

THE EFFECT OF COATING ON CORROSION BEHAVIOR OF STEEL IN LIQUID LEAD-LITHIUM

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Abstract

Corrosion behavior of ferritic-martensitic steel Eurofer in stagnant liquid PbLi was studied. Eurofer is under consideration to be the structural steel for fusion reactors. The aim of this study was to describe behavior of the steel in a static liquid lead-lithium eutectic (PbLi) and improvement of corrosion resistance by application of protective coating. Radio frequency inductively-coupled plasma spray (RF-ICP) was used for deposition of the coating. The experiment was realized at 600 °C for 500 and 1000 hours, and post-test examination of surface and cross-section of the specimen was performed by Scanning Electron Microscope with Energy Dispersive Spectroscopy. Microscopical investigation identified the solution-based attack and Pb penetration into the material as the dominant corrosion damage of steel and coatings showed a promising resistance to the corrosive medium. Pb penetration zone deepened with increasing time of exposure. Evaluation of steel protected by Fe coating revealed no Pb penetration into the coating and no solution-based attack was found. Steel was protected from any kind of elemental dissolution or microstructural degradation.

Keywords: Ferritic-martensitic steel, liquid PbLi, coating, nuclear application, solution-based attack

1. INTRODUCTION

Reduced activation ferritic-martensitic (RAFM) steel such as Eurofer is one of the candidates for structural materials for PbLi-cooled breeder blanket concepts for nuclear fusion reactors [1-5]. PbLi has a potential to be used as a cooling media owing to its favorable chemical-physical characteristics, such as high thermal conductivity that can be employed for rapid and efficient heat transfer. However liquid metal-based cooling media represents very aggressive environment and corrosion resistance of structural materials need to be solved.

The applicability of conventional RAFM steels is limited by temperature below 600 °C. In future nuclear technologies increase of operating temperature is supposed. For this reason, improvement of corrosion resistance must be solved. Investigation of Eurofer compatibility to PbLi revealed a uniform corrosion attack based on dissolution of Fe and Cr from the steel and PbLi penetration into the solid structure material. The degree of the attack depends mainly on the temperature and flow rate of the liquid metal [2,4,6-11]. Konys et al. evaluated the corrosion rates at 480 °C and 550 °C and found out that the value critically increased from 90 µm/year to 700 µm/year [12]; Flament et al. presented a similar trend at 400 °C and 500 °C [3]. These values are similar to the measurements for Eurofer-97 in flowing PbLi at 550 °C presented by Konys et al. and Krauss et al. [9,10].

In molten Pb stable protective oxides can be used to slow down the diffusion process and subsequent degradation of steel. Unfortunately, this cannot be applied for PbLi environment. Decrease of surface solubility and reduction of PbLi penetration can be provided by deposition of protective coating. Most of the effort on the coating development is focused on self-healing properties and decrease of solubility. For this reason Al based

coatings are under consideration [13-16]. FeAl coating offers a good resistance too, but more data and research are needed [17,18]. The alternative solution for protective coatings may be elements such as W, Mo, Fe, Al, Si and their combination. In this study we have employed radio frequency inductively-coupled plasma spray (RF-ICP) to deposit Mo and Fe coatings onto structural steel. Evaluation of corrosion resistance was performed in Pb-Li environment at 600 °C.

2. EXPERIMENTAL

2.1. Material and coatings

Low-activation ferritic steel Eurofer was used for experiments. The Eurofer steel was produced by melting and rolling to a thickness of 25 mm (Böhler-Uddeholm, heat nr. 993402). After the rolling, a normalization heat-treatment at 980 °C for 30 min and cooling in air followed by tempering at 760 °C for 90 min and cooling in air were carried out by the manufacturer. The chemical composition is listed in **Table 1**.

Table 1 Chemical composition of Eurofer [wt%]

Element	Cr	Mn	W	V	Ta	Fe
Eurofer	8.95	0.55	1.04	0.20	0.14	balance

RF-ICP was used for coatings deposition. Gas-atomized Mo powder (14-45 µm, 99.9% purity, Tekna, Canada) and water atomized Fe powder (45-90 µm, 99.8% purity, Hoganas, Sweden) were used. Morphology of powders can be seen in (**Figure 1**).

