

EFFECT OF STEEL COMPOSITION ON ITS BEHAVIOUR IN THE LIQUID LEAD ENVIRONMENT

¹Martina PAZDEROVÁ, ¹Anna HOJNÁ, ¹Jan VÍT, ²Hynek HADRABA, ²Jan ČÍŽEK

¹Centrum výzkumu Řež, Husinec-Řež, Czech Republic, EU, martina.pazderova@cvrez.cz

²Institute of Physics of Materials, Czech Academy of Sciences, Brno, Czech Republic, EU

³Institute of Plasma Physics of the Czech Academy of Sciences, Prague, Czech Republic, EU

<https://doi.org/10.37904/metal.2023.4700>

Abstract

Ferritic-martensitic Eurofer-97 and oxide dispersion strengthened (ODS) Eurofer steels are potential candidates for structural applications in advanced nuclear reactors. Influence of scandium, yttrium, and aluminum addition was studied at 600 °C using 10-6 wt.% oxygen concentration. Microstructure and corrosion behaviour was evaluated after 500 h and 1000 h of exposure to liquid lead. Microscopical investigation identified oxidation, solution-based attack, and Pb penetration into the material. Addition of scandium and aluminum changed the mechanism of corrosion attack. Eurofer-97 was partially protected by outer oxide and inner oxidation and Pb penetration was found. In contrast ODS-Eurofer steels after 1000 h of exposure showed mainly inner oxidation and SBA including Pb penetration into the steel. The inner oxidation consisted of Pb+Cr-O and Cr-O+Al-O layers mixture. Degradation of ODS steel was significantly lower than Eurofer-97. It seems that the inner oxidation layer beneath the surface did not prevent the Pb penetration but protected the surface from dissolution.

Keywords: Ferritic-martensitic steel, ODS, liquid Pb, oxidation, nuclear application

1. INTRODUCTION

Ferritic/martensitic steels are promising structural candidates for the future fusion and fission applications. Performance of these structural materials in liquid lead is one of the main problems [1-9]. The applicability of reduced activation ferritic-martensitic steel such as Eurofer is limited by the temperature. It was found that FM steels have high corrosion rates at operating temperatures above 550 °C [2,3,8,9]. So, it is necessary to improve the properties of the FM steels. Oxide dispersion strengthened (ODS) steels are foreseen as structural materials with operating temperature up to 700 °C. Incorporation of Y-oxide nanoparticles to the microstructure decreases the loss of the carbide strengthening effect at high temperatures. As compared to conventional FM/RAFM steels, the 9-14Cr ODS steels are more resistant to corrosion in heavy liquid metals (Pb/PbBi) with a higher oxygen content ($\geq 10^{-7}$ wt.% O) owing to the formation of protective oxide scales. This is explained by their finer-grained microstructure with high intrinsic local stress and strain resulting from their manufacturing route, which strongly affect diffusion processes [10]. On the other hand, in the liquid Pb without oxygen ($\leq 10^{-14}$ wt.% O), the fine-grained structure promotes intergranular corrosion attack and inward lead penetration [10].

Higher operating temperature means worse corrosion damage. Corrosion aggressiveness of liquid metals to the steels increase significantly with increase of temperature. Therefore, the compatibility of ODS steels with lead melts at high temperatures need to be verified. The incorporation of 1 wt.% of Al into the alloy matrix was carried out to promote a formation of fine strengthening phases as well as to improve the corrosion properties in liquid metals.

2. EXPERIMENTAL

Conventional Eurofer-97 steel and two ODS Eurofer variants were used for the experiment. Chemical composition of steels can be seen in **Table 1**. The Eurofer-97 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 ODS Eurofer steels strengthened by Sc-Y and Al-Sc-Y oxides were prepared by a mechanical alloying process from the feedstock powders according to [11]. For that, a 100 g blend of powders was mechanically alloyed using a planetary ball mill (Pul- verisette P-6, Fritsch). The milling was carried out in a hardened steel vial with 25.4-mm steel balls for 24 h under vacuum. The ball-to-powder ratio was 15:1 and the revolutions of the main disc were set to 350 rpm. Cylindrical-shape pellets with dimensions of $\varnothing 30 \times 6$ mm were prepared from the alloyed powder using spark plasma technique (SPS, SPS HP D10-SD, FCT Systeme GmbH, Germany) at a sintering temperature of 1150 °C, dwell time of 5 min, pressure of 50 MPa, and heating/cooling rates of 100 °C/min. A twostep heat treatment was applied to the sintered pellets, consisting of a primary annealing at 1100 °C for 30 min and cooling in the air to room temperature and secondary heating to 750 °C for 2 h and cooling in air.

