Thick protective Fe coatings for PbLi coolant environments

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ABSTRACT

The introduction of generation IV nuclear fission reactors and fusion systems foresees the potential to use liquid metal-based cooling media. Owing to their favorable chemical-physical characteristics, the most promising candidates are heavy liquid metals such as lead-lithium eutectic (PbLi). The usage of PbLi offers several advantages, such as its very high thermal conductivity that can be employed for rapid and efficient heat transfer. However, using such medium triggers the need to prevent degradation (e.g., corrosion) of the structural materials. A potential way could be deposition of protective, long-term stability coatings onto the surfaces. Radio frequency inductively-coupled plasma spray (RF-ICP) is an economical process capable of deposition of thick coatings onto large area surfaces, having a good mutual adherence. Unlike the other, air-based thermal spray methods, its controlled-atmosphere chamber further prevents oxidation, thereby allowing to deposit pure metals and alloys. In our study, we have employed RF-ICP to deposit Fe coatings onto stainless steel demonstration workpieces, manifesting suitability of the method for the task. Following the successful identification of the best-performing powder, the Fe coatings were deposited onto structural material coupons (ferritic-type 9% Cr oxide-dispersion strengthened steel) that are currently tested in the PbLi environment.

1 INTRODUCTION

One of the development directions of DEMO fusion reactor breeder blanket is a PbLi-cooled concept [1]. Unfortunately, despite many advantages, corrosion of the structural materials in the liquid metal environment remains a critical issue to be resolved. The currently considered candidate materials are the reduced-activation ferritic-martensitic steels (RAFM) such as Eurofer [2], [3]. Still, the applicability of these steels is limited to temperatures of approximately 550 °C, which can be increased to slightly over 600 °C by oxide dispersion strengthening (ODS) [4].

The evaluation of long-term (1000-11000 h) corrosion behavior of a conventional Eurofer steel and its Y_2O_3-strengthened ODS variant in a flowing PbLi (0.1 mm/s) at 550 °C showed similar homogenous attack with the corrosion rates around 200 µm/year for both materials, independent on the exposure time [5]. At an increased flowrate of the liquid metal (0.22 m/s) the corrosion rate of the conventional Eurofer doubled to about 400 µm/year at the same temperature [6]. These results suggest that the corrosion of the components during the operational conditions would be high and, needless to say, it would be vitally beneficial to decrease or even avoid the corrosion somehow.

One of the possible routes for a corrosion protection is the application of protective layers on the components surfaces. Iron oxides can form a continuous surface scale if the available oxygen content is sufficient, and also Fe itself has a rather low solubility in liquid metals. For instance, the solubility of Fe in a PbLi environment at 500 °C was only 1 ppm (cf. 10 ppm for Cr and 3000 ppm for Ni) [7]. Pure Fe layers can therefore be considered as a suitable solution for the PbLi environment. For deposition of relatively thick metal layers, thermal spray methods offer several advantages, such as rapid thickness build-up and thicknesses of up to ~10^2 µm (as opposed to, e.g., physical- or chemical-vapor deposition). In thermal spray, feedstock powders are melted and the individual particles are accelerated toward a substrate, where they spread upon the impact and solidify, forming so-called splats. Since employing a conventional atmospheric thermal spray system would lead to a detrimental oxidation of the pure metal, spraying under a controlled atmosphere or vacuum is needed. In this paper, we present first results of thick Fe coatings obtained by spraying various Fe powders using a radio frequency inductively-coupled plasma torch (RF-ICP) in a protective Ar+H_2 atmosphere. The results suggest this may indeed be a viable and economic way to achieve the corrosion protection of the structural RAFM steels for DEMO.

2 EXPERIMENTAL

The Fe deposits were prepared using TekSpray 15 device (Tekna, Canada) equipped with PN-35M RF-ICP torch. The full optimization of the spray process (of which evaluation of the influence of different starting feedstock powders is presented in this paper) was realized using commonly available stainless-steel substrates (AISI 304). Following that, Eurofer and Sc-ODS Eurofer coupons were sprayed and their testing in PbLi is currently underway (as of August 2021, the results could therefore not be included in this paper). Prior to the deposition, the cuboid-shaped 60 × 20 × 3 mm^3 substrates were grit-blasted to increase the substrate-coating adherence and cleaned in ultrasound to minimize embedded residual grit. The substrates were then mounted onto an in-house made water-cooled holder, which revolved at 20 rpm during the spray process (Figure 1). The specimens were pre-heated by a single transversal pass (direction along x-axis) of the holder under the torch at a speed at 0.5 mm/s. The Fe powder feeding was then switched on and, finally, one pass of the holder under the plasma torch was made at 0.2 mm/s.