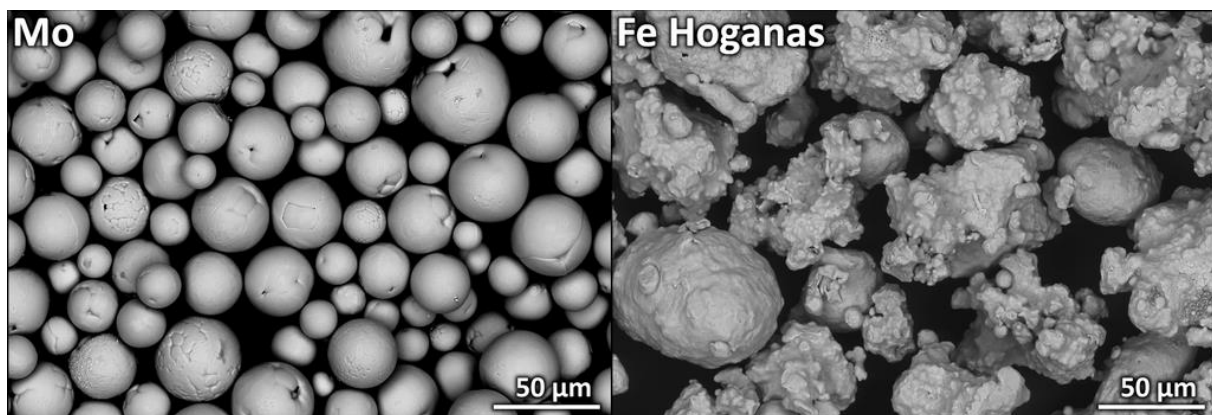


Figure 1 Morphology of feedstock powders used for deposition of coatings

The RF-ICP deposits were prepared using TekSpray 15 device (Tekna, Canada), equipped with PN-35M RF-ICP torch. The used torch power was 15 kW, and the chamber filled with protective (reduction) Ar+H₂ atmosphere was maintained at 0.103 MPa (3% atmospheric overpressure) throughout the spray duration for Fe. This pressure was reduced to 0.069 MPa for the deposition of the high-melting point Mo, to allow for an enhanced heat intake in the longer plasma jet. The stand-off distance was selected as 70 mm. Such a short distance was possible as own, in-house designed water-cooled sample holder was used.

2.2. Corrosion testing in PbLi

The facility for PbLi exposure experiments is an instrumented static tank which consists of a 4.5 l stainless-steel test chamber lined with alumina (Al₂O₃) crucible, containing approximately 13.5 kg of PbLi (16% Li, purity 99.98%). The alumina prevents a direct contact of the steel chamber wall with both the liquid metal and the test specimens. Heating elements reeled onto the chamber outer surface allow controlling the test temperature, while the thermal insulation of the whole setup minimizes potential heat losses and high temperature gradient

in the PbLi bath, see (Figure 2). A ball valve separates the air-lock and the test chamber. In the air-lock, several specimens either fixed in or hung to a movable ceramic holder are kept in an inert gas atmosphere both before and after their immersion into the liquid metal in order to avoid oxidation during heating up and cooling down.

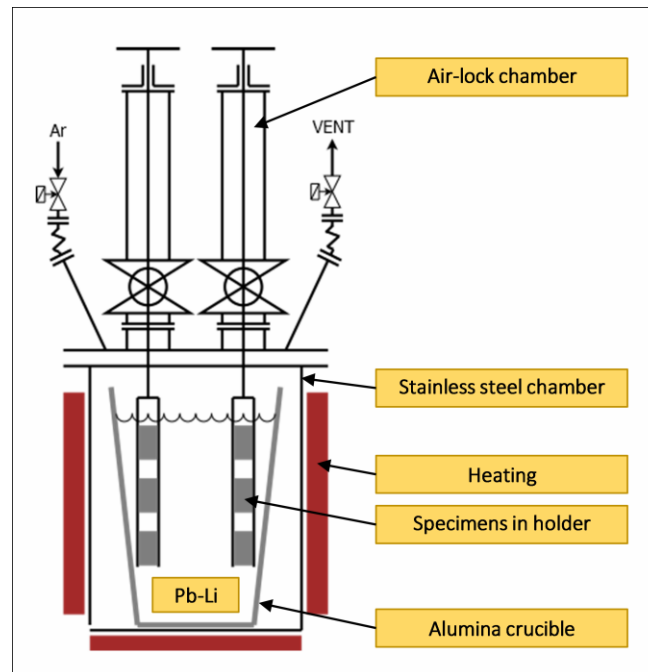


Figure 2 The experimental setup to study the corrosion of Eurofer in a static PbLi environment

Testing at static conditions used a simple immersion method. First, the PbLi alloy was heated up to 600 °C and purged using pure argon. After the melt stabilization, the holders with the fixed test specimens were immersed from the air-tight air-lock chamber into the liquid PbLi. A very low Ar gas flow (5 mL/min) was maintained in the test chamber throughout the whole exposure period to secure approximately 15 kPa overpressure to avoid outside air penetration. After the exposure, the holders were pulled back into the air-lock chamber and the setup was cooled down. The residual PbLi was left on the specimen surfaces. Two dwell times were used for all samples, 500 h and 1000 h. The extended times were used to collect information on a mid-term stability of the materials in such aggressive environment.