Table 1 Chemical composition of Eurofer-97 and ODS-Eurofer steels in wt. %

Element	Fe (wt%)	Cr (wt%)	Mn (wt%)	W (wt%)	V (wt%)	Ta (wt%)	Y (wt%)	Sc (wt%)	Al (wt%)
Eurofer-97	Bal	9.0	0.55	1.0	0.2	0.14	-	-	-
Sc-Y-ODS	Bal	8.9	0.72	0.9	0.2	0.13	0.16	0.28	-
Al-Sc-Y-ODS	Bal	9.2	0.55	0.8	0.2	0.13	0.1	0.2	1.0

An instrumented static tank was used for exposure experiments. The facility consists of a 4.5 l stainless-steel test chamber with inner alumina crucible which prevents the direct contact of the steel walls with the Pb during the test. A reducing Ar+H₂ (6 %) gas mixture was used as a cover gas. Oxygen sensors based on the Bi/Bi₂O₃ ref. electrode were used. Active oxygen control, i.e., maintaining the oxygen concentration in the Pb at the targeted level, was ensured by means of automatic mixing of cover gases (Ar+H₂ (6 %) with Ar+O₂ (10 %)) based on the oxygen sensor signal. 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 1**. A ball valve separates the airlock and the test chamber. In the airlock, 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 to avoid oxidation during heating up and cooling down.

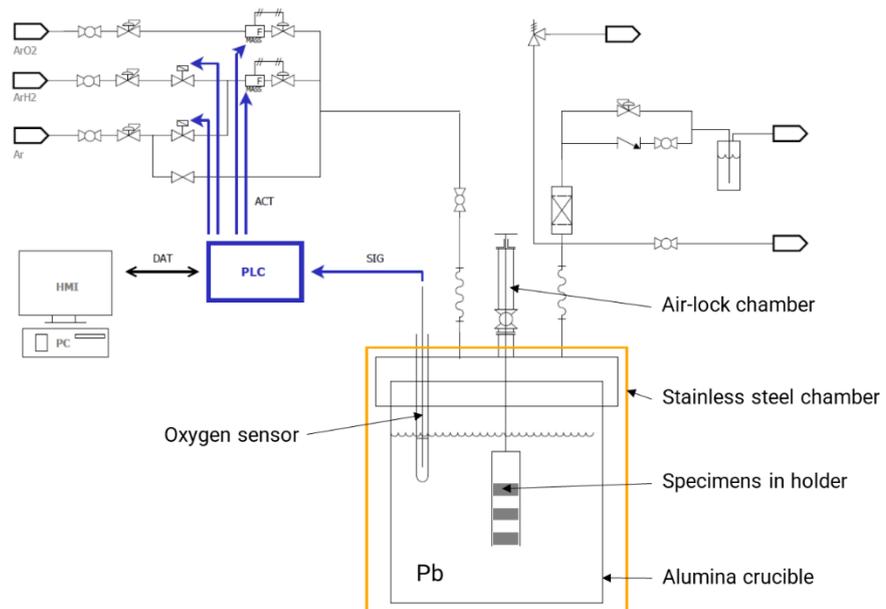


Figure 1 Scheme of experimental setup

3. RESULTS AND DISCUSSION

The corrosion mechanism of the Eurofer-97 can be defined as a combination of outer and inner oxidation, and a solution-based attack by liquid Pb. The outer oxide covered 55% of surface, which improved the resistance to the inner oxidation. The inner oxidation and solution-based attack were found particularly on the surfaces with no outer oxide (see **Figure 2**).

