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Silicon-containing ferritic/martensitic steel after exposure to oxygen-containing flowing lead–bismuth eutectic at 450 and 550 °C

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HIGHLIGHTS

- 9Cr–3Si steel shows basically the same phenomena as 9Cr steels with typically lower Si content.
- Improved performance in comparison to T91 especially at 450 °C and 10^{-6} mass% oxygen in LBE.
- Less clear benefits from Si addition to 9Cr steel at 550 °C.
- Oxygen $>10^{-6}$ mass% seems detrimental for 9Cr–3Si at 550 °C in respect of solution-based corrosion.

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ABSTRACT

A ferritic/martensitic (f/m) steel with 9 and 3 mass% of chromium (Cr) and silicon (Si), respectively, was tested on performance in flowing lead–bismuth eutectic (LBE) at 450 and 550 °C, each at concentrations of solved oxygen of both 10^{-7} and 10^{-6} mass%. The 9Cr–3Si steel generally exhibits the same basic corrosion modes as other f/m materials with 9 mass% Cr and typically lower Si content, namely Steel T91. The Si-rich steel shows an overall improved performance in comparison to T91 at 450 °C and 10^{-7} mass% solved oxygen, but especially at 450 °C and 10^{-6} mass% solved oxygen. The advantage of higher Si-content in 9Cr steel is less clear at 550 °C. Especially high oxygen content in flowing LBE at 550 °C, between $>10^{-6}$ mass% and oxygen saturation, seems detrimental for the high-Si material in respect of the initiation and progress of a solution-based corrosion.

1. Introduction

Liquid lead (Pb) or Pb alloys show thermal, thermo-hydraulic and neutronic properties that render them particularly suited as a coolant in fast-neutron nuclear reactors as well as coolant and spallation neutron source in an accelerator driven system. The latter is considered for the transmutation of long-lived fission products in the residues from currently operating nuclear power plants. The operating temperature envisaged for demonstrators and pilot reactors are in the range of 500 °C or lower, so that steels are favoured as a material for the structural components and fuel cladding in these first-of-a-kind plants. However, there are still open questions in regard of the compatibility of liquid Pb alloys, especially the lead–bismuth eutectic (LBE), with existing steels that may show an unacceptably high level of corrosion (solution) even at the moderate maximum temperatures proposed for the first reactors under design. Furthermore, the mechanical properties of otherwise unaffected (by corrosion) steel may degrade at simultaneous action of liquid metal and mechanical stress.

Based on early work focussing on the minimisation of steel corrosion caused by liquid Pb or LBE at 550 °C [1], addition of oxygen to the liquid metal is regarded as a feasible means of impeding the solution and removal of steel elements at the cost of the formation of an oxide scale on the steel surface. At the same time, a dense surface layer consisting of oxides of the steel elements avoids immediate contact between liquid metal and steel, and, therefore, possible detrimental effects of the liquid metal on mechanical properties of the steel. The benefit from oxygen addition for mitigating steel degradation in the presence of liquid Pb or LBE naturally depends on the growth rate and integrity of the formed oxide scale.

It is well known that silicon (Si) generally promotes the

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formation of a slow-growing surface oxide when Si-containing steel is exposed to an oxidizing environment. Accordingly, Si has been considered an important alloying element also for the strategy of minimizing steel corrosion by oxygen addition to liquid Pb or LBE [1]. Experimental studies on the Si effect reported in the technical literature indicate that austenitic nickel (Ni)–chromium (Cr) steel with 4.8 mass% Si will not show selective leaching of Ni or Cr after exposure for 3000 h to static LBE at 550 °C, in contrast to other commercial austenitic steel grades with the more typical <1 mass% Si [2]. In the cited experiment, oxygen was supplied to the LBE by using argon (Ar) cover gas with 1 vppm impurities, so that the liquid metal was oxygen-saturated (~10^{-3} mass% solved oxygen) at least near the free surface of the provided volume. At 450 °C and otherwise similar experimental conditions, none of the investigated austenitic steels exhibited solution-based corrosion, but only formation of a thin protective oxide scale [2]. While also the somewhat higher Cr content in the particular Si-rich steel that was investigated may have had a beneficial effect on the formation of a protective oxide scale, the thin surface film analysed after exposure at 550 °C primarily shows an enrichment of Si. Protective scales observed on Type 316 austenitic steel after exposure to flowing LBE at 550 °C and 10^{-6} mass% solved oxygen clearly contain both Cr- and Si-rich oxide [3].

For ferritic/martensitic (f/m) steel with 9 mass% Cr, addition of 1.5 mass% Si results in remarkably thinner oxide scales in comparison to 9Cr steel with typical (lower) Si content when being exposed for 1372 h to static LBE at 550 °C and ~10^{-5} mass% solved oxygen [4]. Si enriches especially in the inner part of the comparatively thick oxide scale that is characteristic for oxidation of 9Cr steels like T91 under these conditions. Locally, the scale observed on the Si containing material is exceptionally thin, implying high protectiveness of the formed oxide in respect of corrosion in general. However, a beneficial effect of 1.5 mass% Si in 9Cr steel is no longer noticeable in a respective experiment at 550 °C and low oxygen content around 10^{-8} mass%. The same holds true for Type 316 austenitic steel with increased Si content of 2.4 mass% [4]. The analysis of 10Cr–2Si steel after exposure to flowing (1 m/s) LBE at 550 °C and ~10^{-8} or 10^{-6} mass% solved oxygen shows that the formed oxide scales tend to crack and detach, so that the main part of the scale locally loses contact with the underlying steel, while only a thin, Cr- or Cr- and Si-rich oxide layer still adheres to the surface [5].

