Corrosion behavior of steels in flowing lead–bismuth under abnormal conditions

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Abstract

The project IP EUROTRANS, domain DEMETRA, is primary focused on the study of the technology of the interaction between steels and heavy liquid metals. The characterization of the metal response to sudden changes, simulating accidental conditions in liquid lead–bismuth eutectic was carried out. This paper reports the results of two hot-spot simulations with two different oxygen concentrations (10^{-8} wt%, 10^{-6} wt%). Each experiment was divided in two main periods: the initial, long period at the standard operating temperature 550 °C; the second, short period, at higher temperature, 650 °C. The damage that occurs on the austenitic steel AISI 316L and the ferritic–martensitic steel T91 was investigated. The amount of damage for both steels was higher at lower oxygen contents and the short, hot spot simulation, markedly affected the T91. At higher oxygen content the amount of damage decreased. A few, localized pits, were observed; however, there was no visible increment in the amount of damage after the hot spot simulation.
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1. Introduction

Liquid lead alloys have been evaluated as spallation targets and coolants of accelerated driven system (ADS) on the account of their optimal chemical, thermodynamic, physical and neutron properties. The material compatibility in lead–bismuth eutectic (LBE) is one of the issues in the research and development of liquid metal technologies. Structural materials in contact with heavy liquid metals (HLM) undergo damage due to nickel dissolution and/or liquid metal penetration. The austenitic steel AISI 316L and the ferritic–martensitic steel T91 are the selected structural materials for ADS for transmutation of nuclear waste [1]. These materials can undergo damages in this environment, especially at high temperatures and low oxygen content, when the system is not able to develop and maintain a protective oxide scale on the surface of the metals [2,3].

The aim of this study is a preliminary evaluation of the corrosion resistance of structural materials in contact with LBE when sudden changes (simulating accidental condi-

tions) are imposed. Two main variables have been considered, such as the sudden increase of temperature, hot-spot simulation, and two different oxygen contents.

2. Experimental

2.1. Materials and specimens preparation

The composition of both steels, austenitic AISI 316L and ferritic–matensitic steel T91, is listed in Table 1. The AISI 316L was solution annealed at 1050–1100 °C. The T91 was subjected to normalisation and tempering heat treatment: the normalisation at 1050 °C, 1 mm per minute, followed by water-cooling; the tempering at 770 °C for 45 min and then air cooling. The materials were cut and a set of thin plates (1 × 12 × 30 mm) was machined.

The specimens were exposed in two different surface conditions, ground and passivated. Half of the specimens were selected for pre-oxidation and passivated for 50 h at 400 °C for austenitic steel AISI 316L and at 300 °C for martensitic steel T91 in a gaseous mixture of steam containing 5% of H_2. The aim of the passivation was the development of a layer of magnetite, to act as an initial physical

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Table 1
Composition of steels

Elements (wt%)	Fe	C	N	P	S	Cr	Ni	Mo	Mn	Si	V	Cu	Nb	Al	W	Ti
AISI 316L	Bal.	0.02	0.03	0.03	0.0035	16.9	10.2	2.1	1.8	0.6	–	0.23	–	0.02	0.02	0.006
T91	Bal.	0.1	0.04	0.02	0.0004	8.9	0.1	0.9	0.4	0.2	0.2	0.06	0.06	0.01	0.01	0.003

barrier and prevent leaching of alloying elements (such as nickel) or any generalised corrosion.

2.2. Testing conditions

Two different hot-spot simulations were carried out in the loop COLONRI I [4,5], in LBE. COLONRI I is the convectional loop with flow velocity 1–2 cm/s. This type of loops allows dosing of the inlet $H_2O + H_2$ mixture, in any ratio, both above and below (bubbling through) the level of the liquid metal in the upper equalising tank. The oxygen content is monitored by oxygen sensors placed in three key points of the loop. These sensors are based on the Bi/Bi_2O_3 reference electrode.

The main parameter differentiating these experiments was the oxygen content. However, the general procedure (temperature and exposure times) was identical for both experiments. In fact, each experiment was divided in two main periods: the initial, long period (1000 h) (named PHASE 1) at the standard operating conditions (details in Table 2); at the end of this first phase, one part of the specimens was removed from the loop and a new set of specimens were introduced; then, the experimental conditions were changed for a second, short period of about 6 h (named PHASE 2). At the end of each experiment three sets of specimens were produced: *group 1* were specimens after 1000 h in the operating conditions, *group 2* were specimens after 1006 h in the operating condition and hot spot period, *group 3* were specimens exposed only for 6 h to the hot spot conditions. Furthermore, in all the 3 groups, the specimens were sub-divided as a function of their initial surface state, as only ground (*group 1g, group 2g, group 3g*) and passivated specimens (*group 1p, group 2p, group 3p*). Each group contains four specimens – three for gravimetric evaluation and one for metallographic evaluation.

