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Corrosion investigations of steels in flowing lead at 400°C and 550°C

H. Glasbrenner [a,*], J. Konys [a], G. Mueller [a], A. Rusanov [b]

[a] *Forschungszentrum Karlsruhe GmbH, Inst. fur Materialforschung III, P.O. Box 3640, D-76021, Karlsruhe, Germany*
[b] *IPPE, Bondarenko Square 1, Obninsk, 249020, Kaluga Region, Russia*

Abstract

Experiments were conducted in a liquid lead pumped loop at 400°C and 550°C to examine the corrosion behaviour of ferritic and austenitic steels. The aim of this work is to identify suitable structural containment materials for a lead cooled accelerator driven transmutation reactor (ADS). During exposure to liquid lead containing $3–4 \times 10^{-5}$ wt% oxygen, protective oxide layers grow on the surface of each candidate alloy. The total thickness of the multiphase layers increases parabolically with increasing exposure time. After 3000 h, they reach a maximum of 50 μm on one ferritic steel (Optifer) and of 30–40 μm on electron pulse-treated austenitic steels. Austenites with an untreated surface develop oxide layers of just 1–2 μm thickness. In each case the oxide layers prevent the dissolution attack of liquid lead. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Transmutation of plutonium, minor actinides and long-lived fission products can be accomplished in an accelerator driven system (ADS) to reduce the half-life of these elements [1]. For this purpose protons are injected into a spallation target through a vacuum beam pipe in order to generate free nucleons (neutrons) by a spallation process. The spallation neutrons convert non-fissile isotopes into fissile ones (transmutation). A heavy liquid metal like lead or the eutectic lead–bismuth alloy is needed for the spallation target material to ensure efficient production of neutrons. Furthermore, the molten metal is intended to be used not only as a target but also as a coolant in the accelerator system. It is known that the heavy metals lead and bismuth are much more corrosive than alkali metals [2–4]. As a consequence the behaviour of possible structural containment materials in heavy liquid metal has to be investigated. The alloy elements nickel and chromium have a high solubility in lead at elevated temperatures [5], which leads to a strong dissolution corrosion attack by leaching of nickel and chromium contained in the steel. The formation of a protective oxide layer on the surface of the structural materials can prevent dissolution corrosion attack of liquid lead [6,7]. To maintain the oxide layer stability, the oxygen content in lead should not drop below a critical value which would lead immediately to dissolving of the oxide layer and subsequently to a dissolution corrosion attack. Hence, a continuous monitoring of the oxygen content in the melt is required to avoid corrosion.

2. Experimental section

2.1. Materials

Two ferritic–martensitic steels (Optifer IVc and EM 10) and two austenitic steels (1.4948 and 1.4970) have been selected for corrosion testing in circulating lead. The ferritic-martensitic steels were developed in the framework of the Fusion Technology Project to achieve low activation steels as structural materials. Both austenitic steels tested have good mechanical properties at the loop temperatures [8]. Significant experience exists

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[*] Corresponding author. Tel.: +41-56 310 4712; fax: +41-56 310 2199.

E-mail address: heike.glasbrenner@psi.ch (H. Glasbrenner).

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with the steel 1.4948 which was used as a material for tubes, pressure vessels and other structural components in sodium cooled fast breeder reactors. The chemical composition of the austenitic steels is taken out of the Stahlschlüssel [8] and the chemical composition of the ferritic steels was given by the suppliers. All data are summarised in Table 1.

2.2. Specimen preparation

Cylindrical specimens were machined of the as-received material with a length of about 110 mm and a diameter of 8 mm (see Fig. 1). About 1/3 of the specimens were treated by the pulsed electron beam of Gepulste Elektonen-Strahl-Anlage (GESA). In this process, a thin surface layer (50 cm^2) can be melted and cooled in a very short time. The rapid solidification after the pulse (cooling at 10^7 K/s) results in a very fine grained structure. The GESA installation is described elsewhere [9].

2.3. Lead corrosion loop

The corrosion tests were carried out in a non-isothermal pumped lead loop at IPPE Obninsk. The flow loop consists of a main heater, a cooler, a hot and a cold test section, an electromechanical pump, a purification system, a flow meter and two oxygen meters. Two test sections are available, one at 400°C, the other at 550°C.

The volume of the liquid lead in the loop is around 60 l, and the steady state flow velocity is 1.9 m/s. The temperature is maintained by electrical resistance heating. This heating zone is positioned just upstream of the hot test section. For cooling the circulating lead, a three-wall cooler construction is applied: cooling water – stagnant Pb–Bi alloy – pumped lead. The cooler is placed directly upstream of the cold test section.

