

## The Influence of Al Content in Steels and Oxygen Concentration in Liquid LBE on the Corrosion Protection of Structural Steel Candidates for Generation IV FBRs

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### INTRODUCTION

Heavy liquid metals, such as lead and lead-bismuth eutectic (LBE), have been found to be efficient heat transport fluids in Fast breeder reactors (FBR). However, these heavy liquids are responsible for an extensive degradation of structural materials at high temperatures, through liquid metal corrosion [1], due to the high solubility of constitutive elements from structural material [2, 3]. A controlled passivation, i.e. surface oxidation of steel constituents and formation of protective oxide layers of desired properties can reduce material degradation [3, 4]. Besides that, the use of ferritic or F/M steels instead of austenitic can improve the steel resistivity towards corrosion at higher temperatures, since the solubility of Ni from austenitic materials becomes extensive above 500 °C [5, 6].

Addition of aluminum to the steel composition has shown to be beneficial in preventing corrosion attack and severe oxidation, by forming an Al-rich oxide layer. Alumina layers are transient polymorphs that gradually transform into stable alumina and provide the effective diffusion barrier to Fe, Cr, Pb and Bi [7]. 4-7 wt% of Al in addition to 12.5-17 wt% Cr are found to be sufficient to form an alumina layer in ferritic Fe-Cr-Al alloys at 400-750 °C, while lower Al concentrations (as well as higher Al if there is  $\leq 10$  wt% Cr) lead to the formation of Fe-based spinel-type oxides in LBE [7]. Fe-Cr-Al alloys display a so-called third element effect, where Cr (having an intermediate oxygen affinity, between those of Fe and of Al) is supposed to induce a transition between the internal and external oxidation of Al on ternary alloys under lower Al levels than for binary Fe-Al alloys [8].

By now, numerous experimental techniques have been used to investigate/reveal the structure of these oxide layers grown on Fe-based alloys. However, not enough has been done to reveal the influence of oxygen concentration in LBE and Al content in steel onto the formation of specific oxide structures on Al-doped ferritic steels exposed to LBE. In this study, a combined effect of oxygen in LBE and aluminum in steels onto the formation of specific oxides on two Fe-Cr-Al alloys at 800 °C were analyzed and compared.

### Experimental procedure

Two ferritic Fe-Cr-Al alloys have been selected for testing in LBE, both provided by Sandvik (Kanthal): Alkrothal720 (ALK) and APM (an advanced powder-

metallurgical, dispersion-strengthened Fe-Cr-Al steel), having a major difference in aluminum and chromium content (and minor differences in manganese and titanium content), as represented in Table 1. The goal was to compare the oxide layers formed on lower-Al/lower-Cr alloy (ALK) with those formed on higher-Al/higher-Cr alloy (APM), at two concentrations of oxygen dissolved in LBE. Samples have been exposed to LBE in the two separate tests of the same duration (216 h) and same temperature (800 °C), but containing different amounts of oxygen dissolved in LBE ( $5 \cdot 10^{-6}$  and  $1 \cdot 10^{-6}$  wt%). Each Kanthal sample has been cut into 4 mm  $\times$  50 mm  $\times$  1 mm specimen, placed into alumina-crucible filled with liquid non-flowing  $\text{Pb}_{44.5}\text{Bi}_{55.5}$  and exposed to corrosion conditions for 216 h, in a custom-built setup with precise environmental control. The oxygen content was measured using commercially available oxygen sensors, typically used for measuring oxygen in exhaust gas and smoke stacks. The details about the corrosion test setup and oxygen monitoring have been reported elsewhere [9].

After testing, each sample was removed from still liquid LBE while the test system was cooling down to the room temperature, mounted in epoxy resin serving as a holder, then cut into cross-sections. Cross-sectioned samples in epoxy holder have been polished at first up to 1200 grit by SiC paper, then by 1.0  $\mu\text{m}$  and 0.3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  suspension for final polishing steps. Samples were cleaned in an ultrasonic bath at first with ethanol, then with acetone, and sent for analyses. The samples' surface has been analyzed by Scanning electron microscopy (SEM), Raman spectrometry and Transmission electron microscopy (TEM).

