

Oxidative passivation of Fe–Cr–Al steels in lead-bismuth eutectic under oxygen-controlled static conditions at 700° and 800 °C

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ARTICLE INFO

Article history:

Received 9 February 2019

Received in revised form

16 May 2019

Accepted 2 June 2019

Available online 4 June 2019

ABSTRACT

Lead-bismuth eutectic (LBE) is a candidate heat transfer fluid for fast nuclear reactors and for concentrating solar power energy systems, due to its low melting point and beneficial thermophysical properties. Increasing the maximum operating temperature beyond 600 °C, can increase thermal efficiency of power conversion. However, LBE causes liquid-metal corrosion in many solids used as structural materials at high temperatures, due to increasing solubility of their constituents. A way to mitigate this issue is to establish a controlled oxidative passivation, by maintaining a desirable oxygen concentration in liquid LBE to promote formation of protective oxide scales on structural materials. In this study, the corrosion behavior of three Fe–Cr–Al alloys in LBE at 700 and 800 °C has been tested in two different oxygen concentrations. It was found that oxygen concentration of 1×10^{-6} wt% in LBE at both temperatures promotes formation of protective scales in all tested candidates. At 700 °C, these scales are more compact and well-adhered to bulk in all candidates. At 800 °C, lower-Al-containing candidates develop a thinner but adherent scale containing various oxides, while scales in higher-Al-containing candidates contain mostly Al-oxide and suffer more breaking and spalling off. However, oxygen concentration of 2×10^{-7} wt % proves to be insufficient for protective scales formation in all three Fe–Cr–Al alloys.

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1. Introduction

Liquid lead–bismuth eutectic (LBE) is one of the main candidate heat transfer fluids in the fast-neutrons nuclear reactors [1] and concentrated solar power (CSP) systems [2,3]. The advantages of using LBE in nuclear and in CSP systems are: high boiling and low melting point, competitive volumetric heat capacity, high thermal conductivity, low viscosity, low neutron capture cross section and moderation, high neutron yield (spallation), low chemical reactivity and low costs [4–7]. In addition, good gamma shielding makes LBE-cooled reactors competitive candidates in the Generation IV nuclear reactor design [8–10]. The disadvantage of using LBE is that it causes materials-related issues with steel structural materials including liquid metal embrittlement [4,11] liquid metal enhanced creep [12] and liquid metal corrosion, particularly at high temperatures [9,13–16]. The main cause of structural materials degradation is the solubility of their constituent elements, particularly

nickel above 550 °C, in the liquid LBE [7,8and17] leading to precipitation on the cold leg of a loop and dissolution at the hot leg. The improvement of corrosion resistance can be achieved by alloying the structural materials with strong oxide-forming elements [31,42]. Therefore, the combination of corrosion, long term operation and structural integrity in a wide range of operation conditions make the choice of the structural materials rather challenging at temperatures above 650 °C which are needed in order to achieve high thermal efficiency of the heat transfer system.

The strategy for corrosion mitigation is based on active oxygen control by adding an amount of oxygen to the liquid alloy coolant, while monitoring and controlling the oxygen concentration, thereby allowing the steel to form a protective oxide scale on the solid surface [18–23]. The order of oxidation of the elements from liquid and solid phase depends on temperature, oxygen concentration and chemical potential (Gibbs free energy change, ΔG) of oxidation, as given by the Ellingham diagram [4,43]. Maintaining the targeted oxygen level constant everywhere in the system is difficult and the establishment of the oxygen-depleted zones of static heavy liquid metal (LM) will result in dissolution attack, since the formation of a passivating oxide is suppressed [8]. Numerous

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studies on oxide layers formation in liquid LBE have been carried out leading to several proposed corrosion models [14–16,24–27]. The majority of the studies deal with austenitic and martensitic steels, while only limited studies are carried out in ferritic materials.

In alumina-forming steels a precise oxygen control of the liquid metal is crucial to maintain and control the oxygen content in liquid metals and to grow self-healing protective oxide layers on steel in this environment. By appropriate setting the EMF value, the formation of desired (specific) oxides can be enabled, while the formation of the others prevented. In order to maintain a stable constant oxygen concentration in the testing system, the EMF value must be maintained in a very narrow voltage range, and precisely measured.

It has been found that the oxidation kinetics in LM is different from that in air due to the fact that the LM can leach specific alloying elements and is transported quickly from the structural materials surface, leaving nanopores behind. On the other hand, the high oxygen content in the liquid metal leads to oxidation of Pb (and Bi) as well and clog formation in the loop. Therefore, there is an “oxygen window” (a window of oxygen levels), which defines the range of the optimum oxygen concentrations in the liquid metals needed for a proper operation of the heat transport system [7]. The higher boundary of the oxygen window is defined as a saturation level of oxygen in LBE (the level at which the reaction $\text{Pb}_{(\text{LBE})} + \text{O}_{(\text{LBE})} \rightarrow \text{PbO}_{(\text{solid})}$ is in equilibrium) at the cold leg temperature. The lower boundary is defined as the oxygen concentration at which the reaction $\frac{1}{4}\text{Fe}_3\text{O}_4 \rightarrow \frac{3}{4}\text{Fe} + \text{O}$ is in equilibrium at the hot leg temperature (i.e. the lowest O concentration needed for the onset of oxide scale formation at the highest temperature in the system). It has been found that the oxygen level between 1×10^{-6} and 1×10^{-8} wt% O is a good range at temperatures up to 550 °C [28,34]. At 550–750 °C with the oxygen concentrations of 1×10^{-5} – 1×10^{-6} wt%, the formation of a thin (<2 µm) alumina layer on Fe–Cr–Al steels after 1000 h of the exposure in LBE has been reported [35,36].

The scarce data on materials exposed to LBE at high temperatures triggers this research since some applications especially solar concentrating power calls for operation temperatures of 800 °C. It is known that Al-containing (i.e. Alumina forming) materials perform rather well in heavy LM environment due to the fact that aluminum allows the formation of rather protective Al-rich oxides. Aluminum addition to the steel composition has shown to be beneficial in preventing corrosion attack and severe oxidation, by forming an aluminum-oxide scale [28–31] which is found to be among the best scales preventing metal degradation. Ideally, Al_2O_3 can be formed as shown on Al-alloyed ODS alloys [38] with a high Al concentration at the surface [39,40]. Previous studies in LBE have shown that additions of 4–7 wt% Al to Fe–Cr steel at temperatures 500–750 °C is beneficial in preventing corrosion by forming an Al-oxide scale [31,34,35], whereby even a thin but continuous and adherent Al_2O_3 layer provides a diffusion barrier to heavy metal atoms [31,34].

