

Thick Protective Fe and Mo Coatings for PbLi Coolant Environments Prepared by RF-ICP and Cold Spray

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ABSTRACT

Progress in developing generation IV nuclear fission reactors and fusion systems entails many challenges to overcome. One of the critical ones is related to the planned cooling systems that ensure safety and a proper functionality of the reactors. Among other cooling concepts, the use of liquid metal-based cooling media was proposed, with liquid heavy metals such as lead-lithium eutectic (PbLi) as one of the most promising candidates. This coolant type is planned to be used in, e.g., DCLL type (dual coolant lithium lead) of experimental DEMO fusion reactor, where PbLi is also considered as breeder blanket material [1]. These materials excel in thermal conductivity, which is crucial for rapid and efficient heat transfer needed in the cooling systems of the reactors. However, using such medium requires a proper protection of the structural components to prevent degradation processes such as corrosion. In PbLi, one of the solutions could be a deposition of protective, long-term stable coatings onto the component surfaces. To verify this approach, two thermal spray deposition techniques were used in our study, radio frequency inductively coupled plasma spray (RF-ICP) and cold spray (CS). Both can deposit thick coatings with good adherence and without oxidation of the materials. Owing to their favorable properties, Fe and Mo were selected for the coatings, and they were deposited onto two different steel types (Eurofer, ODS Eurofer). The coated steels were then tested in a

stagnant liquid PbLi environment at 600 °C for 500 and 1000 hours. The results suggest that these coatings are able to prevent the degradation of the structural material.

1 INTRODUCTION

In the nuclear sector, the prospective answers for rapid increasing of the energy consumption may be generation IV fission and fusion reactors. In those, a liquid metal cooling concept is foreseen, bringing many advantages over the present-day technology.

However, the use of liquid metals above their melting point represents an extremely aggressive environment toward the used structural components. Most frequently, reduced-activation ferritic-martensitic (RAFM) steels are discussed for the components, in particular Eurofer steels and its ODS variants. Despite their favorable mechanical properties, their corrosion behavior is still rather poor: the corrosion dissolution rate in, e.g., PbLi environments at 600 °C was estimated as 500 $\mu\text{m}/\text{year}$. This triggers the need to find a suitable and sufficient protection of these steels [2][3]. In Pb or PbBi environments, such protection is typically achieved by maintaining small oxygen levels in the liquid metals, triggering a formation of surface passivation layers. However, this concept cannot be used in PbLi due to the high affinity of Li to O_2 .

One of the solutions may be deposition of protective, long-term stable coatings onto the surfaces. Here, different approaches were tested to achieve the corrosion protection of the components, e.g., aluminum-based coatings prepared by pulsed laser deposition or T92 steel coated by chemical vapor deposition [4][5].

In our study, Fe and Mo were chosen for their favorable properties (mainly their low solubility in PbLi) and deposited onto Eurofer/ODS Eurofer substrates. To expand the range of the study, two thermal spray processes, RF-ICP and cold spray, were used for the deposition, both able to process the materials without oxidation. The coatings were then tested for up to 1000 h in stagnant PbLi at 600 °C. These conditions were approximated to simulate the environmental conditions planned in the coolant media in the future reactors as close as possible. In DCLL DEMO reactors, the conditions are expected to be approximately 530–550 °C and a steady-state flow of approximately 0.005–0.17 m/s. Our testing facility does not allow to test in PbLi under flowing conditions, however, the most promising results (Fe coatings) are planned to be submerged in a PbLi loop, which also simulates the flowing conditions [1].

2 EXPERIMENTAL

2.1 Powder feedstock and substrates

The requirements for an optimal powder differ for RF-ICP and CS, in particular since each method requires different particle sizes. Too big powders (above 50 μm) cannot be deposited using CS. Contrary to this, using too fine powders, which are usable for CS technology (below 20 μm) may lead to a situation where the particles are not able to accelerate enough in the RF-ICP process. The lack of the in-flight momentum then leads to improper flattening of the molten particles, resulting in a poor coating quality [6][7]. Therefore, based on the previous trials [6], different commercial Fe powders were used to deposit the coatings by each technology (Höganäs, Sweden and Nanoval, Germany, Table 1). As opposed to Fe, the plasma atomized Mo powder (Tekna, Canada, Table 1) suited the requirements of both

technologies. The morphologies of the particles are shown in Figure 1, their size distributions were measured using Mastersizer 3000 (Malvern Panalytical, UK) and are shown in Table 1.

