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Microscopic Characterization of various yttrium doped FeCrAl Alloys under High Temperature Steam Oxidation

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1. Introduction

The zirconium alloy cladding has good corrosion resistance in the operating environment of water reactors, but rapid oxidation reaction occurs under the loss-of-coolant accident conditions, which can lead to hydrogen explosion as in the Fukushima nuclear power plant accident [1].

For this reason, various materials are considered as potential candidate for Accident Tolerant Fuel (ATF) cladding such as SiC, Mo and iron-chromium-aluminum (FeCrAl) alloys, which are resistant to corrosion even in a high temperature steam environment, have been developed over the world. Several concepts, such as application of a coating to a conventional zirconium cladding or a multi-metal layer cladding, have been studied. In a short term, it is necessary to study coating technology, but it also has disadvantages such as potential peeling of the coating layer under the accident conditions and difficulty of formation of uniform coating layer at 4-m long cladding. From the long-term point of view, it is necessary to study FeCrAl alloys that can replace existing zirconium cladding.

FeCrAl alloys have excellent oxidation resistance in both a high temperature steam and primary water environment and have resistance to hydrogen embrittlement. However, in order to further improve the oxidation resistance of FeCrAl alloys in high temperature, it is considered to dope the reactive element such as Y, La, Ce and Hf, which is known to affect scale adhesion, growth and microstructure of alumina-forming alloys. In this study, 4 kinds of Fe-13Cr-6Al with varying contents of yttrium (0 ~ 0.27 wt. %) were fabricated to evaluate the optimized chemical composition by the oxidation resistance under high temperature steam environment. Microstructure analysis was conducted to investigate the yttrium behavior. FeCrAlY samples were isothermally oxidized for 10 minutes, 3 hours, and 8 hours under a 1200 ℃ steam/Ar environment.

2. Experimental methods

The compositions of Cr and Al were varied in the range of 13~14 wt. % and 4 ~ 6 wt. %, respectively. Cr has a maximum content limitation of 20 wt. % in order to prevent the α'-α phase separation. At least 13 wt. % Cr is necessary for the stable Cr oxide formation in the primary water. For Al, there is a maximum content limitation of 6 wt. % to ensure fabricability and at least 4 wt. % Al is necessary for the uniform Al_2O_3 formation [2,3,4].

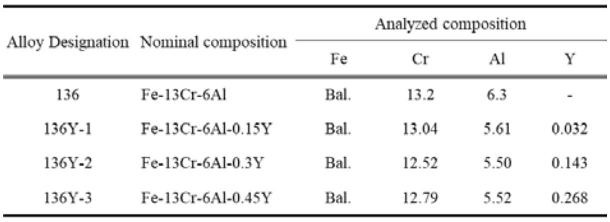
Within this limited range, the chemical composition of 13 wt. % Cr and 6 wt.% Al was fabricated as reference FeCrAl alloy. To evaluate the yttrium behavior under high temperature steam environment, 0.05, 0.1 and 0.15 wt. % Y doped FeCrAl alloys were also fabricated for comparison.

Since yttrium has high reactivity with oxygen, it was difficult to achieve the nominal chemical composition in actual samples. Therefore, the FeCrAl alloys with 0.15, 0.3 and 0.45 wt. % yttrium, which are three times larger than the initial nominal chemical composition, were fabricated by referring to earlier results [5].

The FeCrAlY pre-alloy was manufactured by arc-melting and then induction-melting was conducted to remove yttrium rich oxide slag on the surface of ingots. After the induction-melting, the slag was filtered when pouring the molten alloy into the mold. An ingot with a width of 55 mm, a length of 100 mm and a thickness of 24.8 mm was homogenized at 1200 °C for 2 hours. The homogenized ingot was hot rolled at 700 ℃ and annealed at the same temperature for 1 hour. The final thickness of samples is 3 mm, and the total thickness reduction rate is 87.9%. The chemical composition of samples is shown in Table 1.

To evaluate the oxidation resistance with time, 10 × 30 × 2 mm polished samples were inserted into a tube furnace. Yttrium doped FeCrAl samples were isothermally oxidized for 10 minutes, 3 hours, and 8 hours under a 1200 ℃ steam/Ar environment, non-yttrium doped FeCrAl sample was only oxidized for 3 hours. After oxidation, the samples were cooled in laboratory air.