In this study, three Fe–Cr–Al steels (Alkrothal 720, APM and APMT) have been exposed to LBE at 700° and 800 °C at the two different oxygen concentrations, and analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

2. Materials and testing (experiment and analyses)

2.1. Structural materials tested

Three ferritic Fe–Cr–Al alloys from Sandvik (Kanthal) were used as sample materials in corrosion tests, due to their reported passivation by alumina scales on the steel surface [31,34,35,37]: Alkrothal720 (ALK), APM (an advanced powder-metallurgical,

dispersion-strengthened Fe–Cr–Al steel) and APMT (a version of APM with addition of molybdenum). The composition of the materials used (in wt%) is given in Table 1. The specimens were cut in rectangular 20 mm × 40 mm × 1 mm slices (tetragonal prisms), polished using SiC paper up to 1200 grit, and cleaned with acetone prior to exposure to the molten LBE. The samples were placed in cylindrical crucibles (28 mm diameter, 40 mm height) filled with molten LBE (at ~200 °C) so that the angle between each two samples was around 60° (Fig. 1a) leaving space in the center for an oxygen sensor.

2.2. Experimental setup for static corrosion tests

Samples have been exposed to liquid LBE in a custom-built setup (see Fig. 2) built from commercially available standard stainless steel vacuum components and Swagelok tube fittings, and equipped with precise environmental control. The temperature of the liquid is measured by the R-type thermocouple in the sensor (87% Pt/13%Pt–Rh, 0 °C–1450 °C range), while the temperature of the furnace itself is recorded via a K-type thermocouple (chromel–alumel, –250 °C – 1250 °C range). The oxygen content in the liquid phase was measured using the commercially available Australian Oxytrol Systems oxygen sensors (Fig. 2), commonly used for the oxygen monitoring in exhaust gas [4]. The measurement principle is based on monitoring the oxygen potential difference between a reference (Pt in air) inside the hollow yttria-stabilized-zirconia (YSZ) sensor and liquid alloy surrounding the sensor, by measuring the electromotive force (EMF) signal. The EMF is generated in the oxygen sensor due to the difference in oxygen activities between the oxygen in the air in the sensor's reference (at 20.95%) and the oxygen in the liquid metal [4,41]. Similar to gaseous environments, oxygen sensors in liquid metals are based on the principle that O^{2-} ions are transported through the sensor's material (yttria-stabilized zirconium, YSZ) and allow to measure the electrochemical potential (as the EMF) between the reference (Pt/air in this study) in sensor, and the liquid metal. The oxygen concentration in the liquid LBE can be calculated based on the modified Nernst equation [4,32]:

$$E [\text{mV}] = 790.7 - 0.071 T [\text{K}] - 0.043 T [\text{K}] \cdot \ln C_0 [\text{ppm}]$$

The output EMF signal from the sensor was recorded by a Keithley 181 Nanovoltmeter and fed into an Omega DAQ board together with the thermocouple signal. LabView software was used to record the experimental parameters (EMF, T, time) and to control the oxygen concentration in the liquid metal by operating the automated valves for switching the gas flow (Fig. 2). The oxygen content was maintained actively by switching the gas flow through the autoclave between diluted hydrogen in argon (5% H_2 , balance Ar) and diluted oxygen in argon (3% O_2 , balance Ar), based on the EMF feedback readings from the oxygen sensor. If the EMF value was below the EMF set point (predefined by the user), Ar/3% H_2 would flow, while if the value was above the set point, Ar/3% O_2 would flow. Thus, one gas mixture was ON while the other was OFF (and vice versa) at each moment in real time [37]. Whichever gas was flowing, it would pass through a flow meter that limited the

Table 1

Nominal chemical composition of the tested Fe–Cr–Al steel candidates (in wt. %) [33].

	Cr	Al	Mn	Mo	Si	Ti	C	Fe
ALK	12.0–14.0	4.0	<0.7	—	<0.7	0.25	<0.08	Bal.
APM	20.5–23.5	5.8	<0.4	—	<0.7	—	<0.08	Bal.
APMT	20.5–23.5	5.0	<0.4	3.0	<0.7	—	<0.08	Bal.

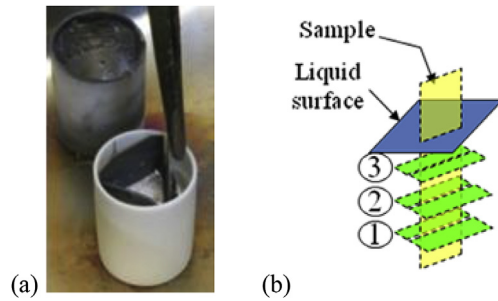


Fig. 1. (a) Samples placement in cylindrical alumina crucible, filled with liquid alloy; (b) Cutting the pieces from specimen bottom, for subsequent structural analysis (numbers denote cutting at 1st, 2nd and final (3rd) pullout, respectively).

flow rate to a constant value. From the time that the valves switched the gases to the time that the oxygen sensor signal changed was typically about 10 s.

2.3. Performance of the corrosion tests and choice of conditions

Based on the oxygen window concept defined in the previous section, in an isothermal case (i.e. corrosion test performed at constant temperature) the boundaries of the window are given by the same reactions as in case of thermal gradient. The maximum oxygen concentration corresponds to the oxygen level in LBE where the oxidation of lead into PbO is in equilibrium (the onset of PbO precipitation), while the minimum oxygen concentration corresponds to the point of onset of iron-oxide scales degradation. Magnetite (Fe_3O_4) was chosen among the iron oxides, as being the most common in detection and mostly reported in the literature [21–23,26,31]. Thus, at 700 °C this window ranges from 2×10^{-3} to 1×10^{-7} wt% O in LBE, while at 800 °C it is from 5×10^{-3} to 5×10^{-7} wt% O in LBE (see Fig. 3). However, the research interest is focused more on minimum boundary and lower oxygen concentrations in these ranges (as it is the goal to keep the oxygen level in the liquid metals to the minimum possible, in order to reduce chances for harsh oxidation and formation of PbO and other undesirable oxides).