Table 1: Properties of the used powders.

Powder	Particle size distribution (volume)			Used for method	Purity (%)
	D10 (μm)	D50 (μm)	D90 (μm)		
Fe Höganäs	52.2	78.6	121.0	RF-ICP	99.8
Fe Nanoval	9.4	18.1	36.6	CS	99.9
Mo	19.1	28.8	44.6	RF-ICP, CS	99.9

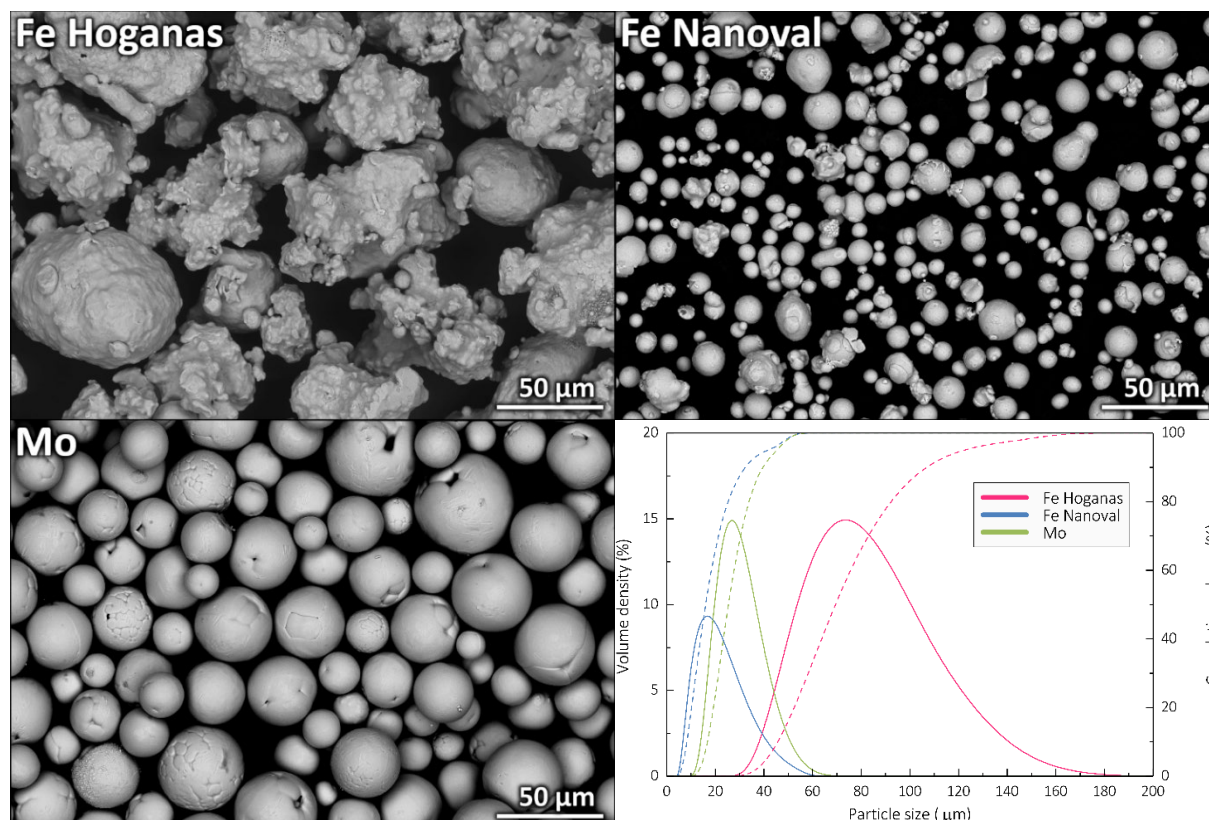


Figure 1: Morphology of the used powders and the respective particle size distributions.

All three powders were deposited onto Eurofer ($60 \times 20 \times 3 \text{ mm}^3$) and Eurofer ODS ($\text{Ø}30 \times 4 \text{ mm}$ round substrates) steels. The ODS variant was strengthened by a dispersion of 0.3 wt.% ScTiO and was prepared by spark plasma sintering process of mechanically alloyed powder. A grit blasting procedure was employed to improve adherence of the coatings through increased surface roughness. Ultrasonic cleaning in acetone was performed for the RF-ICP samples.