Optimization of the spray parameters such as torch power, gases flows, or powder feedrate was realized first. Taking advantage of our previous experience with steel powders [8], the torch power for all the sprayings was 15 kW, the chamber pressure was kept at 103 kPa (a slight overpressure). The flow of argon was set to 35 slpm, 10 slpm, and 8 slpm for sheath, central, and carrier gas, respectively. The flowrate of reductive hydrogen added to the sheath gas was 3.4 slpm. The feedrate for all runs was approximately 2.5 g/min.

In this paper, we would like to present a specific part of this optimization study, focusing on the influence of the starting Fe feedstock (the choice of suitable powders, as well as the respective particle size distribution and morphology). For that, two commercially available powders (Nanoval, Germany and Höganäs, Sweden) and one non-commercial powder (denoted as Tec here) available from R&D partner were used. It turned out that the non-commercial and Höganäs Fe powders had rather broad particle size distributions (measured using Mastersizer 3000, Malvern Panalytical, UK); while the former was sieved into two fractions, the latter was sieved into three, but also its original non-sieved variant was tested. That said, the feedstock influence study was performed using seven pure Fe powders differing in average particle size and shape (Figure 1: In-house made water-cooled specimen holder that allows RF-ICP deposition of coatings onto metallic substrates. The six substrates are mounted onto the surface of a hexagonal prism, forming tiny gaps between them to prevent merging of the coatings.

Table 1, Figure 2).

The best obtained results were then applied for the final spraying on Eurofer and Sc-ODS Eurofer structural materials designated for exposition in liquid PbLi.

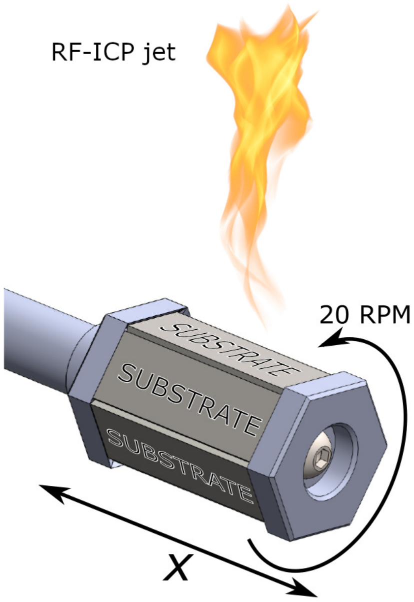

Figure 1: In-house made water-cooled specimen holder that allows RF-ICP deposition of coatings onto metallic substrates. The six substrates are mounted onto the surface of a hexagonal prism, forming tiny gaps between them to prevent merging of the coatings.

Table 1: Designation and average particle sizes of the seven Fe powders tested in this study.

Powder designation	Manufacturer	Particle size distribution (volume %, in µm)			
		Indicated	D_{10}	D_{50}	D_{90}
NAN	Nanoval	10-32	9.4	18.1	36.6
TEC-S	Tec	40-80	48.5	77.3	120.0
TEC-L	Tec	80-125	78.5	115.0	163.0
HOG	Höganäs	45-180	27.9	63.7	136.0
HOG-S	Höganäs	-45	24.4	41.6	68.0
HOG-M	Höganäs	45-90	52.2	78.6	121.0
HOG-L	Höganäs	+90	98.7	148.0	223.0

