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Corrosion behaviour of stainless steels in flowing LBE at low and high oxygen concentration

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Abstract

The corrosion behaviours of austenitic steel AISI 316L and martensitic steel T91 were investigated in flowing lead–bismuth eutectic (LBE) at 400 °C. The tests were performed in the LECOR and CHEOPE III loops, which stood for the low oxygen concentration and high oxygen concentration in LBE, respectively. The results obtained shows that steels were affected by dissolution at the condition of low oxygen concentration ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%) and were oxidized at the condition of high oxygen concentration ($C_{[O_2]} = 10^{-5}$–10^{-6} wt%). The oxide layers detected are able to protect the steels from dissolution in LBE. Under the test condition adopted, the austenitic steel behaved more resistant to corrosion induced by LBE than the martensitic steel.

1. Introduction

The lead–bismuth eutectic (LBE) is foreseen as spallation target and coolant in ADS system, due to its favourable physical, chemical, thermodynamic and neutron properties. But the liquid metal corrosion has to be considered to select an appropriate containment material for the ADS target. The compatibility of structural material with the liquid metal became one of the important issues in ADS when the steels contact with LBE.

During the first phase of the EU 5th framework program, the Program 'Technologies, Materials, Thermal-Hydraulics for lead alloys' (TECLA) was founded. Its objectives are to provide a validation of the envisaged structural materials under varied experimental conditions.

One of the candidate structural materials is the martensitic steel T91, that is a readily available industrial material (stabilized with vanadium and niobium additions), which was qualified as steam generator material for non-nuclear and nuclear power plants. The modified 9Cr–1Mo steel T91 has higher strength, low thermal stress and lower ductile-brittle transition temperature (DBTT) shift after irradiation. Another potential material is austenitic steel AISI 316L that have a good corrosion resistant and superior weldability.

This paper is focused on the corrosion properties of these two materials after exposure in flowing LBE with lower oxygen concentration and with high oxygen concentration, respectively. Corrosion tests of austenitic

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and martensitic steels were performed in the liquid metal loops under continuous controlling of the oxygen concentration in LBE.

2. Experimental

The corrosion tests were performed in two loops with the same test conditions except the oxygen concentration in LBE. The LECOR loop was used for low oxygen concentration test while the CHEOPE III loop was used for high oxygen concentration test. The detailed information about these two loops were previously described in Refs. [1,2].

Two kinds of stainless steel were investigated in this report, one is austenitic steel AISI 316L, the other is martensitic steel T91. The chemical compositions of the materials, which were given by the supplier, are summarized in Table 1.

The as-received steels were machined to cylindrical specimens with 10 mm diameter and 50 mm length. Before placing the specimens into the test sections of the loops, they were degreased and weighed. The dimensions of each specimen were measured. There was no additional heat treatment to the specimens after machining. The specimens were fitted together in the test section by fixing their ends with pins. The test section temperatures of both loops were 400 °C, and the cold branch temperatures of the loops were 300 °C. The oxygen concentration in LBE were maintained in the range of 10^{-8}–10^{-10} wt% and of 10^{-5}–10^{-6} wt% for the LECOR and the CHEOPE III loops, respectively, which represent the low oxygen concentration and high oxygen concentration. The total duration of the tests were 4500 h, some specimens were removed to analyze after 1500 h and 3000 h of exposure time.

After corrosion tests, one specimens of each steels was immersed in a fresh solution ($CH_3COOH:H_2O_2:C_2H_5OH = 1:1:1$) at room temperature to remove the adherent LBE. Specimens were then cleaned and dried for visual examination and weight measurement. Specimens without cleaning were cut and polished for cross section examination by optical microscopy (OM) and scanning electron microscopy (SEM). Energy dispersive X-ray analysis (EDX) was used to analyze the chemical composition of the adherent corrosion products and bulk materials.

3. Results

3.1. At conditions with low oxygen concentration ($C_{[O_2]} = 10^{-8}$–10^{-10} wt% T = 400 °C)

Fig. 1 shows the weight changes over time for all steel coupons that were tested in the LECOR loop. Both austenitic stainless steel AISI 316L and martensitic steel T91 exhibited weight loss after they were exposed in LBE with low oxygen concentration. With increasing test time, the weight loss of specimens increased significantly. The value of weight loss for T91 after 4500 h was 0.184 mg/mm^2, while the value for AISI 316L was 0.155 mg/mm^2.