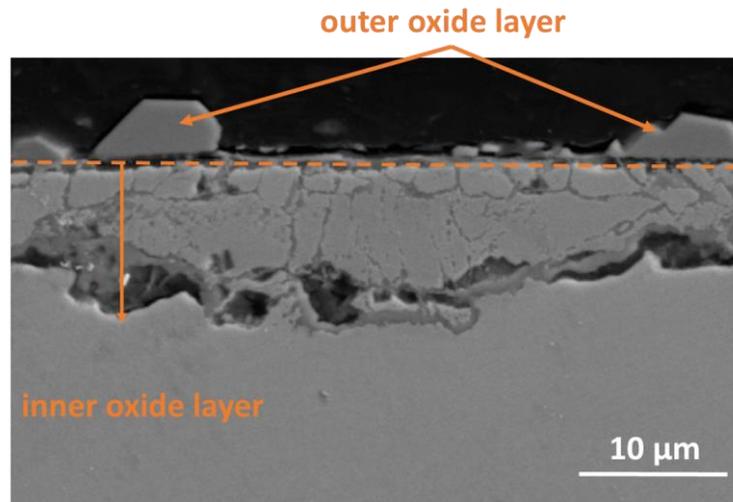


Figure 2 Cross-section of Eurofer-97 after 1000h exposure

Post-test SEM observation of Sc-Y-ODS-Eurofer steel revealed oxidation. Outer oxide layer covered 77 % of the surface with an average thickness of 0.7 μm. The inner oxidation was found on 66 % of the surface. Incorporation of Sc and Y oxides into the matrix increased the ability of Cr to form the oxide layer near the surface. This oxide layer is supposed to protect the surface against dissolution. Cross-section of Sc-Y-ODS-Eurofer after 1000h exposure can be seen in **Figure3**.

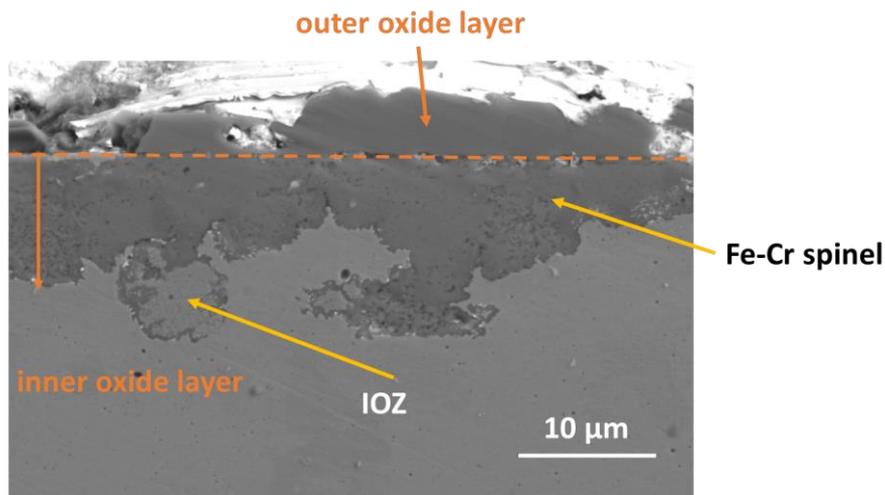


Figure 3 Cross-section of Sc-Y-ODS-Eurofer after 1000h exposure

SEM observation of the Al-Sc-Y-ODS-Eurofer after the liquid Pb exposure revealed oxidation and SBA including Pb penetration into the material. It was found that the 1×10^{-6} wt.% oxygen in the Pb is insufficient to form a compact continuous layer of protective oxide. Instead, outer oxide nodules with an average thickness of 1.1 μm were visible along approximately 40 % of the surface. The inner layer was an inhomogeneous Pb+Cr oxide layer as identified by EDS cross-section analysis. The analysis further confirmed Cr and Al diffusion to

the surface and formation of chromium and aluminum oxides layer visible near the surface (see **Figure 4**). Based on material loss measurements, it can be said that the chromium and aluminum oxides layer decreased the dissolution of the steel.