TABLE I. Composition of the two alloys used in the study

| Sample | Cr    | Al  | Mn   | Si   | Ti   | C     | Fe   |
|--------|-------|-----|------|------|------|-------|------|
| ALK    | 12-14 | 4.0 | <0.7 | <0.7 | 0.25 | <0.08 | bal. |
| APM    | 20-23 | 5.8 | <0.4 | <0.7 | -    | <0.08 | bal. |

### RESULTS

Al-oxide has been found in both samples (ALK and APM) at both oxygen concentrations ( $5 \cdot 10^{-6}$  and  $1 \cdot 10^{-6}$  wt%) used in tests. The differences have been found in the abundance and distribution of the other oxides, seemingly depending on the Al-content or Al : Cr (wt%) ratio in the tested samples. At ALK from  $5 \cdot 10^{-6}$  wt%O test, two oxide layers have been found: inner and outer, with the outer one being subdivided into three sub-layers. EDS, TEM and Raman data showed that the inner layer consists dominantly of Al-oxide, while the outer one is a mixture of dominantly

Fe-oxides and Al-oxide (Fig. 1). Although Al was expected to diffuse and oxidize faster than Fe (also accounting the fact that there is much more Fe than Al in ALK, via the values of  $a_{Al}$  and  $a_{Fe}$  that were used in the calculation of  $\Delta G^0$ ), Fe is more available for oxidation (in a *geometric* sense) than Al: ALK contains  $\geq 10$  Fe atoms per 1 Al atom, Fe is  $\sim 500\times$  more soluble in LBE at 800 °C than Al [3], and LBE is a source of oxygen that oxidizes both Fe and Al. Therefore, Fe oxidizes first as it preferentially dissolves into the LBE next to the steel surface and encounters the oxygen first. The initially formed Fe-oxide layer then reduces the speed of Fe dissolution and of O diffusion, so that the higher diffusion rate of Al than of Fe in the bulk, along with the thermodynamics that favors Al-oxidation over Fe-oxidation, enables the formation of an inner Al-oxide below the initial (outer) layer.

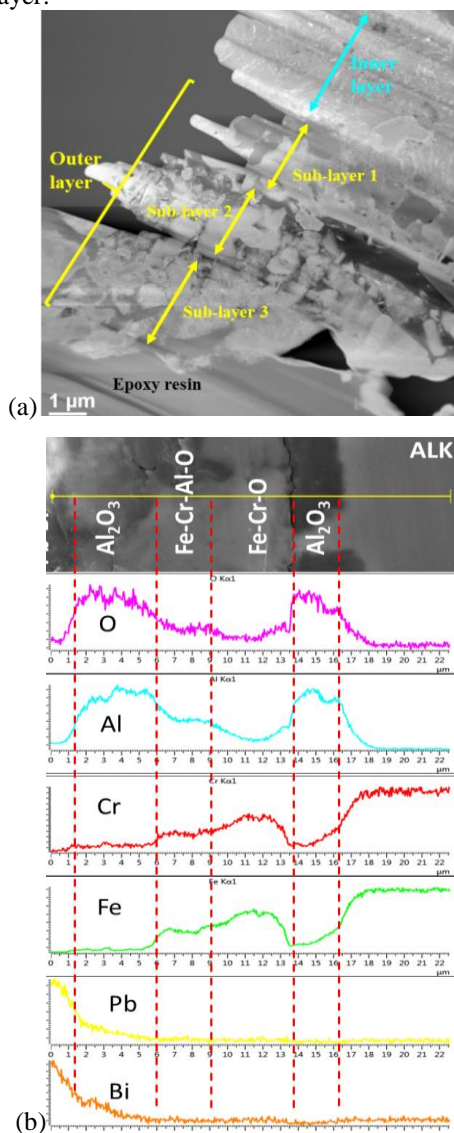


Fig. 1. (a) Morphological appearance (HAADF TEM) and (b) EDX scan of the oxide scale formed on ALK steel in LBE at 800 °C with  $5\times 10^{-6}$  wt% O.