Three static corrosion tests have been performed in this study: (1) at 800 °C for 1000 h with 1×10^{-6} wt% oxygen (O) in liquid LBE, (2) at 700 °C for 1000 h with 1×10^{-6} wt% O in LBE, and (3) at 800 °C for 440 h with 2×10^{-7} wt% O in LBE. The oxygen concentration of 2×10^{-7} wt% O at 800 °C was chosen (although slightly below the equilibrium concentration of magnetite formation/

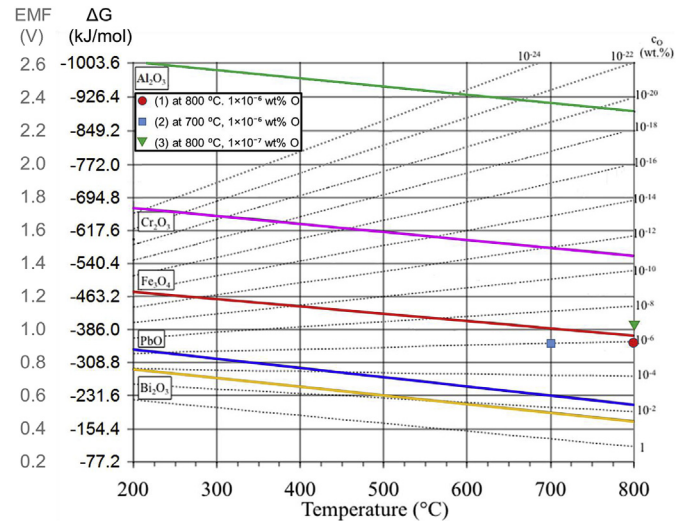


Fig. 3. Ellingham diagram representing Gibbs free energy (and corresponding EMF, based on Nernst equation) of formation of relevant oxides in this study (Fe-, Cr- and Al-oxides on Fe–Cr–Al steels surface, and Pb- and Bi-oxides in LBE). Gibbs free energy (and EMF) of the corrosion tests represented as blue square (700 °C/ 1×10^{-6} wt% O test), red circle (800 °C/ 1×10^{-6} wt% O test), and green triangle (800 °C/ 2×10^{-7} wt% O test). Oxygen concentration in all three tests prevents formation of Pb- and Bi-oxides, while enables Al- and Cr-oxides formation. Magnetite formation is possible in the tests with 1×10^{-6} wt% O in LBE, while disfavored in 800 °C/ 2×10^{-7} wt% O test. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

degradation) in order to test the protectiveness of Cr- and Al- oxides, and to compare the formed oxide scales with those formed at 1×10^{-6} wt% O at the same temperature. The samples were periodically retrieved (mid-term pullouts after 350 h and 700 h in the test (1), after 300 h and 650 h in the test (2), and after 300 h in the test (3), see Table 2) and small sections of the specimens were cut off with a Buehler high speed abrasive cut of saw while the remaining piece was re-submerged in the LBE for further exposure, before the final pullout at the end of test. At each pullout, the samples were temporarily removed at lower temperature from the still molten alloy (at ~200 °C). A small rectangular part from the bottom of each one of the samples was cut (Fig. 1b), then mounted in epoxy. The samples were subsequently cut in halves while in epoxy (to avoid damages potentially caused by cutting), one half of each then polished using SiC paper up to 1200 grit, then by 1.0 and 0.3 μm Al_2O_3 suspensions, and cleaned with ethanol and acetone in

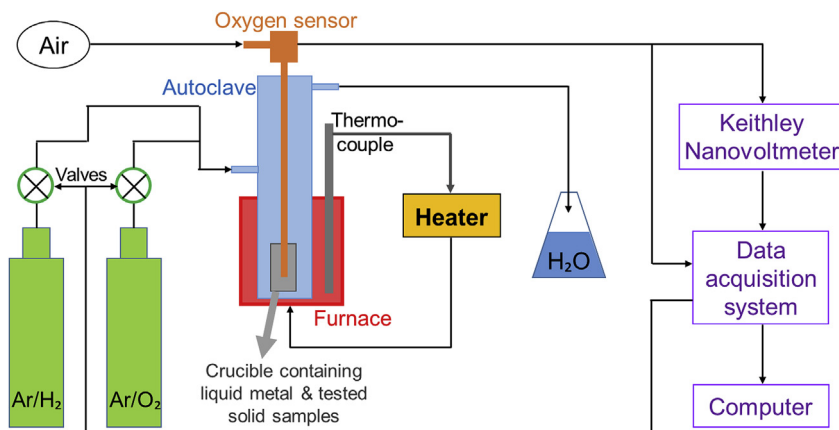


Fig. 2. Schematic of the experimental setup for static corrosion tests in liquid LBE.

Table 2

Parameters of the constant-temperature static corrosion tests in LBE in this study.

Test N°	Temperature of LBE (°C)	Test duration until mid-term pullouts (h)	Max. duration of test (h)	EMF setpoint (V)	Oxygen conc. (wt%)
1.	800	350, 700	1000	0.926	1.0×10^{-6}
2.	700	300, 650	1000	0.918	1.0×10^{-6}
3.	800	220	440	1.014	1.0×10^{-7}

an ultrasonic bath before further investigations. By this way, the analyzed zones of the pieces of each sample were preserved from damaging and far enough from cutoffs done before placing in epoxy.

The EMF signal from each test has been continuously monitored during the experiment and the values are reported in Table 2. These values correspond to the oxygen concentrations (given in the far right column of Table 2) that were chosen to avoid the formation of Pb- or Bi-oxides at the all temperature ranges in which a potential LBE loop may operate ($\sim 250^\circ\text{C}$ low temperature and 800°C high temperature). At the same time, these concentrations provide a high enough amount of the oxygen to grow the oxides of Fe, Cr and Al on the steels surface.

2.4. SEM/EDS analysis of structural material candidates after exposure to liquid LBE

Cross-sectional analysis of the structural material samples was performed using SEM. A Quanta 3D field emission gun scanning electron microscope with focused ion beam (SEM/FIB) has been used in this research. Energy dispersive spectroscopy (EDS) was carried out using an Oxford EDS attached to the SEM/FIB.

3. Results

The evolution of EMF, temperature (T) and oxygen concentration (C_{Ox}) over the time of the tests in LBE performed in this study is represented in Fig. 4. There were some instabilities in oxygen concentration at 700°C test, being occasionally below and above the desired (and averaged) 1×10^{-6} wt % O, mostly due to the lack of precise control of the gas flow rates because they were regulated manually. Occasionally, the Ar/O_2 gas flow rate was significantly higher than the Ar/H_2 gas flow rate. As the result, the oxygen concentration in the liquid LBE was above the saturation concentration during three time intervals (for 22 h, 4 h, and 6 h), meaning that lead-oxide existed at the LBE surface for about 32 h in total during the test at 700°C .

