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Oxidation studies of Fe10CrAl–RE alloys exposed to Pb at 550 °C for 10,000 h

Jesper Ejenstam [a,*], Mats Halvarsson [b], Jonathan Weidow [b], Bo Jönsson [c], Peter Szakalos [a]

[a] KTH Royal Institute of Technology, Division of Surface and Corrosion Science, Drottning Kristinas väg 51, 100 44 Stockholm, Sweden
[b] Chalmers University of Technology, Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden
[c] Sandvik Heating Technology AB, Box 502, 734 24 Hallstahammar, Sweden

HIGHLIGHTS

- Four experimental Fe10CrAl alloys were exposed to liquid Pb at 550 °C up to 10,000 h.
- Influence of the Al content and the impact of reactive elements (RE) were studied.
- Critical Al content was found in the interval of 4–6 wt.% Al, given the RE additions.
- None of the experimental alloys was severely attacked by liquid Pb.
- The effect of RE may be more important than the actual Al content (4–6 wt.%).

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ABSTRACT

Five experimental FeCrAl–RE alloys have been exposed up to 10,000 h in stagnant liquid Pb at 550 °C. The test matrix consisted of three 10 wt.% Cr alloys, with an Al content ranging from 4 to 8 wt.% (10Cr–4Al, 10Cr–6Al and 10Cr–8Al), one alloy without additions of reactive elements (RE) (10Cr–6Al), and one reference alloy with 21 wt.% Cr and 5 wt.% Al (21Cr–5Al). The evaluation showed a clear difference in oxidation properties, and it was possible to divide the alloys into two distinct groups. A critical Al concentration in the interval of 4–6 wt.% at the given RE content was required to form a thin protective oxide. However, the absence of RE addition in one of the two 10Cr–6Al alloys resulted in a significant reduction in oxidation resistance, comparable with 10Cr–4Al. None of the alloys were severely corroded, however Pb penetrated to a relatively large extent into the porous oxide of the low performing alloys. A 100 nm thick oxide scale, partly consisting of alumina (Al_2O_3), was observed for the high performing 10Cr–6Al alloy. The Fe10CrAl–RE alloys showed overall very good corrosion resistance and are hence a promising new alloy category for liquid Pb applications.

1. Introduction

The corrosive natures of Pb and lead bismuth eutectic (LBE) at high temperatures are well known, and have been intensely studied in the literature [1–3]. Attention has recently been turned to Al-alloyed steels due to the protective properties of Al-rich oxides [4–17]. Ferritic FeCrAl–RE alloys are examples of such high temperature materials, commonly used as heating elements at temperatures between 900 °C and 1400 °C [18]. Their high chromium content (20–22 wt.%) makes the ferritic structure prone to spinodal decomposition at approximately 475 °C. Around this temperature, the material will rapidly segregate into an iron rich phase (α), and a chromium rich phase (α'), causing severe embrittlement [19–21]. The amount of embrittling phases can be described as a function of the Cr content in the Fe matrix. A reduction of the Cr content hence decreases, or even suppresses, the spinodal decomposition. Chromium plays a crucial role in the formation of alumina, for the ternary system of FeCrAl alloys [22]. Therefore, a reduction of Cr content would influence the oxidation properties. Reduction of Cr and a parallel increased Al content have shown to restore the ability of these alloys to form a protective surface oxide [9]. Long-term oxidation studies are rare and are crucial to verify these findings. The addition of small amounts of reactive elements (RE), such as Y, Zr, Ti, Hf, Ce, Sc, is essential for the formation of thin, slow growing, protective oxides, hence ensuring long lifetime of the structural component. Effects of RE addition on the oxidation properties of high temperature alloys have been extensively studied elsewhere [23–25]. FeCrAl–RE alloys are currently being proposed as potential surface alloying material on 15-15 Ti cladding tubes in the European Lead Cooled Training Reactor (ELECTRA) [26]. Bulk FeCrAl–RE alloys are also candidate alloys for heat exchangers and of large potential for other applications to improve safety in light water reactors (LWR) by replacing

* Corresponding author. Tel.: +46 8 790 6642.
E-mail address: ejenstam@kth.se (J. Ejenstam).

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Zircalloy cladding tubes [27], in bio and waste fired waste burning power plants, and as structural components for heat exchanger and energy storage systems based on liquid metals in concentrated solar power (CSP) plants [3,28].

The aim of this study is to evaluate the long-term oxidation properties of a new category of "low" Cr containing FeCrAl–RE alloys via pilot corrosion tests in stagnant liquid Pb, at 550 °C, up to 10,000 h. The investigation includes three 10 wt.% Cr alloys, with an Al content ranging from 4 to 8 wt.% (10Cr–4Al, 10Cr–6Al and 10Cr–8Al), one alloy without the addition of RE, (10Cr–6Al–(No RE)), and one reference alloy with 21 wt.% Cr and 5 wt.% Al (21Cr–5Al). The corrosion resistance is evaluated via surface and bulk analytical studies of the oxide scale.