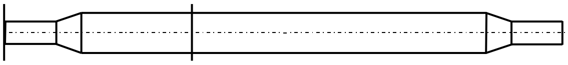

Fig. 1. Shape of the specimens exposed to flowing Pb. Some materials were partly treated by pulsed electron beam (GESA).

The loop consists of tubes with an inner diameter of 30 mm and 4 mm wall thickness. The tubing of the hot section is made of austenitic chromium nickel 20Cr14Ni2Si steel whereas in the cold section (less than (460°C) an ordinary austenitic stainless steel 18Cr10Ni1Ti is employed.

In the present corrosion test the oxygen content in lead was monitored by two oxygen meters placed in the two temperature zones. The oxygen activity in the liquid lead is measured by the electrochemical cells of the oxygen meters. The error of EMF measurements in the Pb–O system with an oxygen meter does not exceed 2% [10]. Up to now the oxygen meters used are not described in the literature and hence no details are available.

2.4. Experimental conditions

The specimens to be tested were fit together in the test sections with fixing their tails by pins in adapter bushes and in upper and bottom grids. The temperature of the hot test section was 550°C, the temperature in the cold test section, 400°C. The concentration of oxygen dissolved in the liquid metal was around 3–4 $\times 10^{-5}$ wt%. The exposed materials and the corresponding test conditions are summarised in Table 2. Specimens were

Table 1
The chemical composition in wt% of the steels tested in Pb

Material	C%	Mn%	Si%	Cr%	Ni%	Mo%	W%	V%	Nb%
1.4970	0.08–0.12	1.6–2.0	0.25–0.45	14.5–15.5	15–16	1.05–1.25	–	–	–
1.4948	0.04–0.08	0–2.0	0–0.75	17–19	10–12	–	–	–	–
Optifer IVc	0.13	0.52	–	9.05	–	–	1.0	0.25	–
EM 10	0.10	0.51	0.37	8.8	0.2	1.0	–	0.03	0.01

Table 2
A list of the materials exposed to flowing lead at 400°C and 550°C

Material	400°C	550°C	400°C	550°C	400°C	550°C
1.4970	1027 h	1027 h	2000 h	2000 h	3027 h	3027 h
1.4970–GESA	–	1027 h	–	2000 h	–	3027 h
1.4948	1027 h	1027 h	2000 h	2000 h	–	3027 h
1.4948–GESA	1027 h	1027 h	–	2000 h	–	3027 h
Optifer IVc	1027 h	1027 h	2000 h	2000 h	3027 h	3027 h
Optifer IVc–GESA	–	1027 h	–	–	–	–
EM 10	–	1027 h	–	–	–	3027 h

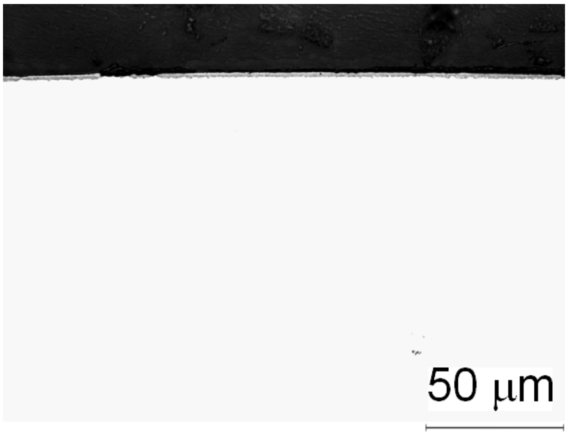

Fig. 2. Metallurgical examination of 1.4970 specimen after 3000 h at 550°C in flowing lead.

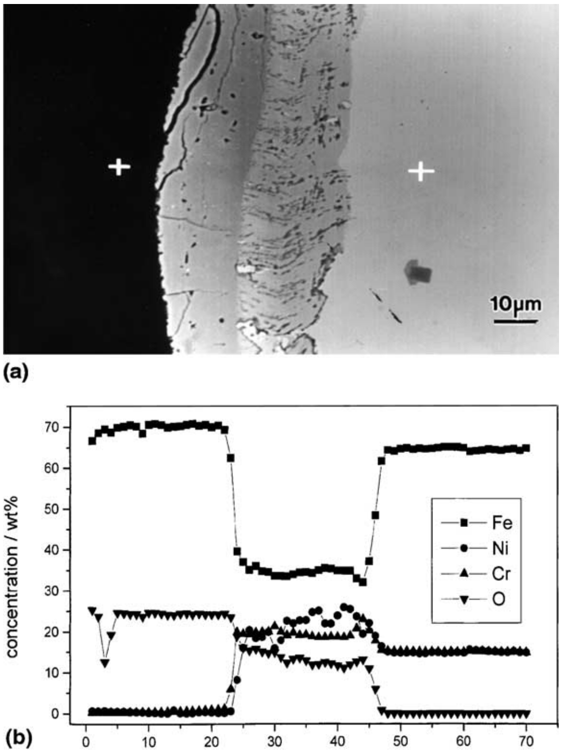

Fig. 3. Micrograph of GESA-treated 1.4970 specimen cross-section and EDX concentration profile after 3000 h at 550°C in flowing lead.

