Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 335 (2004) 185–188

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Corrosion behaviour of steels in lead–bismuth at 823 K

F. Gnecco, E. Ricci *, C. Bottino, A. Passerone

National Research Council, Institute for Energetics and Interphases, Department of Genoa, Via de Marini, 6, 16145 Genoa, Italy

Abstract

The corrosion behaviour of the martensitic T91 steel and the austenitic AISI 316L steel was analysed. The steels were immersed in stagnant molten Pb–55.2wt%Bi alloy at 823 K for different exposure times ($t = 550$–2000 h). The corrosion tests were carried out both under Ar and under Ar–5%H_2 mixture. Under the oxidising conditions ($P_{O_2} = 6 \times 10^{-3}$ Pa), the formation of oxide layers was observed which prevent the penetration of the liquid alloy into the matrix, while under the Ar–5%H_2 mixture ($P_{O_2} = 3.2 \times 10^{-23}$ Pa), two phenomena occurred: a ‘reactive penetration’ at the liquid alloy/steel interface and the competition between oxidation and penetration.

1. Introduction

Lead and lead–bismuth eutectic alloy (LBE) have been proposed as target and coolant material in the accelerator driven system (ADS) [1], due to their physico-chemical properties such as high atomic number, low melting points, low vapour pressure. In spite of these features, liquid lead and its alloys could give rise to corrosion related problems. The selection of appropriate structural materials to be exposed to liquid Pb–Bi alloys is a crucial point in the ADS design and compatibility studies are required. It is known that severe corrosion occurs when steels are in contact with liquid lead or its alloys [2,3]. For this reason the behaviour of different martensitic and austenitic steels has already been compared when exposed both to flowing and stagnant LBE alloy [4,5]. Two basic approach can be used to solve the corrosion phenomena: (a) to choose physico-chemical conditions in which the steel surface is inert; (b) to protect the steel surface by coating or alloying it [5] or by an ‘in situ passive oxidation’ [6,7]. However, as the phenomena affecting the interactions between a liquid metallic material and a solid substrate depend strongly on the particular system and on the operating conditions, specific investigations have to be performed, helping the compatibility behaviour between the materials to be understood. Among them, the wetting experiments represent a preliminary study with particular emphasis on a complete characterisation of the Pb–Bi liquid phase in terms of thermodynamics [8] and surface properties [9]. Moreover, phenomena such as liquid metal embrittlement and penetration of liquid metals along the grain boundaries have also to be taken into account [10,11]. In this work the behaviour of the T91 martensitic steel and the AISI 316L austenitic steel at two different oxygen contents has been analysed. The steel samples were immersed in stagnant molten LBE alloy at 823 K for different exposure times (550, 1000 and 2000 h). The oxygen content was imposed by using different atmospheres: high purity Ar and the Ar–5%H_2 mixture. In the first case the complete saturation of the system was attained in order to compare the results on the oxides formation with those obtained under the

---

[*] Corresponding author. Tel.: +39 010 6475 720; fax: +39 010 6475 700.

E-mail address: e.ricci@ge.ieni.cnr.it (E. Ricci).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.07.013

same conditions in flowing LBE; the second one provided a very low oxygen content in the system in order to obtain a deoxidised steels surfaces with the aim to provide an actual contact between the liquid metal and the substrates [12].

2. Experimental

The corrosion-device consists of a stainless steel vacuum chamber which contains two alumina crucibles ($\phi_{\text{ext}} = 20$ mm, $h = 30$ mm), each of them heated by a Thermocoax® resistance. The temperature was monitored by a K-thermocouple regulated by a digital controller. ENEA-RC Brasimone (IT) supplied the LBE alloy with composition close to the eutectic one (Pb–55.2wt%Bi) [4]. Samples of the T91 steel (composition in wt%: 8.26Cr; 0.13Ni; 0.95Mo; 0.38Mn; 0.20V; 0.075Nb; 0.43Si; 0.105C) and the AISI 316L steel (composition in wt%: 17.3Cr; 12.1Ni; 2.31Mo; 1.8Mn; 0.35Si; 0.02C), sized 20 × 6 × 3 mm were prepared for the corrosion tests by metallographic polishing with SiC paper (up to grit 1200). The LBE alloy was pre-melted under vacuum ($P_{\text{tot}} = 10^{-1}$ Pa) at $T = 723$ K. The steel samples were immersed about 2/3 of their length. The tests were carried out both under pure Argon (AirLiquide-N60) and an Ar–5%H$_2$ mixture, introduced in the vacuum chamber via a metal leak valve. The gas flow in both cases was kept at a rate of 10^{-2} Pa s^{-1}. A solid-state electrode (MicroPOAS-SETNAG©) with a built-in Pd–PdO internal reference monitored the oxygen partial pressure inside the working chamber. Under the pure Ar atmosphere, the oxygen partial pressure $P_{O_2} = 6 \times 10^{-3}$ Pa at $T = 823$ K was measured, providing the conditions of a complete saturation of the system ($C_O > 10^{-3}$ wt%) [13]; while, under the Ar–5%H$_2$ mixture, a $P_{O_2} = 3.2 \times 10^{-23}$ Pa at $T = 823$ K was measured, corresponding to an oxygen concentration in the melt $C_O = 3.9 \times 10^{-9}$ wt%. Referring to the Ellingham diagram as reported in [14], in these last conditions the oxygen partial pressure measured was lower than that required for the magnetite formation: this condition should provide a deoxidised steel surface.