2. Materials and methods

2.1. Materials

In collaboration with Sandvik Heating Technology AB in Hallstahammar, Sweden, five experimental FeCrAl–RE alloys were produced. In the pre-study phase, calculations by means of the Thermo-Calc software indicated that the Cr limit for suppressing spinodal decomposition is approximately 10 wt.% for an FeCrAl–RE containing 4 wt.% Al (Fig. 1). Even at a low temperature of 327 °C (Pb melting point), no embrittling phases are present. The kinetics for the phase separation at this temperature is slow, and may hence not be an issue for a structural component out-of-pile. However, under irradiation, the kinetics of spinodal decomposition has been shown to rapidly increase [29]. These findings show that the resistance to spinodal decomposition is important over the entire temperature range. Moreover, the addition of Al to an Fe–Cr alloy seems to suppress the phase separation according to Thermo-Calc calculations as shown in Fig. 1. This observation is supported in the literature [30–32].

Based on this thermo-dynamical calculation, a Cr content of 10 wt.% was selected for the experimentally produced alloys of this study. The Al content was varied from 4 up to 8 wt.%, with minor RE-additions of Zr and Ti. An FeCrAl–RE alloy of standard composition (Fe21Cr5Al) was produced in the same way as the other experimental alloys and used as reference. Bulk alloy compositions are given in Table 1.

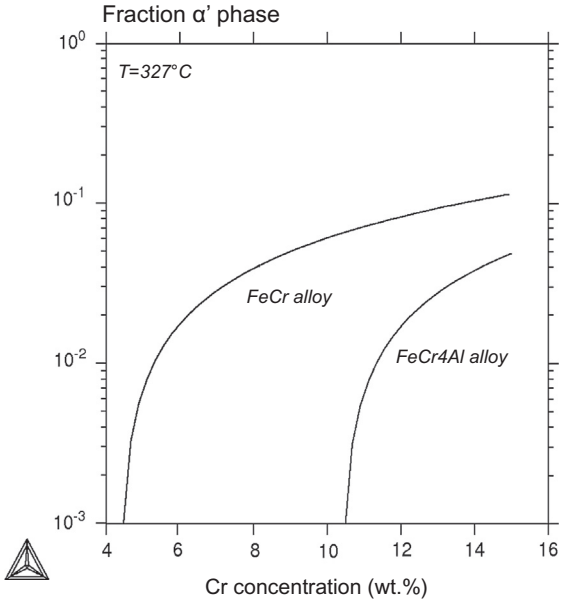

Fig. 1. Fraction of the α′ phase as function of Cr content at 327 °C calculated for an Fe–Cr alloy, with and without 4 wt.% Al, by means of the Thermo-Calc software.

Table 1
Bulk alloy compositions of all experimental alloys, in wt.%.

Alloy ID	Fe	Cr	Al	Si	C	Ti	Zr
21Cr–5Al	Bal.	21	5	0.07	0.03	0.07	0.08
10Cr–8Al	Bal.	10	8	0.07	0.03	0.07	0.08
10Cr–6Al	Bal.	10	6	0.07	0.03	0.07	0.08
10Cr–4Al	Bal.	10	4	0.07	0.03	0.07	0.08
10Cr–6Al-(no RE)	Bal.	10	6	0.07	0.03	–	–

Experimental alloys, roughly 1 kg per batch, were produced in an induction-melting furnace, flushed with argon. The ingots were cut into 20 × 70 mm rods and hot-rolled at 1100 °C into 8 × 1 mm strips in 8 steps, with 5 min heat treatment after each step. Finally, 30 mm samples were cut from the strips and heat treated at 1050 °C for 5 min in air, in order to recrystallize the microstructure. After recrystallization, all samples were polished with #800 SiC paper to remove any surface oxides formed during the heat treatment. Finally the samples were ultrasonically cleaned for 10 min in ethanol.

2.2. Methods for material characterization

2.2.1. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

A JEOL-7001F SEM and an FEI Quanta ESEM equipped with a field emission guns (FEGs), were used to perform the initial characterization. High-resolution micrographs along the entire cross section on one side of the samples were recorded to obtain oxide thickness statistics. The samples, polished in about a 45° angle along one edge, were placed vertically in the sample holder, tilting the polished surfaces away from the incident electron beam. In this way, the electrons see the true surface, as the projected area is corrected with the same angle as the samples were initially polished with. All micrographs were collected with an acceleration voltage of 10 kV. 80 mm^2 X-Max Silicon Drift EDS Detectors (SDDs) from Oxford Instruments were used for line scans, point analyses, and elemental maps.

2.2.2. Electron Backscatter Diffraction (EBSD)

The FEG-SEM used in this work for EBSD analyses was a LEO 1530 with a Gemini column and a Nordlys F+ EBSD camera. The EDS detector was a 50 mm^2 X-Max SDD from Oxford Instruments. All measurements were performed using an accelerating voltage of 15 kV.

2.2.3. Focused Ion Beam Scanning Electron Microscopy (FIB-SEM)

Cross sections, for studying the thin oxide scales by means of SEM and Transmission Electron Microscopy (TEM), were produced in two DualBeam instruments; an FEI Strata 235 DB and an FEI Versa 3D. These instruments are a combination of an SEM and a Focused Ion Beam (FIB) microscope. For both the cross sections and the TEM-specimens, platinum was deposited on the specimen surface and then, Ga^+-ions were used to perform the sputtering next to the platinum layers. In the case of producing TEM-specimens, the *in-situ* lift-out technique was employed [33].

2.2.4. Broad Ion Beam (BIB) milling

In order to produce cross sections on slightly thicker oxide scales without the aid of grinding and polishing, which possibly could smear Pb present on the surface into the oxide cross section, BIB milling was used. A Gatan Ilion+ working at 6 kV was used.