb–Bi eutectic was mechanically cleaned at low temperature (around 180 °C) to remove the oxides present in the liquid alloy. Zinc was then added under the form of metallic needles (Prolabo Rectapur) at low temperature and the liquid alloy was again mechanically cleaned. Then, the temperature was increased up to the testing temperature under a static Ar + 5%H₂ gas mixture. When the tests were completed, the pots were opened, the specimens removed from the bath and cooled in the glove box.

Concerning the zinc solubility limit, no data have been found in Pb–Bi. Therefore we considered the data obtained in pure lead [1]. At 350 °C, the zinc solubility limit in pure lead is: $C_{Zn} = 10750$ wppm [1] (which is well above the concentration during the experiments). At 150 °C, no data are available as the lead melting point is 327 °C.

Two materials, 316L austenitic and T91 martensitic steels were tested as plates or U-bend specimens. The T91 martensitic steel was supplied by Creusot Loire Industrie as a plate of 30 mm thickness with an austenitization treatment at 1050 °C followed by an air cooling and a tempering treatment at 770 °C for 40 min followed by an air cooling. The 316L austenitic stainless steel was supplied by COGNE France as a rod of 10 mm diameter. Some of the specimens were tested in their as-received surface state and some other were preliminary electropolished. Some of the plates were stressed as U-bend after test.

After the tests, the residual Pb–Bi adhering to the specimen surface was removed by either immersion in a chemical mixture constituted of 1/3 ethanol, 1/3 acetic acid and 1/3 hydrogen peroxide or by immersion in a glycerine bath at 180 °C. Microscopic observations and analyses of the specimen surface and cross-sections were performed. Chemical analyses of the liquid Pb–Bi were performed before and after the tests by ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectrocopy) to determine the zinc concentration. The Pb–Bi samples were taken at the testing temperature.

3. Results

3.1. 316L steel

After 3000 h of exposure at 150 °C in Pb–Bi with zinc as well as at 350 °C in Pb–Bi without and with zinc, the 316L austenitic steel specimens, plates and U-bend, did not show any corrosion. No weight variation was measured and the specimen surfaces had the same roughness (Ra = 0.55 μm) than the reference one. The steel/Pb–Bi interface observed by optical microscopy after immersion confirmed this behaviour and the X-ray images did not indicate any modification of the distribution of the steel elements. At these temperatures, the results which were obtained agreed with those previously obtained [2]: even for such a low oxygen concentration (which is below the oxygen concentration required to form the most stable of the iron oxides which is magnetite at this temperature, Fe₃O₄), the native oxide layer which is partly made of chromium oxide and spinel is stable at these temperatures. It is a protection against corrosion by dissolution in the tested conditions. At 350 °C, the dissolution rate of the 316L steel is too low to evidence some variations due to the presence of zinc. However, the presence of zinc, even in small quantities,

induces a decrease of the oxygen content in Pb–Bi (10^{-14} wt% compared to 10^{-8} wt%) which could modify, at higher temperatures the corrosion processes, the oxide layer becoming no longer stable.

After immersion at 600 °C in Pb–Bi without zinc, the surface of the 316L austenitic steel specimens (plates and U-bend) exhibited an about 200–220 μm thick regular superficial corrosion layer (Fig. 1). SEM and microprobe analyses showed that it is composed of two parts. The about 50–80 μm thick external part is porous and shows an irregular external surface (in this part the microprobe analysis cannot lead to 100% due to the high porosity of the layer). It mainly consists of Fe and is almost completely depleted in Mn (0.1 wt%), Ni (0.2 wt%) and severely depleted in Cr (8 wt%). The pores of this external ferritic layer were filled with Pb–Bi. The about 140 μm thick internal layer mainly consists of Fe. It is almost completely depleted in Mn (0.1 wt%), severely depleted in Ni (1.5 wt%) and slightly depleted in Cr (10 wt%). Such a ferritic layer was already observed, even at lower temperatures [2,3]. Moreover, at 600 °C, even for higher oxygen concentrations (10^{-6} wt%), the 316L steel suffered significant damages in Pb–Bi and could not be used for long durations [2].

Finally, in all the tested conditions and even in the most stressed part of the U-bend specimens, no cracks were observed at the surface of the specimens. Some cracks were only observed in the corrosion layer of the plates put in U-bend shape after test at 600 °C in the tension zone of the U-bend. Thus, these results show no LME with and without zinc.

3.2. T91 steel

After 3000 h of exposure at 150 °C in Pb–Bi with zinc, the T91 steel specimens, plates and U-bend, did not show neither corrosion nor cracks. No weight variation was measured.