The SEM/EDS analysis of the tests revealed the differences in oxide formation behavior depending on temperature and sample composition.

a) $700^\circ\text{C}/1 \times 10^{-6}$ wt% oxygen:

Only ALK developed a complex oxide structure, labeled as Fe–Cr–Al–O (Fig. 5a) containing all three major steel constituents in oxide phase, while the other two steels had only one Al-oxide layer. After the maximum test duration of 1000 h, this oxide phase was found occasionally crushed (partially) and a slight dominance of Al–O over the other elements was found (Fig. 5b). On the other hand, APM and APMT steels formed one layer at 700°C that consists mostly of Al-oxide, with a presence of some Cr-oxide.

b) $800^\circ\text{C}/1 \times 10^{-6}$ wt% oxygen:

At 800°C , all three samples developed two oxide layers: the inner one being Al-oxide, and the outer consisting mostly of Cr-

oxide. The ALK steel tended to form an adherent, inner aluminum-oxide layer of $3\text{--}4\ \mu\text{m}$ thickness after full exposure time of 1000 h, and an outer, chromium-oxide layer of about the same thickness (with some Al-oxide). An example of such Al- and Cr-oxide layers formed on ALK after 1000 h exposure is shown in Fig. 6. Two layers were detected in APM and APMT too: the inner one being dominantly Al-oxide, while the outer one dominantly Cr-oxide with presence of Fe and Al (see Fig. 7c). However, in these two an occasional dissolution has been observed at longer immersion durations. It progresses radially into the steel from specific locations on the steel's surface where the Al-oxide layer failed. A residual oxide layer was frequently found detached near the original steel surface (Fig. 7a and d). At other places where the oxide layer adhered, little to no dissolution occurred (Fig. 7b and c).

c) $800^\circ\text{C}/2 \times 10^{-7}$ wt% oxygen:

The third test in LBE has been performed at 800°C with a lower concentration of oxygen in LBE (2×10^{-7} wt % O), but was stopped after 440 h (having only one mid-term pullout, at 300 h), due to the evident lack of protective oxide formation (and subsequent steel elements dissolution into liquid) already at the midterm pullout. This test has proven that the mentioned oxygen concentration is too low for oxidative passivation (protective oxide scale formation) on all three tested steel samples (Fig. 8). The analysis at 300 h revealed a lack of compact and continual oxide layers formation almost over the entire surface of all three samples (Fig. 8 a–c), with the steel elements (Fe, Cr, Al) and their oxides being surrounded by LBE (or dissolved in it).

4. Discussion

A weak point in this research, as well as in all similar tests with oxygen level control/maintenance in the liquid metal, is the distribution of oxygen in the liquid phase. Nothing is known about the oxygen concentration gradient in the crucible filled with LBE. Thus, we have chosen to take the oxygen concentration measured by the sensor as being a representative average value. The different portions of each sample might have experienced higher or lower oxygen level than this value, depending upon their depth in the LBE. Besides that, in the test at 800°C with 1×10^{-6} wt % O, the oxygen concentration exceeded 1×10^{-6} wt% considerably during a significant portion of the total test time (and even above 1×10^{-3} wt% for 32 h).

APM and APMT steels have a higher Al content (5.0 and 5.8 wt%, respectively, vs. 4.0 wt% in ALK), and therefore developed only one layer at 700°C being mostly consisted of Al-oxide (with possibly some smaller amount of Cr-oxide). However, at 800°C the chemical structure of the oxide changed, so there were two layers detected. Moreover, the Al-oxide formed below the initial steel surface (sub-surface), indicates the existence of internal oxidation (Fig. 7b).

The oxides formed on APM and APMT were proven more brittle and less adherent at both temperatures, with the consequence that dissolution was observed in places in both steels at longer immersion durations (Fig. 7e). Breaking and spalling of oxide scales in APM and APMT was followed by scales re-formation, however not as efficient as in case of ALK. The dissolution occurs transversely

