

# Effect of oxygen concentration and temperature on compatibility of ODS steel with liquid, Stagnant $\text{Pb}_{45}\text{Bi}_{55}$

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## Abstract

Exposure tests of an oxide dispersion strengthened martensitic type steel (ODS) were performed in stagnant lead bismuth eutectic (LBE) containing  $10^{-4}$ ,  $10^{-6}$  and  $10^{-8}$  wt% of oxygen at 500–650 °C up to 10000 h. It resulted that the base metal was protected from corrosion by the formation of a magnetite and spinel layer in liquid  $\text{Pb}_{45}\text{Bi}_{55}$  containing  $10^{-6}$  wt% of oxygen at 550 °C or less, not however, at higher temperatures. At 650 °C and  $10^{-8}$  wt% of oxygen, the ODS steel showed good compatibility with LBE by formation of a thin mixed high chromium spinel layer, while at  $10^{-4}$  wt% multilayers of magnetite and spinel develop at this temperature which break off but are renewed by oxide layers which protect the steel again.

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## 1. Introduction

Lead bismuth eutectic (LBE) is a candidate material for the coolant of a fast breeder reactor (FBR) and for the coolant and spallation target of an accelerator driven subcritical reactor system (ADS). One of the main problems in the development of these systems is compatibility of the steels with LBE.

In 1998 experiments were reported in which the formation of oxide scales on the surface of steel was shown to protect the steel from dissolution attack by LBE [1]. For stabilization of these oxide scales a controlled con-

centration of dissolved oxygen in LBE has to be maintained. The concentration applied in the experiments was  $10^{-6}$  wt%. Recent work on corrosion of austenitic and martensitic steels gives an overview on the corrosion effects and processes and its prevention in stagnant and flowing Pb and LBE [2–12]. However, few data only were presented on the processes taking place in LBE with different oxygen concentrations and also at temperatures above 550 °C.

In this study, an oxide dispersion strengthened martensitic type steel (ODS) as a candidate material for the fuel cladding of a LBE cooled FBR is examined to analyse its corrosion behavior. The experiments are conducted in stagnant LBE of 500–650 °C up to 10000 h under controlled oxygen concentration of  $10^{-4}$ ,  $10^{-6}$  and  $10^{-8}$  wt%. After the test, each specimen was investigated based on metallurgical analyses.

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## 2. Experimental

The chemical composition of ODS tested in this study is listed in Table 1.

The arrangement of the specimens in the crucible is shown in Fig. 1. Specimens of  $27 \times 6 \times 2$  mm dimension were mounted in molten LBE filled into an  $\text{Al}_2\text{O}_3$  crucible. Each crucible contains two specimens only.

The apparatus for exposure tests is shown in Fig. 2. The oxygen concentration in LBE is controlled by an atmosphere that contains argon hydrogen and water with a definite ratio that determines the chemical potential of oxygen in the gas atmosphere and within the LBE bath. The experimental conditions and the resulting oxygen partial pressures are shown in Table 2. Experiments with  $10^{-4}$  and  $10^{-8}$  wt% oxygen are carried out only at  $650^\circ\text{C}$  and up to 5000 h, while those at  $10^{-6}$  wt% cover the temperature range of  $500$ – $650^\circ\text{C}$  up to 10000 h of exposure. Analysis of corrosion effects is performed after 800, 2000, 5000 and 10000 h using a scanning electron microscope (SEM) with energy dispersive X-ray analyzer (EDS), a X-ray diffractometer (XRD) and field emission transmission electron microscope (FE-TEM) with EDS.

## 3. Results

### 3.1. Corrosion behavior in LBE containing $10^{-6}$ wt% of oxygen

The corrosion behavior of ODS steel in LBE containing  $10^{-6}$  wt% of oxygen during 2000 h of exposure was already described in a previous report [11]. The follow on experiments conducted here deal with the effects observed after exposure times of 5000 and 10000 h under the same conditions.

The cross-section of the steel exposed at  $550^\circ\text{C}$  for 5000 h is presented in Fig. 3. This figure shows the corrosion of the steel at the interface between LBE and gas region. In the LBE region, the outer oxide layer consisting of magnetite ( $\text{Fe}_3\text{O}_4$ ) spalled off and appeared on the surface of the LBE. However, the Fe–Cr–O layer (spinel) stuck on the base metal and protected it from liquid metal corrosion. At  $500^\circ\text{C}$ , however, the magnetite layer did not brake off even after 10000 h of exposure.