cleaned after exposure in hot oil to remove residues of lead.

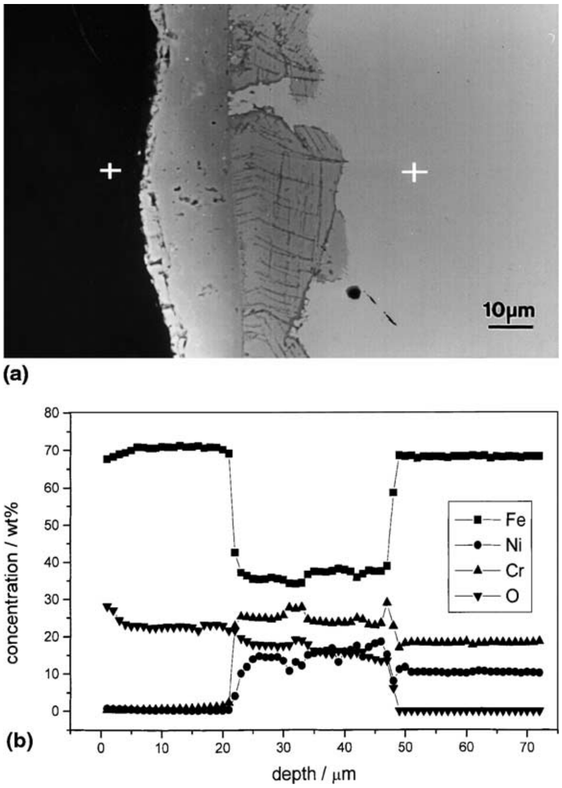

Fig. 4. Micrograph of GESA-treated 1.4948 specimen cross-section and EDX concentration profile after 3000 h at 550°C in flowing lead.

Post-test analysis consisted of: (1) weighing of the cleaned specimens, (2) X-ray spectral microanalysis of the surface of the specimens, (3) metallurgical examination and (4) EDX line scan analysis on the cross-sections of the specimens.

3. Results

The cleaned specimens showed no sign of damage (i.e. no surface roughing, no porosity etc.) by dissolution attack. The visual inspection revealed an oxide formation with varying thickness on the surface of each specimen. Austenitic steels exposed to lead up to 2000 h revealed a golden shiny surface even when exposed to 550°C, which indicates the existence of a thin oxide layer. With increasing exposure time the colour of the surface turned darker, but even then it remained shiny. The surfaces of the ferritic steels (GESA-treated and untreated) and also the GESA-treated austentic steels were black coloured without any shiny area, i.e. thick oxide layers were formed.

X-ray diffraction patterns obtained from the surface of the ferritic steels showed the formation of the compound $(\mathrm{Fe,Cr})_3\mathrm{O}_4$ already after 1000 h of exposure at 400°C and 550°C. No other compounds could be

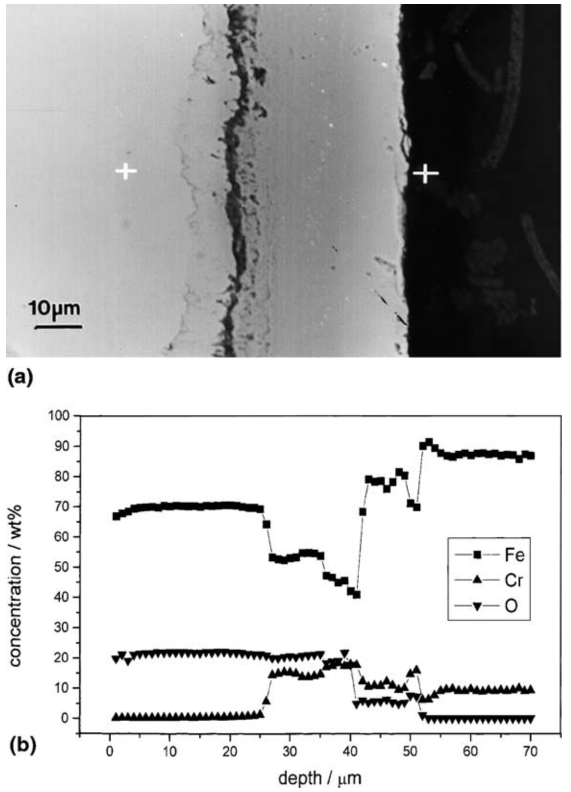

Fig. 5. Micrograph of Optifer IVc specimen cross-section and EDX concentration profile after 2000 h at 550°C in flowing lead.