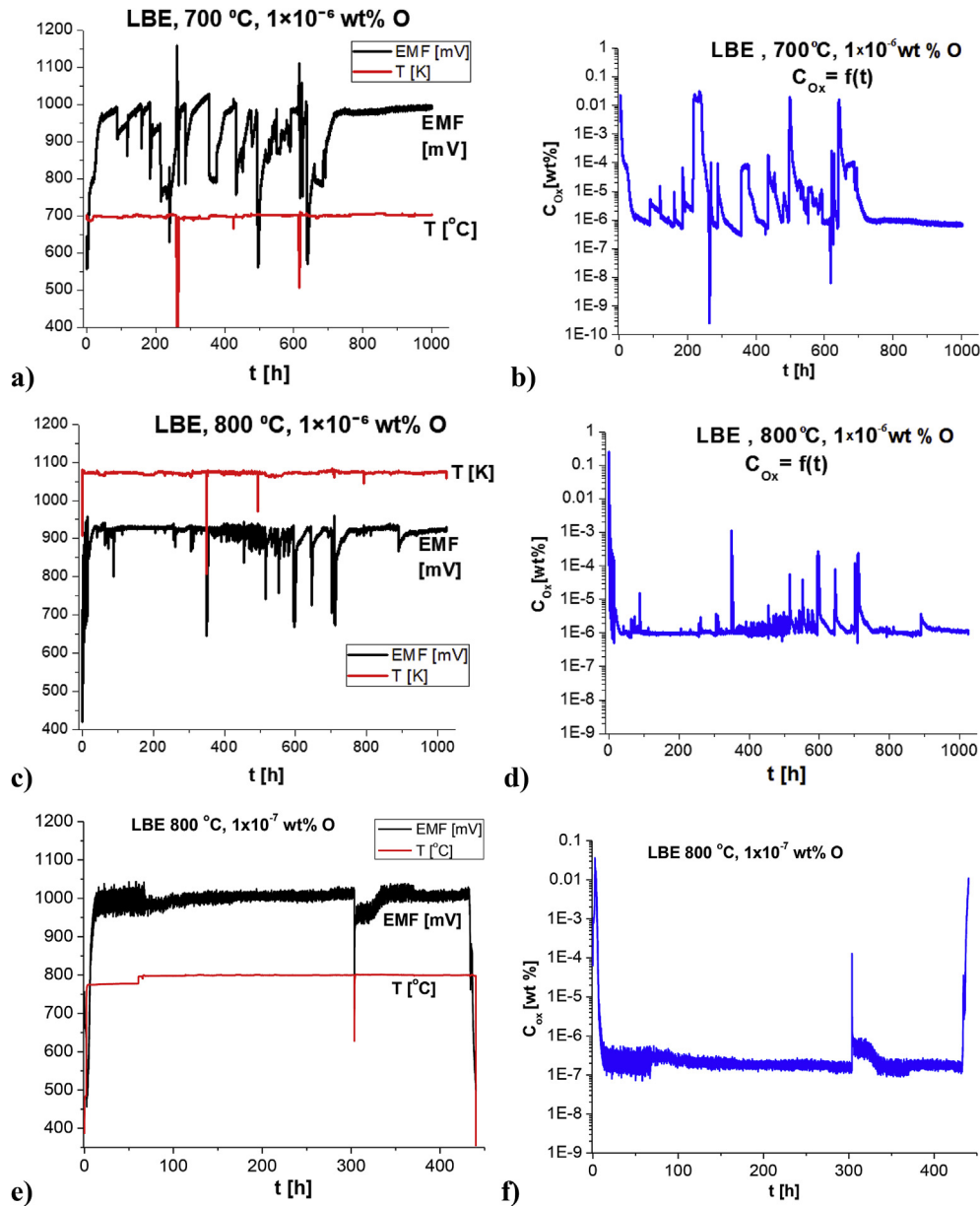


Fig. 4. Electromotive force (EMF) signal, temperature, and oxygen concentration (C_{ox}) of three corrosion tests of this study: (a–b) at 700 °C with 1×10^{-6} wt% O in LBE, (c–d) at 800 °C with 1×10^{-6} wt% O in LBE, (e–f) at 800 °C with 2×10^{-7} wt% O in LBE.

into the steel from specific locations on the steel's surface where Al-oxide layer failed: a residual oxide layer was frequently SEM-detected floating near the original steel surface (Fig. 7a and d). Thus, the corrosion performance depends significantly on the steel composition (i.e. on Al and Cr content) and therefore on the structure/chemistry of the oxide scales formed.

The oxide-scale thickness did not consistently grow larger with time, probably because the scale detached and reformed one or more times, as is indicated by the presence of remnants of aluminum oxide that float in the LBE near the surface of the steel at the longer immersion durations (see Fig. 7, b and d). The detachment of the oxide layer could have been caused by the thermal cycling when the mid-term pullouts of samples were performed. If the dissolution is estimated as being $\sim 12 \mu\text{m}$, based on SEM micrographs of dissolution zones of this depth into the steel, then the total corrosion depth of oxide plus dissolution can be estimated at

$16 \mu\text{m}$ after 1000 h of immersion. This corrosion rate corresponds to less than $140 \mu\text{m}$ per year.

The detachment of an oxide scale during sample handling (while performing the cross-section sample cutting) could be identified in the SEM results as a gap or crack, between the oxide layer and the substrate steel, filled with epoxy. In contrast, some of the detachment of the oxide layers clearly occurred while the sample was immersed in the LBE, as evidenced by the filling of the gap or crack with LBE. If the gap or crack was narrow and little to no dissolution of the exposed steel surface occurred, it was surmised that the detachment of the layer happened during the cooling down of the sample prior to extraction. In this case, the cause of the detachment would have been the difference in the thermal expansions of the oxide layer and of the substrate steel. In addition to this explanation, another factor may be that the oxygen content may not be homogenous throughout the LBE.

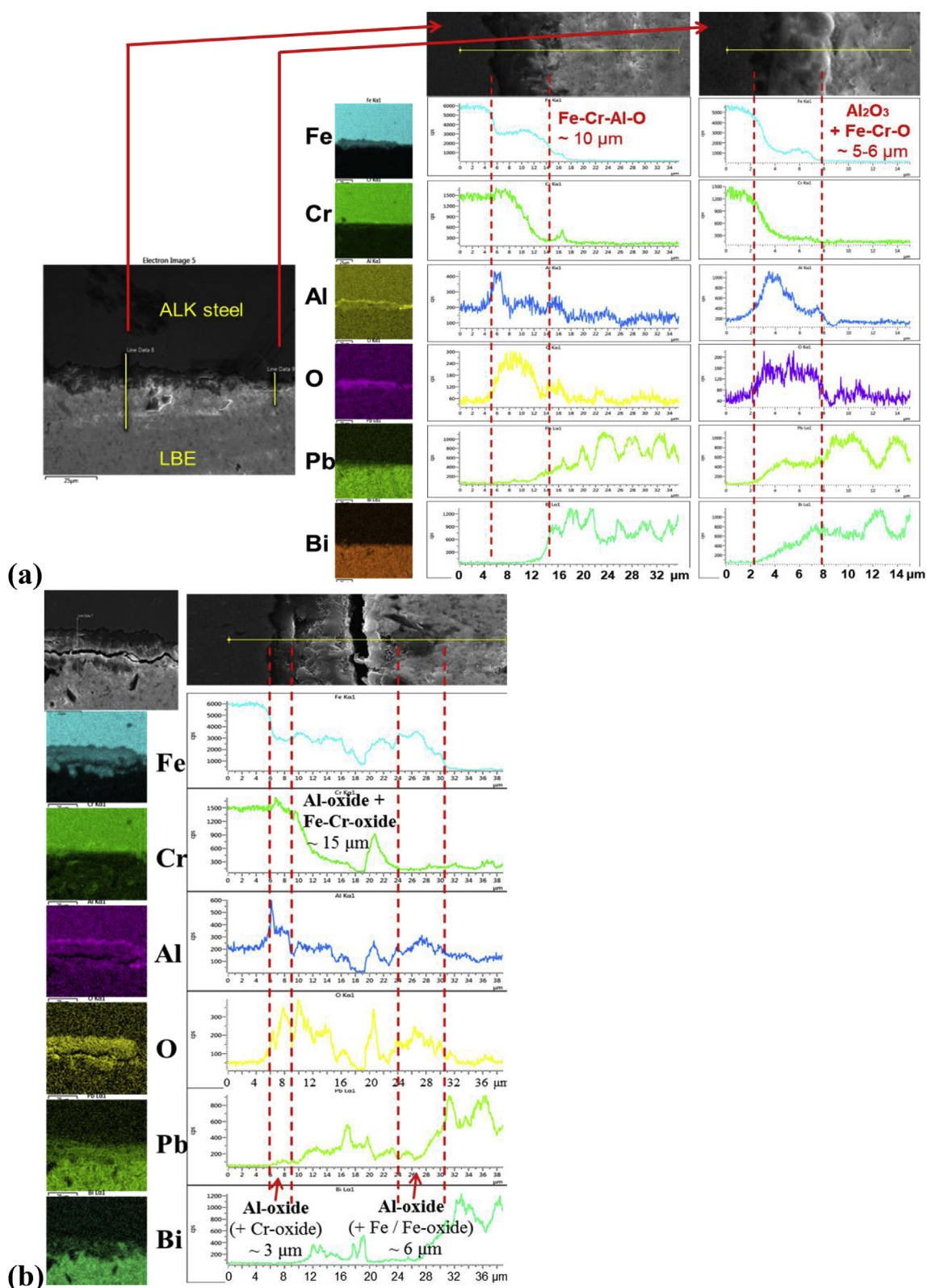


Fig. 5. (a) SEM and EDX of a cross section of the interface between ALK Kanthal steel and LBE, after exposure for 650 h to LBE at 700 °C with 10^{-6} wt% O (EMF = 0.918 V); (b) EDX line- and map-scan of SEM-imaged area (top) of ALK steel after exposure to LBE at 700 °C for 1000 h.