The growth of the oxide layer on ODS in the gas atmosphere above the LBE and in the LBE at  $550^\circ\text{C}$

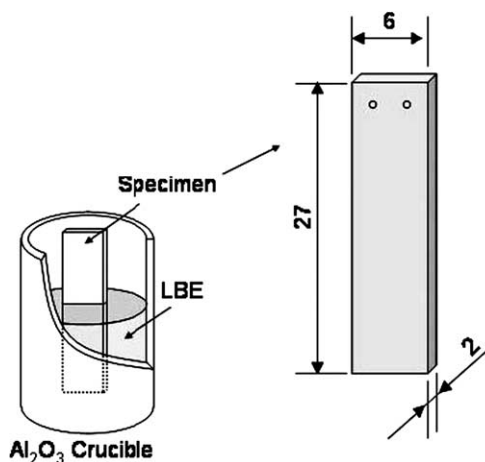


Fig. 1. Specimen and LBE test crucible.

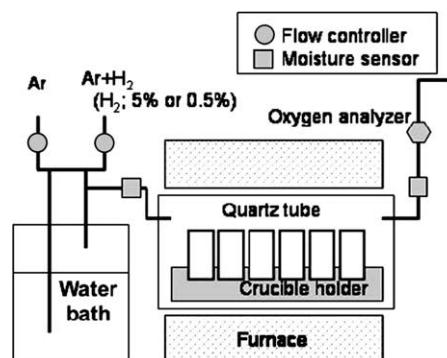


Fig. 2. Corrosion test apparatus. left: gas conditioning, right: specimen crucibles inside the furnace and gas sensors.

is presented in Fig. 4. The total layer thickness measured at three different positions of each specimen includes magnetite-, spinel- and diffusion-zone is growing faster in the gas atmosphere than in the LBE. Between 2000 and 5000 h, the thickness in LBE gets smaller because the magnetite broke off. The thickness of the spinel layer grows only slowly and is the same in the atmosphere and LBE.

The oxidation behavior changed at  $600^\circ\text{C}$ . At temperatures of  $600$  and  $650^\circ\text{C}$  a thin Fe–Cr spinel layer appears on the surface. Up to 2000 h of exposure it protects the whole surface with exception of a few places

Table 1  
Chemical composition of ODS-M (product, wt%)

C	Si	Mn	P	S	Ni	Cr	W	Ti	Y	O	N	Ar
0.13	<0.005	<0.01	0.001	0.003	0.01	8.85	1.94	0.2	0.27	0.17	0.011	0.005

Heat treatment:  $1050^\circ\text{C}$  – 1 h (AC),  $800^\circ\text{C}$  – 1 h (AC).

Table 2

H<sub>2</sub>/H<sub>2</sub>O mixture gas supply condition for oxygen control at different temperatures and oxygen concentrations

Oxygen concentrated in LBE [wt%]	10 <sup>-4</sup>	10 <sup>-6</sup>	10 <sup>-8</sup>			
Temperature [°C]	650	500	550	600	650	650
H <sub>2</sub> /H <sub>2</sub> O ratio [-]	1.2E-04	1.6E-02	4.0E-02	8.8E-02	1.9E-02	1.2E+01
P <sub>O<sub>2</sub></sub> [atm]	3.16E-17	1.16E-24	1.93E-23	2.35E-22	2.10E-21	3.16E-25

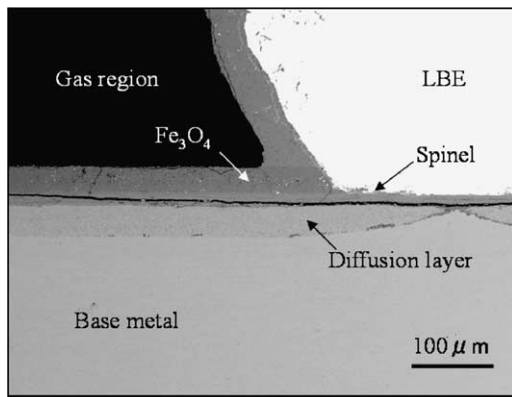


Fig. 3. Cross-section of ODS steel specimen through the surface region of the LBE containing 10<sup>-6</sup> wt% of oxygen at 550 °C for 5000 h.

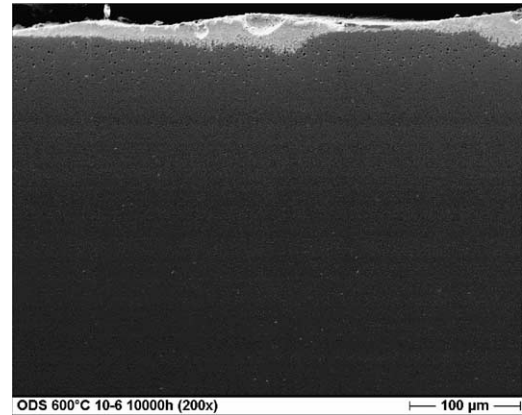


Fig. 5. Cross-section of ODS tested in LBE with 10<sup>-6</sup> wt% of oxygen at 650 °C after 10000 h showing dissolution attack at the surface.