2.3. Post-exposure examination

The measurement of metal loss by gravimetric method was used to quantify the metal loss of each material. Each

specimen was weighed before and after exposure to LBE, following the removal of residual LM deposits with a fresh solution of CH_3COOH: H_2O_2: $C_2H_5OH = 1:1:1$. The weight difference, in grams, was converted into linear thickness loss, in metres, for comparison purpose.

The specimens prepared for metallographic examination were cut in two parts: one half was cleaned in the above-mentioned solution and in the other half the deposit was left on the specimen. Both half of the same specimen were embedded in resin and polished to 1 μm finish for metallographic examination. The embedded specimens were used for the observation of the damaged areas with the light and scanning electron microscope (SEM).

3. Results and discussion

Two experiments were carried out in order to simulate a sudden increase of temperature (from 550 °C to 650 °C), in different conditions of oxygen content, with the aim of quantifying the effect of accidental conditions on the rate of metal loss for steels in contact with liquid LBE. Moreover, the effect of surface conditions was considered, in terms of comparison between ground and pre-oxidised surfaces.

3.1. AISI 316L

The main results of the weight loss measurements were summarized in Fig. 1 for the both hot-spot simulations. The main difference between specimens with ground surfaces after the phase 1 and phase 1 + 2 was an increase in metal loss. The specimens from *group 3*, in the ground conditions, showed clear signs of initiation of damage. For the specimens with passivated surface the weight losses were lower. Moreover, the exposure of the passivated specimens for 6 h to the higher temperature was not sufficient to initiate any measurable damage to the specimens.

From the metallographic study in the light microscope, it was observed that the specimens of AISI 316L with both surface finish underwent abundant metal loss, with large

Table 2
Test parameters

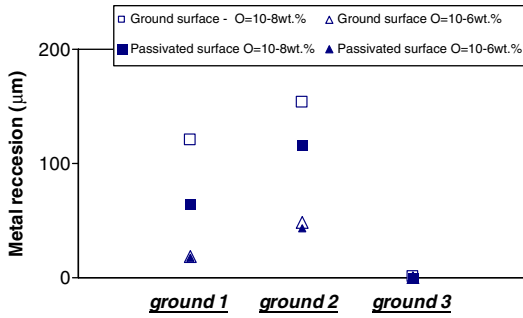|	Hot-spot simulation 1				Hot-spot simulation 2			
Liquid medium		LBE				LBE		
	Phase 1		Phase 2		Phase 1		Phase 2	
$T_{test\ section}$ (°C)	550 ± 1 °C		650 ± 1 °C		550 ± 1 °C		650 ± 1 °C	
Duration (h)	1000		6		1000		6	
Velocity (cm/s)		1–2				1–2		
Ratio H_2/H_2O		1:0.36				1:11		
Oxygen (wt%)	3×10^{-8}		1.4×10^{-7}		1×10^{-6}		4.3×10^{-6}	

Fig. 1. Comparison of the metal recession of AISI 316L, with two different surfaces finish (ground, passivated), after the hot-spot simulations (O = 10^{-8} wt% and 10^{-6} wt%).