The metallographic examination of the samples extracted from the melt were accomplished by optical microscopy, SEM, EDS and XRD.

3. Results and discussion

At the end of the experiments performed under the saturation conditions, the surface of the T91 specimens were covered by an oxide layer homogeneously distributed with thickness ranging between 7 and 12 μm after 550 and 1000 h, respectively. The oxide scale had a fractured structure and was formed by two zones composed of iron and oxygen with a different chromium content: 12 at.% in the inner part and about 9 at.% in the outer one. By the EDS and XRD analyses, an oxygen diffusion zone about 4 μm thick with spinel formation along grain boundaries was also detected (Fig. 1). No dissolution of any T91 components into the melt was found. These results are in agreement with those obtained by long-time tests (up 3000 h) performed under flowing or stagnant conditions at a lower temperature as reported in Ref. [15,16]. These authors reported comparable results on martensitic steels: the presence of an outer layer consists of magnetite (Fe_3O_4) with an inner layer being a mixed spinel oxide $(Fe,Cr)_3O_4$.

Under the same conditions, AISI 316L specimens developed partly a two-phase oxide scale (thickness about of 7–8 μm after both the two exposure times), consisting of a magnetite and a spinel zone underneath. The relative contents of iron, chromium, nickel and oxygen lead to consider the internal layer as a $Fe(Fe_{1-x},Cr_x)_2O_4$ spinel plus nickel. In a few areas of the samples a double oxide layer was also found composed by magnetite containing lead in the external part while the inner part consisted of spinel. In fact, the EDS analysis showed the presence of lead in the magnetite layer (Fig. 2), with a concentration decreasing from 6 at.% in the external part to 3 at.% in the internal one. In addition, Ni enrichment at the matrix/oxide interface was detected. As in the case of the T91 samples, the results obtained are comparable to those performed under flowing or stagnant conditions at a lower temperature and for longer time (up to 5000 h) as reported in Ref. [4,17]. These results show that under saturation conditions, both the austenitic and the martensitic steels produce stable protective oxide layers, which prevent the liquid metal attack.

Under reducing atmosphere conditions (Ar–5%H$_2$) the corrosion behaviour of both steels, maintained in

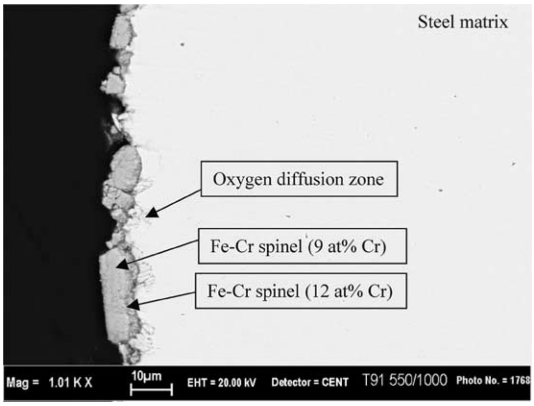

Fig. 1. SEM micrograph of T91 steel after immersion in LBE at $T = 823$ K for 1000 h under an Ar atmosphere.

