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Influence of the Pb–Bi hydrodynamics on the corrosion of T91 martensitic steel and pure iron

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Abstract

The Pb–Bi eutectic liquid alloy is considered as spallation target material in hybrid systems due to its suitable nuclear and physical properties. One of the parameters which may have a significant influence on the corrosion of steels in contact with molten lead alloys is the hydrodynamic regime. Corrosion tests have been performed in the CICLAD device at 400 and 470 °C at low oxygen concentrations and for various cylinder rotating speeds with T91 martensitic steel. The results obtained show that increasing the rotating speed leads to an increase of the corrosion rate. Moreover, the need for controlling finely the Pb–Bi physico-chemistry as well as the surface state of the samples is also shown by these tests. Finally, a comparison is made between the experimental corrosion rates and calculated values obtained by using equations expressing the mass transfer coefficient.

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1. Introduction

Liquid eutectic lead–bismuth is considered as candidate for the spallation target material to produce neutrons for the transmutation of long-lived nuclear wastes. However, one of the concerns with the use of liquid metals is their compatibility with the containment structure. Concerning liquid eutectic Pb–Bi, it was shown that one of the major parameters influencing the corrosion process is the oxygen concentration in the liquid alloy [1]. For low oxygen concentrations (approximately below the magnetite formation), dissolution of the steels should occur. In that case, another parameter which strongly influences the corrosion process of the steels is the Pb–Bi hydrodynamics.

Corrosion tests performed in the CICLAD device [2] on T91 martensitic steel and on pure iron at different temperatures and rotating speeds are presented. A comparison is also made between the experimental corrosion rates and the calculated values obtained with equations expressing the mass transfer coefficients.

2. Experimental data

2.1. The CICLAD device

The CICLAD device is devoted to the study of the Pb–Bi velocity effect on the corrosion of austenitic and martensitic steels. Its main part consists in a rotating cylinder which allows to analyse the effect of the Pb–Bi velocity on the corrosion of steels under controlled hydrodynamic conditions [2]. All the parts of the facility

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in contact with the liquid metal have been aluminized in order to protect them from dissolution. The efficiency of this coating has been proven in Pb–Bi for temperatures up to 550 °C even for low oxygen concentrations [3].

In this paper, all the tests were performed at low oxygen concentrations (10^{-9}–10^{-12} wt%). The concentration was maintained by imposing a constant pressure of 1 bar of an Ar–4%H_2 mixture in the testing pot. The oxygen concentration was continuously measured with an oxygen sensor designed and built by DEN/DER/STR in CEA/Cadarache [4] except for the last test performed on pure iron. For some of the tests performed at 400 °C, zinc was also added to the liquid Pb–Bi (≈ 100 wppm) to ensure a low oxygen concentration. A prewetting step was also performed by immersion of the samples in Pb–Bi with a low oxygen concentration of 3–4×10^{-10} wt% at $T = 480$ °C for 16 h, to ensure a satisfying wetting of the surfaces of the steels.

Concerning the addition of zinc in the liquid alloy, it allows to decrease the oxygen concentration below the magnetite formation as zinc oxide is much more stable than magnetite. Concerning an eventual effect of zinc on the corrosion rates, static corrosion tests have been performed which showed no specific effect of zinc [5]. Moreover, if an oxide layer is present at the surface of the steel, the prewetting step which is performed at a higher temperature than the corrosion test should normally allow the removal of an oxide layer at the surface of the steel: as the temperature is higher, for a same oxygen concentration, magnetite (if the oxide layer is constituted of magnetite) can become unstable and therefore dissolve in the liquid melt.

The purification of the Pb–Bi by the cold trap was not functioning. This system allows the purification of the liquid lead–bismuth by trapping the dissolved corrosion products in the liquid alloy (Fe, Cr) by considerably decreasing the temperature of the medium in order to decrease also the solubility limits of these species. For a testing temperature of 400 °C, the temperature of the cold trap should have been around 200 °C in order to achieve a very low metallic species concentration at the exit of the cold trap. In fact, due to technical problems, for the corrosion tests performed at 470 °C, the bottom of the cold trap was at 425 °C. For the tests performed at 400 °C, a plugging of the loop occurred and in order to avoid the accumulation of corrosion products in the testing pot, a cold point was set at the bottom of the pot acting as a cold trap. Regular analyses of Pb–Bi showed no increase in the corrosion products concentration (Fe, Cr). However, the iron solubility limit in Pb–Bi at 400 °C being around 0.3 wppm [6], as the analytical technique used (ICP–AES: inductive coupled plasma–atomic emission spectroscopy) does not allow a precise measure below 1 wppm, there is no guarantee that the iron concentration had not reached the solubility limit.

