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Corrosion behaviour of aluminized martensitic and austenitic steels in liquid Pb–Bi

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Abstract

The Pb–Bi liquid alloy is under consideration as a spallation target material in the hybrid systems due to its suitable nuclear and physical properties. In order to limit the risks of corrosion of the structural elements in contact with the liquid Pb–Bi, protection by means of aluminized coatings was investigated for 316L austenitic steel and T91 martensitic steel. For both steels, no damages were observed after immersions in static Pb–Bi up to 500 °C for low oxygen concentrations and long durations. However, at 600 °C in the same conditions, a non-uniform degradation of the coatings was observed. Only coated 316L was tested in dynamic conditions. The results were generally satisfying for temperatures from 350 to 600 °C and for fluid velocities up to 2.3 $\mathrm{m\,s^{-1}}$. However, in both the IPPE loops and the CICLAD device, some localized damage of the coatings, attributed to erosion, was observed.

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1. Introduction

Liquid eutectic lead–bismuth is considered as a 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. In order to limit the corrosion risks to the structural elements, protection by means of aluminized coatings has been investigated. The efficiency of this coating has been proven in the case of Pb–17Li [1] for fusion applications. In this paper, coatings applied on 316L austenitic steel and coatings developed for T91 martensitic steel are described and a summary of the corrosion tests performed on these coatings in various conditions of temperature, oxygen concentration and hydrodynamic conditions is provided.

2. Experimental data

2.1. Coating procedure

For 316L austenitic stainless steel, the aluminizing process is performed industrially by a pack-cementation process. The experimental procedure is:

- a deposition treatment in the presence of the powder at 750 °C for 1 h 40,
- a diffusion phase performed under an argon atmosphere at 900 °C for 6 h.

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The thickness of the resulting aluminized coating was between 50 and 100 μm.

For T91 martensitic steel, as no industrial process is available, the development of different processes was carried out by CEA/Grenoble [2–4]. The objectives were:

- to perform Fe–Al deposition at 'low' temperature (i.e. below 750 °C which is the steel tempering temperature) in order to avoid any modification of the structural material properties and without forming brittle intermetallic phases;
- to deposit an Al_2O_3 top layer using specific means to also guarantee a deposition temperature below 750 °C.

Three different processes were investigated:

(a) Fe–Al deposition by pack-cementation.

The deposition is produced by the thermal decomposition at 750 °C for one h of a powder containing:

- 70 wt% Fe + 30 wt% Al which is the *donor* (constituted of the metallic element, Al, to transport to the surface to be coated);
- NH_4Cl as an *activator* to encourage transport of the metallic species;
- Al_2O_3 as the *inert filler* to minimize sintering of the powder.

(b) Fe–Al deposition by pack-cementation + in situ oxidation.

Fe–Al deposition by pack-cementation (as for coating 1) followed by an air oxidation at 750 °C for 1 h.

(c) Fe–Al deposition by pack-cementation + Al_2O_3 deposition by Pyrosol method.

Fe–Al deposition by pack-cementation (as for coating 1) followed by an Al_2O_3 deposition using a Pyrosol (=Pyrolysis of an aerosol) technique. A solution is prepared with a metalorganic precursor (aluminium acetylacetonate) and a solvent (methanol). An aerosol of this solution is generated and transported to a heated zone where it vaporizes. A chemical reaction occurs between the vapour and the substrate. This treatment is performed at 370 °C for 1 h.

The thickness of the coatings including the Al diffusion zone are between 40 and 120 μm depending on the process. The compositions of the different coatings performed on T91 martensitic steel are given in Fig. 1 and all the coatings are described more precisely in Section 3.1.

2.2. Corrosion tests

Corrosion tests were performed in the COLIMESTA (stagnant Pb–Bi) and the CICLAD facilities (rotating cylinder in Pb–Bi leading to conditions 'equivalent' to flowing Pb–Bi [5]) in CEA/Saclay [5] and in the static (stagnant Pb–Bi) and dynamic facilities (circulating Pb–Bi at a velocity of 1.9 $m\,s^{-1}$) of IPPE/Obninsk [6]. Various experimental conditions were tested which are summarized in Table 1. For the tests performed in COLIMESTA at 600 °C and for all the tests performed in CICLAD, the oxygen concentration was continuously measured with an oxygen sensor designed and built by CEA/Cadarache [7]. For the tests performed in