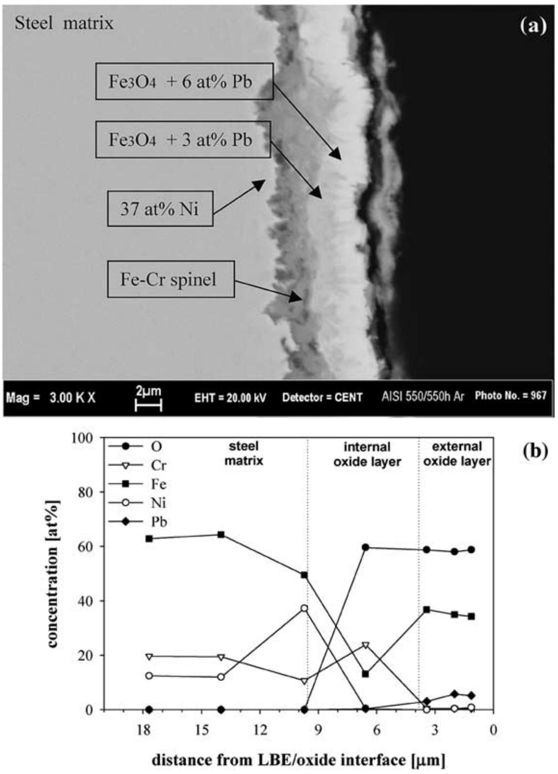

Fig. 2. AISI 316L steel after treatment with LBE at $T = 823$ K for 550 h under an Ar atmosphere: (a) SEM micrograph of the cross-section; (b) EDS concentration profiles.

the molten alloy for 550 and 2000 h changed completely. After 550 h the T91 steel surface exhibited a limited intergranular attack, while at longer time (2000 h) the penetration of lead and bismuth into the matrix was more evident (Fig. 3). The penetration increases with increasing of exposure time: up to 30 µm after 2000 h. However the corrosion did not occur uniformly: despite the low oxygen content in the surrounding atmosphere, some portions of the T91 specimen were covered by a thin layer of oxide (<10 µm) composed mainly by magnetite in the outer part and by Fe–Cr spinel in the inner part. No penetration occurred where the oxide layer was present, confirming the protection efficiency of a surface oxide layer even if very thin.

On the AISI 316L samples, the liquid metal attack after 550 h was found not uniformly distributed on the entire surface of the specimen, while after 2000 h the entire surface of the specimen was attacked (Fig. 4). The LBE penetration was deeper than that observed on the T91 samples and increased with the increasing of the exposure time reaching a depth of about 60 µm after 2000 h. At variance with T91, no oxide layers on the surface were detected, but the EDS-analysis showed the presence of oxygen in the LBE. The whole penetration zone resulted in depleted Ni and Cr (Ni < 1 at.%, Cr < 10 at.%).

As already mentioned, the choice of a reducing atmosphere would have assured a solid/liquid interface free of oxygen. That partially happened during the experiments under the Ar–5%H_2 atmosphere: the surface of the austenitic steel was completely free of oxygen while the formation of a thin oxide layer was sporadically observed on the T91 surface. Moreover, as detected by the EDS analysis, where the penetration occurred, the LBE in the matrix was oxidised. The presence of oxygen in the molten alloy lead to suppose that the penetration occurs by erosion of the GBs (‘reactive penetration’). In this case, the particular ‘interconnected-network’ aspect of the penetration zone could be explained by the oxygen-driven corrosion mechanism which bring the oxidised LBE to follow some preferential way inside the matrix due to the different energetic

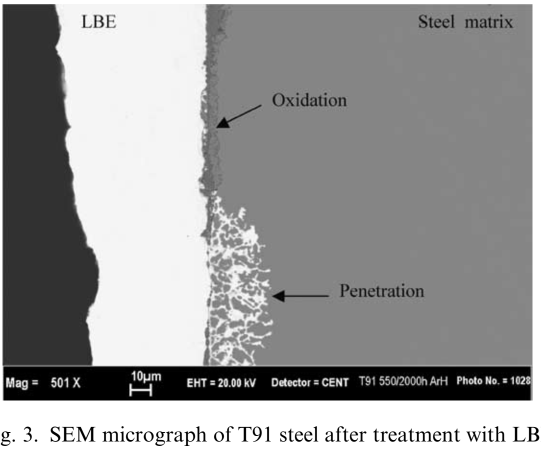

Fig. 3. SEM micrograph of T91 steel after treatment with LBE at $T = 823$ K for 2000 h under an Ar–5%H_2 atmosphere.

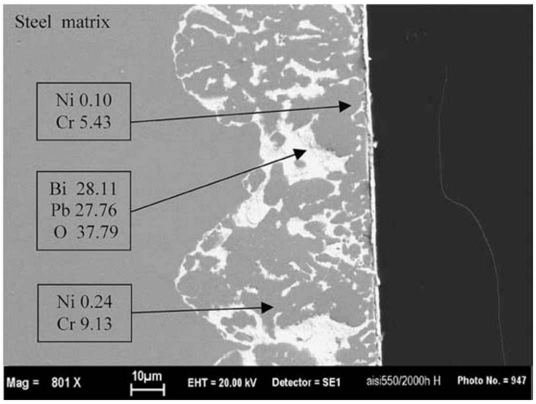

Fig. 4. SEM micrograph of AISI 316 steel after treatment with LBE at $T = 823$ K for 2000 h under an Ar–5%H_2 atmosphere (element concentrations in at.%).

state of the different boundary interfaces between the solid grains and the liquid alloy. However, the simpler explanation of a corrosion mechanism due to the dissolution of the steel elements in the liquid metal have not to be excluded.

