

Initial Oxidation Behavior of a Commercial FeCrAl-based Alloy Under 1200°C Steam Environment

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1. Introduction

Owing to their low cross section of thermal neutron absorption, adequate oxidation resistance and materials properties, zirconium-based alloys have been widely used for fuel cladding materials in nuclear power plants. However, the accident in Fukushima Daichi reactors has highlighted the importance of using fuel cladding materials with higher tolerance to the severe accident condition, i.e. exceptional oxidation resistance under high temperature steam environment. FeCrAl alloys are recently considered to be in the top lists of candidate materials for this purpose [1].

Oxidation resistance of FeCrAl alloys relies on the formation of a protective dense α -Al₂O₃ (corundum) scale. However, the formation of this slow growing oxide and how it behaves especially during early stage of oxidation at high temperature still need to be understood better in order to improve predictive capability for its protective properties. The present study focused on the early stage behavior of α -Al₂O₃ scale formed on a commercial FeCrAl alloy and various microstructural changes with time during early stage of oxidation have been investigated.

2. Experimental Technique

A commercial FeCrAl alloy was the material being investigated in the present study. It contains small refractory inclusions of yttrium and hafnium oxides dispersed in its matrix and has chemical composition as shown in Table 1. From the given material, 10 × 30 × 2 mm samples were cut. Prior to exposure, the samples were polished, cleaned, dried and weighed.

Table 1: Chemical composition of material

Element	Fe	Cr	Al	Mo	Si	Y	Mn	Hf
wt.%	Bal.	22.2	5.1	3.1	0.2	0.2	0.1	0.06

The samples were exposed in a resistance heating horizontal tube furnace for a 100 sec, 1h, 3 h, and 24 h. The steam and Ar gas were supplied into the furnace at a rate of 500cc/hr, respectively after heating them to 350°C. After the furnace was heated and stabilized, the samples were inserted into the furnace, heated at a rate of ~ 6.5°C/s and then taken out after being oxidized at 1200°C for the designated durations. This rapid heating

rate was deliberately set in order to simulate LOCA condition in LWR. After the exposures, the samples were cooled to room temperature in laboratory air.

After the steam oxidation tests, the samples were weighed for weight gain measurement. The oxide scales formed on the samples were observed using a SUPRA40VP (Zeiss) Scanning Electron 129 Microscope (SEM) at an accelerating voltage of 15 kV equipped with Energy Dispersive X-ray 130 Spectroscopy (EDS), and a TALOS F200X (Thermo Fisher Scientific) Transmission Electron 131 Microscope (TEM) at an accelerating voltage of 200 kV.

3. Results and Discussion

Weight gain as a function of time is shown in Fig. 1. As expected that the weight gains were quite small. As a comparison, the measured weight gain after 100 s steam exposure in this study was 0.007 mg/cm², which is much smaller than 10.07 mg/cm² gained by Zr-Nb-Sn alloy that was previously reported using similar experimental set-up and condition [2]. This clearly indicates that FeCrAl-based alloys exhibit a significantly superior oxidation resistance compared to Zr-based alloys. The oxidation kinetics is parabolic, indicating that parabolic rate law is obeyed in the present study.

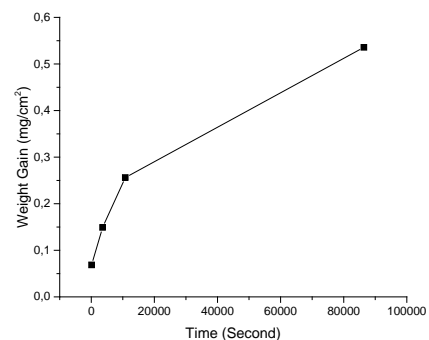


Fig. 1. Weight gain vs time

SEM and TEM images (Fig. 2 and 3) show that all oxidized samples were covered by continuous Al₂O₃ scales with varying thicknesses. No spallation of the scale was observed. All oxide scales had a band enriched by Cr that divides the scales into two layers, an outer layer located above the band and an inner layer located below the band. With an exception of oxide

scale formed after 100 s exposure that contained both inner and outer layers with equiaxed grains, all other oxide scales consisted of an inner layer with elongated or columnar grains and an outer layer with more equiaxed grains. Except for oxide scale on 100s exposed sample that consists of outer and inner layers having relatively similar thicknesses, inner layers were relatively thicker than outer layers in all other oxide scales. Both outer and inner oxide layers become thicker as the time increases but the inner layer has a noticeably greater growth rate compared to that of the outer layer.