Table I: Chemical composition (in wt. %) of samples



Alloy Designation	Nominal composition	Analyzed composition			
		Fe	Cr	Al	Y
136	Fe-13Cr-6Al	Bal.	13.2	6.3	-
136Y-1	Fe-13Cr-6Al-0.15Y	Bal.	13.04	5.61	0.032
136Y-2	Fe-13Cr-6Al-0.3Y	Bal.	12.52	5.50	0.143
136Y-3	Fe-13Cr-6Al-0.45Y	Bal.	12.79	5.52	0.268

3. Results & discussion

3.1. Weight gain

The high temperature oxidation resistance of each alloy was evaluated by comparing the weight gain and the results are shown in Fig. 1. It is interesting to note that there seems to be the optimum yttrium content in terms of high-temperature oxidation resistance. Therefore, addition of proper yttrium content is very important for high temperature oxidation resistance of FeCrAl alloys.

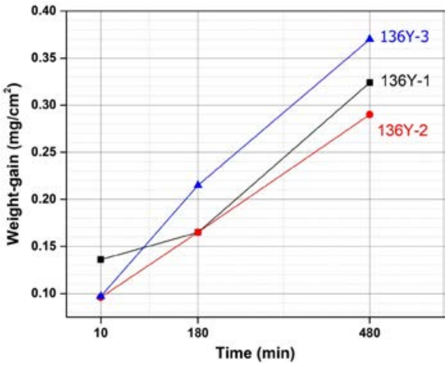


Fig. 1. Weight gain comparison of FeCrAl-Y alloys corroded for 10 minutes, 3 hours and 8 hours under 1200 °C steam/Ar environment.

3.2. Oxide morphology of corroded samples

In the case of non-yttrium doped 136 alloy corroded for 3 hours, most of the oxide layer was spalled out as shown in Fig. 2. However, in the case of the yttrium doped alloys, the uniform aluminum oxide was formed on the surface with the reticular structure in which yttrium peaks were highly detected in the EDS mapping results as shown in Fig. 3. These reticular structures were decreased in size as the exposure time increased.

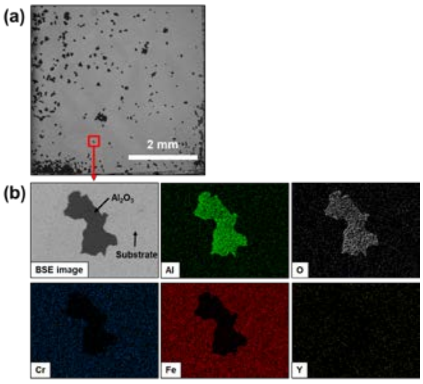


Fig. 2. (a) SEM image of top view and (b) EDS analysis results of remained aluminum oxide of non-yttrium doped 136 alloy corroded for 3 hours under 1200 °C steam/Ar environment.

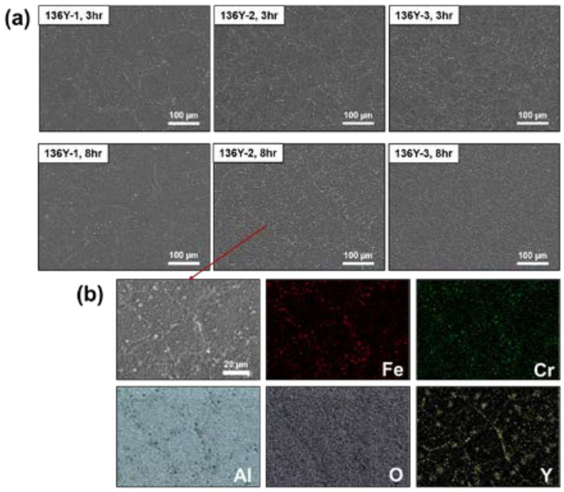


Fig. 3. (a) Reticular structure on 3 hours and 8 hours corroded 136Y-1, 136Y-2 and 136Y-3 and (b) EDS analysis results of reticular structure formed on 8hr corroded 136Y-2 under 1200 °C steam/Ar environment.

3.3. Relationship between reticular structure and $Y_3Al_5O_{12}$

The detail reticular structure can be described by four areas through EDS mapping analysis as shown in Fig. 4. The reticular structure present as spot with Y content, which can be distinguished into the large spot marked in yellow circle and the small spot in red circle. Near the reticular structure, there is the region (blue circle) in which the Fe and Cr are mainly detected in EDS analysis. In the other regions (marked in black circles), the contents of Al and O contents are mainly detected.

