Cross-Sectional Investigations of Oxide Scale Nanocrystalline FeCr Alloys after High-Temperature Oxidation Test at 900°C

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Abstract. The cross-sectional examinations of oxide films formed by oxidation on the surface of FeCr alloys with various crystallite sizes were observed and investigated. X-ray diffraction (XRD) analysis was used to characterize the oxide scale morphology and to identify the phases and oxidation products. Furthermore, Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) have been used to study the cross-sectional oxides produced by specimens after oxidation process. The cross-sectional investigation shows that the oxide scale formed on the surface of FeCr alloys consisted roughly of Cr2O3 with a small amount of FeO mixture. The outward diffusivity of Chromium to form Cr2O3 protective layers varies significantly on the surface of FeCr alloy with smallest crystallite size (38.51 nm), the scale had an enriched Cr content which improves the adherence of the oxide scale to the substrate, in another word, it increases the oxidation resistance. While the oxide scale formed on the surface of FeCr alloy with largest crystallite sizes (76.60 nm) had an enriched Fe content which reduces the resistance to oxidation, and adherence to the substrate. The thickness of oxide scale formed on nanocrystalline FeCr alloy with smallest crystallite sizes was found around 8 μm thick, which three-time thinner than FeCr alloy with largest crystallite sizes.

1. Introduction

The interconnect is a critical component in the stack of solid oxide fuel cells (SOFC), which act as a physical separation between anode and cathode gasses and provide the electronic connection between the single cells of the stack. Technical requirements to be used as interconnect in SOFC should fulfill a number of specific requirements, i.e. a high oxidation resistance, a high electrical conductivity of the surface oxide scales, gas tightness, and a coefficient of thermal expansion matched to the electrolyte and the electrodes [1,2]. Cr based alloys and high-Cr ferritic steels seem to be the most promising metallic interconnect materials [1].

The oxidation performance of FeCr used in high-temperature applications (such as Interconnector in SOFC) depends on their potential to form and maintain a Cr2O3 oxide scale under SOFC atmospheres [2, 7]. The main phenomena taking place during reactions of metals with oxygen. Initially, the gas absorbs on the metal surface as atomic oxygen; then oxide nucleation and growth to form a complete thin film [3]. Scale growth results from the concomitant moving of electrons, oxide ions, metal ions and oxygen diffusion through the scale [4]. As the scale grows up, cavities and micro cracks may be created from generated stresses, leading to failure of the scale [5, 6, 12]. When Cr based alloys and high-Cr ferritic steels are exposed to an oxidizing environment at elevated temperatures, an oxide layer is formed on the surface, acting as a barrier between the metal and the gas. Chromium increases the oxidation resistance of stainless steels by the formation of a chromia (Cr2O3) scale on the surface. Other oxides
which are often encountered in the layers are iron oxides (wüstite FeO, magnetite Fe3O4, or hematite Fe2O3). Refer to our previous study [7, 9], the effect of the smallest crystallite sizes can significantly improve the high-temperature oxidation and corrosion resistance of FeCr alloy that oxidized at 900°C. However, it focused only on investigating of oxidation kinetic, oxide phase and surface morphology characterization of specimens, but did not investigate the characterization of oxide scale on a cross-sectional analysis and the growth mechanism of oxide scale. Therefore, the objective of this study is to investigate the cross-sectional characteristics of oxide scale that formed on the surface FeCr alloys after being oxidized at 900°C.

2. Specimens and Experimental Procedure

2.1. Specimens
The studied specimens of developed nanocrystalline FeCr alloys were prepared by the following process. As starting element materials, high purity (99.99%) powders of Fe and Cr with mean particle size of about 2 µm were prepared by powder metallurgy technique, the powders of Fe and Cr with nominal composition of 80wt%Fe and 20wt%Cr were mechanically alloyed into RETCH PM400 planetary ball mill with variations of milling time for 40 h, 60 h, and 80 h. The ball milled alloy powder specimens were then hot compacted at 1000°C into samples of the dimension of 33 mm diameter and 3 mm thickness, under a uniaxial pressure of 25 Mpa pressure in a vacuum atmosphere for 45 min.

2.2. Oxidation Test
The samples of oxidation test were cut from the specimens to the size of 4x5x3 mm. The samples were subjected to oxidation tests in laboratory air at atmospheric pressure in a PROThERM box furnace at 900°C for 100 h in laboratory air at the atmospheric pressure. The linear heating and cooling rates were controlled at 5°C/min. The electronic analytical microbalance with an accuracy of 0.01 mg was used to determine the weight of the specimens after each interrupted cycle.

