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Al_2O_3 coating as barrier against corrosion in Pb-17Li

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Alumina coating, with a thickness of 1 μm, has been manufactured by Pulsed Laser Deposition on EUROFER. A whole characterization of the interface, bare and coated, with stagnant Pb-17Li eutectic for 1000 hours at 550 ºC were performed using scanning electron microscopy, energy dispersive x-ray spectroscopy and secondary ion mass spectrometry. The results show that uncoated samples are damaged and suffer loss of material due to a solution process of the steel into the liquid metal, while corrosion process is insignificant for coated samples. Therefore, these results suggest a good performance of the alumina coatings under the test conditions.

Keywords: Alumina coatings, corrosion, compatibility, EUROFER, lead-lithium, stagnant conditions.

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1. Introduction

The reduced activation ferritic-martensitic steel EUROFER is considered as reference structural steel for different concept of Pb-Li breeding blanket (Water Cooled Lithium-Lead (WCLL), Helium Cooled Lithium-Lead (HCLL) and Dual Coolant Lithium-Lead (DCLL). In early studies the corrosion behavior of EUROFER in Pb-17Li was described and concluded in an excessive corrosion rate for the working conditions [1-2].

On the other hand, due to its characteristics, aluminum-based coatings are proposed as anti-corrosion barrier in those concepts which use Pb-Li as breeding blankets. Such coating should work also as anti-permeation barrier. [3],

Recent investigations on Pulsed Laser Deposition Alumina coating (PLD-Al_2O_3) revealed high mechanical performances and chemical compatibility in liquid lead at 550°C, making it promising also for the application in liquid Pb-Li alloy [4, 5].

In this work, 1 μm Al_2O_3 coatings were been prepared at Istituto Italiano di Tecnologia (IIT) on EUROFER by the PLD technique and qualified in stagnant Pb-17Li as a first approximation to evaluate its suitability as protective agent against corrosion.

Full characterization of the samples, before and after the corrosion tests, has been carried out using different analysis techniques, such as scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and secondary ion mass spectrometry (SIMS) to evaluate the migration of Li into the EUROFER. Results show a good performance of the coatings for the test conditions.

2. Experimental procedure

2.1 Description of the experimental set-up

The corrosion tests of bare and PLD-Al_2O_3 coated EUROFER in stagnant Pb-17Li were carried out within an experimental cylindrical steel vessel. Figure 1 shows the experimental set-up.

The heating of the Pb-17Li was ensured by a heating element wrapped around the external surface of the cylinder. The thermal insulation was given by mineral wool and aluminum sheets folded around the external surface of the cylinder. The vessel was provided with an inlet and an outlet for the argon gas cover (purity 99.9999%, 0.1 ppmv of O_2), opposite to one another in the cylinder body. An alumina crucible (φ=125 mm, H=220 mm) located inside and at the bottom of the vessel was used as a container for the liquid Pb-Li. The crucible prevented the contact between the liquid metal and the cylinder steel wall and so avoided the contamination of Pb-17Li with metallic elements not directly coming from the corrosion of the samples. The flange lid of the vessel was equipped with holes and fittings for the insertion of the components required for the test execution: three specimen-holder bars, a thermocouple for the continuous monitoring of the liquid metal temperature, one connection for the vacuum system (pump) and another one for the Pb-17Li ingress from the melting tank into the alumina crucible. The temperature was monitored by means of a PC software.

Before its use, Pb-17Li melted at 239.9±1.4°C (the nominal melting temperature of the Pb-17Li eutectic alloy is 235 °C).

The Pb-17Li (about 12 Kg) was loaded into the steel vessel from the molten state using a melting tank operating in slight argon overpressure. The outlet section of the melting tank was then connected to the flange lid for the purpose. A filter placed in the outlet section of the melting tank allowed to catch oxides or slag contained in the Pb-17Li ingot pieces, preventing their ingress into the vessel. During the melting in the melting tank, the steel vessel was purified by the atmospheric oxygen by means of a vacuum pump. The following procedure for the load of the Pb-17Li into the vessel was carried out:

1. Vacuum at 130°C for 2 days both in the melting tank and steel vessel;
2. Pb-17Li melting in the melting tank in slight argon overpressure;
3. Pb-17Li load from melting tank to the steel vessel;
4. Heating up to 550°C and samples dipping into Pb-17Li under argon overpressure (0.8 bar).