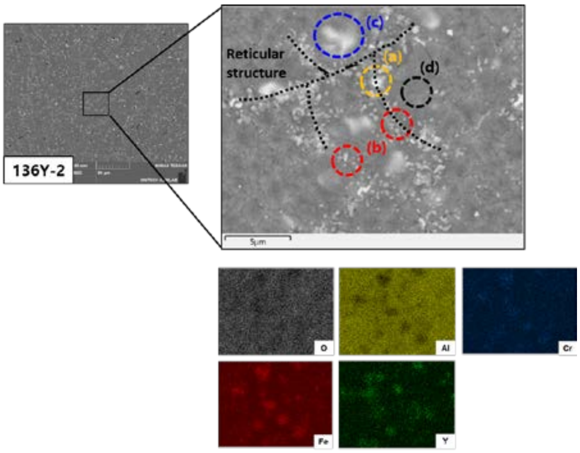


Fig. 4. Results of EDS analysis of oxidized surface of 136Y-2 specimens corroded for 3 hours under 1200 °C steam/Ar environment.

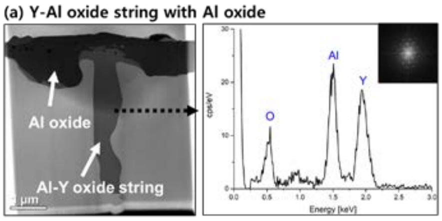
The detail microstructure by Transmission electron microscopy (TEM) for the areas of Fig. 4 (a), (b), (c) and (d) are shown in Fig. 5. In the large spot (region (a)) where the Y content was relatively high in the reticular structure, Y rich oxide was observed at the metal grain boundary. This Y rich oxide was determined as the $Y_3Al_5O_{12}$ by TEM crystallography diffraction pattern.

On the other hand, the $Y_3Al_5O_{12}$ was observed inside of uniform aluminum oxide as shown in Fig. 5 (b) where the cross-section of region of small spot with high Y content was detected on the corroded surface.

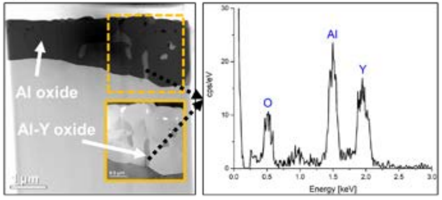
At the cross section of the Fe and Cr contents were mainly detected (Fig. 4(c)), relatively thin aluminum oxide films were observed as shown in Fig. 5 (c). Due to this thin aluminum oxide layer, it is believed that the Fe and Cr contents from the base metal existing below the thin oxide was easily detected.

Lastly, the non-reticular area designated in (d) of Fig. 4 showed only the uniform aluminum oxide (see Fig. 5(d)). All of the aluminum oxide formed under the 1200 °C steam environment shows that the large number of voids and Fe or Cr rich nano-particles are linearly aligned to lateral direction of aluminum oxide. Detail explanation of voids and nano-particles will be discussed in a next section.

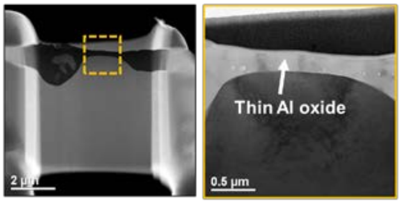
(a) Y-Al oxide string with Al oxide



(b) Y-Al oxide in the Al oxide



(c) Thin Al oxide layer



(d) Non reticular structure

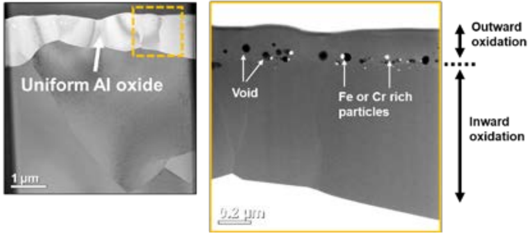


Fig. 5. TEM analysis results for cross-section of the oxidized surface of 3 hours corroded 136Y-2 under 1200 ℃ steam/Ar environment.

3.4. Cr rich band with void and nano-particles

In the aluminum oxide of 136Y-2 corroded for 10 minutes or 8 hours, the Cr rich band was commonly observed with voids and nano-particles. However, grain shape and thickness of outer oxide and inner oxide were different according to the exposure time with Cr rich band as interface.

In the case of the 136Y-2 specimen corroded for 10 minutes, the thickness of the outer oxide and inner oxide was almost the same and existed as equiaxed grain or as one grain. The chemical composition of nano-particles inside the Cr rich band was mainly observed as Fe or Cr. These Fe or Cr rich particles are believed to be the remnant of α-Fe_2O_3 and Cr_2O_3 formed at the transient stage before the temperature of specimen reaches to 1200 ℃ [6].