2.2. Corrosion tests

Tests performed are summarized in Table 1. In this table, the experimental conditions of each test are presented. In this table, is also presented the test performed in the LECOR loop available in ENEA/Brasimone [7,8].

Specimens were cylinders 10 or 20 mm long with a 30 mm diameter for the rotating cylinder system. For the pipe flow test section, specimens were cylinders 20 mm long with a 6 mm diameter. Samples were placed in the pipe flow test section only for the test performed at 470 °C. The samples were tested in their as-received surface state.

After the corrosion tests, examinations were performed by scanning electron microscopy. Chemical analyses were performed by energy dispersive spectrometry (EDS).

The Pb–Bi velocity in a pipe (of hydraulic diameter corresponding to the LECOR loop) leading to an equal mass transfer coefficient in pipe (calculated with the Berger and Hau equation [9]) and for the rotating cylinder (calculated with the Eisenberg equation [10]) is also given in the table.

3. Corrosion results

3.1. T91 martensitic steel

The values of the corrosion rates obtained for each test are given in Table 2 from the upper sample (which is situated downstream) to the lower sample.

Table 1
Experimental conditions of the corrosion tests + conditions of the LECOR test [7,8] (RC: rotating cylinder)

	Test	T (°C)	t (h)	ω rpm	Equiv. v_{pipe} (m s^{-1})	C_O (wt%)	Other
T91	1 Pipe	470	1203	–	0.069	–	–
	2 RC	470	376	2300	1.65	2.6×10^{-12}	–
	3 RC	400	282	540	0.53	8.5×10^{-10}	–
	4 RC	400	512	2714	1.98	9.5×10^{-12}	Zn + prewett
	LECOR	400	4500	–	1	3.1×10^{-10}–7.3×10^{-8}	80 ppm Mg
Fe	5 RC	400	435	870	0.79	1.6×10^{-11}	Zn + prewett
	6 RC	400	339	2845	2.06	–	Zn + prewett

Table 2
Experimental and calculated corrosion rates of the rotating cylinder samples after immersion in Pb–Bi for a low oxygen concentration (upper value = upper sample)

	Exp. $v_{\text{corrosion}}$ ($\text{mg}\,\text{m}^{-2}\,\text{s}^{-1}$)	Calc. $v_{\text{corrosion}}$ ($\text{mg}\,\text{m}^{-2}\,\text{s}^{-1}$)
1	0.0136 4.4×10^{-3}	0.0978
2	0.3278 0.1771	0.849
3	1.3×10^{-2} 1.7×10^{-2}	8×10^{-2}
4	2.2×10^{-2} 5.4×10^{-4}	0.25
5	1.87×10^{-2} 4.83×10^{-3}	0.113
6	8.96×10^{-2} 0	0.260

At 400 and 470 °C, weight losses were measured for all samples. In almost all cases, the weight loss of the upper sample (situated downstream) was more important than the weight loss of the lower sample. SEM observations and X-ray analyses showed that the samples' surface was uniformly attacked with penetrations containing Pb–Bi for some of the samples showing that the Pb–Bi removal was not completely efficient leading to an underestimation of some corrosion rates (test 3). Some wetting concerns were encountered which were attributed to the existence of a very thin oxide layer (thickness lower than 1 μm) at the surface of the steel (probably constituted of an Fe–Cr spinel oxide).

3.2. Pure iron

The last two corrosion tests were performed on pure iron at 400 °C in order to determine if the extremely different behaviour observed on the T91 martensitic steel samples of the same test could be attributed to a local protection of the steel by a very thin chromium oxide or Fe–Cr spinel oxide layer.