and extensive damage, homogeneously distributed along all the surfaces. A more detailed examination of the specimens with the SEM (Fig. 2) revealed that the damaged areas were characterised by an outer deposit of LBE and an interface, between deposit and substrate where the liquid metal penetrated into the surface and subsequently removed parts of the steel (Fig. 2(a)). Penetration depths up to about 50 μm were observed in the areas where the damage started, but no removal of material occurred (Fig. 2(b)). In this initial stage of the interaction between the steel and the liquid metal penetration of LBE occurred, together with the simultaneous outwards diffusion of nickel and chromium. In fact, qualitative line scans (Fig. 2) revealed that these areas (where the liquid metal penetrated) are completely depleted of Ni and Cr. In particular, where widespread damage was observed (Fig. 2(a)), the area where the liquid metal penetrated contained only iron and negligible amounts of minor alloying elements. On the other side, in areas where only the penetration of liquid metal into the specimen was observed (Fig. 2(b)), a double-layer structure was observed. The line scans revealed
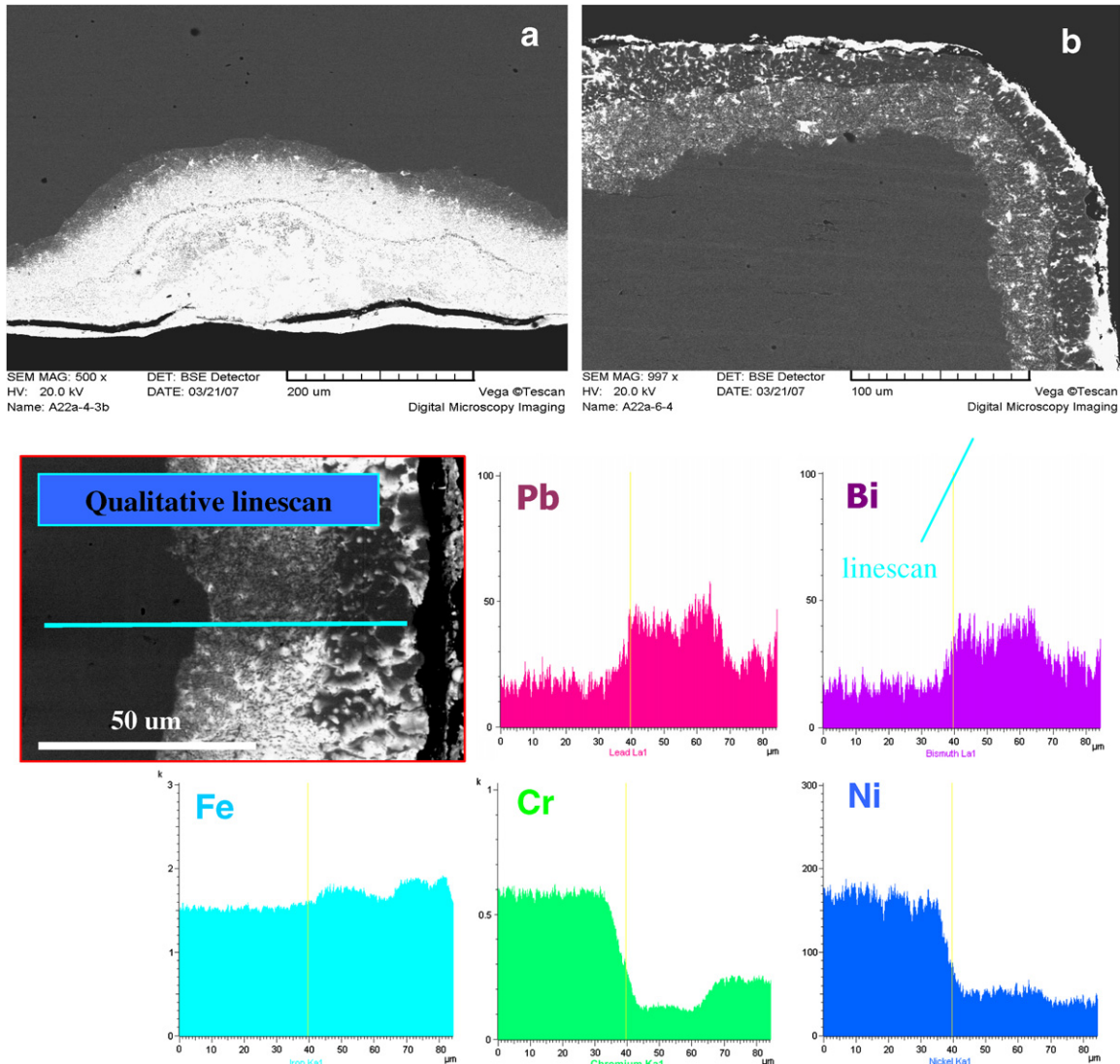

Fig. 2. SEM micrographs of AISI 316L steel, pre-passivated surface, exposure time 1000 h, $T = 550$ °C, O = 10^{-8} wt%, (a) damaged area, (b) lateral side of damaged area and its linescan.

that from the bulk metal to the intermediate layer, depletion of Ni and Cr occurred. However, in the outer layer only the Ni was missing and the Cr was found to be present in combination with Fe.

The weight measurements and the following calculation of metal recession in the second hot-spot simulation with higher oxygen content indicated that with increasing exposure time and temperature (hot spot condition), the corrosion rate calculated by metal recession significantly increased for both surface finishes with respect to temperature and exposure time. However, the metal losses, with higher oxygen content, are much lower than in the experiments with low oxygen content. Moreover, the specimens exposed only in the hot spot conditions did not show any visible damage.