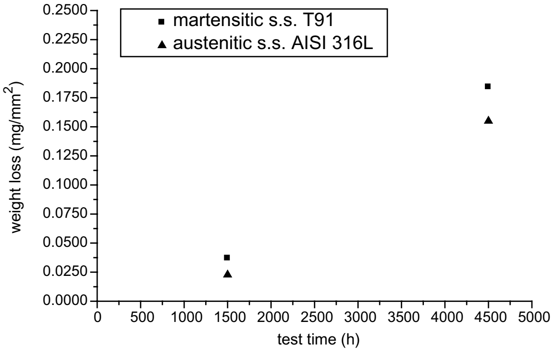


Fig. 1. Specific weight change of steels after exposure in LECOR loop ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, T = 400 °C).

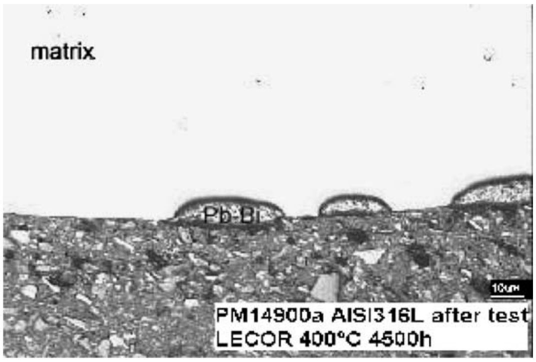


Fig. 2. Optical micrograph of austenitic steel exposed in LECOR loop after 4500 h ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, T = 400 °C).

Table 1
The chemical compositions of the stainless steels (wt%, balance Fe)

Element	Cr	Ni	Mo	Mn	V	Nb	Si	C
AISI 316L	17.3	12.1	2.31	1.8	–	–	0.35	0.02
T91	8.26	0.13	0.95	0.38	0.20	0.075	0.43	0.105

Optical microscopy analysis on the cross section of both steels showed that they suffered a very limited attack after 1500 h of exposure. With increasing exposure time, the specimens were corroded evidently (see Fig. 2). In order to reveal the microstructure of the corroded layer, the specimens were etched with a solution of oxalic acid. Fig. 4 is the SEM micrograph of an AISI 316L specimen after exposed in flowing LBE. As shown in this figure, a corroded layer was detected already after 1500 h. The EDX point analysis performed on this layer, but on the not etched part, revealed that the depletion of Ni and Cr had occurred in this layer (see Fig. 3(b)). This means that the austenitic steel AISI 316L was corroded by dissolution of the alloying elements to the liquid metal and formed a ferritic layer. This is consistent with the result of weight loss of the specimens.

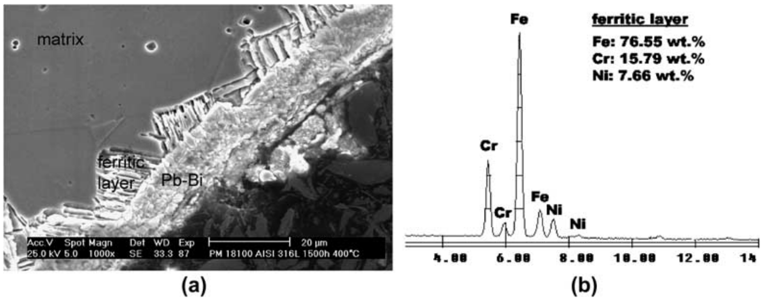
Concerning the martensitic steel T91, an uniform attack on the surface of the specimen after 4500 h of exposure (see Fig. 4) was detected. The SEM results showed the liquid metal penetrated into the matrix of steel (see Fig. 5).

The corrosion rates of steels have been estimated with the measurement of weight variation (Δm) assuming a linear evolution of the weight loss. After 4500 h of exposure, the calculated corrosion rate of austenitic steel AISI 316L is: $V_{\text{corrosion}} = 6.8\ \text{mg}\,\text{dm}^{-2}\,\text{d}^{-1}$; while the corrosion rate of martensitic steel T91 is: $V_{\text{corrosion}} = 10.2\ \text{mg}\,\text{dm}^{-2}\,\text{d}^{-1}$.