The samples both prior to and after the corrosion immersion were metallographically cut and polished. The cross-sections of the samples were cut about 5 mm from the specimens' longest edge, in a direction parallel to it. Lyra3 XMU field emission SEM (Tescan, Czech Republic) equipped with the energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, Abingdon, UK) was used to observe the changes in the materials, in particular those associated with penetration of Pb. BSE mode was used to help differentiate between the heavy Pb-containing regions and those free of Pb.

3. RESULTS AND DISCUSSION

Post test SEM observation of Eurofer specimen revealed solution-based attack (SBA) including Pb penetration into the material (see Figure 3). The cross-sections evaluation revealed the presence of protective Cr-rich passive layer. During the first 500 h of exposure a non-continuous dissolution of the passive layer occurred and surface with no passive layer was attacked directly. The SBA zone deepened with increasing time of exposure, with average value of 4.7 μm and 9.3 μm after 500 h and 1000 h of exposure. An EDS analysis of the Eurofer cross-section revealed the Cr-Pb zone at the surface, and an accompanying Cr-depleted zone in the base material beneath the penetrated Pb (Figure 4). The Cr depleted zone reached up to 8 μm and 15 μm

after 500 h and 1000 h of exposure, respectively. The Eurofer steel material loss was determined from the specimen thickness measurement before and after the exposure and from cross-section corrosion depth statistical evaluation (**Figure 5**). It was found that after the 500h exposure, 31.1 μm of the specimens' thickness was dissolved, while, after the 1000 h, this value grew up to 56.9 μm . Combined with the average SBA depth of 9.3 μm , the Eurofer total material loss reached 66.2 μm after 1000 h, corresponding to a rate of 580 $\mu\text{m}/\text{year}$.