For these two tests, a very different behaviour was observed between the upper sample and the lower sample. For the fifth test, the magnitude of the corrosion rate was close to what was obtained for T91 for close rotating speeds. For the sixth test performed at a higher rotating speed, a very severe dissolution was observed on the upper sample leading to a corrosion rate around 360 $\mu\text{m}\,\text{yr}^{-1}$. No weight loss was measured for the lower sample. Observations of the iron samples showed for both rotating speeds a uniform attack of the surface except for the sample with no weight loss measured for which no attack was observed. An electrochemical attack in an oxalic acid bath showed some penetrations initiated at the grain boundaries. Analysis of the samples showed no traces of Pb–Bi remaining on the surface after the removal of the liquid alloy.

4. Discussion

All these experiments performed at low oxygen concentrations show a quite heterogeneous behaviour for the T91 martensitic steel as well as for pure iron.

4.1. Analysis of the corrosion results

First conclusions can be made:

- for all the tests performed at low oxygen concentrations (below the formation of magnetite), dissolution occurs for T91 and pure iron,
- for the same temperature, increasing the fluid velocity leads to an increase in the corrosion rate,
- for the similar fluid velocity, increasing the temperature leads to an increase in the corrosion rate.

The surprising result is the very important difference observed between the corrosion rates obtained for the upper and the lower sample of the rotating cylinder system of the same test. This difference was also observed for the samples placed in the pipe flow of the CICLAD device. Different hypotheses can be made:

- *An oxygen effect*: the lower sample (which is situated upstream) could use the oxygen present in the liquid Pb–Bi to form a protective chromium or spinel oxide layer (stable at the oxygen concentration tested here) and due to the very low oxygen concentration in Pb–Bi, the downstream sample would not have enough oxygen available to form such a layer leading to much higher corrosion rates. However, a similar behaviour was observed for pure iron showing that the presence of a thin chromium or Fe–Cr spinel oxide layer cannot solely explain this difference.
- *An hydrodynamic effect*: a specific hydrodynamic configuration of the rotating flow could lead for the upper sample to very turbulent conditions which could cause high corrosion rates. Moreover, as the purification system was not efficiently operating during these tests as it was already explained in Section 2.1, a different hydrodynamic configuration between the two samples could lead to a different iron concentration in the liquid Pb–Bi close to the samples and thus to different corrosion rates: for example by modifying the renewal rate of the dissolved products close to the surfaces of the samples (if their concentration in solution was not negligible).

- *A surface state effect*: roughness, presence of a native oxide layer, ... Concerning the influence of the surface conditions, a specific study was carried out by Ilincev [11]. Corrosion tests were performed on various materials in a Pb–Bi convection loop ($v_{\mathrm{Pb\text{–}Bi}} = 0.01\ \mathrm{m\,s^{-1}}$ for $\Delta T = 100$ between the hot leg at 500 °C and the cold leg at 400 °C) at two oxygen concentrations 3–4 × 10^{-6} wt% and 2 × 10^{-5} wt% [11]. They showed that, even if these oxygen concentrations are above the magnetite formation for the temperatures tested, dissolution of the steels can occur leading to high corrosion rates especially at 500 °C depending on the material tested and on its surface condition. In fact, ground and untreated specimens were generally more corroded than ground and passivated specimens. This result was observed at Eurofer where the composition (9Cr–1W–0.4MnVTa) can be compared to T91 [11]. However, concerning this hypothesis, it has to be noted that if the surface state of the samples was the only parameter that led to the important differences between the corrosion rates of the CICLAD samples, the difference would not be systematic as it is observed between the upper and the lower sample but it would be a more random phenomenon.

Concerning the hydrodynamic effect, a specific study of the rotating flow is actually performed at CNRS/LEGI in Grenoble. The aim of this study is to perform both a numerical analysis of the flow in the CICLAD pot together with experimental visualizations and measurements of the velocities in a water pot simulating the CICLAD testing pot (the hydrodynamic configuration being independent of the fluid density). These observations and measurements of the different components of the fluid velocity (radial, axial and tangential) close to the surface of the specimens are performed as a function of the cylinder rotating speed and as a function of the specimen (upper or lower sample). It appears from the first results obtained in LEGI that the hydrodynamic configuration in the testing pot of the CICLAD device could play an important role on the corrosion rate differences observed.

Static corrosion tests are also being performed on samples with different surface treatment (electropolished, passivated, preoxidized) for a low oxygen content in the liquid Pb–Bi to determine the influence of the initial surface state of the sample on the corrosion rate.