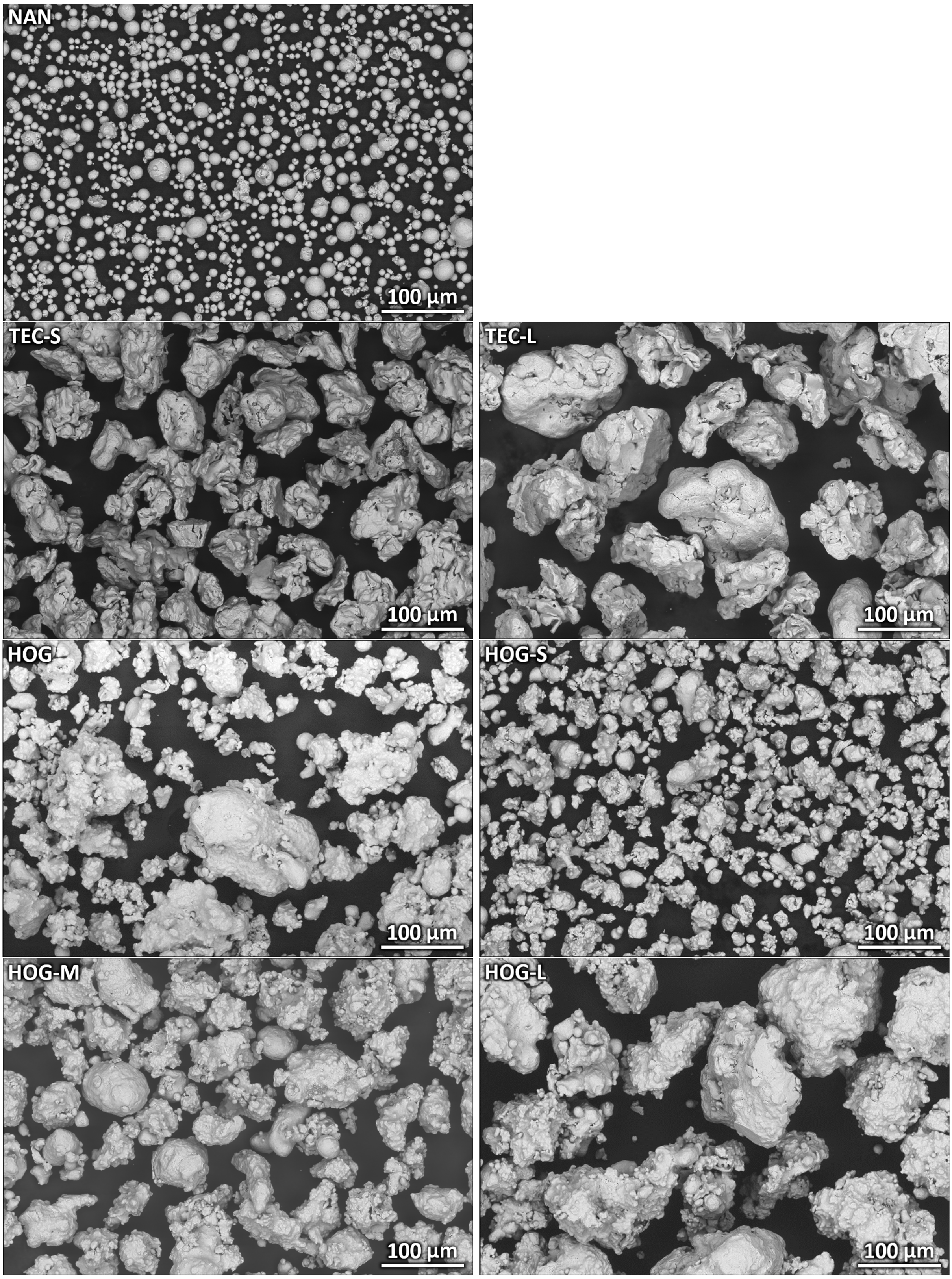

Figure 2: Morphology of the seven Fe powders tested in this study.

All prepared samples were cold-mounted under vacuum and ground using a standard metallographic procedure (Tegramin-25 automatic polishing machine, Struers, Denmark). The final polishing was done using colloidal silica. The microstructures were then evaluated using scanning electron microscope (Zeiss EVO MA 15).

3 RESULTS AND DISCUSSION

The microstructure of the seven coatings is presented in Figure 3. The powder supplied by Nanoval was water-atomized, having a regular, spherical shape. Contrary to expectations, the respective coating was not good. It consisted of poorly connected fragments of materials, with vertical voids exposing the substrate at some places. Such coating would without doubt lead to inferior protective properties. A closer investigation revealed that the flattening of splats upon their impact was not sufficient. This was probably caused by the small size of the powder particles: in a low-velocity plasma such as RF-ICP, they have obviously not acquired enough in-flight momentum to trigger a proper spreading and flattening. This phenomenon was already observed earlier for this technology (compared to the conventional thermal spray technologies) [9], [10]. At the topmost region of the coatings, structures signifying potential material boiling were observed; this too suggested the used powder was too small.