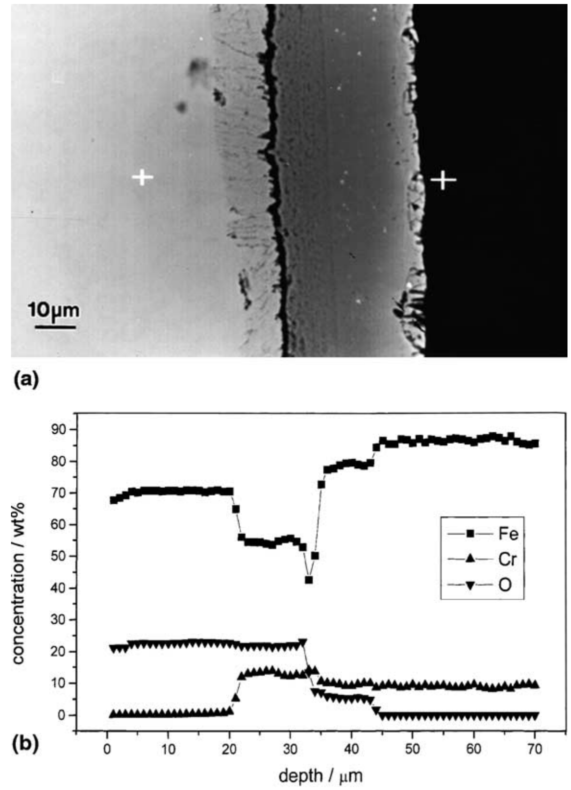

Fig. 6. Micrograph of EM 10 specimen cross-section and EDX concentration profile after 3000 h at 550°C in flowing lead.

detected even after longer exposure time. In contrast oxide patterns were not visible in the spectra of the austenitic steels, because the oxide layers were too thin. Metallurgical examination of the austenitic steels showed an oxide layer thickness of about 2 µm after 3000 h of exposure at 550°C (see Fig. 2). This film prevents the dissolution attack of the liquid lead at least during the limited time of exposure.

A two-phase oxide scale was found on all austenitic steels treated by GESA. Both layers vary in thickness. The adherence seems to be very good. The cross-sections of GESA-treated 1.4970 and 1.4948 steels after 3000 h of exposure at 550°C and the corresponding EDX concentration profiles are presented in Figs. 3 and 4. The outer layer has a composition of pure magnetite which is in agreement with the X-ray diffraction results obtained from specimens exposed to stagnant lead [11]. Other alloy steel elements like nickel and chromium were not detected. The inner layer contains iron, chromium nickel and oxygen. This corresponds to an iron chromium spinel plus nickel. The concentration of iron and chromium stays constant in the whole layer whereas the oxygen content decreases slowly and nickel increases slightly towards the steel side. In both austenitic steels the content of chromium and nickel is higher in the internal layer than in the steel matrix because of the release of iron into the magnetite layer.

In ferritic steels no obvious influence of the GESA treatment was observed [11]. The EDX concentration profiles with the corresponding cross-sections of Optifer IVc (2000 h at 550°C in lead) and EM 10 (3000 h at 550°C in lead) are shown in Figs. 5 and 6. The micrographs of the cross-sections show the typical corrosion attack with three different zones. The zone at the top consists of magnetite without appreciable chromium concentration. The layer in the middle contains Cr–Fe spinel that roots in a porous belt. Within the spinel zone, the chromium content reaches a maximum that is 1.5 times higher than the concentration in the bulk material due to iron depletion caused by the magnetite scale formation. In the interior, an oxygen diffusion zone can be observed in which oxides precipitate along grain boundaries. In the case of EM 10 the thickness of all three zones formed is smaller than that on Optifer IVc.