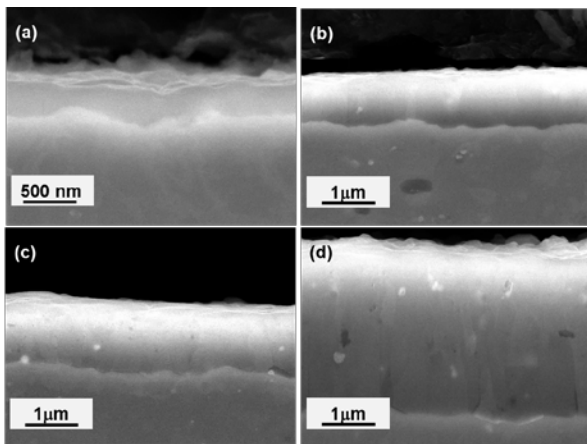


Fig. 2. SEM cross section images showing oxide scale grown after (a) 100 s, (b) 1 h, (c) 3 h, and (d) 24 h.

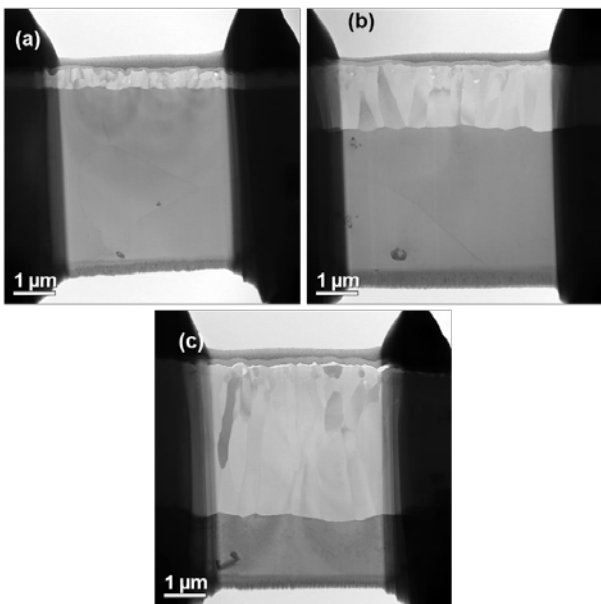


Fig. 3. TEM cross section images showing oxide scale grown after (a) 100 s, (b) 3 h, and (d) 24 h.

According to distances and angles between spots in FFT patterns constructed from both outer and inner layers of all oxide scales, it is concluded that α - Al_2O_3 was the dominant phase. It has been reported that

initially at low temperatures, between 600–900°C, α - Al_2O_3 may not form and instead metastable aluminas form [3,4]. Metastable aluminas will afterward transform to stable α - Al_2O_3 . This transformation will be faster at high temperatures beyond 1000–1100°C. In the present study, the phase transformation of Al_2O_3 was very fast as the sample has already been covered by a continuous α - Al_2O_3 scale after 100 s exposure at 1200°C.

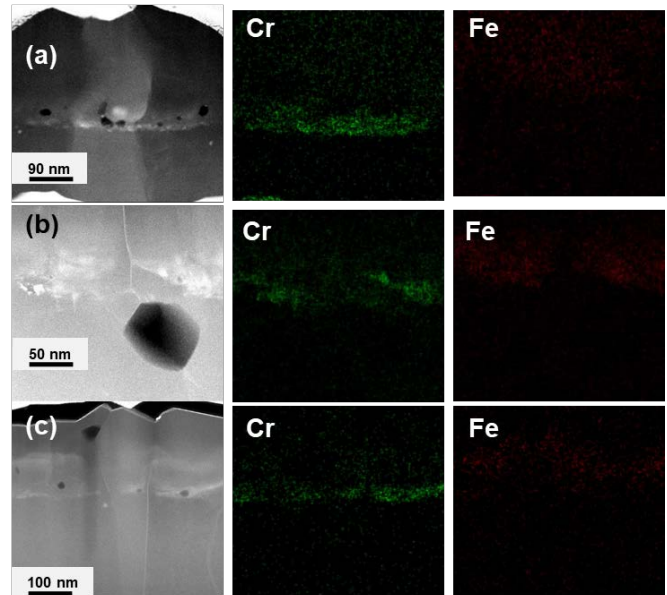


Fig. 4. TEM/EDS maps showing Cr-rich band oxide scale grown after (a) 100 s, (b) 3 h, and (d) 24 h.