The situation significantly improved by changing the powder for a bigger one (TEC). First, the bigger fraction powder was used (80-125 µm, TEC-L). The coating structure of the bottom ~100 µm was very dense and the region contained a significant proportion of unmelted particles. Those later lead to a high porosity in the upper coating regions, again potentially detrimental for the planned application. A smaller fraction of the same powder was therefore used (40-80 µm, TEC-S). The porosity of the obtained coating was low enough and the pores were not interconnected. As much as both these facts suggested the coating could actually be used for the exposition in liquid PbLi, the two Fe TEC powders are not readily available at the market. Based on the successful results, though, we have searched for a commercially produced powder of similar properties to achieve the desired good results using a market-available solution.

The Höganäs powder exhibited morphology and sizes similar to the Fe TEC powders (45-180 µm, HOG). The distribution was very broad and, as a consequence, the coating contained (similarly to TEC-L) a certain proportion of unmelted particles, thereby giving rise to a relatively high number of big pores. Still, the results were promising and suggested the powder could be used to obtain high quality coatings, provided its thorough sieving was realized. This was done and the powder was sieved into three fractions (Table 1). Analogous to Fe TEC-L powder, the negative influence of big particles on the coating microstructure was then confirmed after spraying of the largest powder fraction (> 90 µm, HOG-L).

The best result was achieved using the middle-sized fraction of the Höganäs powder (HOG-M). The microstructure was compact and dense, with only negligible porosity (Figure 3). The interface did not contain any void chains or microcracks (aside from some residual grit particles observed in the region). The coating seemed very suitable for the task and, therefore, this fraction was used for the spraying onto the Eurofer and ODS-Eurofer steels.

Surface roughness represents a potential problem considering corrosion of any component. In the liquid PbLi tests, two different states of the coatings were therefore planned – as-sprayed (cheaper, faster, but generally more susceptible to corrosion attack) and polished (extra technological step needed, better resistance). The cross-section of the polished coatings sprayed on Eurofer (approximately 130 µm thickness) and Sc-ODS Eurofer steels (approximately 150 µm thickness) is shown in Figure 4. As of August 2021, these samples are now being tested in liquid PbLi and their corrosion resistance as well as the influence of the surface state should be available before the end of 2021.