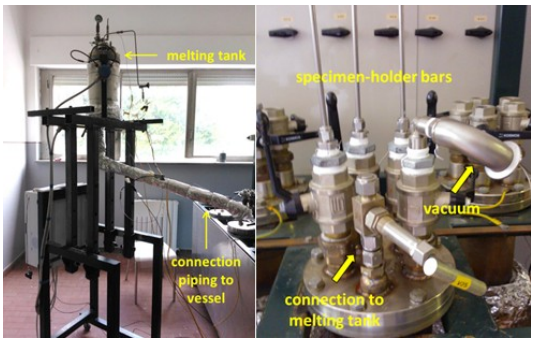

Fig. 1. Experimental set-up of the corrosion test showing the melting tank for the purification of the Pb-Li (left) and the steel vessel for the exposure test (right).

2.2 Materials and methods

Six samples of bare and coated EUROFER (80x8x3mm plates) [2, 6], were exposed in Pb-17Li at 550 ºC for 1000 hours in the experimental steel vessel described in the previous paragraph. Three of the six samples were coated with Al_2O_3 [7]. The thickness of

Al_2O_3 layer deposited on EUROFER was about 1 µm, as illustrated, figure 2.

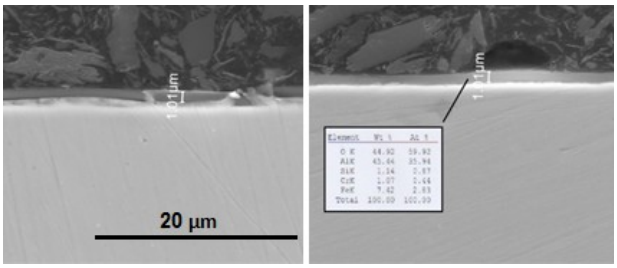

Fig. 2. Cross-section at SEM of a PLD-Al_2O_3 coated EUROFER plates, with indication of the thickness (about 1µm) (left) and the composition wt. % (obtained by EDX) of the coating (right).

After testing, both samples, bare and coated, were washed in an ethanol solution of CH_3COOH, H_2O_2 and deionized H_2O in a 1:1:3 ratio to remove the corrosion layer and observe the EUROFER naked surface.

Metallographic studies on the polished surfaces were performed in the cross-section for all samples by SEM (Zeiss Auriga Compact) configured with a thermal Schottky field emission electron column (0.1 – 30 kV acceleration voltage and 4 pA – 100 nA electron probe current and 0.9 nm resolution at 30 kV). Elemental analysis of the surfaces through line-scan and mapping were performed by EDX (Bruker Nano, XFlash Detector 5010, 127 eV).

Light ions (as lithium) were analyzed by SIMS (HYDEN Analytical). The facility includes a Hiden's MAXIM quadrupole mass analyzer (1 – 510 amu, 5 % resolution), a Hiden IG-20 O2 or Ar gas primary ion gun (ions are accelerated up to 5 keV). SIMS analyses were carried out using a current up to 500 nA after confirming that it enough to get through the corrosion layer and reach the base material.

3. Results

3.1 Characterization of the EUROFER surface after testing

Representative SEM images of the surfaces are shown in figure 3. At left, it can be seen that bare sample surface seems damaged by the liquid metal. On the contrary (right), alumina coating protects the steel surface remaining insignificant the corrosion process.

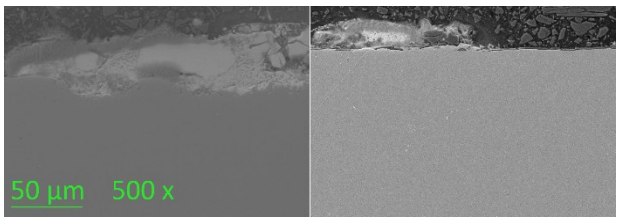

Fig. 3. SEM image of bare (left) and alumina coated (right) EUROFER surface after exposure in PbLi.

3.2. Results for bare samples

For bare samples, some dark areas appear in the bulk of the steel, figure 4 (left). The EDX mapping shows that such zones correspond to Cr disintegrations, figure 4 (right). These disintegrations appear all around the PbLi immersed zone. Two strips are recognized. The first, next to the sample edge, where disintegrations are very popular and reach, has a depth of around 35 µm, the second one, immediately after, is more than 20 µm depth. The total damage depth is estimated around 55 µm.

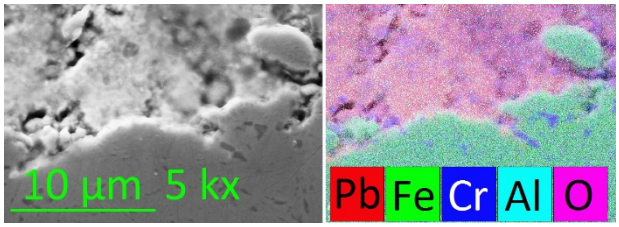

Fig. 4. SEM image (left) and mapping EDX analysis (right) of a corroded bare sample.