2.3. Preparation of cross-section specimens
Cross-section samples are mounted using “cold-mounting” resins. Samples were placed on a commercial sample holder (cylindrical), fixed through a drop of wax. Resin (plus hardener and accelerant) is then poured in the sample. Next, after 12 hours, the sample and resin becoming a hard block. Furthermore, the samples were polished on the cross-sectional face up to 1500 grade SiC paper and final polishing using 0.05 µm diamond paste.

2.4. Microstructure Characterization
The oxidized alloys were investigated by a BRUKER D8 Advance X-ray diffraction (XRD) equipped with CuKα radiation and phase identification as referred to the ICDD PDF-2 database. The surface and cross-sectional morphology analyses of oxidized specimens were carried out with a JEOL JSM-6380 scanning electronic microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) analyzer. The EDS analyses were performed as point analysis and line/mapping analysis.

3. Results and Discussion

3.1. Previous Results
The previous results on developed of FeCr Alloys, oxidation test, and parabolic rate were collected in Table 1 and Fig.1 [7, 8, 9, 10 & 11], where the parabolic rate constant (k_p) is determined by the mass gain (∆W) per unit surface area of a specimen (A) and exposure time (t) [9-10].

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(\frac{\Delta W}{A})^2 = k_p t
\]
Table 1. Mass gain change and parabolic rate constant ($k_p$) of FeCr alloys after oxidized at 900°C.

| Specimens  | Crystallite size (nm) | Mass Gain (mg/cm²) | Parabolic Rate, $k_p$ (mg²/cm⁴) |
|------------|-----------------------|--------------------|---------------------------------|
| FeCr “A”   | 53.33                 | 21.81              | 6.191                           |
| FeCr “B”   | 38.51                 | 7.72               | 0.794                           |
| FeCr “C”   | 76.60                 | 35.18              | 13.58                           |

Figure 1. Surface morphology characterization of oxide scale FeCr alloys oxidized at 900°C [10].

Fig. 1 shows the surface morphology of oxide scale on the specimens that oxidized at 900°C. The surfaces of FeCr “A” and FeCr “B” were covered with compact oxide scale consisting of fine grain scales. The oxide scales showed that the mainly consisted of Cr₂O₃ which indicates the scale had an enriched Cr content which improves the adherence of the oxide scale to the substrate. This occurrence can be explained due to the chromia growth mechanism, where chromium preference diffused outward to react with oxygen. However, the oxide scale that formed on the surface FeCr “C” indicated covered and distributed evenly with the main composition of FeO approximately 98.57 at%. This indicates that Cr₂O₃ as the protective layer becomes non-protective, due to the formation of cracks and volatile Cr₂O₃ upon exposure to oxidizing atmospheres for extended periods [10].

Figure 2. X-rays diffractograms of FeCr alloy oxidized at 900°C
Fig. 2 above shows the diffraction patterns of FeCr “A” and FeCr “B” that were oxidized at 900°C. The x-rays diffractograms show some peaks of the original alloys and the corundum oxides of Cr₂O₃. The presence of the peak of the original alloy indicates that oxide scale was formed as a thin layer which dominated by the presence of Cr-rich oxide and small peaks of solid solution chromium iron oxide (Fe,Cr)₂O₃ [10-11]. On the contrary, FeCr “C” after oxidized 900°C, all strong peaks were dominated by the presence of hematite Fe₂O₃. The results have also identified the presence of mixed oxides and a solid solution of chromium iron oxide (Fe,Cr)₂O₃ are present. While the presence of the peaks of the original alloys still found with a small intensity which indicates that oxide scale was growing rapidly with the dominating presence of Fe-rich oxide due to largest crystallite size effect.

3.2. Results of the current study

The cross-sectional morphologies of the oxide scale formed on FeCr alloys that oxidized at 900°C for 100 h in air atmosphere are presented in Fig 3.

![Figure 3. Morphological characterization of oxide scale FeCr “A” oxidized at 900°C.](image)

Fig. 3 shows the SEM/EDS analyses on the cross-sectional view for oxidation of FeCr alloys, Fig.3 clearly shows that the internal layer of oxide scale was dominated by the presence of Cr₂O₃. While on the outer layer of the oxide scale was dominated by the presence of FeO. SEM micrograph of cross-sectional investigation of the specimens have also shown the thickness of oxide scale formed on FeCr “A” and FeCr “B” was found around 20 and 8 μm thick respectively, while the thickness of oxide scale formed on FeCr “C” as the specimen with the largest crystallite sizes was found around 30 μm thick. This indicates that the crystallite sizes have a significant effect to improve the oxidation resistance of the alloys. In order to understand more detail about the mechanism of oxide growth on the surface of specimens, EDX line/mapping analysis was used to verify the results in the formation of the oxide scale as shown in Fig.4, 5 and 6.