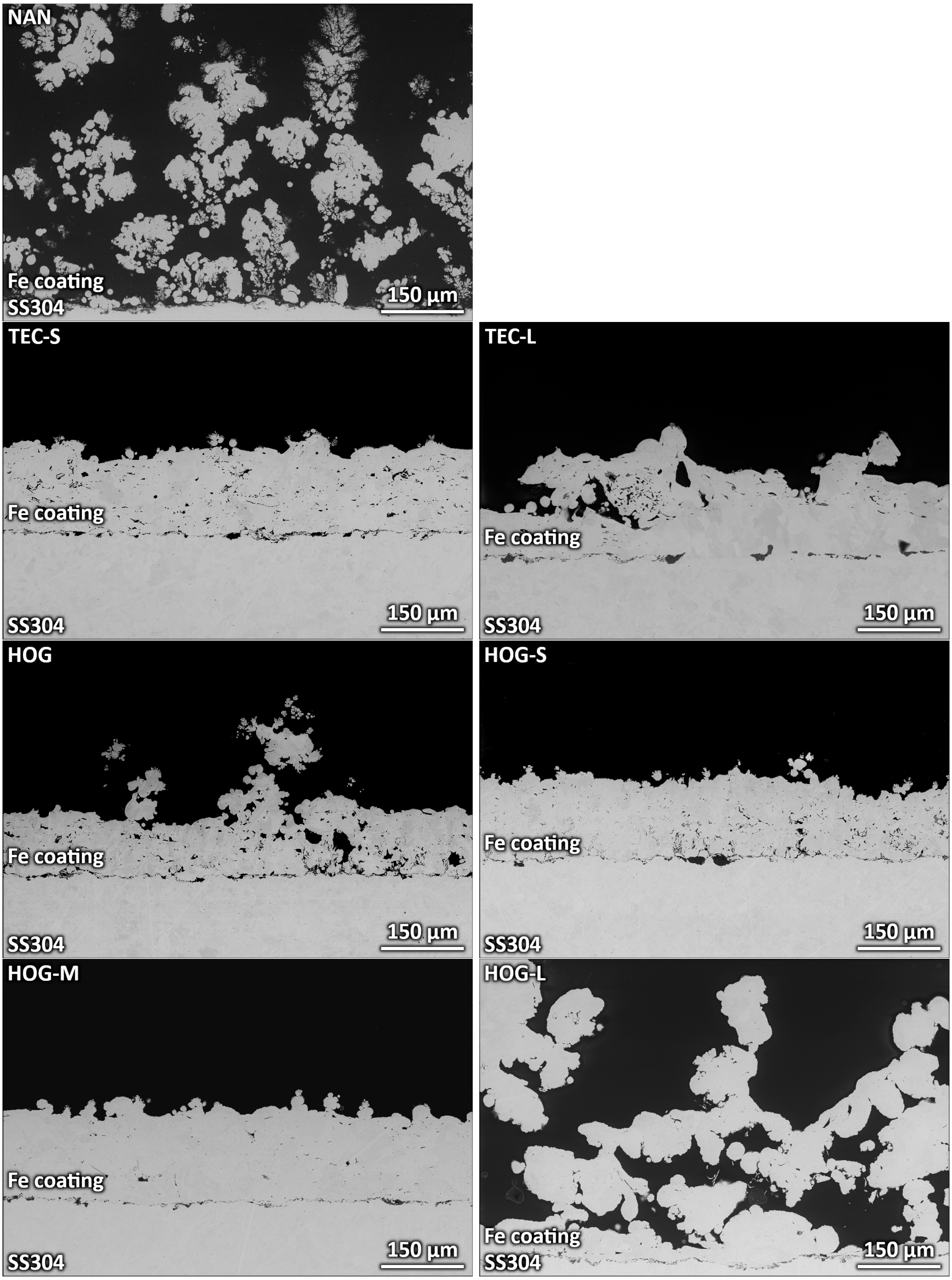

Figure 3: Microstructure of the seven Fe RF-ICP coatings sprayed from three different powders, sieved into different particle size fractions.

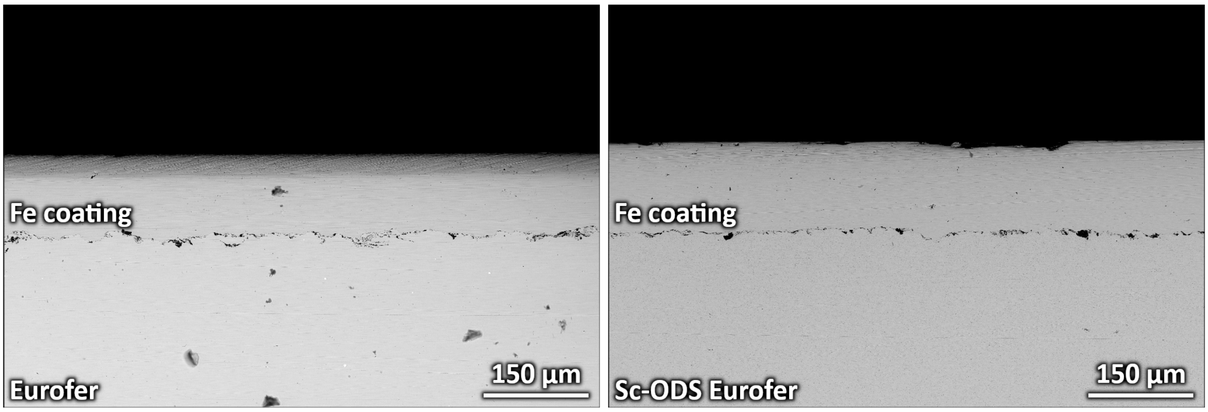

Figure 4: Microstructure of the final Fe coatings deposited onto Eurofer and Sc-ODS Eurofer steels for the liquid PbLi exposition. The as-sprayed surface roughness was removed by polishing. Please note that due to the following processing, these specimens could not be mounted into resin and were only hand-ground, resulting into inferior quality of the two cross-section images.

4 CONCLUSION

We have demonstrated that RF-ICP method can be used to deposit thick, dense, non-oxidized Fe coatings intended as protection for the liquid PbLi environment. In this paper, seven different Fe feedstock powders were deposited onto AISI 304 steel coupons and evaluation of the produced coatings microstructure helped in identifying several underlying governing factors. This included the role of morphology as well as the size distribution of the input powders.

Importantly, the best results in this study were achieved using a commercially available, reasonably priced powder. It is critical to note that the produced coupons were small (60 mm in length), but the RF-ICP technology is fully scalable and significantly bigger components can be sprayed using other torch/chamber models.

Finally, the optimized powders were used for spraying onto coupons made of structural materials that are ultimately planned for DEMO (Eurofer and ODS-Eurofer). These are now being exposed in a liquid PbLi environments and the protective abilities of the RF-ICP sprayed iron coatings will be evaluated by end of 2021.

ACKNOWLEDGMENTS

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