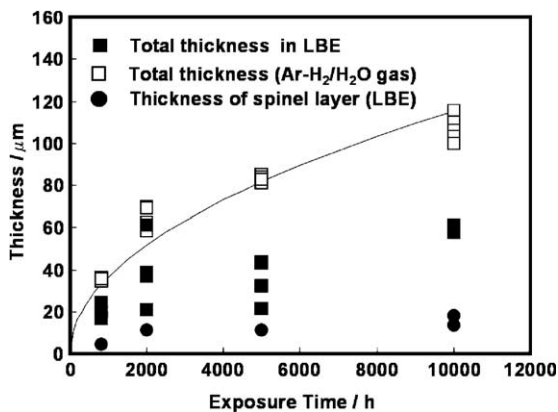


Fig. 4. Results of measurements of the oxide thickness formed on ODS steel at 550 °C at three different positions on each specimen and of the Fe–Cr layer thickness.

at which dissolution attack is observed. After 5000 h this protective layer disappears partly but after 10000 h completely with the consequence of an overall dissolution attack (Fig. 5). Measurement of the concentration in the Fe–Cr spinel layer resulted in 25–30 wt% in the 650 and 600 °C and 15–20 wt% Cr in the 550 °C specimens.

### 3.2. Corrosion behavior in LBE containing 10<sup>-4</sup> and 10<sup>-8</sup> wt% of oxygen

As described in Table 2 the experiments with 10<sup>-4</sup> and 10<sup>-8</sup> wt% oxygen in LBE are only conducted at 650 °C. The maximal exposure time for those experiments is 5000 h.

From the experiments with 10<sup>-6</sup> wt% oxygen in LBE it was expected that magnetite and spinel layers grow on the specimens with the high oxygen concentration of 10<sup>-4</sup> wt%. This behavior is demonstrated in Fig. 6(a). However, between 2000 and 5000 h of exposure the oxide scale breaks off and a renewed scale is observed after 5000 h of exposure, Fig. 6(b). This is different to the result obtained in LBE at 650 °C with 10<sup>-6</sup> wt% oxygen, where a thin spinel layer appeared which allowed partial dissolution attack. The Fe–Cr spinel layer below the magnetite scale contains 13–15 wt% Cr.

A thin protective Fe–Cr spinel layer covers the ODS steel surface completely up to 2000 h of exposure at 650 °C in LBE with 10<sup>-8</sup> wt% oxygen. Only at a few places LBE penetrates through the oxide scale into small pores below the surface. However, the surface inside the pores is also covered by a Fe–Cr spinel layer which seems to constitute a stable condition with no further dissolution attack. The Fe–Cr spinel contains 35–41 wt% Cr.

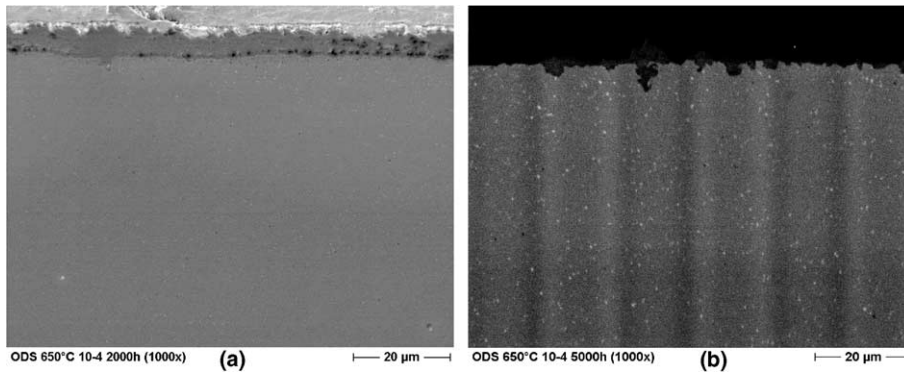


Fig. 6. Cross-section of ODS tested in LBE containing  $10^{-4}$  wt% of oxygen at 650 °C after 2000 h with a magnetite layer on top (a) and after 5000 h with renewed oxide layer (b).