2.2 RF-ICP deposition

TekSpray 15 (Tekna, Canada) RF-ICP system was used for the deposition. It operates in the power range up to 15 kW. The process takes place in a controlled atmosphere (mainly Ar) chamber, which protects the metals against any detrimental oxidation during the deposition. Using a self-developed, water-cooled sample holder (Figure 2), it was possible to simultaneously spray onto up to six rectangular samples. The round ODS samples were attached to standard rectangular samples using welded screws.

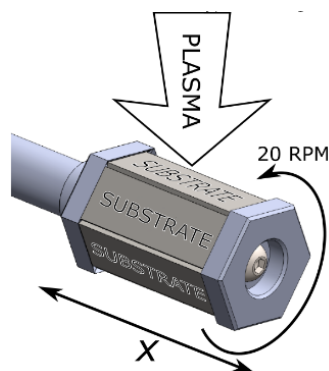


Figure 2: Self-developed water-cooled specimen holder for the RF-ICP process, allowing to deposit onto metallic substrates without their melting.

The substrates mounted to the holder revolved at the speed of 20 RPM below the plasma torch. To improve the coating adherence, substrate preheating was carried out using the plasma jet. At this stage, the holder was moved below the plasma torch at the speed of 0.5 mm/s with the powder feeding turned off. Immediately after the preheating process, the powder feeding was switched on and the spraying was done in one pass at the speed of 0.2 mm/s with the torch power of 15 kW. The substrate stand-off distance (measured from the end nozzle) was relatively short, 70 mm. Ar was used as the plasma-forming, sheath, and carrier gas. H₂ was mixed into the sheath gas and contributed to the plasma formation. For Fe, the atmosphere was maintained at 103.4 kPa (3% atmospheric over-pressure) throughout the spray duration. This pressure was reduced to 68.9 kPa for the deposition of the high-melting point Mo, to allow for an enhanced heat intake in the longer plasma jet.

In total, four combinations were tested, with the respective parameters shown in Table 2.

Table 2: Overview of RF-ICP coatings deposition parameters.

Sample	Substrate type	Used powder	Chamber pressure (kPa)	Gas flow (slpm)	
				Ar (Central, sheath, carrier, option)	H ₂ (Sheath)
RF-E-H	Eurofer	Fe Höganäs	103.4	61	3.4
RF-O-H	ODS Eurofer	Fe Höganäs	103.4	61	3.4
RF-E-M	Eurofer	Mo	68.9	61	3.4
RF-O-M	ODS Eurofer	Mo	68.9	61	3.4

2.3 CS deposition

The CS coatings for this study were produced at partner laboratories (Impact Innovations, GmbH, Germany). High-pressure ISS 5/11 system was used for the deposition. For Fe, nitrogen was used the process gas at 4 MPa pressure. Molybdenum is known to be a very demanding metal for CS deposition [8], helium was therefore used instead. The remaining deposition parameters are considered an intellectual property of the partner and cannot be shared.

2.4 PbLi testing

After the deposition, the samples were mounted into a sample holder using molybdenum wire and immersed in stagnant PbLi at the temperature of 600 °C for 500 and 1000 h. 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.

2.5 Evaluation

The cross-sections from all the samples were prepared using standard metallography methods. After the final polishing, the microstructures were evaluated before and after PbLi exposition using EVO MA 15 and Lyra 3 XMU microscopes, respectively (Carl Zeiss, Germany and Tescan, Czech Republic).

3 RESULTS AND DISCUSSION

The microstructure of the RF-ICP coatings is shown in Figure 3. The thickness of the Fe coating was around 200 μm , while for Mo it reached almost 500 μm . Both Fe and Mo coatings possessed a compact structure with well merged splats, showing only relatively low porosity and virtually no un-melted particles. Only a limited imperfections were observed at the coating-substrate interface, indicating a good mutual adherence.