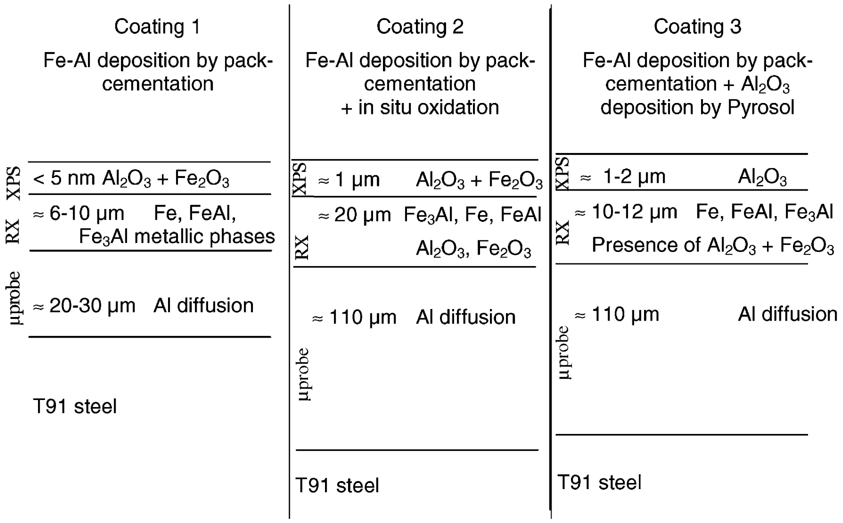


Fig. 1. Composition of the aluminized coatings performed on T91 martensitic steel. (XPS: X-ray photoemission spectroscopy; RX: X-ray diffraction; μprobe: electron microprobe.)

Table 1
Synthesis of the corrosion tests performed on aluminized steels

			T (°C)	t (h)	$C_{[O]}$ (wt%)
T91	Static	Colimesta	350	3000	10^{-8}–10^{-9}
			500	3000	10^{-8}–10^{-9}
			600	3000	10^{-8}–10^{-9}
316L	Static	Colimesta	350	10000	10^{-8}–10^{-9}
			500	10000	10^{-8}–10^{-9}
			600	3000	10^{-8}–10^{-9}
		IPPE	470	1000	4×10^{-9}
			470	1000	2.5×10^{-4}
			600	1000	4.3×10^{-13}
			600	1000	9×10^{-4}
	Dynamic	IPPE	470	1000	$10^{-6} + 10^{-7}$–10^{-8}
		$v = 1.9\ \mathrm{m\,s^{-1}}$	600	1000	$10^{-6} + 10^{-7}$–10^{-8}
		CICLAD $v = 0.6$–$2.3\ \mathrm{m\,s^{-1}}$	400	≈500	10^{-11}–10^{-12}

COLIMESTA at 350 and 500 °C, a measurement was performed after the tests. IPPE sensors were used in their devices.

Post-test observations were performed by scanning electron microscopy. Chemical analyses were performed by energy dispersive X-ray (EDX) and electron microprobe analysis.

3. Results and discussion

3.1. Characterization of the coatings before the corrosion tests

The aluminized coating deposited on 316L austenitic steel has already been described in a previous paper [1]. This coating is about 60–70 μm thick and is constituted of two layers. The external layer is about 30–40 μm thick and contains Al, Fe, Cr, Ni and O with a higher Al content than the inner layer which is richer in Cr. Between the two layers, precipitates rich in Ni and Al are found. A thin (5–10 μm) Cr and O enrichment is also observed at the surface of the coating.

For the T91 martensitic steel, the characteristics of the different coatings are presented in Fig. 1 [2–4]. We can see that the different aluminization processes lead to similar coatings. However, the thickness of the aluminium diffusion layer is more important for coatings 2 and 3 than for coating 1. This can be attributed to the fact that for coatings 2 and 3, the treatment is twice longer. The oxygen content in the layer containing the Fe–Al metallic phases is also higher for coatings 2 (13–17 wt%) and 3 (10–33 wt%) than for coating 1 (0–3 wt%). This can be attributed to the fact that, for these two treatments, a specific oxidation step follows the deposition step. A very thin (around 1 μm for coatings 2 and 3 and lower than 5 nm for coating 1) Al and O enrichment is also observed at the surface of the coating.