The EDX line-scan analysis shows how Li and Pb follow the same pattern figure 6, (up). From figure 6 (down), it can be observed that Pb, and therefore also Li, goes into the steel progressively. In this case, the Pb-17Li-steel interphase takes around 1 µm depth.

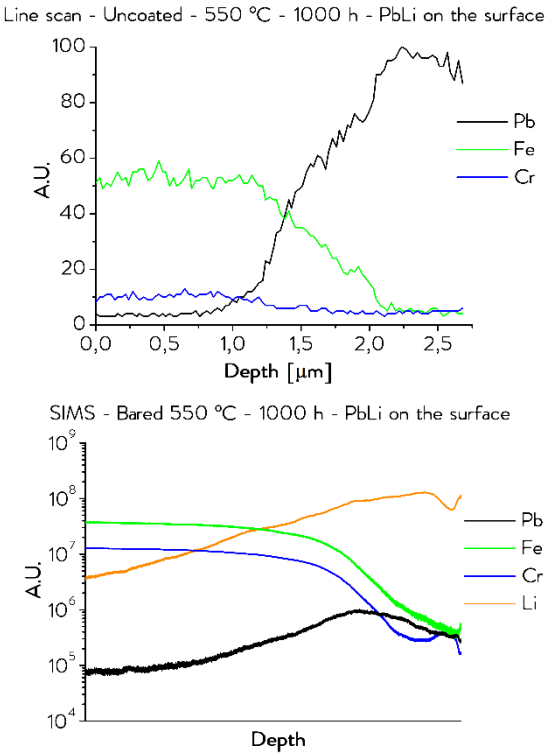

Fig. 6. Line-scan EDX analysis (left) and SIMS analysis (right) of bare sample.

3.3. Results for coated samples

Coating cracks have been detected all around the sample, even on the as-coated samples, figure 2, and on not PbLi immersed zones, figure 7.

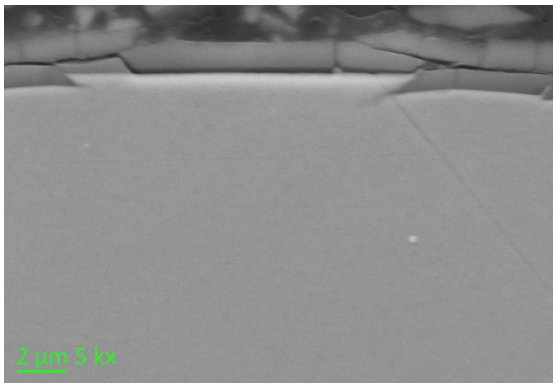

Fig. 7. SEM image of coated sample cross section.

Mapping EDX image of the coated sample on a Pb-17Li immersed zone is shown in figure 8. No evident signs of corrosion appear, despite original cracks, it has been protected.

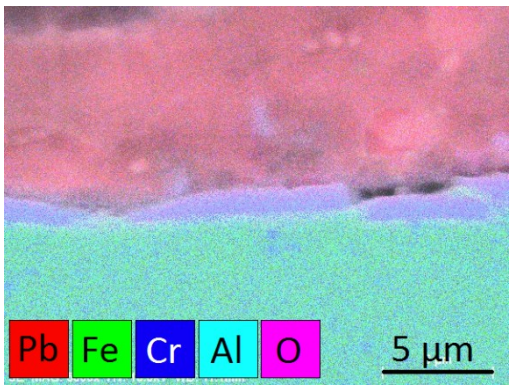

Fig. 8. Mapping EDX analysis of a coated sample on a PbLi immersed zone.

To evaluate corrosion effects in the sample, several line scan analysis all around the specimens have been performed, figure 9 (up). The results are reproducible all around the specimens. The zone of the analysis corresponds to the same one shown in figure 8, i.e. a Pb-17Li immersed zone of the sample. The first data on the depth axis correspond to EUROFER, in the central zone of the depth axis alumina coating is represented and at the end of the axis we can recognize Pb on the sample. As can be seen, Pb makes an interface close to the coating, but it is not able to penetrate into the steel.