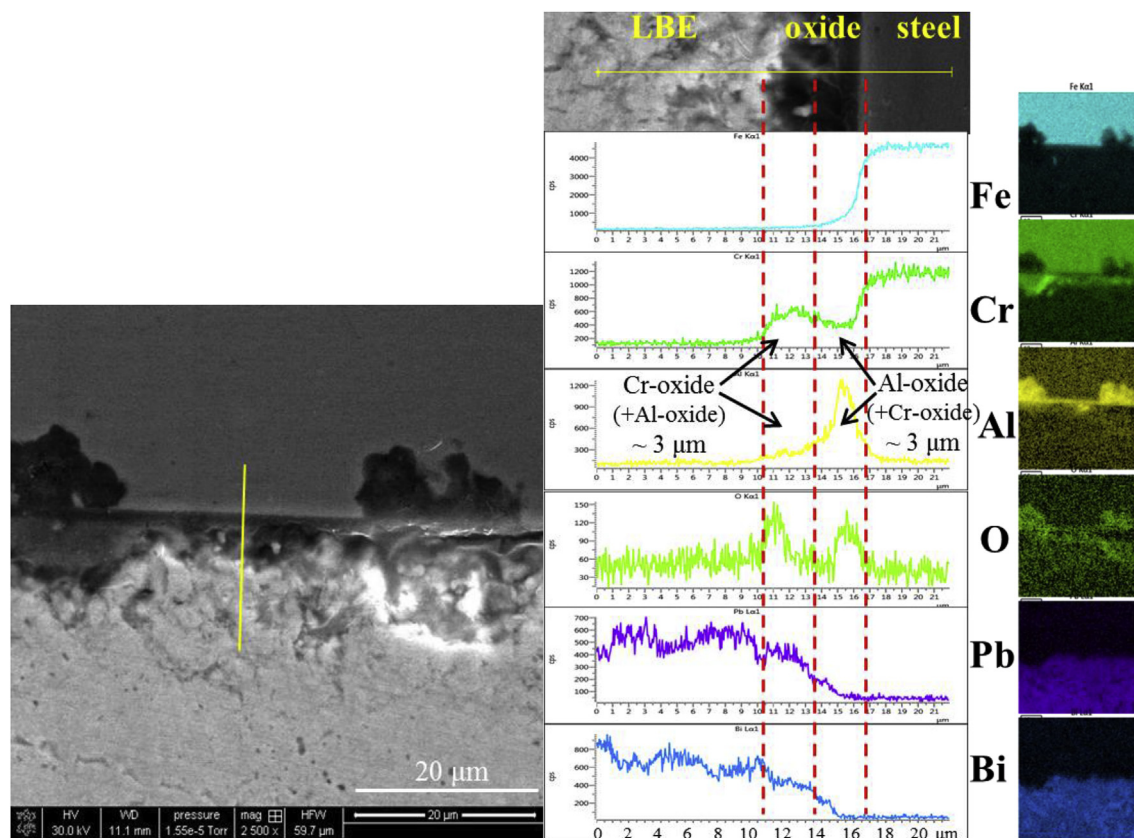


Fig. 6. SEM and EDS line- and map-scan of a cross-section of the interface between ALK and LBE, after 1000 h of exposure at 800 °C with 10^{-6} wt% oxygen (EMF = 0.926 V). Inner layer (mostly Al-oxide, with some Cr-oxide) and outer layer (mostly Cr-oxide, with some Al-oxide) both found to be ~ 3 µm thick.

4.1. The assessment of material loss – method validation

The oxide layer thickness was measured for all areas scanned by the SEM/EDX on each sample after all three pullouts, and used as a material loss measurement on Kanthal steels. Material loss was characterized through the change in sample thickness, i.e. as a thickness loss. The direct, gravimetric measurement of the mass loss (weight loss) was impracticable in this case, mostly due to the impossibility to determine the exact amount of oxygen from LBE that reacted with steel elements and got incorporated in the oxide scales (per unit surface). Therefore only thickness loss was analyzed, from where mass loss can be assessed. Material thickness loss was characterized as one-dimensional parameter. There are three different ways that one can measure the material thickness loss: (1) a change in sample thickness on the one and same spot before and after the exposure (of several hundred hours) in liquid alloy; (2) liquid metal penetration depth (when we measure the linear difference between the initial position of bulk-liquid interface line and the deepest/furthest point of the liquid penetration, in the direction perpendicular to the bulk-liquid borderline); (3) as the average oxide layer thickness. Because of the everlasting uncertainty regarding the determination of the initial bulk-liquid borderline position, it was difficult to perform methods (1) and (2). Hence, method (3) was used – oxide layer thickness measurement. This was based on a reasonable assumption of the existence of positive correlation between the oxide thickness and the extent of material loss in structural material. This method is the least quantitative (since we still do not know what is the exact thickness loss once we know total oxide thickness, and there might be several – at least two-oxide layers, each one re-growing after

sample was pulled out, cut and immersed back), but is enough informative, and the only possible in the lack of labeling the initial bulk-liquid borderline.

The oxide layer thickness measurement and averaging in the first and second test has been performed in the following way: after samples were pulled out after different portions of time in each pullout, and a piece of each one of three samples was cut off in cross-section and polished, every piece was SEM/EDS-analyzed on several spots. At each one spot, the thickness of detected oxide layers was measured and averaged (for the one spot), then oxide layers' thicknesses of all the spots of one Kanthal sample and one exact pullout have been averaged per sample per one pull-out. The results of the time evolution of the thickness of oxide scales on tested samples in LBE (with 1×10^{-6} wt% oxygen at 800° and 700 °C) are represented in Fig. 9.