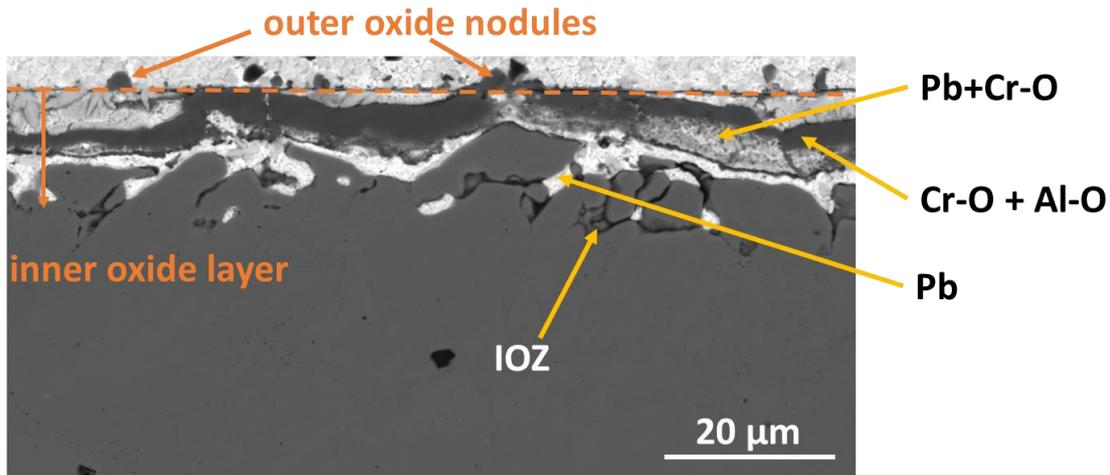


Figure 4 Cross-section of Al-Sc-Y-ODS-Eurofer after 1000h exposure

Comparison of total material loss of Eurofer-97 and ODS variants can be seen in **Figure 5**. The material loss was determined from the specimens' thickness measurement before and after the exposure and from the cross-sections' corrosion depth statistical evaluation. It was found that after the 500h exposure, 63.8 μm of the Eurofer-97 thickness was dissolved, while, after the 1000 h, this value grew up to 97.8 μm. Combined with the average corrosion depth of 4.1 μm, the Eurofer-97 total material loss reached 101.9 μm after 1000 h, corresponding to a rate of 893 μm/year. Significant decrease of metal loss values was measured for the Sc-Y-ODS-Eurofer. It was found that after the 500h exposure, 23.4 μm of the Sc-Y-ODS-Eurofer thickness was dissolved, and after the 1000 h, this value grew up to 35.4 μm. Combined with the average corrosion depth of 4.4 μm, the Sc-Y-ODS-Eurofer total material loss reached 39.8 μm after 1000 h, corresponding to a rate of 349 μm/year. The incorporation of Al into the matrix ensured a further decrease of material's loss. After the 500h exposure, 10.4 μm of the Al-Sc-Y-ODS-Eurofer thickness was dissolved, and after the 1000 h, this value grew up to 19.8 μm. Combined with the average corrosion depth of 9.2 μm, the Al-Sc-Y-ODS-Eurofer total material loss reached 29.0 μm after 1000 h, corresponding to a rate of 255 μm/year.

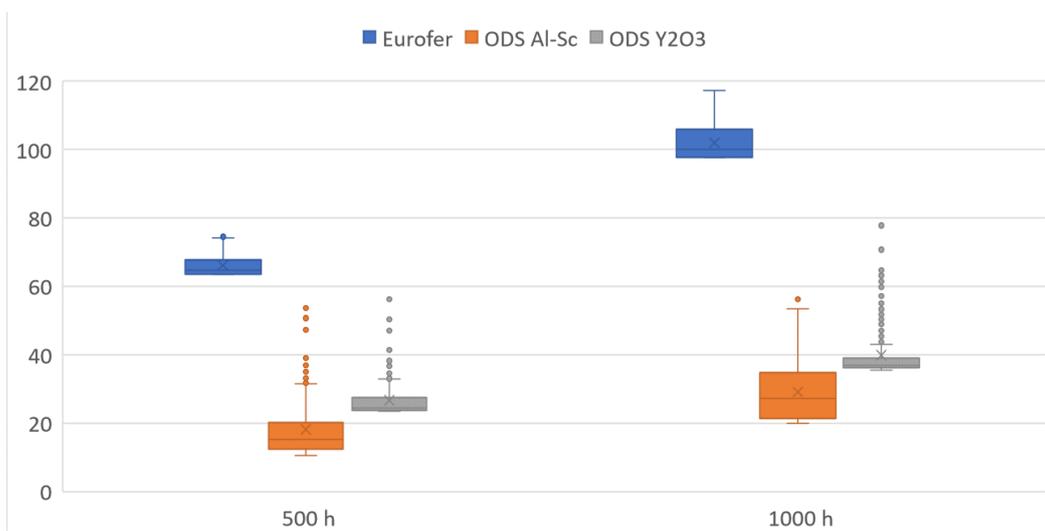


Figure 5 Statistical evaluation of total material loss

4. CONCLUSIONS

In this study the effect of mechanical alloying on Eurofer steel's corrosion resistance was evaluated. Oxide dispersion strengthened steels were exposed to Pb environment at 600 °C with 1×10^{-6} wt.% of oxygen and after 500 h and 1000 h of exposure, it can be concluded that:

