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The influence of silicon on the corrosion properties of FeCrAl model alloys in oxidizing environments at 600 °C

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ABSTRACT

The present study investigates the influence of Si on the high temperature corrosion behaviour of FeCrAl model alloys in O_2, O_2+H_2O and O_2+H_2O + KCl at 600 °C for up to 168 h. The investigation by SEM/EDX showed that all alloys displayed a protective behaviour in dry O_2. In the more corrosive environments (O_2+H_2O and O_2+H_2O + KCl) the addition of Si affected the oxidation properties in two ways; Alloys containing Si resisted breakaway oxidation caused by Cr-evaporation (O_2+H_2O) and the thickness of the oxide formed after breakaway oxidation decreased with increasing amount of Si (O_2+H_2O + KCl).

1. Introduction

FeCrAl alloys, and the corrosion resistance of these, has been studied extensively at high temperatures (900–1300 °C) where FeCrAl alloys (about 20 wt% Cr and 1–5 wt% Al) may form a protective α-alumina. The α-alumina is reported to be the most protective alumina oxide scale giving an excellent corrosion resistance up to 1300 °C in O_2/H_2O-containing environments, see e.g. [1–3]. Due to the formation of the protective α-alumina FeCrAl alloys are commonly used as heating elements for various different applications, including the electrical elements of gas burners, furnace rollers, ignitors etc. It has been shown that FeAl alloys can form α-alumina as well but when adding chromium to the alloy, the amount of aluminium needed to form the protective layer, is decreased [4]. This is beneficial since high Al-contents have negative impacts on mechanical properties such as fabricability.

At medium high temperatures, between 700 °C and 900 °C, depending on environment and alloy composition, it is well known that the protective α-alumina layer may not form and instead transient alumina forms. The properties of the transient alumina are less known and consequently stainless steels are normally used at this temperature span as they form a protective chromia-layer [1]. However, in more corrosive environments, containing alkali salts such as KCl as well as water vapour, the protective chromia formed on stainless steels has been shown to the react with water vapour, leading to chromium evaporation [5] or alkali, leading to the formation of chromates [6–9]. Studies of the corrosion behaviour of FeCrAl alloys below 900 °C has shown that in an environment containing O_2 and H_2O, FeCrAl alloys are able to form a thin protective transient alumina layer at as low as at 600 °C [10]. The transient alumina contain small amounts of both Fe and Cr [11]. Thus, the transient alumina is less sensitive towards reaction with water vapour/alkali compared to pure chromia. However, upon introducing KCl on the sample prior to exposure, the corrosion process has been shown to drastically accelerate as a result of a rapid formation of iron-rich oxide [10]. Pre-oxidation of a FeCrAl alloy to form a thin protective alfa/transient alumina layer, prior to exposure, has shown to have a significant beneficial effect on the corrosion behaviour [12] but was sensitive towards flaws in the scale. However, a transient alumina formed on AlNi coatings has been shown to be able to resist reactions with small amounts of KCl [13]. In highly corrosive environments, the protective oxides of both alumina and chromia-formers tend to break down and form fast growing iron-rich oxide. The microstructure of this oxide has been shown to be similar for austenitic and ferritic stainless steels (FeCr and FeCrNi) as well as FeCrAl alloys at 600 °C and consists of an outward growing iron oxide as well as an inward growing spinel oxide [14–17].

Adding small amounts of specific elements may influence the corrosion properties of the alloy by increasing the protectiveness of the alumina/chromia or by altering the growth rate of the iron-rich oxide after the thin protective oxide has been lost. This is not fully understood for FeCrAl alloys in the temperature range around 600 °C.

It is well known that small amounts of alloying elements, e.g. reactive elements (RE) or Si, may strongly influence the corrosion properties of alloys. The RE effect has been studied extensively over the years and has been summarized in three extensive review articles

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[18–20]. Studies has shown that small additions of rare earth elements, other reactive metals or stable oxide dispersions to chromia- or alumina-forming alloys have significant beneficial effects on the corrosion properties of the material. Two important effects of the addition of RE is the reduction of the scale growth rate as well as the enhanced adhesion of chromia and alumina scales [21,22]. Even though there are a large number of studies in this area, the RE effect is still not fully understood, however, there are a few hypothesis regarding the mechanisms of the effects. One suggested mechanism is that the RE may act as nucleation sites on the surface of the material, resulting in a more fine-grained initial oxide film as well as the stabilization of transient alumina phases. A suggested mechanism for the enhanced scale adhesion is the formation of “oxide pegs” extending from the oxide to the alloy substrate. In alumina forming alloys, these oxide pegs has been shown to consist of alumina which is forming by enhanced inward growth. The majority of studies regarding the effect of RE addition has been performed at higher temperatures. The influence of RE additions on the corrosion properties of stainless steels at lower temperatures (600 °C) is less studied.

Adding small amounts of silicon to stainless steels (FeCr, FeCrNi) is known to have large positive impact on the corrosion protection at high temperatures [23–25]. Continuous as well as discontinuous silica layers have been observed at high temperatures (700–900 °C). These layers may act as diffusion barriers, reducing the oxide growth rate. However, the effect of Si on FeCrAl alloys at 600 °C has not been investigated.