3.2. T91

Fig. 3 summarises the results of the weight loss measured for T91 after the both hot-spot simulations. The main difference between the specimens with ground surfaces, after the 1000 h and 1006 h exposure, is a general increase in corrosion rate due to the hot spot conditions.
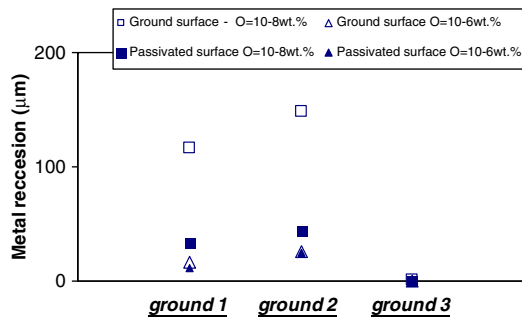

Fig. 3. Comparison of the metal recession of T91 steel with two different surface finishes (ground, passivated) after the hot-spot simulations ($O = 10^{-8}$ wt% and 10^{-6} wt%).

For the specimens with passivated surface the metal recessions were markedly lower. Moreover, the exposure of specimens for 6 h to the higher temperature was not sufficient to initiate any measurable weight difference. The specimens of the steel T91 had a different behaviour, in fact, the influence of the surface finish was more evident in the amount of damage, as well as the effect of the hot spot simulation. However, in general, the amount of damage was markedly higher than for the AISI 316L steel.

A more detailed observation of the specimen that was first passivated and then exposed during the 1000 h was carried out with the SEM. Surface where no removal of material was observed (Fig. 4(a)) had residual, disrupted oxides. However, in the damaged surfaces (Fig. 4(b)) the LBE was observed to penetrate through grain boundaries and the removal of small particles of material can be observed in the residual LBE deposit on the damaged surface.

The weight measurements and the following calculation of metal recession for the T91 in the second hot-spot simulation, with higher oxygen content, indicated that with increasing exposure time and temperature, the corrosion rate significantly increased for both surface finishes. However, in general, metal recessions with higher oxygen content were much lower. Moreover, the specimens exposed only in the hot spot conditions did not show any visible damage.

The detailed examination of the unaffected areas with the SEM (Fig. 5(a)) revealed that on the surface of the specimen passivated and then exposed for 1000 h, there was a very thin oxide scale (about 2 μm). The qualitative analyses of this layer revealed that there was enrichment of O, Si and Cr, with an outer layer enriched in Mo and Ti. Furthermore, it was observed that where there was the onset of damage (central part of Fig. 5(a)) a residual, thin oxide layer was still visible at the level of the original surface. Analyses of this layer revealed that it was a spinel type oxide, with Fe and Cr. However, even in areas with
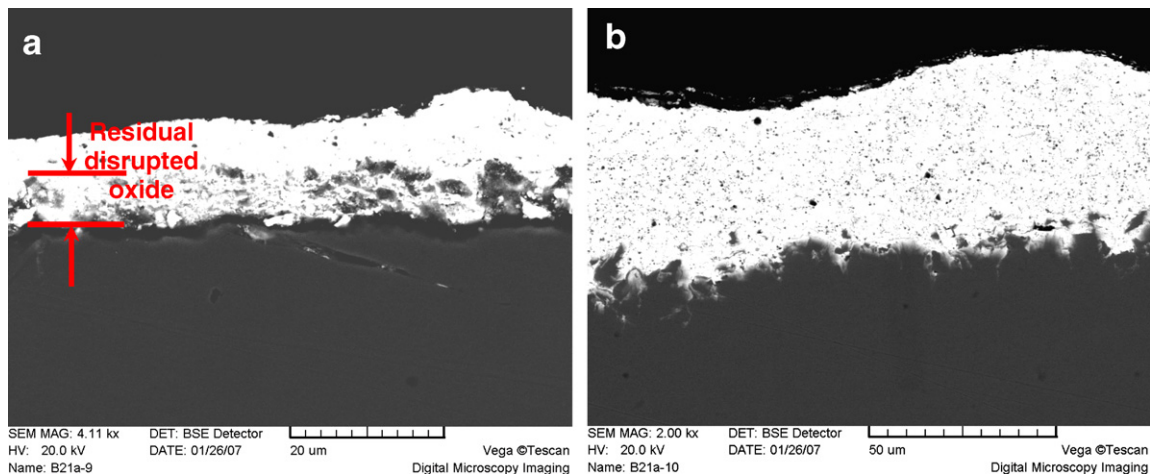