The total oxide layer thickness increases with time and temperature, most dramatically for the ferritic steels and GESA-treated austenitic steels. The largest thickness is achieved on Optifer IVc, followed by the GESA-

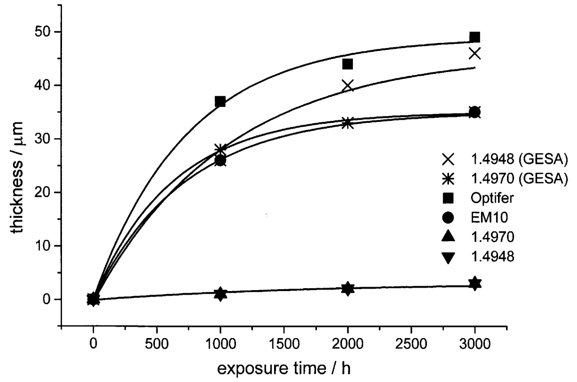

Fig. 7. Total thickness of oxide layers versus the duration of corrosion tests of steels in flowing lead at 550°C.

treated austenitic steel 1.4948. The steels EM 10 and 1.4970 (GESA-treated) showed more or less the same growth rate. The oxide layer thickness versus exposure time in liquid lead at 550°C is given in Fig. 7. It can be seen that the growth of the oxides on the ferritic steels and GESA-treated austenitic steels obeys the parabolic law.

4. Discussion

Multiphase oxide scales were formed on the steel surfaces of the ferritic steels and the two GESA-treated austenites during exposure to flowing lead. These scales protect the steels against dissolution attack. Lead was not detected in any region of the specimens, i.e. no penetration of lead into the scale or the base material had occurred. Alloy components do not diffuse at the same rate in the oxide layers and the alloy, therefore a multiphase oxide scale is formed during oxidation of the alloys. The stratified oxide layer structure and composition agrees with descriptions by Hauffe [12] and Talbot [13] for oxidation of steels below 570°C in air.

Three distinct oxidation zones were developed at the steel surfaces: an outer magnetite scale (Fe_3O_4) which is placed on top of the original surface; other than Fe and O, elements do not appear in an appreciable amount in this scale. The intermediate layer below the magnetite scale consists of a spinel $Fe^{2+}(Fe^{3+}_{1-x}Cr^{3+}_{x})_2O_4(+Ni)$. The innermost layer is an oxygen diffusion zone with spinel formation along grain boundaries.

The proposed oxidation mechanism for this multiphase oxide scale can be described as follows [14–16]: firstly, oxygen reacts with iron and chromium to form the Fe–Cr spinel. Oxygen has the capability to diffuse inward through the oxide scale and reacts with steel elements to a spinel type structure. As a result of this O-ion diffusion the Fe–Cr spinel grows inward. The outer layer grows by Fe-ion diffusion to the surface, which creates the magnetite scale that grows on the surface. Cr diffuses more slowly and is only present in the inner part of the scale.

The thickness and compositions of the multiphase oxide scales formed on the ferritic steels with and without GESA treatment do not show any difference. Hence, the additional surface treatment did not have an obvious influence on the oxidation behaviour of Optifer IVc and EM 10. Not so for the GESA-treated austenitic steels 1.4970 and 1.4948, in which multiphase oxide scales were developed like observed for the ferritic steels. In the case of untreated austenitic steel surfaces a thin dense oxide layer was formed.

All the oxide scales developed on the examined steels provide protection against dissolution attack at 400°C and 550°C up to an exposure time of 3000 h in a liquid lead loop with controlled oxygen concentration. This corresponds well with the results of corrosion tests in stagnant lead during the same exposure time [11]. Those tests also included austenitic and ferritic steels in which aluminium was alloyed into the surface by GESA pulse heating. In that case, a thin alumina scale appeared during the tests on the surface that prevented not only the dissolution attack of liquid lead but also oxidation of the steel components. This treatment may provide a superior corrosion protection especially for exposure times much longer than 3000 h.

5. Conclusions

Ferritic and austenitic steels appear to be suitable structural materials for liquid lead loops up to 550°C if the dissolution attack is prevented by a dilute solution of oxygen in the liquid metal. The concentration of oxygen must be controlled at a value at which a protective oxide scale builds up at the steel surface but no PbO is formed. Oxide scales on ferrites that develop under these conditions in lead agree in structure with those for oxidation in air. Austenitic steels have such scales only when the surface is treated by the GESA process. Untreated austenites show only very thin oxide layers of about 1–2 µm. Results obtained so far are representative for exposure times up to 3000 h only. It remains to be determined whether this conclusions is valid for longer times and also whether the thick oxide scales provide a better protection than the thin scale observed on austenitic steel. However, oxidative corrosion may become a problem with long exposure times. Alloying of aluminium into the surface of the steels has to be considered as a prospective treatment for a protection against corrosion because the alumina scale prevents not only dissolution attack but also oxidation of steel components.

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