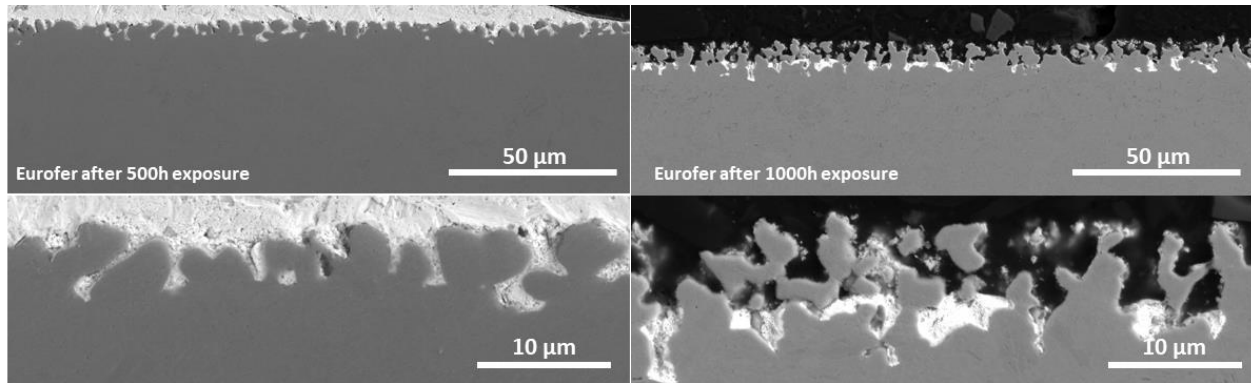


Figure 3 SEM BSE images of Eurofer steel after 500 h and 1000 h exposure

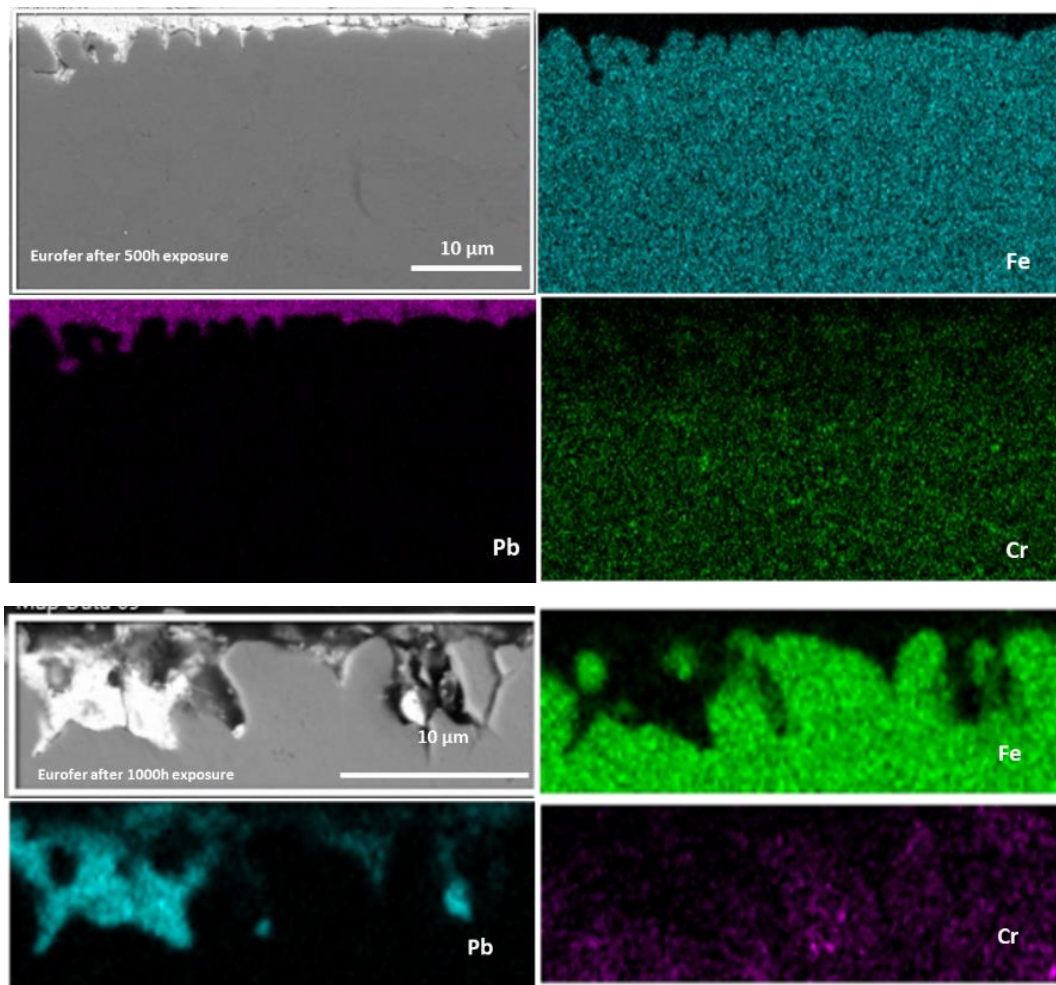


Figure 4 Near-surface EDS elemental distribution in the Eurofer steel after 500 h and 1000 h of exposure showing the Pb penetration and accompanying Fe and Cr-depletion zone beneath it

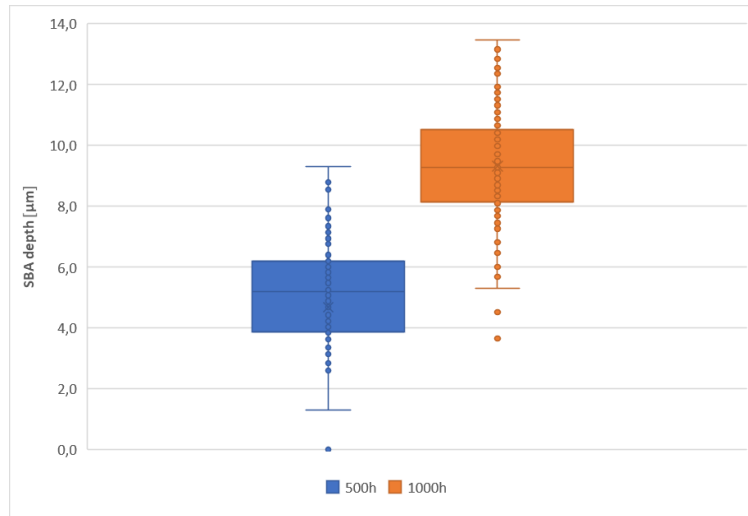


Figure 5 Statistical evaluation of SBA depth

In **(Figure 6)** as-sprayed microstructure with typical splat morphology and some non-connected porosity and inter-splat linear voids of deposited coatings can be seen. At the interface, clear regions with different Cr/Fe/Mo stoichiometry were observed, suggesting an inter-diffusion on the major elements.