3.2. *At conditions with high oxygen concentration ($C_{[O_2]} = 10^{-5}$–10^{-6} wt% $T = 400$ °C)*

The weight measurement of specimens indicated that there was a weight gain for both steels after exposure in the CHEOPE III loop. Fig. 6 shows the weight gain over the exposure time for austenitic steel AISI 316L and martensitic steel T91. It can be seen that with the increasing of test time, weight gain of specimens increased, and the value of T91 was higher than that of AISI 316L. Presently, the corrosion tests on CHEOPE III loop are on-going. The oxidation kinetic will be estimated after the conclusion of the whole experimental campaign.

The visual examination of the specimens showed that both steels did not suffer strong liquid metal attack effects, but modification of the steels surfaces in contact with the liquid metal was detected for both steels after 1500 h of exposure. Metallographic analysis results



(a)

(b)

Fig. 3. (a) SEM cross-section and (b) EDX spectrum of austenitic steel in LECOR loop ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400$ °C, $t = 1500$ h).

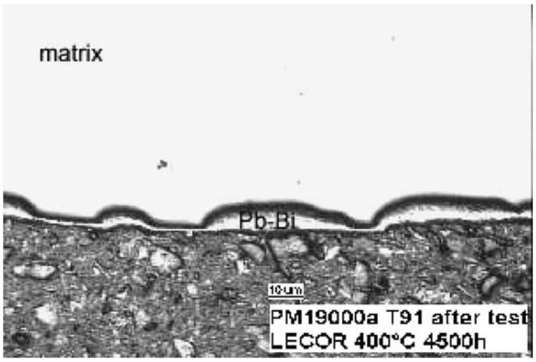


Fig. 4. Optical micrograph of T91 exposed in LECOR loop after 4500 h ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400$ °C).

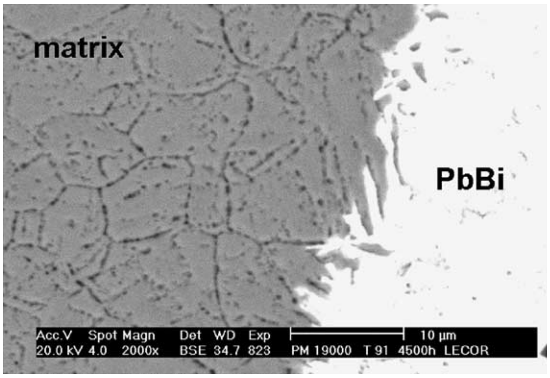


Fig. 5. SEM cross-section of T91 after exposure in LECOR loop ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%, $T = 400$ °C, $t = 4500$ h).

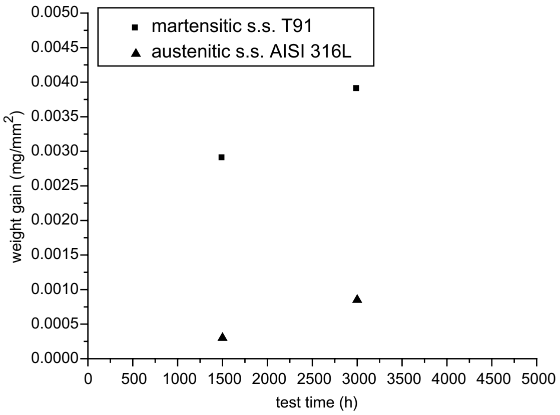


Fig. 6. Specific weight change of steels after exposure in CHEOPE III loop ($C_{[O_2]} = 10^{-5}$–10^{-6} wt%, $T = 400$ °C).

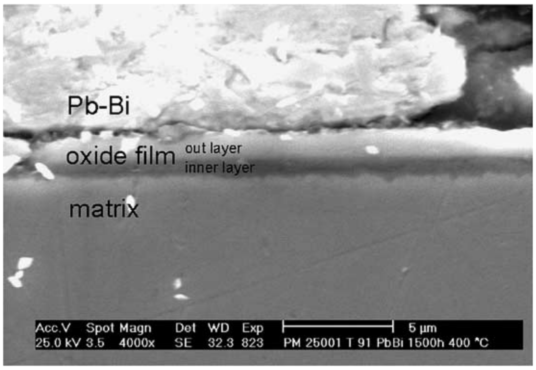


Fig. 7. SEM cross-section of T91 after exposure in CHEOPE III loop ($C_{[O_2]} = 10^{-5}$–10^{-6} wt%, $T = 400$ °C, $t = 1500$ h.

revealed that a thin and uniform oxide scale was formed on the steels surfaces. For austenitic steel AISI 316L, a less than 1 μm thickness oxide layer was formed on the surface of specimen. However, since the oxide layer formed on the surface of austenitic steel was so thin, its composition could not be analyzed by the techniques used in our tests. For martensitic steel T91, the thickness of oxide layer was ∼3 μm after 1500 h, and it grow to 6 μm after 3000 h of exposure. Fig. 7 shows a cross section of the oxide layer formed on the surface of T91 specimens. It can be seen that the oxide layer is composed of two sub-layers: the outer part consist of porous magnetite, while the inner is a compact spinel $(Fe, Cr)_3O_4$.