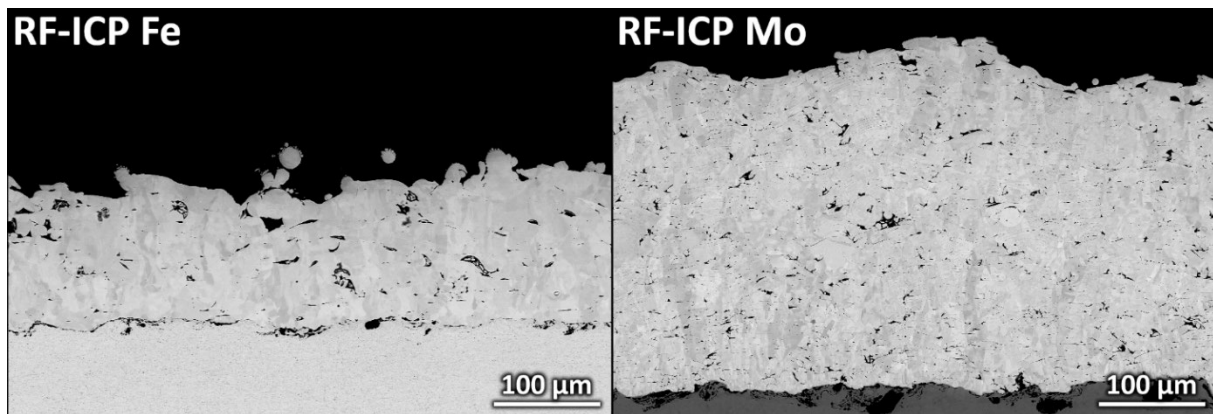


Figure 3: Microstructure of the RF-ICP coatings.

The microstructure of the CS coatings is shown in Figure 4. These coatings also showed great adherence of the splats. The Fe coating was almost 900 μm thick, and virtually pore-free. The Mo coating had the same thickness and showed a significantly increased porosity and reduced mutual interconnection of the particles in its upper part (above 300 μm thickness). This is connected to the difficulty in cold spraying of Mo (even using expensive helium as the propellant gas) and the lower number of oncoming particles that would compact the layers beneath.

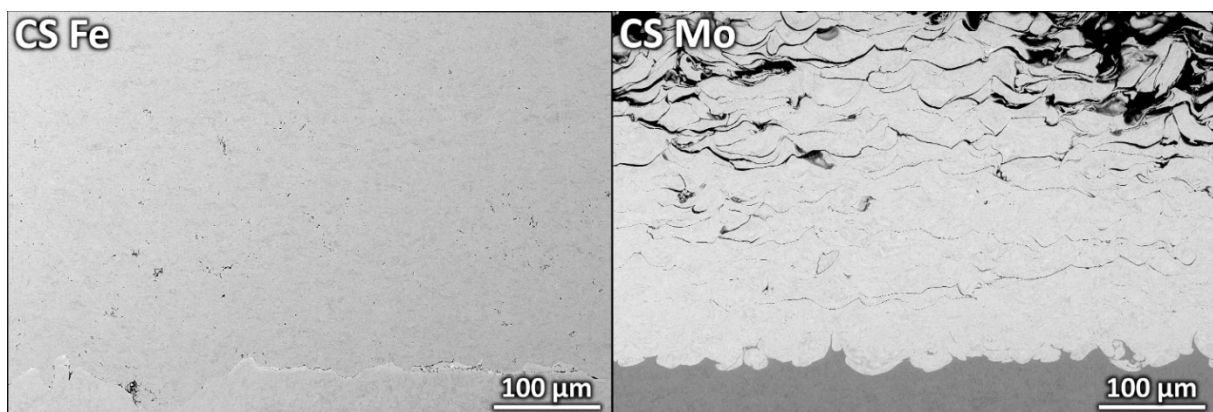


Figure 4: Microstructure of the CS coatings.

The severity of the PbLi attack is shown in Figures 5 and 6. All four coatings were able to prevent dissolution of the steels. The Mo coatings were not able to prevent PbLi penetration, mostly because of the inter-splat porosity that gave rise to a capillary effect (some of the penetration spots are highlighted by yellow circles in Figures 5 and 6). As opposed to Mo, both RF-ICP and CS Fe coatings showed almost no signs of PbLi penetration into the coating even after the 1000 h period. These are very promising results, in particular since the dissolution was also prevented and therefore it seems thermally sprayed Fe coatings have a strong potential to protect structural materials against the degradation in the severe liquid PbLi environment.