In ALK from the test at 800 °C/ $1\cdot 10^{-6}$  wt%O in LBE, mostly Al-oxide has been detected, usually as a mono-layer, with some Cr-oxide and Fe-oxides present outwards, as the outer oxide layers in ALK (Fig. 2). Reducing the oxygen concentration while keeping Al content and temperature same leads to a decrease in the number of oxide species in the layers, particularly in the outer one. The outer layer consists of mostly FeAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>, while inner is almost only Al<sub>2</sub>O<sub>3</sub> (Fig. 2). Since oxygen is the fastest diffusing species among the six relevant (O, Fe, Cr, Al, Pb and Bi) both through Fe bulk [10] and through the relevant oxides (Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe-spinels) [11], in case of a higher oxygen concentration ( $5\cdot 10^{-6}$  wt% O), kinetics is the governing factor, and oxidation occurs first at the more abundant elements (Fe, Cr). Iron is oxidized to Fe<sub>3</sub>O<sub>4</sub>, then even further to Fe<sub>2</sub>O<sub>3</sub> next to the LBE, and there is Cr<sub>2</sub>O<sub>3</sub> both in the inner and in the outer layer (also a detectable amount of TiO<sub>2</sub> is in both layers, and Mn-oxide in outer). Due to the faster diffusion of Al than of Fe and Cr through the steel matrix, a lot of Al is secondarily oxidized, forming the inner Al-oxide layer (mixed with some Cr- and Ti-oxides). However, in five times lower oxygen concentration ( $1\cdot 10^{-6}$  wt% O), thermodynamics dominates: oxides containing Al are dominantly formed (Al<sub>2</sub>O<sub>3</sub> and FeAl<sub>2</sub>O<sub>4</sub>), whereby Al<sub>2</sub>O<sub>3</sub> is present almost exclusively in inner layer, and still is prevalent even in the outer (while FeAl<sub>2</sub>O<sub>4</sub> is found occasionally). Al<sub>2</sub>O<sub>3</sub> is obviously more stable than the most of the relevant binary oxides (as given by Ellingham's diagram), while FeAl<sub>2</sub>O<sub>4</sub> has the standard Gibbs free energy of formation ( $\Delta G^0$ ) significantly more negative than magnetite and FeCr<sub>2</sub>O<sub>4</sub> [12]. These facts support the experimental findings of Al-oxide and Fe-spinel domination over the other oxide species under these conditions.

In case of the APM steel, having higher Al (5.8 wt%) and higher Cr content (20.5 - 23.5 wt%) than ALK, at both oxygen concentrations in LBE ( $5\times 10^{-6}$  and  $1\times 10^{-6}$  wt%), two morphological oxide structures (oxide layers) are distinguishable: the inner one mostly Al<sub>2</sub>O<sub>3</sub> with some Fe-oxide, and the outer one containing more Fe-oxides (Fig. 3).

### Conclusions

Based on the presented data we conclude the following: Oxide scale formed on ALK in 800 °C LBE containing  $5\times 10^{-6}$  wt% O is a complex structure. The inner oxide layer is a dense and compact, adherent to the bulk steel and consists mainly of Al<sub>2</sub>O<sub>3</sub>, with no Fe-oxides and no Pb/Bi penetration in it. The outer oxide layer is more heterogeneous and consists of several oxides (mainly Fe-oxides), which are differentiated into three sub-layers based on the chemical structure. A slight lowering of the oxygen content to  $1\times 10^{-6}$  wt% in LBE results in reduction of the diversity of oxides in the two layers formed on ALK: the outer one consists mostly of Fe-spinel and Al-oxide, while the inner is almost only Al-oxide. Higher Al content in case of APM alloy (5.8 wt%) leads to only one layer formed,

consisting of mostly  $\text{Al}_2\text{O}_3$  and some areas of  $\text{FeCr}_2\text{O}_4$  and  $\text{Cr}_2\text{O}_3$  immersed in the Al-oxide matrix.