After 3000 h of exposure at 350 °C in Pb–Bi with and without zinc, all the specimens exhibited the same behaviour. They all suffered an homogeneous dissolution with no formation of a corrosion layer (as it was observed for 316L specimens) and no intergranular attack (Fig. 2). However, it was not possible to measure the weight variation of the U-bend specimens after tests because it was not possible to remove completely the solidified Pb–Bi between the bolt and the nut of these specimens. On the other hand, for plates, small weight losses were measured and assuming a linear dissolution kinetics, we obtained a very low mean dissolution rate (0.1–0.2 μm year^{-1}). The observations of all U-bend specimens in their most stressed part did not show any crack. Analyses indicated that no preferential dissolution occurred. Moreover, no intergranular attack was observed.
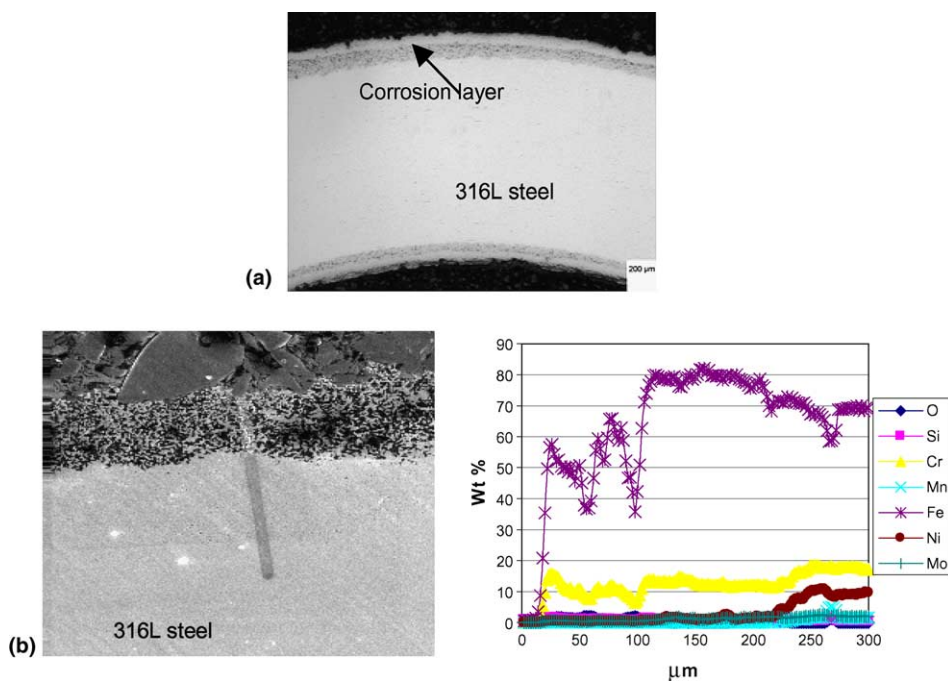

Fig. 1. 316L austenitic steel U-bend after 3000 h immersion at 600 °C in static isothermal liquid Pb–Bi without Zn: (a) SE cross-section micrograph and (b) SE cross-section micrograph with the associated concentration profiles.
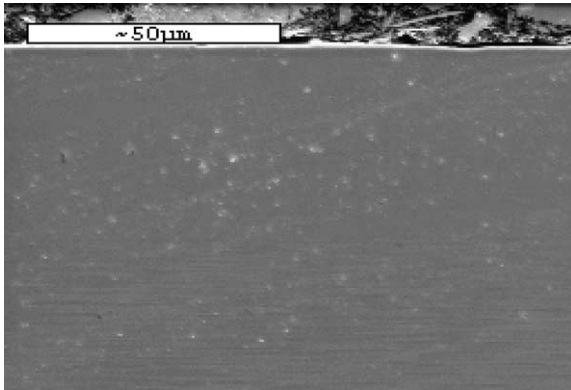
Fig. 2. Cross-section of T91 martensitic steel U-bend (in its most stressed part) after 3000h immersion at 350 °C in static isothermal liquid Pb–Bi with 80wppm of Zn.

All the T91 martensitic steel specimens after contact at 600 °C with static isothermal liquid eutectic Pb–Bi without zinc showed a non-uniform corrosion (Fig. 3). The difference of depth between a corroded and a non-corroded zone reached 150–200 μm. In the corroded zones, a superficial porous 20–50 μm thick layer was observed. The morphology of the steel-layer interface suggested that the corrosion proceeded by both intergranular and transganular dissolution as it was already observed elsewhere [4]. The thick porous layer could be due to a local Pb–Bi saturation in Fe due to the fact

that the liquid Pb–Bi was stagnant. Microprobe analysis showed that it mainly consisted in Fe and Cr and that it was severely depleted in Mn (0.1wt%). Moreover, the zones without visible attack were also depleted in Mn up to 20 μm depth. According to thermodynamics, at 600 °C and for an oxygen concentration of 8×10^{-10} wt%, no iron oxide is stable and dissolution of the T91 steel is expected as it was previously observed at lower temperatures [4]. However, chromium oxide as well as Fe–Cr spinel which are part of the native oxide layer on such a steel are stable in the tested conditions and it could explain that some parts of the specimen were corrosion free. An oxide layer on T91 steel specimens was already observed at the same temperature and in nearly the same experimental conditions [2].

Moreover, in all the tested conditions and even in the most stressed part of the specimens, no cracks have been observed at the surface of the specimens.