#### 4. Discussion

The behavior of the oxide scales which develop on the surface of ODS steel exposed to LBE depends on the temperature and the oxygen concentration in LBE. For a concentration of  $10^{-6}$  wt% the activity in oxygen is high enough to ensure iron oxide formation at temperatures up to 650 °C. Fe/FeO is in equilibrium with the oxygen in LBE along the  $\text{Fe}_3\text{O}_4/\text{FeO}$  line above 570 °C and  $\text{Fe}/\text{Fe}_3\text{O}_4$  below this temperature (Fig. 7). The concentration of  $10^{-6}$  wt% is, however, high enough for formation of the magnetite,  $\text{Fe}_3\text{O}_4$ , scale. In spite of these conditions magnetite scales are not present on the specimens at temperatures of 600 and 650 °C, but

only on those of 500 and 550 °C. The change in the oxidation process is due to two conditions which minimize the iron migration to the surface above 550 °C, one is the fact that the oxygen concentration in LBE approaches the decomposition condition of the magnetite, the other is the low mobility of Fe ions in Fe–Cr spinel with high Cr concentration (25–30 wt%). As a consequence, thin Fe–Cr spinels grow at the surface of the specimens at 600 and 650 °C. They are, however, not protective. Dissolution attack starts first partially and extends after 5000 h over the entire surface.

The Cr concentration in the Fe–Cr spinel below the magnetite scale of the 550 °C specimen in LBE with  $10^{-6}$  wt% oxygen is only 15–20 wt%. Thick magnetite scales grow on this specimen which brake off between 2000 and 5000 h of exposure and are replaced by new oxide scales. This behavior was already observed for the martensitic OPTIFER IVc and MANET II steels [13].

The surface of the specimens exposed to LBE with  $10^{-8}$  wt% oxygen at 650 °C have a similar spinel oxide scale like observed on specimens in LBE with  $10^{-6}$  wt% at the same temperature. The Cr concentration in the Fe–Cr spinel is, however, up to 41 wt%. The result is practically no dissolution attack up to 5000 h exposure with the exception of some LBE inclusions in pores which do not change because the pores are covered with a protective spinel layer. There is practically no important driving force for Fe to move to the surface because the oxygen concentration of  $10^{-8}$  in LBE is below that for FeO decomposition.

As opposed to the low oxygen concentrations, the one of  $10^{-4}$  wt% in LBE at 650 °C is far above the oxygen concentration for decomposition of magnetite. As a consequence, magnetite scales are formed also at 650 °C above the Fe–Cr spinel surface layer which contains only 12–14 wt% Cr. The magnetite scale grows very fast and breaks away already after 2000 h. However, new scales are developed and provide protection up to the applied exposure time of 5000 h.

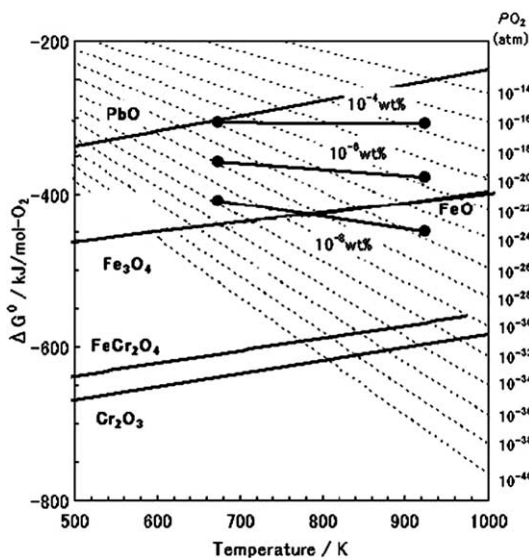


Fig. 7. Ellingham diagram with oxides of interest containing lines of constant oxygen partial pressure and oxygen concentrations in LBE.

## 5. Conclusions

At  $10^{-6}$  wt% of oxygen and higher concentration in LBE ODS steel can be employed up to 550 °C and at least 10000 h of exposure as a structural material, while for  $10^{-4}$  wt% this was confirmed up to 5000 h also at temperatures up to 650 °C. ODS steel is compatible with LBE containing only  $10^{-8}$  wt% of oxygen also at least up to 5000 h of exposure at 650 °C. Thus it can be concluded that for 650 °C either a high oxygen concentration around  $10^{-4}$  wt% or a low one around  $10^{-8}$  wt% is favorable for a good compatibility not, however,  $10^{-6}$  wt%. The low concentration of  $10^{-8}$  wt% has the advantage that no oxide scale spallation takes place. Additional experiments in the high and low oxygen content region especially in flowing LBE are necessary to explore the potential of the ODS steel as a fuel cladding material in LBE cooled systems.

## Acknowledgment

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