- Sc-Y-ODS-Eurofer had 2.5 times lower material loss than Eurofer-97
- Al, Sc, and Y oxides addition decreased corrosion rate more than 3 times

Mechanical alloying improved the corrosion resistance of the Eurofer steel. Incorporation of higher Al content could ensure the formation of a uniform layer with better protective character.

ACKNOWLEDGEMENTS

This work was financially supported by the Czech Science Foundation project No. 20-20873S. At CVR, the presented work has been realized within Institutional Support by the Ministry of Industry and Trade of the Czech Republic.

REFERENCES

- [1] ALEMBERTI, A., SMIRNOV, V., SMITH, C.F., TAKAHASHI, M. Overview of lead-cooled fast reactor activities, *Prog. Nucl. Energy*. 2014, vol. 77, pp. 300-307.
- [2] CINOTTI, L., SMITH, C.F., SEKIMOTO, H., MANSANI, L., REALE, M., SIENICKI, J.J. Lead-cooled system design and challenges in the frame of Generation IV International Forum. *J. Nucl. Mater.* 2011, vol. 415, pp. 245-253. Available from: <https://doi.org/10.1016/j.jnucmat.2011.04.042>
- [3] FAZIO, C., BENAMATI, G., MARTINI, C., PALOMBARINI, G. Compatibility tests on steels in molten lead and lead-bismuth. *J. Nucl. Mater.* 2001, vol. 296, pp. 243-248.
- [4] KOSEK, L., ROZUMOVA, L., HOJNA, A., PAZDEROVA, M. Performance of 9Cr ferritic-martensitic steels in flowing lead for 8000 h. *J. Nucl. Mater.* 2021, vol. 554, 153092.
- [5] GLASBRENNER, H., KONYS, J., MUELLER, G., RUSANOV, A. Corrosion investigation of steels in flowing lead at 400 °C and 550 °C. *J. Nucl. Mater.* 2001, vol. 296, pp. 237-242.
- [6] ZHANG, J. A review of steel corrosion by liquid lead and lead-bismuth. *Corr. Sci.* 2009, vol. 51, pp. 1207-1227.
- [7] KURATA, Y., FUTAKAWA, M., SAITO, S. Comparison of the corrosion behavior of austenitic and ferritic/martensitic steels exposed to static liquid Pb-Bi at 450 and 550 °C. *J. Nucl. Mater.* 2005, vol. 343, pp. 333-340. Available from: <https://doi.org/10.1016/j.jnucmat.2004.07.064>
- [8] SCHROER, C., WEDEMEYER, O., NOVOTNY, J., SKRYPNIK, A., KONYS, J. Performance of 9% Cr steels in flowing lead-bismuth eutectic at 450 and 550°C, and 10^{-6} mass% dissolved oxygen. *Nucl. Eng. Des.* 2014, vol. 280, pp. 661-672.
- [9] BRIMBAL, D., BECK, L., TROEBER, O., GAGANIDZE, E., TROCELLIER, P., AKTAA, J., LINDAU, R. Microstructural characterization of Eurofer-97 and Eurofer-ODS steels before and after multi-beam ion irradiations at JANNUS Saclay facility. *J. Nucl. Mater.* 2015, vol. 465, pp. 236-244.
- [10] YELISEYEVA, O., TSISAR, V., ZHOU, Z. Corrosion behavior of Fe-14Cr-2W and Fe-9Cr-2W ODS steels in stagnant liquid Pb with different oxygen concentration at 550 and 650 °C. *J. Nucl. Mater.* 2013, vol. 442, pp. 434-443.
- [11] HUSAK, R., HADRABA, H., CHLUP, Z., HECZKO, M., KRUML, T., PUCHY, V. ODS EUROFER Steel Strengthened by Y-(Ce, Hf, La, Sc, and Zr) Complex Oxides. *Metals*. 2019, vol. 9, p. 1148.