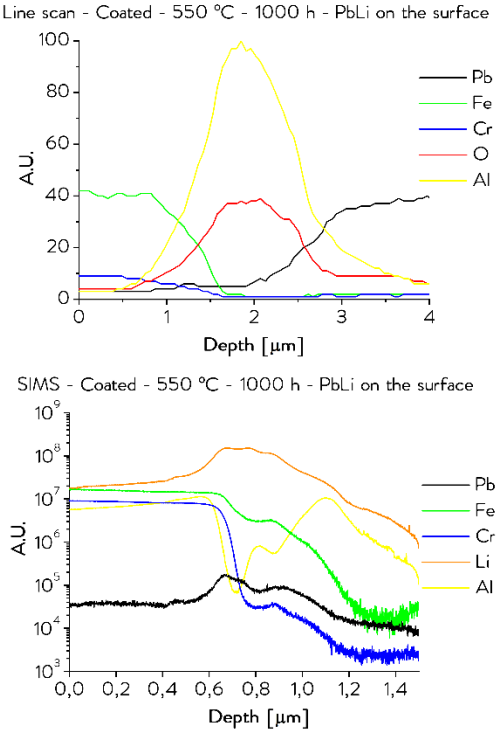

Fig. 9. Line scan EDX analysis (left) and SIMS analysis (right) through coated sample.

In order to corroborate this result, SIMS analysis have been made with the same configuration, figure 9 (right). In this case, Lithium is also detected. If we compare Li and Pb signals in figure 9 (down), both have the same behavior, what means that eutectic composition remains constant during the test.

4. Discussion

According to previous works, dissolution is the corrosion mechanism for Eurofer in Pb-Li [1-3], as well Cr depleted layer has already been seen [2]. This affected zone, identified in the literature, varies and it behavior depends on the experimental condition, in our case this layer is around 50 μm and, it is stuck to the steel, what agrees with similar experiments.

On the other hand, PLD-Al_2O_3 coatings are designed to be resistant to thermal stress since in previous tests no sign of thermal-stress damage was observed [5], hence cracks could depend on a non-correct deposition occurred casually for this batch. Further tests are needed in order to confirm this hypothesis.

For coated samples, EDX results underline the good performance of PLD coating, figure 9 (left), while SIMS results suggest that Pb-17Li is able to penetrate into the coating and achieve the steel, figure 9 (right). These contradictory results can be explained taking into account the operational set-up in each case. Line-scans EDX analysis are punctual, the analyzed zone is as wide as the electron beam, and hence crack zones are avoided while taking line-scans EDX data. By contrary, SIMS analysis are made in a 600 x 700 μm2 area, the obtained data are an average of all the material from a smaller region, 100x100 μm2, in the center of the crater, cracks can be included in this area, therefore, the Pb-17Li-steel interface detected in figure 9 (right) can correspond to a crack, a locally not protected zone, where Pb-17Li achieve the steel easily

For both cases, bared and coated samples, SIMS has revealed the same behavior for lead and lithium species through the coating and the steel in each case. This fact suggests that Pb-17Li composition keeps constant while the test.

5. Conclusions

Experimental results confirm the dissolution as corrosion mechanism for bare EUROFER in Pb-17Li. Such process includes the erosion of the surface, the formation of a wide zone with Cr disintegration and the creation of an interphase with a complex nature. Furthermore, Li penetration into EUROFER has been observed by SIMS.

By contrast, the corrosion is negligible for PLD-Al_2O_3 coated sample, even in those areas where coating was cracked. On these surfaces, it is observed that Li and Pb go through the alumina coating forming a thick interface between the coating and the steel.

According to these results, we can conclude the good performance of the PLD-alumina as anticorrosion coatings for the test conditions.

Acknowledgments

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References

[1] J. Konys et al., Corrosion behavior of EUROFER steel in flowing eutectic Pb-17Li alloy, Journal of Nuclear Materials 329-333 (2004), pp. 1379-1383

[2] G. Benamati et al., Mechanical and corrosion behavior of EUROFER 97 steel exposed to Pb-17Li, Journal of Nuclear Materials, 307-311 (2002), pp. 1391-1395

[3] J. Konys et al., Comparison of corrosion behavior of bare and hot dip coated Eurofer-steel in flowing Pb–17Li, Journal of Nuclear Materials, 367–370 (2007), pp. 1144-1149

[4] F. García Ferré et al., The mechanical properties of a nanocrystalline Al2O3/a-Al2O3 composite coating measured by nanoindentation and Brillouin spectroscopy, Acta Materialia 61 (2013) 2662–2670.

[5] F. García Ferré et al., Advanced Al2O3 coatings for high temperature operation of steels in heavy liquid metals: a preliminary study, Corrosion Science 77 (2013) 375–378

[6] R. Lindau et al., Thermal and mechanical behavior of the reduced-activation-ferritic-martensitic steel EUROFER, Fusion Eng. Des., 61-62 (2002), pp. 659-664

[7] S. Bassini, Production of Al2O3 coating developed by Pulsed Laser Deposition and Screening Tests, IDM reference, Deliverable No EFDA_D_2MFLYA (2015), Breeding Blanket project.