4.2. Influence of the fluid velocity on the corrosion rate

The experimental results show that increasing the fluid velocity leads to an increase in the corrosion rate. Therefore, for the experimental conditions tested here, the corrosion process seems to be controlled by the corrosion products diffusion from the solid/liquid interface to the bulk. However, the analysis of the results has to be performed with great care given the uncertainties on the results.

If we assume a diffusion controlled process, the corrosion rate can be expressed according to

$$v_{\mathrm{corrosion}} = K(c_{\mathrm{s}} - c_0)$$

with K: mass transfer coefficient ($\mathrm{m\,s^{-1}}$), c_{s}: solid/liquid interface iron concentration. This concentration is considered to be equal to the iron solubility limit as the interface reaction is considered at the equilibrium ($\mathrm{g\,m^{-3}}$). c_0: iron bulk concentration ($\mathrm{g\,m^{-3}}$).

It is sure that this equation considers only local hydraulic effects and that the non-isothermal characteristic of the loop is not taken into account as it is in other publications [12,13]. However, the CICLAD loop, apart from the corrosion specimens, is entirely constituted of aluminized 316L. Therefore no dissolution or oxidation of the loop occurs. Moreover, for the tests performed at 400 °C, only the testing pot was operational due to the plugging of the loop. Therefore, in that case, a nearly isothermal system is obtained (apart from the cold point at the bottom of the pot which allows the purification of the liquid Pb–Bi).

For a rotating cylinder geometry, the mass transfer coefficient can be expressed [10]:

$$K_{\mathrm{Eisenberg}} = 0.0487\omega^{0.70} d_{\mathrm{cylinder}}^{0.4} \nu^{-0.344} D^{0.644}$$

with ω: cylinder rotating speed ($\mathrm{rad\,s^{-1}}$), d_{cylinder}: cylinder diameter (m), ν: Pb–Bi kinematic viscosity ($\mathrm{m^2\,s^{-1}}$), D: iron diffusion coefficient in Pb–Bi ($\mathrm{m^2\,s^{-1}}$).

The values of the data used for the calculations at the two testing temperatures are given in Table 3. For the iron diffusion coefficient, as no data is available at these temperatures in the literature, values obtained in pure lead were considered [14]. Concerning the iron concentration in solution, for the tests performed at 400 °C, it is assumed to be negligible as the bottom of the pot is cold and therefore the iron dissolved in the Pb–Bi alloy is assumed to precipitate there, leading thus to the purification of the liquid Pb–Bi. For the tests performed at 470 °C, the dissolved iron concentration in the bulk was estimated by performing a mass balance considering the dissolved iron in the pot containing the rotating cylinder system. This was performed only for the rotating cylinder test (test 2) as the steady state was not reached during the pipe flow corrosion test. For the pipe flow test (test 1), c_0 which is initially equal to zero increases up to approximately 3.3 $\mathrm{g\,m^{-3}}$. In the calculations, c_0 was considered equal to zero even if we know that in that case, the calculated corrosion rate is overestimated compared to the measured value. These calculations are detailed in a previous report [15].

Table 3
Experimental data

T	D [14] (m^2s^{-1})	ν (m^2s^{-1})	c_s Fe [6] (gm^{-3})	Test	c_0 Fe (gm^{-3})
470	3.98×10^{-10}	1.32×10^{-7}	13.14	1	≈ 0
				2	5.72
400	1.93×10^{-10}	1.49×10^{-7}	3.24	3–6	≈ 0

For the pipe flow geometry, another expression of the mass transfer coefficient has been used, the Berger and Hau equation [9]:

$$K_{B\text{–}H} = 0.0165v^{0.86}d_h^{-0.14}\nu^{-0.530}D^{0.670}$$

with v: Pb–Bi velocity (ms^{-1}), d_h: hydraulic diameter (m).

It is then possible to represent the variation of the corrosion rate as a function of an equivalent fluid velocity in pipe calculated by equalizing the expressions of the mass transfer coefficients obtained for both flow geometries. Fig. 1 shows the results obtained for the experimental corrosion rates obtained for the upper sample (the most corroded) compared to the calculated ones at 400 °C. In this figure is also represented the corrosion rate measured in the LECOR loop available in ENEA/Brasimone [7,8]. In this figure, the corrosion rate is put to zero at zero velocity. Of course, this is not strictly exact. However, the corrosion rate measured for T91 in stagnant Pb–Bi for low oxygen concentrations at 500 °C after 3000 h of immersion is around 2×10^{-3} $mgm^{-2}s^{-1}$ which is negligible compared to the velocities measured in dynamic conditions [2].