Fe was observed to be present above the Cr-rich band, in other words in the outer oxide layer (see Fig. 4). In line with hypothesis stated by authors [3-5,8], the Fe and Cr-rich band in the present study are believed to be a remnant of oxide scale that has formed earlier (i.e. during sample heat up). Previous investigations of oxidation behavior of FeCrAl alloys at medium high temperatures, between 600°C and 900°C, have reported that oxides of Fe and Cr form along with metastable aluminas [4,5]. After phase transformation of metastable aluminas to α - Al_2O_3 , some of Fe and Cr oxides will remain in oxide scale as α - Al_2O_3 , α - Fe_2O_3 and Cr_2O_3 are mutually soluble [5]. It can be thought thus that the outer layer of the scales has been formed by outward diffusion of aluminum and the inner layer has been formed by inward diffusion of oxygen. This conclusion is supported by previous studies, which have shown the inward and outward growing of Al_2O_3 scales to occur simultaneously [6,7]. Nano-sized particles enriched with Fe and Cr were also observed, which is in agreement with previous study investigating the formation of Al_2O_3 on a FeCrAl-based alloy using atom probe tomography (APT) [8].

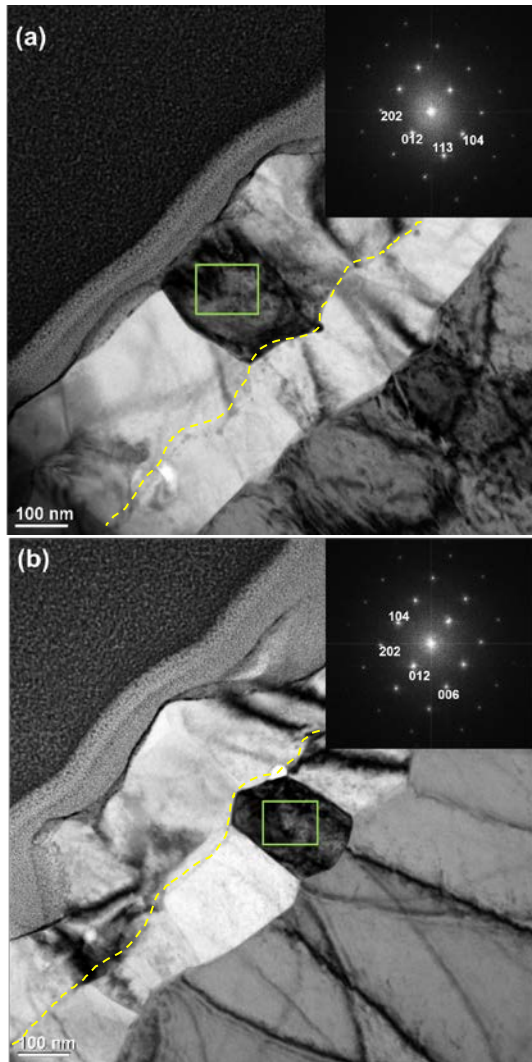


Fig. 5. FFT patterns taken in (a) outer layer and (b) inner layer of 100 s oxide scale, yellow dashed lines are Cr-rich band.

The behavior of reactive elements (REs) such as Y, Zr, Hf, Ti, Ce or La is also important to be paid attention. The sample in the present study contained small additions of Y and Hf. Segregation of Y at oxide scale grain boundaries was observed after 3 h and 24 h exposures but not visible after 100 s. Segregation at oxide scale grain boundaries has been a common behavior of REs [9,10]. The presence of RE ions at the scale grain boundaries results in the suppression of native cation transport [9,10], which is believed to have happened in the present study. Very low concentration of Y at the scale grain boundaries after very short exposure durations especially after 100 s, which is possibly below the detection limit of TEM/EDS, can be thought to result in the difficulty in detecting Y grain boundary segregation in the scale in the present study. The same argument can also be used to explain why

grain boundary segregation of Y is more observable than that of Hf.