On the other hand, in case of the 136Y-2 specimen corroded for 8 hours, the thickness of outer oxide was the same as that of 10 minutes corrosion, but the thickness of the inner oxide increased drastically. The oxide was grown as a columnar grain to inward direction. And some Y rich particles were also additionally observed in the Cr rich band. As shown in Fig. 6, yttrium was segregated at the grain boundary of inner aluminum oxide, but yttrium segregation could not be observed at the grain boundary of outer oxide from Cr rich band. The yttrium particles observed at the Cr rich band of the 136Y-2 alloy corroded for 8 hours were believed to relate to the yttrium segregation observed at grain boundaries below the Cr rich band. The yttrium rich particles were not observed after the 10 minutes exposure time but observed in the 8 hours corroded samples. It is thought that the yttrium ions can diffuse along the grain boundary in aluminum oxide as the corrosion time increases. This yttrium segregation at the grain boundary could delay the oxygen diffusion, which is in agreement with previous study about the role of reactive elements in aluminum oxide as grain boundary segregation [7, 8].

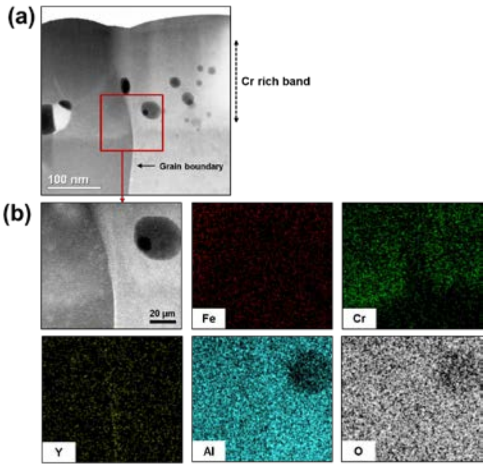


Fig. 6. Yttrium segregation at the inner aluminum oxide and Cr rich band of 8 hours corroded 136Y-2 under 1200 ℃ steam/Ar environment.

4. Summary

Microstructural analysis of oxide formed on FeCrAl and FeCrAlY alloys were performed by TEM and SEM to characterize the oxide formed after isothermal high temperature steam oxidation test.

In the case of non-yttrium doped 136 alloy corroded for 3 hours, most of the oxide layer was spalled out. But in the case of yttrium doped 136Y alloys, aluminum oxide fully cover the corroded surface with yttrium rich reticular structure.

Weight gain results show the oxidation resistance is not linearly increase as yttrium content, it seems to be the optimum yttrium content in terms of high-temperature oxidation resistance. Therefore, addition of proper yttrium content is very important for high temperature oxidation resistance of FeCrAl alloys.

The Reticular structure is related to $Y_3Al_5O_{12}$ formed in the oxide layer and $Y_3Al_5O_{12}$ peg formed in the grain boundary of metal below the aluminum oxide. Cr rich band and Fe or Cr rich nano-particles were observed in aluminum oxide at 10 minutes, 3 hours, and 8 hours corroded alloys, and Y segregation was observed at grain boundaries below the Cr rich band. For 8 hours exposure time, Y rich particles were observed in the Cr rich band. It is thought that the yttrium ions can diffuse along the grain boundary in aluminum oxide as the corrosion time increases. This yttrium segregation at the grain boundary could delay the oxygen diffusion.

ACKNOWLEDGMENT

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REFERENCES

[1] P. Hofmann, Current knowledge on core degradation phenomena, a review. Journal of Nuclear Materials Vol.270, p.194-211, 1999.

[2] S. Kobayashi, T. Takasugi, Mapping of 475°C embrittlement in ferritic Fe–Cr–Al alloys. Scripta Materialia Vol.63, p.1104-1107, 2010.

[3] J. Bischoff et al., "Proceedings of the Third Meeting of the OECD-NEA Expert Group on Accident Tolerant Fuels for LWRs, 3-5 March 2015, OECD-NEA HQ", Organisation for Economic Co-Operation and Development, 2015

[4] Y. Yamamoto, "Development and quality assessments of commercial heat production of ATF FeCrAl tubes", Oak Ridge National Lab. (ORNL), Oak Ridge, TN, United States, 2015.

[5] Y. Yamamoto et al., Development and property evaluation of nuclear grade wrought FeCrAl fuel cladding for light water reactors. Journal of Nuclear Materials Vol.467, p.703-716, 2015.

[6] J. Engkvist, S. Canovic, K. Hellström, A. Järdnäs, 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 O_2 and in $O_2 + H_2O$, Oxidation of Metals Vol.73, p.233–253, 2010.

[7] 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.

[8] D. Naumenko, B.A. Pint, and W.J. Quadakkers, Current thoughts on reactive element effects in alumina-forming systems – in memory of John Stringer, Oxidation of Metals Vol. 86, p.1-43, 2016.