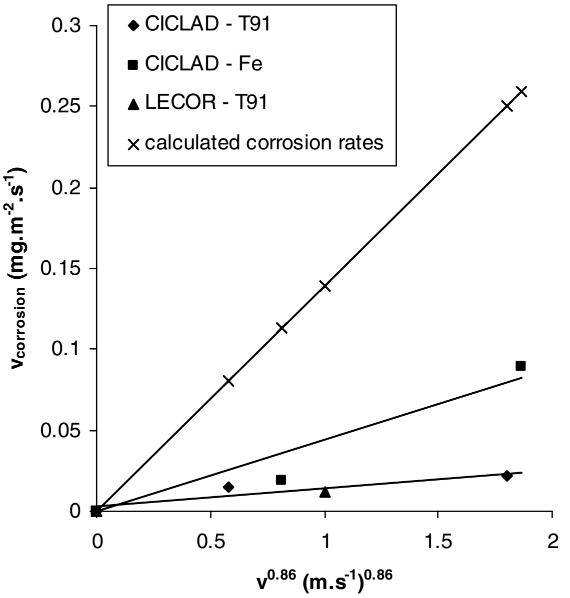

Fig. 1. Variation of the corrosion rate as a function of the fluid velocity + LECOR results [7,8] – comparison between experimental (for the upper sample – the most corroded) and calculated results at 400 °C.

These results show that, for a given temperature, increasing the rotating speed at the power 0.7 (which corresponds to increasing the fluid velocity at the power 0.86 as no other parameter is modified), leads to a linear increase in the corrosion rate. This shows that the corrosion process can be considered *for the velocities tested* as controlled by the iron diffusion from the solid/liquid interface to the bulk. We can also see that the experimental corrosion rates are much lower than the calculated ones. This is also the case at 470 °C for T91 martensitic steel but with a smaller difference between the results. Moreover, the results obtained on T91 martensitic steel are also lower than the results obtained on pure iron especially at a high rotating speed. Different parameters could explain these differences:

- For T91, a thin oxide layer (chromium or Fe–Cr spinel) could partially protect the steel and decrease the corrosion rate compared to pure iron.
- Many uncertainties remain on some physico chemical data like the iron solubility and the iron diffusion coefficient.
- The iron concentration in solution, c_0, remains also uncertain as the analytical techniques currently used do not allow measurements below 1 wppm. This concentration could be higher than supposed leading to overestimated values of the calculated corrosion rates.

5. Conclusions

These tests performed at 400 and 470 °C with iron and T91 in the CICLAD device show that for low oxygen concentrations:

- The corrosion proceeds by dissolution.
- The upper sample (situated downstream) of the rotating cylinder system but also of the pipe flow system is generally more corroded than the lower sample.
- The corrosion rate increases linearly when the fluid velocity increases at the power 0.86 (at the power 0.7 for the cylinder rotating speed) which shows that,

the dissolution process seems to be controlled by the iron diffusion from the solid/liquid interface to the bulk.
- The CICLAD results can be accurately represented with the expression of the corrosion rate obtained assuming a diffusion controlled process.
- The CICLAD results are in agreement with the LECOR results using the mass transfer coefficients for different flow geometries, therefore these equations seem to be valid to represent the results.
- The experimental corrosion rates are much lower than the calculated values.

The major interrogations that remain are:

- The precise effect of the surface state of the samples on the corrosion process: presence of a native oxide layer, roughness, ... In order to study this parameter, static corrosion tests are being performed with electropolished samples, preoxidized samples, ...
- The effect of the hydrodynamic configuration of the rotating flow on the corrosion rate of the cylinders (difference between the samples). A specific hydrodynamic study is being performed at the CNRS/LEGI in this subject.
- The values of the physico chemical parameters such as the iron solubility limit and diffusion coefficient in the liquid alloy. Electrochemical determinations are performed at the laboratory.
- The control of the Pb–Bi purity and the assumption that the iron concentration in solution is negligible (this assumption could be unrealistic compared to the experimental purification system). More precise analyses are planned to allow a determination of the iron concentration below 1 wppm.

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