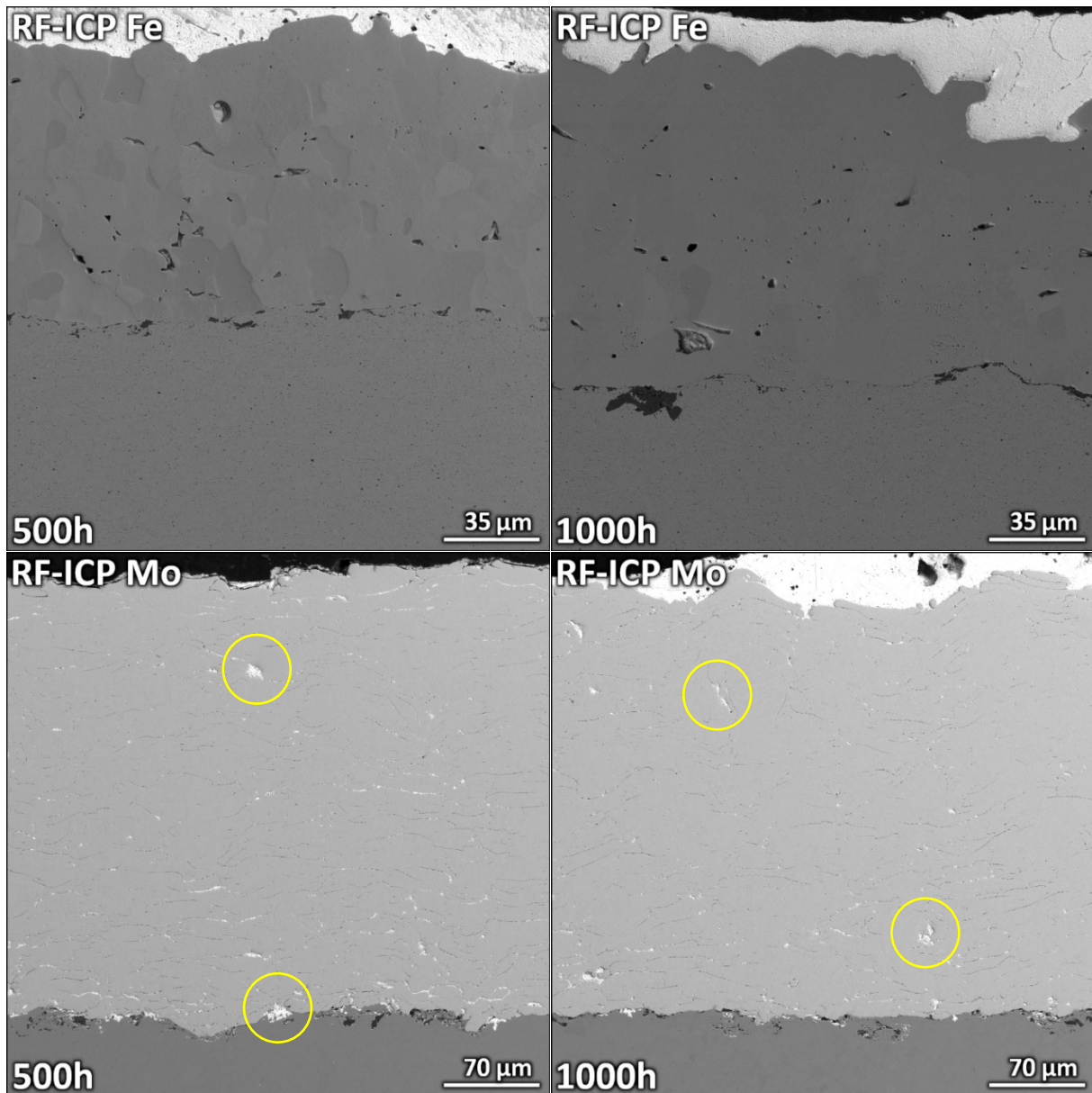


Figure 5: Microstructure of the RF-ICP coatings after the PbLi testing. Some of the PbLi penetration spots are highlighted by yellow circles.