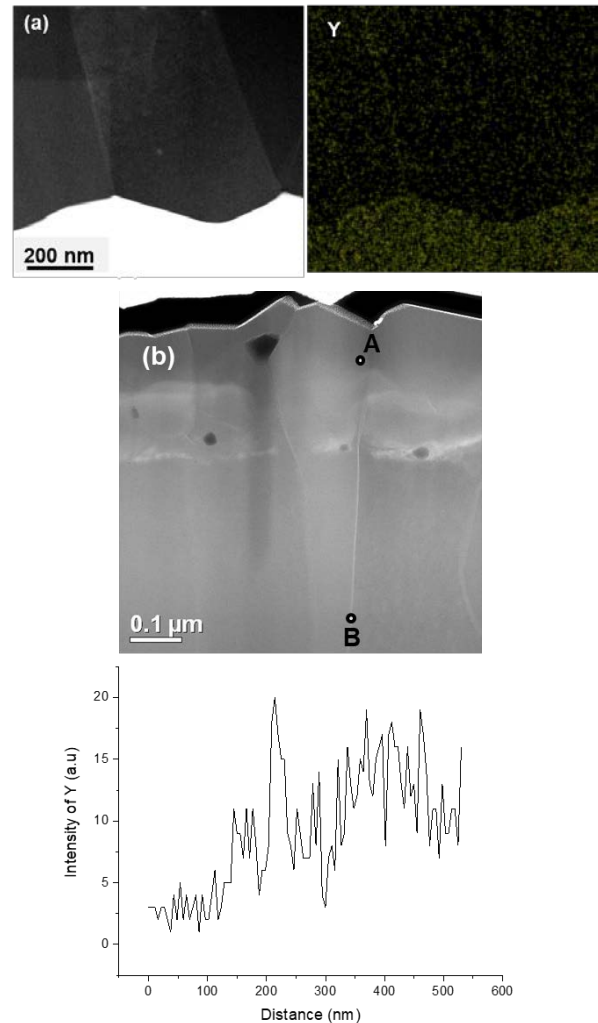


Fig. 6. (a) EDS map showing Y segregation in 3h oxide scale grain boundaries, (b) EDS line analysis taken from point A to B showing increased Y concentration along a grain boundary in 24 h oxide scale

Void formation was observed in all oxide scales. The sizes of the observed voids ranged from 4 to 50 nm, 4 to 80 nm, and 2 to 100 nm in 100 s, 3 h, and 24 h oxide scales respectively. In 100 s oxide scale, voids were mainly observed to be in or close to the Cr-rich band. Voids existed across the thickness of 3h scale with number and size of voids increased in closer region to the Cr-rich band. The outer layer of 24 h scale had some relatively large voids. The scale grain boundaries appear to be preferential sites for void formation in all oxide scales. Void formation at alloy/scale interface, which has been associated with scale spallation or loss of adhesion [11,12], was not observed in all oxide scales.

Based on the observations in the present study and existing literatures, it is worthwhile to explain the mechanism for oxide scale formation. It is believed that during earlier stage of oxidation (i.e. sample heat up),

the formed transient oxide scale consists of metastable aluminas, Fe and Cr oxides. After a certain time, high metastable aluminas will transform to stable α -Al₂O₃. As metastable aluminas are less dense compared to α -Al₂O₃, the phase transformation of Al₂O₃ results in loss of oxide volume and may therefore contribute to the void formation observed in the scale [3,12]. After the formation of α -Al₂O₃, some of Fe and Cr oxides, such as α -Fe₂O₃ and Cr₂O₃, will remain at least partially in oxide scale as α -Al₂O₃, α -Fe₂O₃ and Cr₂O₃ may form a solid solution. At high temperature (1100-1200°C), inward oxygen diffusion begins to be more predominant than outward aluminum diffusion, resulting in the increased rate of oxide formation at or near the alloy/scale interface. The suppression of outward aluminum diffusion is believed to be due to REs effect. Scale growth proceeds with simultaneous inward-outward growing dominated by inward growing, resulting in faster growth of inner layer than that of outer layer of the scale.