4. Conclusions

The behaviour of the T91 martensitic steel and the AISI 316L austenitic steel in contact with LBE alloy has been analysed at 823 K and at two different oxygens. High purity Ar and an Ar–5%H_2 mixture were used as working atmospheres in order to attain two opposite limiting conditions for the LBE: the complete oxygen saturation and very low oxygen content.

Under oxygen saturation conditions the protection efficiency of the oxide layer formed on the surface of both steels has been confirmed. Although the oxides scale of the AISI 316L samples was thinner than that grown on the T91 steel, it seems sufficient to prevent preferential dissolution of the steel elements in the melt.

On the other hand, under reducing atmosphere, the intergranular attack of both steels was observed, accompanied by liquid metal penetration. The thickness of penetration increased with the exposure time. A competition between corrosion and oxidation has been evidenced on the surface of the T91 samples, while a larger and uniform attack on the whole specimen has been observed on the AISI 316L surface. The presence of oxygen in the LBE penetrated along the grain boundaries associated to Ni and Cr depletion could be thought as the progressive step of a reactive LBE attack beginning with the erosion of the steel microstructure.

The results herein reported indicate that the two steels investigated are resistant in Pb–Bi when the oxygen content in the system is such as to assure the formation of a passive oxide layer on the surface. However this is valid at the testing temperature and times used in this work: $T = 823$ K, $t \leqslant 1000$ h. Further investigations in a wider temperature range will be reported [18] to confirm the physico-chemical conditions for both the stable oxide formation and the corrosion phenomena.

Acknowledgments

This work has been financially supported by the E.C. project TECLA, contract no. FIKW-CT00092-2000.

References

[1] C. Rubbia, J.A. Rubio, S. Buono, F. Carminati, CERN/AT/95-44 (ET), 1995.

[2] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.

[3] G. Benamati, P. Buttol, V. Imbeni, C. Martini, G. Palombarini, J. Nucl. Mater. 279 (2000) 308.

[4] C. Fazio, G. Benamati, C. Martini, G. Palombarini, J. Nucl. Mater. 296 (2001) 243.

[5] G. Müller, A. Heinzel, J. Konys, G. Schumacher, A. Weisenburger, F. Zimmermann, V. Engelko, A. Rusanov, V. Markov, J. Nucl. Mater. 301 (2002) 40.

[6] G.S. Yachmenyov, A. Rusanov, B.F. Gromov, Y.S. Belomytsev, N.S. Skvortsov, A.P. Demishonkov, in: Proceedings of Heavy Liquid Metal Coolants in Nuclear Technology, Obninsk, Russian Federation, 5–8 October 1999, p. 133.

[7] I.V. Gorynin, G.P. Karzov, V.G. Markov, V.A. Yakovlev, Met. Sci. Heat Treat. 41 (1999).

[8] B.F. Gromov, B.A. Shmatko, Nucl. Energy 4 (1996) 35.

[9] R. Novakovic, E. Ricci, D. Giuranno, F. Gnecco, Surf. Sci. 515 (2002) 377.

[10] A. Legris, G. Nicaise, J.B. Vogt, J. Foct, J. Nucl. Mater. 301 (2002) 70.

[11] J.B. Monchoux, E. Rabkin, Acta Mater. 50 (2002) 3159.

[12] P. Protsenko, A. Terlain, M. Jeymond, N. Eustathopoulos, J. Nucl. Mater. 307–311 (2002) 1396.

[13] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th Ed., Pergamon, Oxford, 1993.

[14] G. Müller, A. Heinzel, G. Schumacher, A. Weisenburger, J. Nucl. Mater. 321 (2003) 256.

[15] F. Barbier, G. Benamati, C. Fazio, A. Rusanov, J. Nucl. Mater. 295 (2001) 149.

[16] D. Gomez Briceño, F.J. Martin Muñoz, L. Soler Crespo, F. Hernandez Arroyo, J. Nucl. Mater. 296 (2001) 265.

[17] H. Glasbrenner, J. Konis, G. Müller, A. Rusanov, J. Nucl. Mater. 296 (2001) 237.

[18] F. Gnecco, C. Bottino, E. Ricci, in preparation.