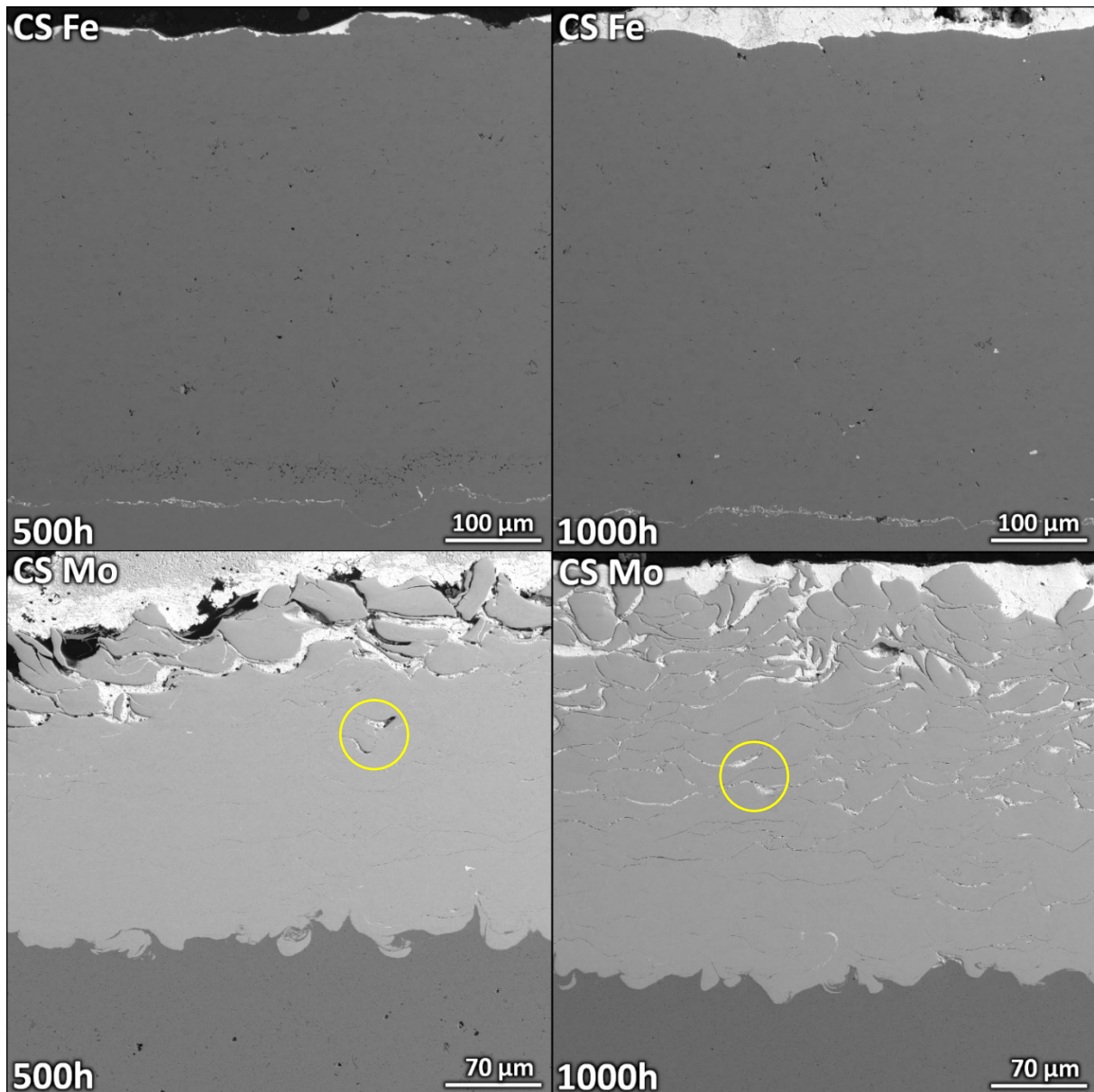


Figure 6: Microstructure of the CS coatings after the PbLi testing. Some of the PbLi penetration spots are highlighted by yellow circles.

4 CONCLUSIONS

Pure Fe and Mo coatings intended as protective barriers for liquid PbLi environment were successfully deposited onto Eurofer/ODS Eurofer substrates by two thermal spray methods, RF-ICP and CS. All coatings successfully prevented the severe dissolution of the steels, amounting to $>500 \mu\text{m}/\text{year}$ for uncoated Eurofers [2]. Both Mo coatings suffered from PbLi penetration, which happened due to capillary effect between its splats. Nevertheless, the Fe coatings shown here promising resistance against the aggressive environment without any signs of dissolution or PbLi penetration for at least 1000 h. Both RF-ICP and CS Fe coatings are therefore suitable candidates for a further study.

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