Liquid metal embrittlement (LME) may be defined as the brittle fracture, or loss in ductility, of a usually ductile material in presence of liquid metal. Abundant experimental and theoretical literature exists on LME model systems [5–11]. However, few data exists on the embrittlement of Fe–9Cr martensitic steels by LBE. Recently, Nicaise et al. [12] studied the behaviour of T91 martensitic steel specimens in the temperature range 350–500 °C in both air and liquid lead in order to evaluate the LME sensitivity of the couple steel/lead. The T91 martensitic steel was submitted to heat treatments in order to modify the precipitation state and therefore
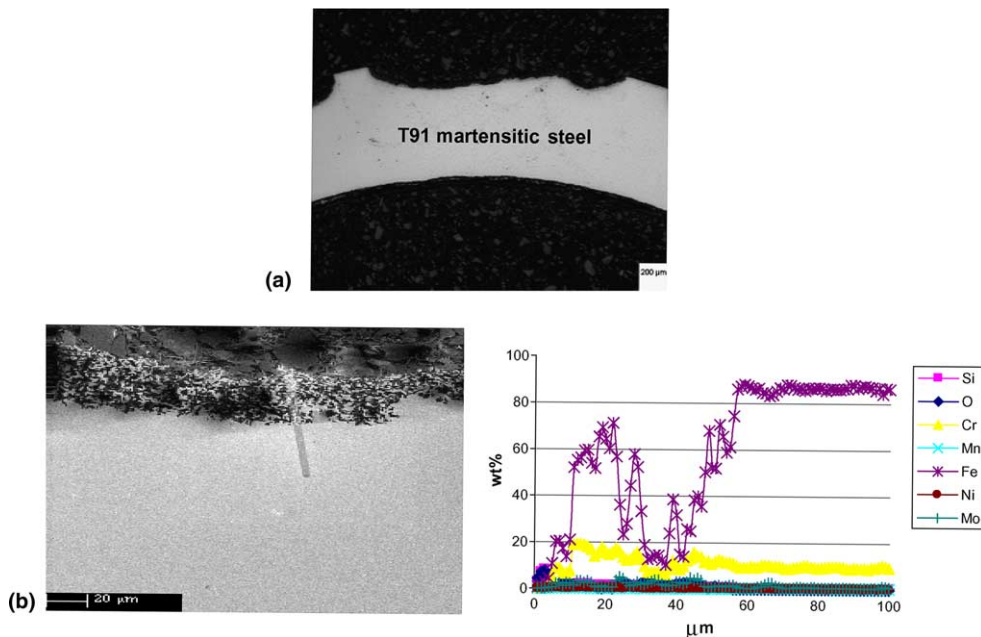

Fig. 3. T91 martensitic steel U-bend after 3000h immersion at 600 °C in static isothermal liquid Pb–Bi without Zn: (a) SE cross-section micrograph and (b) SE cross-section micrograph with the associated concentration profiles.

its hardness and also to produce either ferritic or martensitic grains. During all these tests, the liquid metal was in contact with the ambient atmosphere and no particular care was taken to control the oxygen activity. They found out that by combining adapted heat treatments and the notch effect, it was possible to create conditions leading to LME. For initial T91 martensitic steel (UTS ≈ 700 MPa), no embrittlement was observed in air and liquid lead saturated in oxygen, but for prenotched specimens an embrittlement by liquid lead was observed. The same behaviour was obtained in Pb–Bi at 260 °C [13] and was interpreted with a model based on the surface energy reduction by liquid metal adsorption. Ab initio atomic scale simulations combined to a thermodynamic model allowed to establish a theoretical embrittlement scale corresponding to the experimental results [13]. Other significant results were obtained by performing tensile tests on T91 or MANET II specimens in Pb–Bi which showed a loss of ductility at temperatures between 250 °C and 350 °C in comparison to samples tested in gaseous atmospheres [14,15].

The effect of added elements to lead was mainly studied with low alloyed steels with high and low percentages of carbon. For high mechanical resistance steels, it was reported that additions of zinc (10^{-6} to 10^{-1}%), antimony (4×10^{-3} to 2%) and tin (10^{-1} to 9%) increased the intensity of the embrittlement [16–18]. For lower resistance steels, an embrittlement was highlighted when zinc (0.9% and 2%), antimony (13% and 20%) or copper (1%) were added [19]. It can be noticed that concentrations for which the embrittlement occurs were much higher in the case of the low mechanical resistance steels.

4. Conclusion

To assess the effect of spallation products in the liquid eutectic Pb–Bi on materials, corrosion tests of unstressed and stressed specimens have been carried out in pure liquid Pb–Bi and Pb–Bi with 80 wppm of Zn additive. Tests were carried out at 150 °C, 350 °C, 600 °C. The 316L and T91 steel specimens were tested as plates and U-bend specimens.

The observations of the U-bend specimens surface in their most stressed part without and with Zn spallation product did not show any cracks. The observations of the unstressed specimens showed that 80 wppm of Zn did not influence the corrosion mechanisms and did not promote liquid metal embrittlement.

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