4. Discussion

The results of corrosion tests performed in the LECOR and CHEOPE III loops, respectively, revealed that oxygen concentration in LBE affects the corrosion mechanism of steels at present test temperature ($T = 400$ °C).

At low oxygen concentration ($C_{[O_2]} = 10^{-8}$–10^{-10} wt%) both steels exhibited the dissolution of alloy elements, and a weight loss was measured. For austenitic steel 316L, Ni depletion has been detected, with the formation of a ferrite layer in the corrosion area. This seems due to the high solubility of Ni in LBE (the solubility of Ni in LBE at 400 °C is about 16000 wppm [1]). For martensitic steel T91 a uniform attack by LBE was observed, and the liquid metal penetration appears on the interface between steel and liquid metal. However, no preferential dissolution of alloy elements was detected in the attack area. Comparing the corrosion rates of AISI 316L and T91, the corrosion rate found for the martensitic steel is higher than that for austenitic steel. As previously referred, the optical analysis on the corroded specimen showed a very limited attack after 1500 h for both steels. The corrosion became evident on the whole surface of the T91 specimen after 4500 h, as shown in Fig. 4. The same is not true for the AISI 316L. For this steel in fact, after 4500 h of test, the surface appears not corroded in several zones (see Fig. 2). This behaviour could be explained assuming that a thin layer of natural oxide is present on the specimens at the beginning, and it acts as barrier against the liquid metal attack. Before that the corrosion can take place, this layer has to be removed. Under the test condition adopted in the LECOR loop, the natural oxide film on the martensitic steel is more easily removed by the LBE in comparison to the austenitic steel. This could be the reason for the higher corrosion rate obtained for the martensitic steel and could also explain the increase in the corrosion rate observed with increasing the time exposure.

At high oxygen concentration ($C_{[O_2]} = 10^{-5}$–10^{-6} wt%) a protective oxide layer on the specimens surface have been detected, and a weight gain was measured for both steels. The oxide layers can protect the steels from dissolution attack induced by LBE. Notwithstanding these layers are stable and compact for both steels, the one formed on the surface of austenitic steel is much more thin than that one formed on the surface of martensitic steel. From the data of weight gain and SEM analysis, the AISI 316L shows a higher resistance to oxidation, at the present test conditions. This result is in agreement with a well-known result in the case of oxidation in air [3], where a continuous Cr_2O_3 protective layer is more easy to form on the surface of Fe–Cr–Ni alloy than Fe–Cr binary alloy. But because the layer on the surface of AISI 316L is too thin ($\leqslant 1$ μm), it could not be identified by our analysis techniques. Concerning to the oxide layer formed on the surface of martensitic steel, it consists of two sub-layers: the outer is magnetite while the inner is Fe/Cr spinel. This result was consistent with the results of static tests performed in our labs and with other researcher's works [4,5].

5. Conclusion

The main conclusions are summarized as follows:

Oxygen concentration in LBE affects the corrosion mechanism of steels at present test temperature: at low oxygen concentration both steels exhibited weight loss, and the corrosion was due to the dissolution of alloy elements. At high oxygen concentration both steels exhibited weight gain, and the formation of protective thin oxide layer on the surface of specimens has been detected.

At low oxygen concentration the austenitic steel was affected by preferential dissolution of Ni and Cr in the LBE, and the grew of a ferritic layer on the surface has been detected. Under the same condition the martensitic steel is affected by uniform corrosion, and no preferential dissolution has been noted.

The higher corrosion rate found for the martensitic steel in comparison to the austenitic steel, at low oxygen concentration, could be explained by the presence of an initial thin natural oxide layer on the surface of the specimens. Under the test conditions adopted this layer is more resistant to the LBE attack in the case of the austenitic steel, so the corrosion proceeds faster in the case of T91, at least until the complete removal of this oxides on the AISI 316L surface.

Acknowledgments

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