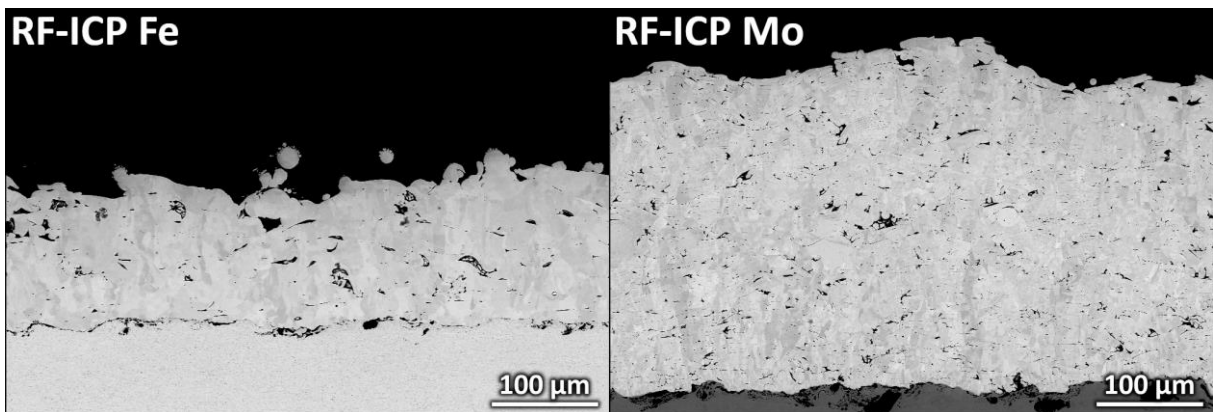


Figure 6 Microstructure of Fe and Mo coatings

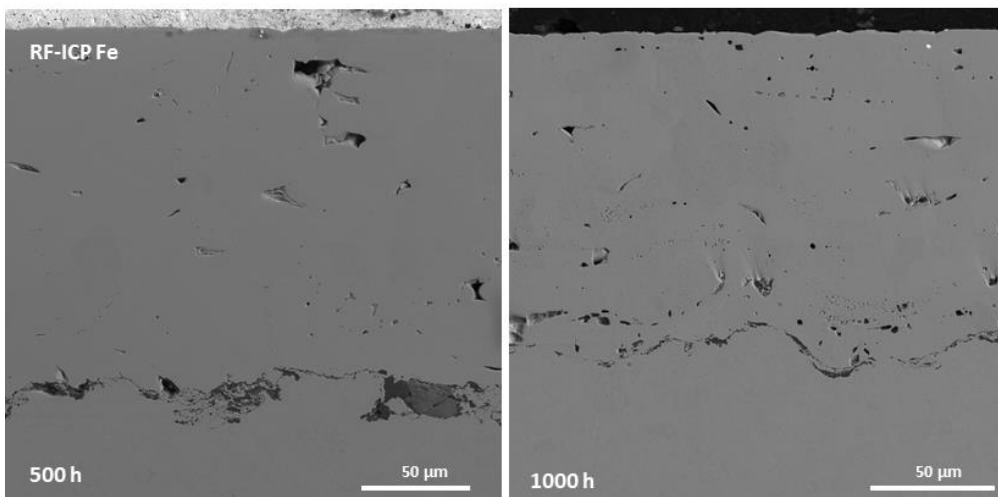


Figure 7/1 Microstructure of Fe and Mo coatings after 500 h and 1000 h exposure

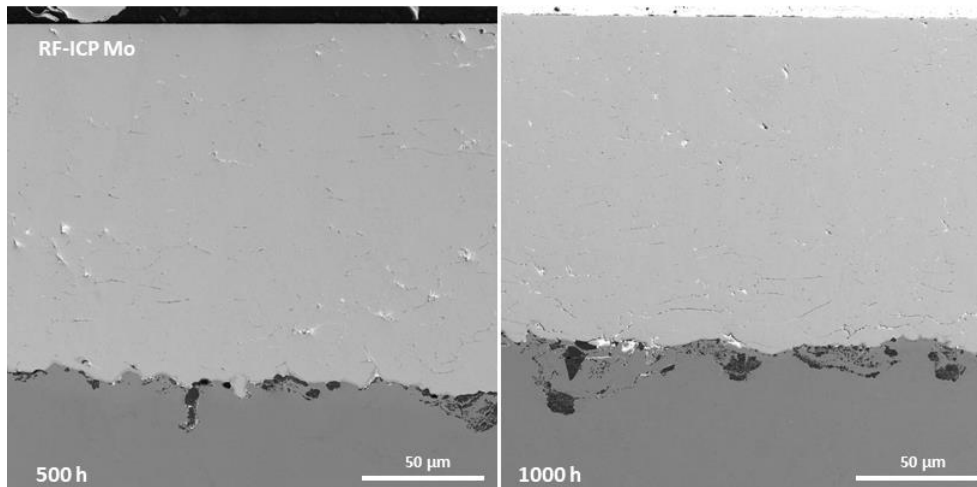


Figure 7/2 Microstructure of Fe and Mo coatings after 500 h and 1000 h exposure

The microstructure of coatings after exposure in PbLi at 600 °C can be seen in **(Figure 7)**. Most surface of the samples was covered by PbLi. Analysis of cross-sections after the exposure revealed that Fe coating prevented the attack completely and no penetration was recorded. In contrast, Mo coating was penetrated by Pb and the penetration was caused by splat-like structure of the coating. Even 500 h of exposure was enough for Pb to reach the steel substrate. Subsequent SBA of Eurofer was observed on coating/substrate interface. Statistical evaluation of cross-section enabled to define the Pb penetration depth, i.e. depth of Pb penetration into the coating related to the coating's thickness. In the **(Figure 8)** is clearly visible