Fig. 4. Steel T91 after exposure for 1000 h, at 550 °C with $O = 10^{-8}$ wt%. Details of (a) the surface without damage, with residual, disrupted oxides and (b) the damaged surface with LBE penetrates through grain boundaries, in addition to the residual deposit rich in particles of removed metal.
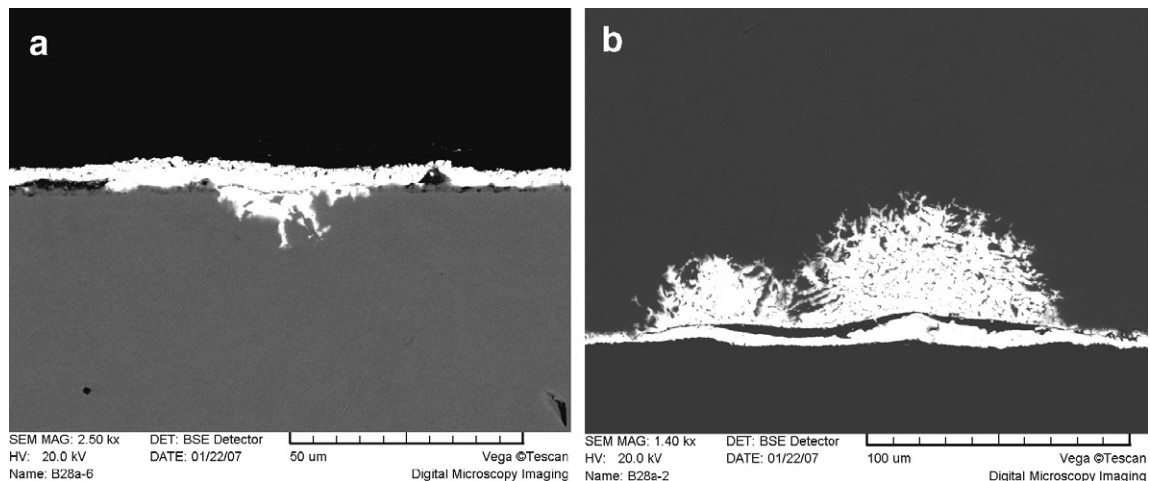
Fig. 5. Steel T91 after exposure for 1000 h, at 550 °C with O = 10^{-6} wt%. Details of (a) the unaffected surface and with the onset of damage and (b) the damaged surface where the LBE penetrates through grain boundaries, in addition to the residual deposit and initial oxide scale.

more extended damages (Fig. 5(b)) the thin layer was observed to 'float' on the more abundant liquid metal inside the pit. Profile analyses on the damaged areas revealed that on the surface of the corrosion front (interface damaged specimen/LBE deposit) there was enrichment of O and Si. While the metal particles detached from the bulk specimen, were identified as Fe and O rich.

The specimens exposed for 1000 h + 6 h in the hot spot conditions, showed the same characteristics. Residual oxide layers were observed to remain on the surface of the damaged zones and elemental analyses confirmed the same compositions.

The general trend observed was that the 'hot spot' simulations had a strong effect in specimens that were in the optimal oxidising conditions (experiment 2, O = 10^{-6} wt%), and although they had moderate corrosion rates in the 'standard' conditions, they were very sensitive to the increase of temperature. Moreover, the passivation, previous to the exposure to LBE, was markedly beneficial to the T91, by delaying the onset of damage, in the experiment 1 (O = 10^{-8} wt%).

Passivation of the steels, previous to the exposure to the LBE, was aimed to grow an initial protective oxide scale (such as Fe_3O_4) to prevent the penetration of the HLM in the steel or leaching of Ni. However, it was observed that the oxide can delay the onset of damage but not completely prevent it. The two materials had a different response to this pre-treatment because the oxide on the T91 had longer resistance to damage.

4. Conclusion

- The amount of damage with low oxygen content was higher (10 times) than the damage measured with the high oxygen content for the materials in both surface finish.

- The effect of the hot-spot simulation in the low oxygen environment did not affect markedly the amount of damage in the specimens.
- Hot-spot simulations had a stronger effect for specimens under the high oxidizing conditions (10^{-6} wt%), hot-spot simulation markedly increase the metal loss for both materials.
- For AISI 316L steel characteristics of damage were typical Ni and Cr depletion at the surface layer, LBE penetration and loss of bulk materials were observed.
- For T91 LBE penetration along the grain boundaries and other preferential paths (such as martensitic laths) was observed.
- The specimens with ground surfaces had corrosion rates comparable for both materials under the both experimental conditions.
- The T91 steel with passivated surfaces showed higher corrosion resistance under the both oxygen content.

Acknowledgement

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