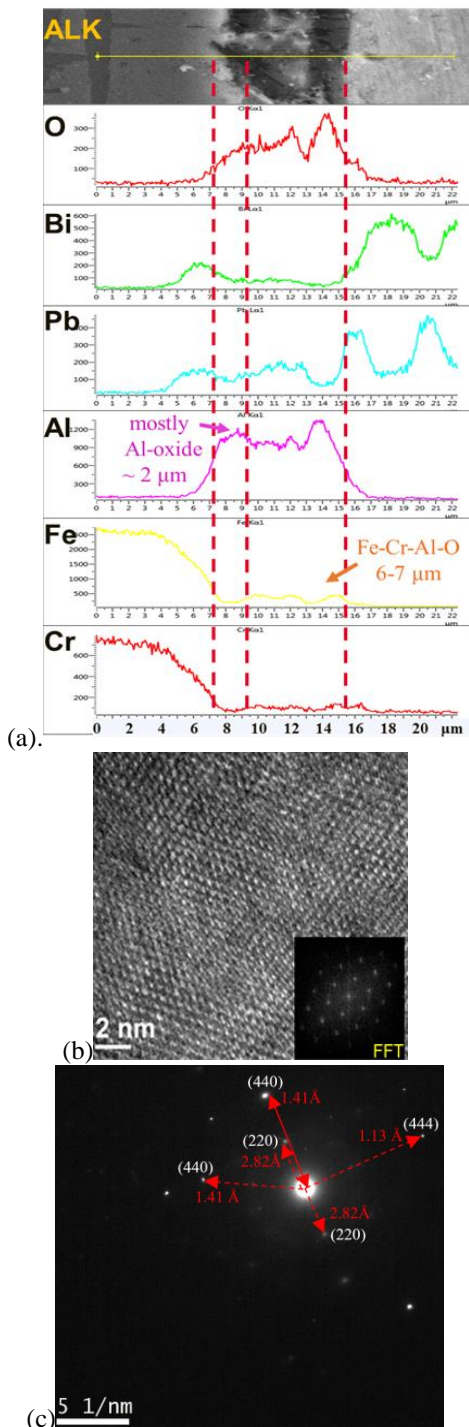


Fig. 2. An analysis of the oxide scale formed on ALK steel in 800 °C LBE with  $1 \times 10^{-6}$  wt% O: (a) EDS scan shows two layers, the inner one mostly Al-oxide, and a complex outer one containing Fe, Cr and Al oxides; (b) Fe-spinel structure in the outer layer revealed by HR TEM; (c) e-diffraction patterns from the inner layer, corresponding to diamond-cubic and monoclinic  $\text{Al}_2\text{O}_3$ .

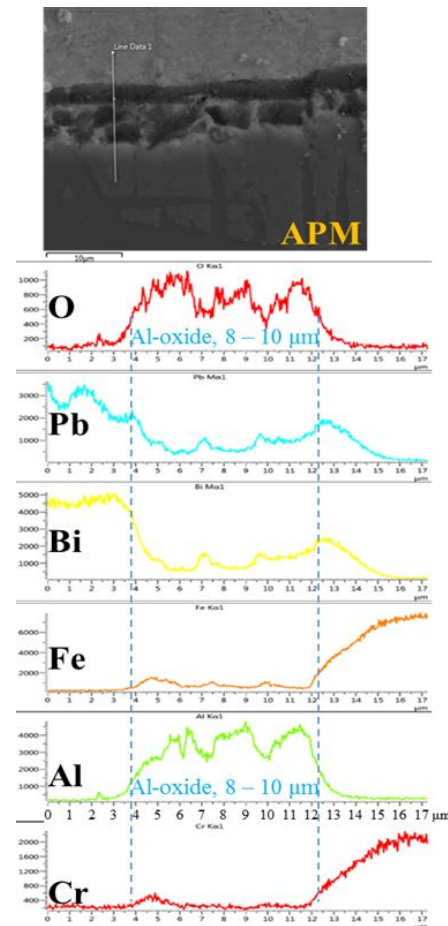


Fig. 3. APM steel from LBE test at 800 °C for 216 h in  $1 \times 10^{-6}$  wt% oxygen: dominantly Al-oxide formation; doubled-layer of Al-oxide occasionally detected.

## NOMENCLATURE

$a_{\text{Al}}$  = activity of aluminum in FeCrAl alloy (ALK or APM)

$a_{\text{Fe}}$  = activity of iron in FeCrAl alloy (ALK or APM)

$\Delta G^0$  = standard Gibbs free energy of formation

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