that Fe coating was almost intact and insoluble during the whole experiment. Mo coating was penetrated even after first 500 h of exposure up to 60 % - 100 %. At the end of 1000h exposure almost 100 % of coating was penetrated by Pb.

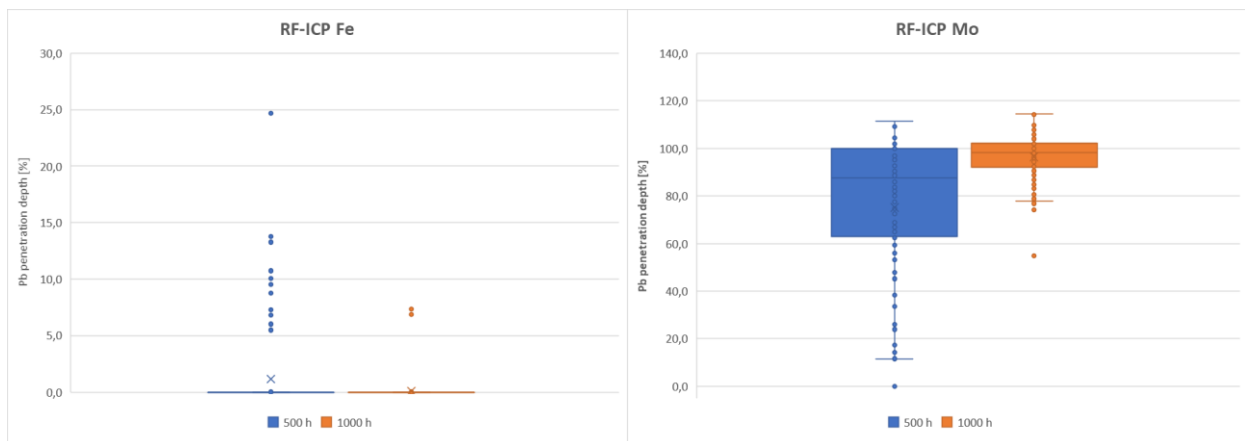


Figure 8 Statistical evaluation of Pb penetration depth

4. CONCLUSION

In our study RF-ICP coatings were deposited onto Eurofer steel to improve the resistance of material to PbLi environment. Fe and Mo coatings were deposited in sufficient thickness and without oxidation of the metals. Resistance of the system was evaluated in the PbLi environment at 600 °C. After 500 h and 1000 h of exposure, it can be concluded that:

- Application of protective coating can prevent severe dissolution of Eurofer.
- Mo coating did not prevent Pb penetration, due to the capillary effect inside the imperfectly bonded structure.

- Fe coating exhibited excellent resistance to the aggressive environment. No dissolution and only sporadic Pb penetration was observed.

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