Particular attention has been paid to 12Cr–2Si steel EP-823, because this material is said to be the most promising candidate for fuel cladding in Pb-cooled reactors designed in Russia. When being exposed to flowing (2 m/s) LBE at 470 °C and ~10^{-6} mass% solved oxygen, EP-823 forms overall thinner oxide scales in comparison to other f/m steels like Optifer IV or T91 [6]. Si enriches in the inner portion of a bi-layer oxide scale that basically consists of a spinel-type iron (Fe)–Cr mixed oxide. During the course of respective experiments performed for up to about 3000 h, EP-823 does, however, not reach the, under these conditions, apparently more favourable oxidation behaviour of austenitic steel 1.4970 with 15 mass% Cr [6]. At 550 °C and otherwise comparable conditions, the oxide scale on EP-823 tends to become single-layer, i.e., an outer portion consisting of magnetite (Fe_3O_4) is almost completely missing [7]. Exposure of EP-823 for about 5000 h to static LBE at 490 °C and oxygen approaching saturation produces an internal oxidation zone (IOZ) that consists of oxides precipitated in the steel matrix, in addition to Fe–Cr spinel and magnetite [8]. Si again enriches in the spinel layer, and probably also in the oxidic portion of the IOZ.

In oxygen-saturated static Pb at 550 °C, internal oxidation of EP-823 is evident only for the first 1000 h of exposure [9]. Samples further exposed for another 1000 or 2000 h do not show internal oxidation anymore, but only spinel and magnetite layers. The bi-layer scale seems to periodically detach from the steel surface, possibly in association to short interruptions of the exposure and drop in temperature when samples were removed from the testing device after each 1000 h, initiating a cyclic oxidation without appreciable reduction in rate by the oxide scale that developed during the preceding cycle(s). After overall 3000 h of exposure, the material loss caused by oxidation is higher for EP-823 than for similar steel with only 0.5 mass% Si [9]. When increasing temperature to 650 °C, a porous multi-layer scale forms on EP-823 that is penetrated by liquid Pb. Although solution-based corrosion does still not occur, the scale grows to a remarkable 500 μm in 100 h [10]. Nano-indentation tests on the oxide scale that formed on EP-823 during exposure for 1500 h to oxygen-saturated static LBE at 550 °C, results in cracking of the Fe–Cr spinel layer, perpendicularly to as well as along the spinel/steel interface [11]. Mechanical instability in the inner part of the scale that is indicated by such cracking, can possibly explain a special susceptibility to spalling and detachment of oxides formed on the Si-containing material.

In the framework of corrosion tests conducted in the CORRIDA loop at KIT, potential effects of Si have been addressed by including 9Cr–3Si steel 1.4718 (X45CrSi9-3) in the selection of investigated materials. The results from characterizing this steel in respect of the performance in oxygen-containing flowing LBE at 450 and 550 °C, each at concentrations of solved oxygen of both 10^{-7} and 10^{-6} mass % are presented in the following. Additionally, the findings after exposure at 550 °C and varying oxygen concentration are reported and discussed.

2. Characterisation of the sample material

1.4718 is a heat-resistant f/m steel with nominally 9 and 3 mass% of Cr and Si, respectively. The Ni content is limited to ≤0.50 mass%. This steel is typically used for exhaust valves in combustion engines, where high-temperature oxidation resistance and fair elastic properties are required. The particular sample material tested in the CORRIDA loop was bought from an external supplier in the form of rods with 9.5 mm diameter.

The chemical composition of the investigated material was analysed in-house using different techniques, including optical emission spectroscopy (OES), inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray fluorescence spectroscopy (XFA) and energy-dispersive X-ray micro-analyses (EDX). Infrared detection (IR) of combustion products (at >2000 °C) was used as an alternative method of analysing carbon (C) and sulphur (S). The results are summarised in Table 1. Elements with allowed concentration ranges being specified for 1.4718 in the currently valid industrial standard (DIN EN 10090 1989-03) are listed above the dividing line in this table. The measured concentrations of these elements are in accordance with the specifications, especially for Cr and Si. The indicated C content is at the lower edge of the allowed range from 0.40 to 0.50 mass%. Average Cr and Si concentrations determined from EDX point analyses correspond fairly well to the results from the other methods applied.

The qualitative metallographic examination of the as-received material in the light-optical (LOM) and scanning electron microscope (SEM), both after etching of the polished cross section, revealed a fine-grained martensitic structure (Fig. 1). The identification of martensite from the produced micrographs alone remained ambiguous, but was corroborated by comparison of the peaks in the X-ray diffraction (XRD) spectra recorded from 1.4718 and a clearly martensitic reference material, namely 9Cr steel T91. The 1.4718 sample material shows some titanium (Ti)-rich