4. Conclusion

- All oxide scales, mainly consisted of α -Al₂O₃, had two layers separated by the Cr-rich band. Oxide scale formed after 100 s exposure contained inner and outer layers having equiaxed grains and all other oxide scales consisted of an inner layer with elongated or columnar grains and an outer layer with more equiaxed grains. Both outer and inner oxide layers become thicker as the time increases but inner layer has a noticeably greater growth rate compared to that of outer layer.
- The outer layer of the scales has formed by outward diffusion of aluminum and the inner layer has formed by inward diffusion of oxygen.
- Fe was observed to present above the Cr-rich band. Fe and Cr-rich band are believed to be a remnant of oxide scale that has formed earlier (i.e. during sample heat up).
- Segregation of Y at oxide scale grain boundaries was observed after 3 h and 24 h exposures but not visible after 100 s possibly due to very low concentration of Y at the scale grain boundaries.
- Void formation was observed in all oxide scales. No void formation was visible in all oxide scales indicating that the scales have good adherence.

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REFERENCES

- [1] R. B. Rebak, Versatile Oxide Films Protect FeCrAl Alloys Under Normal Operation and Accident Conditions in Light Water Power Reactors, JOM Vol.70, p.176-185, 2018.
- [2] J. Moon, S. Kim, W. D. Park, T. Kim, S. W. McAlpine, M. P. Short, J. H. Kim, and C. B. Bahn, Initial oxidation behavior of Fe-Cr-Si alloys in 1200°C steam, Journal of Nuclear Materials Vol.513, p.297-308, 2019.
- [3] F. Liu, H. Götlind, J.-E. Svensson, L.-G. Johansson, M. Halvarsson, Early stages of the oxidation of a FeCrAl alloy (Kanthal AF) at 900°C: A detailed microstructural investigation, Corrosion Science Vol.50, p.2272–2281, 2008.
- [4] J. Engkvist, S. Canovic, F. Liu, H. Götlind, J.-E. Svensson, L.-G. Johansson, M. Olsson & M. Halvarsson, Oxidation of FeCrAl foils at 500–900°C in dry O₂ and O₂ with 40% H₂O, Materials at High Temperatures Vol.26, p.199-210, 2009.
- [5] J. Engkvist, S. Canovic, K. Hellström, A. Järnäs, J.-E. Svensson, L.-G. Johansson, M. Olsson, Alumina Scale Formation on a Powder Metallurgical FeCrAl Alloy (Kanthal APMT) at 900–1,100°C in Dry O₂ and in O₂ + H₂O, Oxidation of Metals Vol.73, p.233–253, 2010.
- [6] K. Abbasi, M. Zahiri Azar, and A. H. Heuer, Study of Scale Formation on Al₂O₃-Scale Forming Alloys by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), Materials Performance and Characterization Vol. 6, No.3, p.292-297, 2017.
- [7] J. A. Nychka and D. R. Clarke, Quantification of Aluminum Outward Diffusion During Oxidation of FeCrAl Alloys, Oxidation of Metals Vol. 63, p.325-352, 2005.
- [8] F. Liu, M. Halvarsson, K. Hellström, J.-E. Svensson, L.-G. Johansson, First three-dimensional atomic resolution investigation of thermally grown oxide on a FeCrAl alloy, Oxidation of Metals Vol.83, p.441-451, 2015.
- [9] B. A. Pint, Experimental Observations in Support of the Dynamic-Segregation Theory to Explain the Reactive-Element Effect, Oxidation of Metals Vol. 45, p.1-37, 1996.
- [10] D. Naumenko, B.A. Pint, and W.J. Quadackers, Current thoughts on reactive element effects in alumina-forming systems – in memory of John Stringer, Oxidation of Metals Vol. 86, p.1-43, 2016.
- [11] B. A. Pint, On the Formation of Interfacial and Internal Voids in a-Al₂O₃ Scales, Oxidation of Metals Vol. 48, p.303-328, 1997.
- [12] J. L. Smialek and R. Gibala, Structure of Transient Oxides Formed on NiCrAl Alloys, Metallurgical Transaction A Vol. 14, p.2143-2161, 1983.