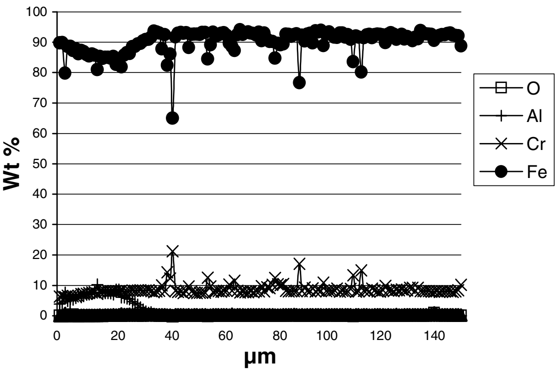
3.2. Results of the corrosion tests

In stagnant Pb–Bi, aluminized 316L and T91 exhibit a very good behaviour up to 500 °C for low oxygen concentrations (below 10^{-8} wt%). No weight change (loss or gain) was measured for the different samples and no modification (change in the thickness and in the composition) of the coating was observed. However, at 600 °C, for low oxygen concentrations, damage to all of the coatings was observed. Moreover, in dynamic conditions, localized erosion phenomena were observed at 600 °C for the IPPE tests (no damages were observed at 470 °C) and at 400 °C for all the CICLAD tests. However, concerning the last point, other characterizations should be performed to confirm that the damages observed on the coatings are due to erosion phenomena in the liquid alloy rather than to cleaning, cutting and polishing procedures.

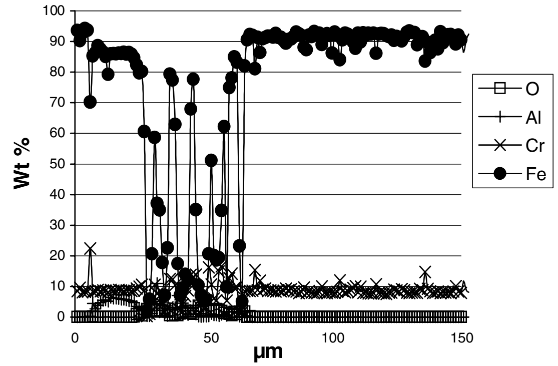
3.2.1. Static tests

Up to 500 °C, a satisfying behaviour of the coatings performed on T91 and 316L was obtained. No weight change (loss or gain) was measured for the different samples and no modification (change in the thickness, the composition) of the coating was observed. In comparison, after 3000 h of immersion in stagnant Pb–Bi at 500 °C with an oxygen concentration around 10^{-7}–10^{-8} wt%, unprotected 316L and T91 underwent weight losses of respectively 124 and 3 $\mathrm{mg\,cm^{-2}}$ [5].

At 600 °C, for T91, an heterogeneous behaviour was observed for the low oxygen concentrations tested (below 10^{-8} wt%). Some parts of the samples remained unwetted and apparently not modified and in some other parts the coating was partially or completely removed from the material and a corrosion layer was observed. The depth of metal loss was around 100–150 μm and a 50 μm thick corrosion layer was also observed (which is identical to what was previously observed on unprotected T91 in the same conditions [8]). Fig. 2



(a) Zone without corrosion damage



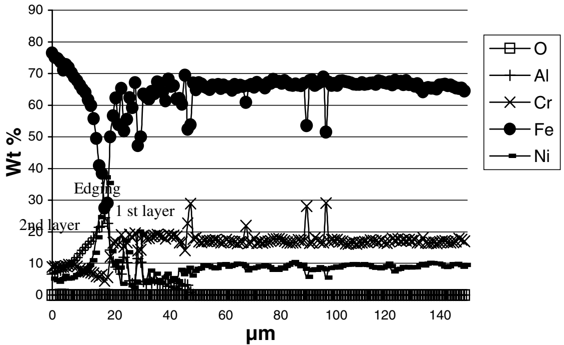
(b) Zone with corrosion damage

Fig. 2. Concentration profiles of a cross section of T91 martensitic steel aluminized with coating 1 in an unwetted (a) and a wetted zone (b) after immersion in Pb–Bi at 600 °C for 3000 h.

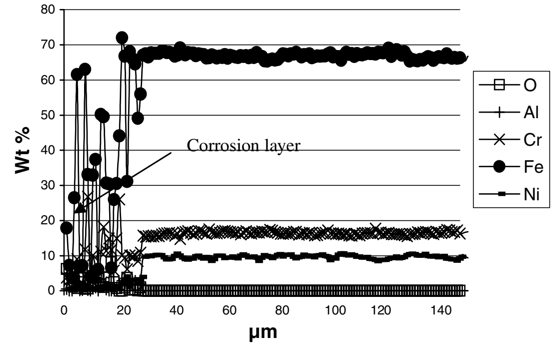
shows the concentration profiles of a sample protected by the coating 1 after 3000 h of immersion in Pb–Bi at 600 °C in wetted and unwetted zones. Similar results were obtained for the two other coatings. For the unwetted parts, the concentration profiles of the elements remained close to what was observed prior to the immersion, however the external layer rich in oxygen and aluminium was no longer observed. Moreover, the aluminium content seems to be lower than what was obtained prior to the tests. For the wetted parts, a corrosion layer (made of Fe and Cr and without Al), about 50 μm thick was observed. Apparently, aluminium has diffused from the coating towards the liquid alloy leading to an Al depletion in the coating and to a decrease of its protective properties which finally led to its destruction and to the dissolution of the steel.