The general problem of this method is the thermal disturbance of the samples (and oxide scales formed on them) by cooling and heating again, each time the samples were pulled out for analysis. This can cause breaking and detachment of the scales, due to the difference in thermal constriction/expansion coefficient of oxides vs. bulk. It means that one may not be able to detect and measure all the oxide layers (after the re-immersion and oxide re-growth) – if they exist, but were detached and sunk into liquid – but probably only the last one formed. If the oxide layers detached, previously formed oxide layers can be seen near the surface. These oxide layers can be added to the total oxide layer thickness since it can be characterized as the material loss. The other problem was the cutting and further exposure of the same specimen. Applied mechanical stress in cutting can be an additional origin of oxide scales damaging. In order to prevent it, the samples were wrapped by

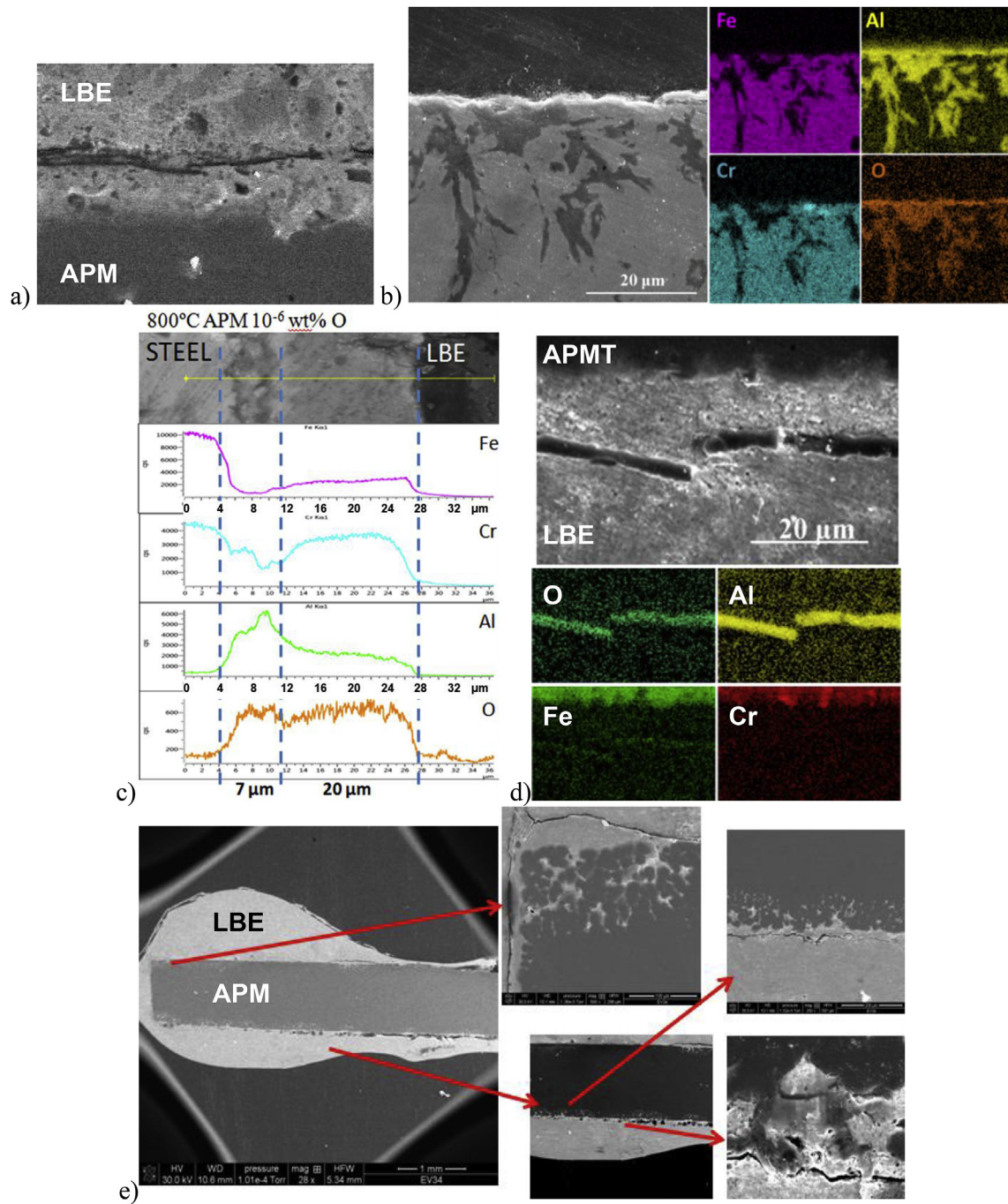


Fig. 7. APM and APMT in LBE at 800 °C with 1×10^{-6} wt% oxygen: (b) SEM/EDS imaging of APMT, after 700 h - internal oxidation detectable; (a) SEM imaging of APM after 700 h; (c) EDS line-scan of oxide layers in APM after 1000 h; (d) SEM imaging and EDS map-scan of APMT after 1000 h: oxide spalling off; (e) occasional dissolution of APM steel substrate after breaking/spalling of oxide scales after 1000 h of exposure to LBE at 700 °C.

several layers of protective towel paper during the clamping in saw, and then each piece was immersed in epoxy resin and cut in halves after freezing (as described above). However, as the second and the third pullout still remain less reliable than the first one due to the thermal effects, the conclusions were limited mainly on the first pullouts. The material loss in ALK in the first two tests (1×10^{-6} wt % O) was calculated to be $< 150 \mu\text{m}/\text{year}$, from the interpolation based on the results of oxide layers thickness after the first pullouts, whereas APM and APMT experience larger material removal and even occasional dissolutions.

The test at 800 °C with 2×10^{-7} wt% O indicated that this oxygen

concentration is not sufficient, i.e. too low, for enabling oxidative passivation (controlled oxide layer formation) on Fe–Cr–Al steels in LBE at 800 °C. SEM/EDS analysis showed a lack of compact protective layer formation combined with steel components dissolution and LBE penetration (see Fig. 8). This indicates either that formed oxide is porous or discontinuous (so that diffusion control is insufficient), or that there is a lower oxide formation rate than the oxide (and steel) dissolution rate. The Ellingham's diagram (Fig. 3) shows that this oxygen concentration lies above (i.e. is more negative than) ΔG of magnetite formation (see green triangle on Fig. 3), which means that oxidation of iron is disfavored.