![Figure 4. EDS line mapping analysis across the interface of the FeCr “A” oxidized at 900°C.](image)
Fig. 4 above shows that the scale formed on FeCr “A” consisted of outer iron oxide layers, while the inner layer of oxide scale is richer in Cr. Based on the image of EDX mapping analyses, the results showed the occurrence of internal oxidation in the substrate of the alloy. This phenomenon indicates that the diffusion is predominated by oxygen ion diffusion into the substrate alloy and reacting with Cr$^{3+}$ ions then form a local oxidation of Cr$_2$O$_3$.

**Figure 5.** EDS line mapping analysis across the interface of the FeCr “B” oxidized at 900°C.

Fig. 5 above shows that the inner layer of oxide scale is richer in Cr, which can be clearly seen from the cross-sectional scale morphology of the specimens. The Cr, Fe, and oxygen as measured from the substrate/oxide interface to the outer surface of the oxide scales are similar in both of the specimens. The oxide scale that formed on the surface of FeCr “A” and FeCr “B” where the enhancement of Cr diffusion guarantee the stable growth of the Cr-rich in the inner of the oxide scales, which significantly improve oxidation resistance, even a Cr$_2$O$_3$ scale may be formed at higher temperatures owing to the higher diffusion rate of Cr. However, EDS line/mapping analysis indicates that the presence of internal oxidation in FeCr “A” and FeCr “B”. It may be caused by oxygen that through diffusing into the alloy and reacting with Cr$^{3+}$ ions that higher oxygen affinity before Cr$^{3+}$ ions diffuses to the surface of the specimens.

**Figure 6.** EDS line mapping analysis across the interface of the FeCr “C” after oxidized at 900°C.
Fig. 6 above shows that the Cr concentration in FeCr “C” is still not sufficiently high to allow the formation of a more protective Cr2O3 layer, while the iron ions dissolve in and diffuse rapidly through the Cr2O3 scale and eventually an outer layer of fairly pure iron oxides will result. It may be caused by Fe and Cr ion transport is predominant then make the scale growth will proceed outwards, the oxygen transports through the FeO layer to the Cr2O3 layer and the Cr ions diffuse to the same layer; both of them react with each other, which make the oxide scale become thicker. Furthermore, due to the loose and incompact scale, thus causing the crack in the surface of the specimen (see Fig. 1) which increase the rate of Cr evaporation. The oxygen may diffuse to the oxidation/alloy interface through the cracks and pores in the oxide scale. This phenomenon was confirmed by XRD results as shown in Fig. 2, where the result shows that the oxide phase that formed on the FeCr “C” is dominated by the presence of Fe3O4. It’s also reinforcement by mass gain change and parabolic rate constant (kp) as presented in Table. 1, where FeCr “C” was found as the specimens with the largest mass gain change and parabolic rate (kp) which indicates that the oxide scale has grown rapidly on the surface of the specimen. It can be noticed that a discontinuous Cr2O3 scale was formed, but could not protect the alloy from internal oxidation. At the same time, Fe became enriched and diffused outwards, which caused the formation and rapid growth of FeO.

4. Conclusion

Based on the results obtained in the oxidation of nanocrystalline FeCr alloys at 900°C for 100 h the following conclusions can be formulated:

1. The specimens developed with smaller crystallite size have a significant effect to improve the oxidation resistance and the adherence of the oxide scale to the substrate of the alloys and also relatively less mass gain is found in the developed alloy with the finer crystallite size of FeCr “B”.

2. The FeCr “B” show better promoting the formation of Cr2O3 in large amount compositions which indicated that chromium preference diffused outward to form a Cr2O3 layer. The thickness of oxide scale formed on nanocrystalline FeCr “B” was found around 8 μm thick, three times thinner than FeCr “C” which indicates that developed specimen with smallest crystallite size can significantly reduce the growth of the oxide scale and reduce the rate of Cr evaporation.

3. The oxide scale that formed on the surface of FeCr “C” as the larger crystallite size was formed as thicker oxide scale which significant increase in oxidation weight gain. It can be noticed that a discontinuous Cr2O3 scale was formed, but could not protect the alloy from internal oxidation. At the same time, Fe became enriched and diffused outwards, which caused the formation and rapid growth of FeO. Blocked by Cr2O3, FeO nucleated and grew at the discontinuous areas such as the incompact Cr2O3 scale or its micro-defective areas; leading to some bulges and cracks.

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