The aim of the present work is to study the effect of small additions of silicon on the corrosion behaviour of FeCrAl model alloys with RE at 600 °C. FeCrAl model alloys with varying silicon contents (between 0 and 2 wt% while other elements are kept fixed) have been isothermally exposed in three differently corrosive environments (Dry O_2, $O_2 + H_2O$ and $O_2 + H_2O$ with KCl present at 600 °C) and subsequently analysed using SEM as well as XRD.

2. Experimental procedure

2.1. Sample preparation

Three different FeCrAl model alloys were used in this study (composition of the alloys are shown in Table 1). The Cr-content in the alloys were kept low to reduce the negative effects of Cr on the mechanical properties. The alloys were first melted in a vacuum induction furnace into a 1 kg ingot. This ingot was later hot-rolled into a strip and further machined to the get a thickness of about 2 mm. The strip was also heat treated at 950 °C to achieve a more even grain size distribution. The strip was then cut into coupons with a dimension of 10 x 12 mm. A small hole with a diameter of 1.5 mm was also drilled into the sample to simplify weighing. A second heat treatment at 950 °C for one hour was performed to relax elongated grains in the bulk of the samples. However, even after the second heat treatment, the grain size varied slightly between different coupons of the same alloy. The average grain size was in the range of 110–130 µm. Prior to exposure, the sample coupons were ground to 500 grit with SiC paper and then polished down to 1 µm with a diamond suspension until a mirror-like surface had been achieved.

2.2. Exposure

Prior to exposure the samples were weighed using a Sartorius™ balance with microgram resolution. KCl was deposited onto both large surfaces of the samples by spraying a 20:80 water-ethanol solution in which KCl had been dissolved. While spraying the solution, a flow of warm air was directed towards the sample which accelerate the drying of the solution. The samples were weighed again in order to register the amount of KCl deposited on the sample. The procedure was repeated until an amount of 1 mg/cm^2 had been deposited on each sample.

Table 1
Nominal chemical composition (wt-%) of FeCrAl model alloys.

Alloy	Cr	Al	Si	Zr
FeCrAl**0Si**	10	4	0	0.29
FeCrAl**1Si**	10	4	1	0.29
FeCrAl**2Si**	10	4	2	0.29

The samples were exposed in a horizontal silica tube furnace in three different environments at 600 °C for 168 h. The gas flow was calibrated using a Bios Definer 220 M to achieve a total flow rate of 3 cm/s and two different gas compositions consisting of 5% O_2 + N_2(bal.) and 5% O_2 + 20% H_2O + N_2 (Bal.). In the latter gas composition, the samples were exposed both with and without KCl deposited on the surface. In the environment in which KCl was present, a short term exposure of three hours was performed for all three alloys. Samples were mounted vertically in alumina sample holders consisting of three slits in the same direction as the tube furnace. After exposure the samples were weighed again and mass gain was registered. The tube furnace set up used in this study was described by Pettersson et al. with a schematic illustration in [9].

2.3. Analysis

Cross sections of the samples were prepared by first gluing on a thin silicon wafer onto the surface of the sample. After the glue had dried for about 24 h they were dry cut with a low speed diamond saw and subsequently milled using broad ion beam (BIB) with a Leica TIC 3X instrument to achieve a smooth surface for more accurate analysis. The three argon guns of the BIB instrument were operated at 6.5 kV for 12 h.

The surface morphology and the cross sections of the resulting oxides of the exposed samples were analysed by means of scanning electron microscopy (SEM) (using both backscattered electrons (BSE) and secondary electrons (SE)) and energy dispersive X-ray (EDX) with an accelerating voltage of 10–20 kV using an FEI Quanta 200 equipped with an Oxford Instruments X-Max^N 80 T EDX detector. In order to closely analyse the oxide grain size on specific samples, a FEI Versa3D LoVac DualBeam FIB-SEM was used. Already prepared cross sections were polished with ions to achieve a smoother surface, making the oxide grains more distinguishable. Ion induced secondary electrons (with accelerating voltage of 30 kV and a beam current of 10 pA) were detected to achieve the image. The average oxide grain size was calculated after measuring the largest diameter of the grains in an image processing software.

Analysis with X-ray diffraction (XRD) using a Siemens Diffraktometer D5000 was also performed as a complement to the EDX-analysis to determine the crystal structure of the oxide layers of the outward growing oxide. The XRD program consisted of a locked couple scan ranging from $2\theta = 0$ to 80°.

3. Results

3.1. Gravimetry

3.1.1. 5% O_2 + N_2

The alloys were exposed to a dry gas mixture of oxygen with nitrogen in balance. All samples exhibit low mass gains after 168 h exposure (Fig. 1), indicating the formation of a thin protective oxide. Based on chromia/alumina the calculated thicknesses vary between 32/42(FeCrAl**2Si**) and 143/189 nm (FeCrAl**0Si**). Small differences in mass gain is observed between the samples in the zoomed in box (the right-hand corner of Fig. 1). FeCrAl**0Si** exhibits a lower mass gain than FeCrAl**1Si** while FeCrAl**2Si** shows the lowest mass gain in this environment.

3.1.2. 5% O_2 + 20% H_2O + N_2

In the O_2/H_2O-containing environment FeCrAl**0Si** exhibits a large