At 600 °C, for 316L, as for T91, damages to the coating were observed for low oxygen concentrations (below 10^{-8} wt%). The same kind of heterogeneous behaviour was observed i.e. some unwetted zones, and some zones where the coating was partially or completely removed with the formation of a corrosion layer. The depth of metal loss was about 100 μm and a 100 μm thick corrosion layer was also observed (which is close to what was previously observed on unprotected 316L in the same conditions [8]). Fig. 3 shows the concentration profiles of a sample protected by the coating 1 after 3000 h of immersion in Pb–Bi at 600 °C in wetted and unwetted zones. For the unwetted zones, the thickness of the two layers constituting the coating remained unchanged. However, the concentration profiles show a decrease of the aluminium content associated to an increase of the iron content in the external layer of the coating. For the wetted parts, a porous corrosion layer about 100 μm thick was observed, constituted mainly of Fe and Cr and strongly depleted in Ni.

Concerning 316L, the static tests performed at IPPE at 600 °C for a low oxygen concentration confirm the unsatisfying behaviour of the coating at this temperature as after 1000 h, important cracks up to 40 μm deep were observed. However, for the higher oxygen concentration tested (around 10^{-4} wt%), no damage was observed up to 1000 h of immersion.



(a) Zone without corrosion damage



(b) Zone with corrosion damage

Fig. 3. Concentration profiles of a cross section of 316L aluminized austenitic steel in an unwetted (a) and a wetted zone (b) after immersion in Pb–Bi at 600 °C for 3000 h.

3.2.2. Dynamic tests

Dynamic tests were performed on 316L austenitic steel in IPPE/Obninsk and CEA/Saclay. For the tests performed in IPPE, the behaviour of the coating was generally satisfying for both tested temperatures, 470 and 600 °C and both oxygen concentrations (10^{-7}–10^{-8} and 10^{-6} wt%). No destruction or modification of the coating were observed even at 600 °C. However, for these tests, the oxygen concentrations were higher than the oxygen concentrations of the static tests. Moreover, the dynamic corrosion tests were also much shorter (1000 h) than the static tests. For the IPPE tests, some localized corrosion phenomena were observed only at 600 °C for both oxygen concentrations. The localized corrosion points which sometimes led to severe corrosion damages were mainly located close to the conical section of the samples near the grid of the samples' holder. It has to be noted that these points were also especially observed on one specific holder corresponding to the short testing durations. This shows that the hydrodynamic configuration of this holder and of the grid where the samples were fixed must have been extremely turbulent leading to these localized corrosion phenomena.

For the CICLAD tests, localized attack of the coated 316L was also observed. This attack was observed on the surface of the steels for all the tested conditions. These attacks concerned only the external part of the coating and they never led to a strong dissolution of the material. However, these tests were performed at a moderate temperature, 400 °C, for short durations (maximum of to 500 h), but for very low oxygen concentrations and high rotating speeds (up to 2.3 $\mathrm{m\,s^{-1}}$).

4. Conclusion

Different aluminized coatings have been tested to determine if they could be efficient corrosion barriers against Pb–Bi for the structural steels of the ADS systems. For 316L austenitic steels, the aluminization process has been developed industrially whereas for T91 martensitic steel, three coating processes have been developed at the laboratory scale in CEA/Grenoble. For both steels, and for all coating processes, adequate protection has been obtained in static conditions for low oxygen concentrations (for which dissolution of the unprotected steels occurs) for temperatures up to 500 °C. At 600 °C and for low oxygen concentrations (below 10^{-8} wt%), significant damages of the coatings occurred for both T91 and 316L leading to severe corrosion of the materials. For higher oxygen concentrations, no damages of the coating were observed for the test duration of 1000 h.

In dynamic conditions, only aluminized 316L austenitic steel was tested. For both moderate (400 °C) and high temperatures (600 °C) localized corrosion points, which can be attributed to a particularly turbulent flow, were observed. Therefore, it seems that the aluminized coating is quite sensitive to a dynamic flow. However, other observations should be performed as, for example, for the CICLAD tests, it has to be confirmed that the localized damages observed on the external part of the coating are due to 'erosion' phenomena and not to the sample preparation procedure (cutting, polishing, ...).

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