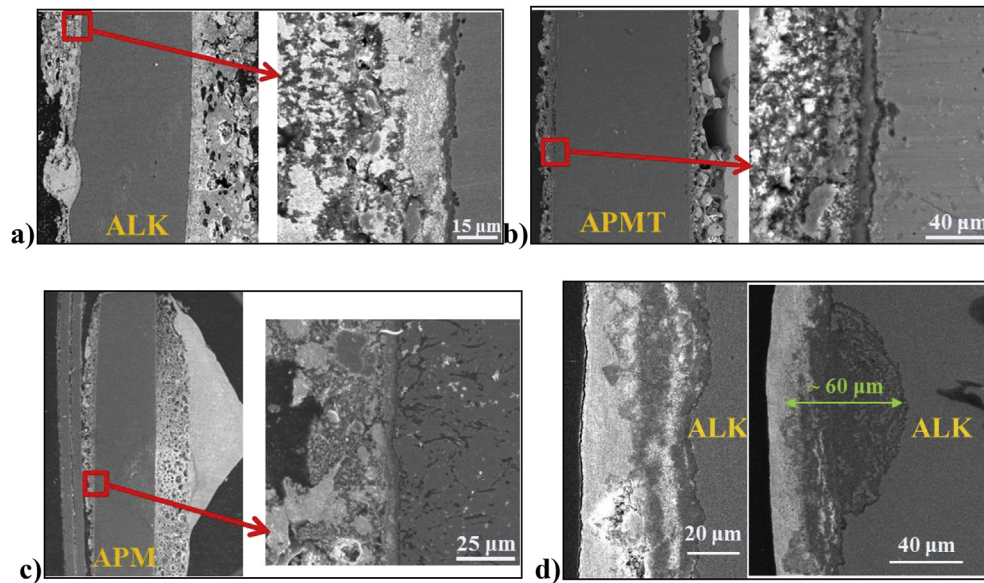


Fig. 8. (a–c) ALK, APMT and APM samples (respectively) after 216 h of exposure in LBE at 800 °C with 10^{-7} wt% oxygen; (d) the example of the “oxidation + dissolution” zone measurement.

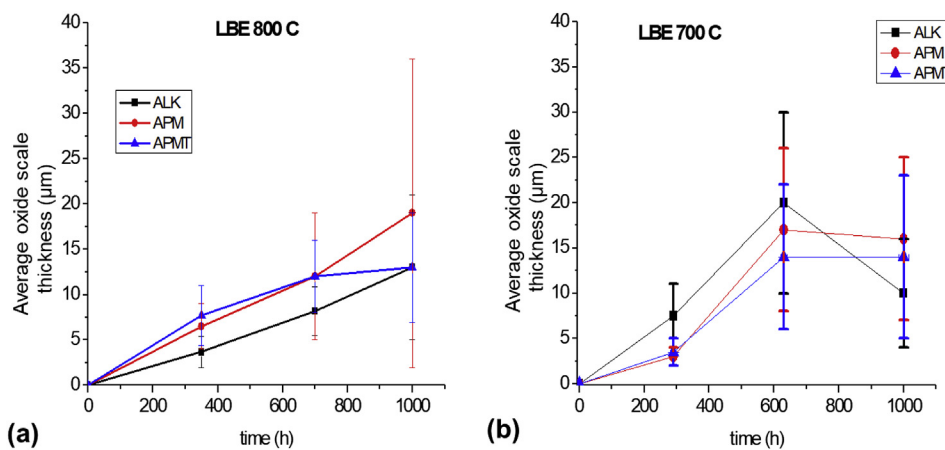


Fig. 9. Averaged oxide scales thickness after 1st, 2nd and 3rd pullout of each sample, in the LBE static corrosion tests with 1×10^{-6} wt% oxygen: (a) at 800 °C and (b) at 700 °C.

The “oxidation + dissolution” zone thickness has been measured/assessed via EDS line scan (at each spot analyzed by EDS), as the distance between the liquid/solid (or liquid/oxide) interface and the maximum penetration depth of LBE into steel bulk along the X-axis. These values were averaged in the same fashion as for the oxide scales thickness measurement. An example of the measurement is given in Fig. 8.d. The oxide layer thickness was determined by taking the average of 3–7 measurements within each image. The material loss is assumed to be one half of this measured thickness since the oxide layer grows outward and inward from the original surface.

The material thickness loss in the three tested steel samples at this low oxygen content has been in the range of 40–180 μm after only 300 h (90 ± 30 μm in ALK, 140 ± 40 μm in APMT and 60 ± 20 μm in APM), meaning a huge loss and confirming that concentration of 2×10^{-7} wt% O in LBE at 800 °C is too low, i.e. insufficient to form protective oxide layers on Fe–Cr–Al alloy samples. The similar outcome in steel samples has been found after 440 h of test operation, with material thickness loss assessed to be in 100–180 μm range.

5. Conclusion

- 1) The results of performed static corrosion tests in LBE at 700 and 800 °C showed that Fe–Cr–Al alloys have sustainable corrosion behavior if the oxygen concentration in LBE is sufficiently high, and therefore are a good choice for Pb–Bi systems.
- 2) Oxygen concentration of 1×10^{-6} wt% in LBE proves to be beneficial in order to form a stable, continuous and well-adhered oxide scales on three tested Fe–Cr–Al alloys, in the high temperature range of 700–800 °C. The most protective behavior (character) of oxide phases formed was found in ALK, a low-Al (4.0 wt% Al) Kanthal steel, with subsequent minimum material thickness loss (<150 μm/year).
- 3) The oxide layers developed at 700–800 °C on higher-Al containing samples (APM and APMT) consist of mostly Al-oxide, while ALK (lower-Al) develops slightly higher amount of Fe- and Cr oxides.
- 4) Oxygen concentration of 1×10^{-6} wt% in LBE at 800 °C promotes formation of complex oxide structure (containing more than one layer) on ALK, which is a mixture of Al-oxide and possibly

Fe- and Cr-oxides, while higher-Al containing steels (APM, APMT) form mostly Al-oxide, with some Fe and Cr (as diffusing atoms from bulk) or their oxides. However, the results should be taken with care, as the oxygen concentration exceeded 1×10^{-6} wt% during several intervals in this test.

- 5) Oxygen concentration of 2×10^{-7} wt% O is too low for promoting formation of compact and well-protective oxide scales.

Acknowledgement

Funding for this research was provided by the U.S. Department of Energy (DOE) SunShot program (Award # DE-EE0005941). The authors thank the California Institute for Quantitative Biosciences (QB3) and Biomolecular Nanotechnology Center (BNC) at UC Berkeley for making the Quanta 3D FEG DualBeam SEM available.

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