

Development of yttrium doped FeCrAl alloy for LWR cladding

Sungyu Kim^{a*}, Joonho Moon^a, Chi Bum Bahn^{a**}

^a School of Mechanical Engineering, Pusan National University, Busan 46241, South Korea

*Presenting author: sgkim@pusan.ac.kr

**Corresponding author: bahn@pusan.ac.kr

1. Introduction

Zirconium alloy cladding has good corrosion resistance in the operating environments of pressurized water reactors and boiling water reactors, but a rapid oxidation reaction occurs when the loss-of-coolant accident occurs as in the Fukushima nuclear power plant accident. If the hydrogen generated by this oxidation reaction accumulates inside the containment, hydrogen explosion may occur [1].

FeCrAl alloys are known to have excellent oxidation resistance in a high temperature steam environment. They also have resistance to corrosion under primary water environments and to hydrogen embrittlement. But the optimized composition for light water reactor environments has not been determined yet.

The FeCrAl alloys are known to have ductility degradation as the '475 °C embrittlement' occurs. This phenomenon is considered to be due to the phase separation of the α -(Fe, Cr) ferrite phase and Fe-rich ferrite (α') with the formation of the Cr-rich ferrite (α') phase of the miscibility gap below ~500 °C in the Fe-Cr binary system. Therefore, hardening occurs when stainless steel having a Cr content exceeding ~12 wt. % is exposed for a long-term at temperatures about 475 °C. Although the temperature of the cladding is about 320-350 °C under the operating conditions of the nuclear power plant, it may be lower than 475 °C, but the '475 °C embrittlement' may occur if phase separation is promoted by enhanced diffusion process due to neutron irradiation. It is necessary to design the optimized chemical composition of FeCrAl alloy to prevent this phenomenon and apply to the fuel cladding of light water reactor.

In this study, 6 samples of FeCrAl alloys with varying contents of Cr, Al and Y were prepared to evaluate the optimized chemical composition by conducting the oxidation testing under the high temperature steam condition.

2. Experimental methods

2.1. Materials

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. And at least 13 wt. % Cr is necessary for the stable Cr oxide scale 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 Al₂O₃ formation [2,3,4].

Initially, the nominal chemical composition of yttrium was set at 0.05, 0.1 and 0.15 wt. %. However, 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 °C 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 are shown in Table 1.

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

Alloy		Fe	Cr	Al	Y
144Y-1	Nominal	81.85	14	4	0.15
	Analyzed	81.848	14.199	3.924	0.03
144Y-2	Nominal	81.7	14	4	0.3
	Analyzed	82.199	13.872	3.78	0.149
144Y-3	Nominal	81.55	14	4	0.45
	Analyzed	81.873	14.092	3.781	0.254
136Y-1	Nominal	80.85	13	6	0.15
	Analyzed	81.32	13.039	5.609	0.032
136Y-2	Nominal	80.7	13	6	0.3
	Analyzed	81.83	12.526	5.501	0.143
136Y-3	Nominal	80.55	13	6	0.45
	Analyzed	81.419	12.79	5.523	0.268

2.2. High temperature steam oxidation test

To evaluate the oxidation resistance with time, 10 × 30 × 2 mm polished samples were inserted into a tube furnace. FeCrAlY samples were isothermally oxidized for 10 minutes, 1 hour, and 3 hours under a 1200°C steam/Ar environment. After oxidation, the sample were

cooled in laboratory air. The schematic of the tube furnace is shown in Fig. 1.

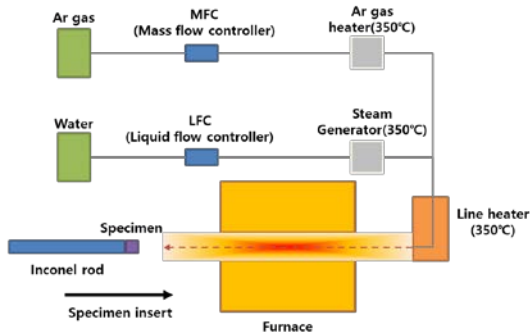


Fig. 1. Schematic of high temperature steam oxidation furnace

2.3. Analysis methods

The grain size and shape of as-received samples were analyzed using optical microscopy (Nikon LV150N). A scanning electron microscope (SEM) was used to observe the surface (top view) and cross section of the corroded specimen.

The specimens were cut by a low speed saw at the central part of the sample and polished. Each of the polished specimens was etched with a solution containing 45 ml of glycerol, 30 ml of hydrochloric acid and 15 ml of nitric acid, and then ultrasonic cleaning was conducted with ethanol and distilled water in sequence.

3. Results & discussion

3.1. As-received samples

The microstructural images of the longitudinal plane (cross-section) of the samples are shown in Fig. 2. The average grain size was less than $100\mu\text{m}$, and the grain refinement was observed as the yttrium content increased. The dark spots are traces of the yttrium rich particles, spread evenly throughout the matrix, and are also linearly aligned in the rolling direction.

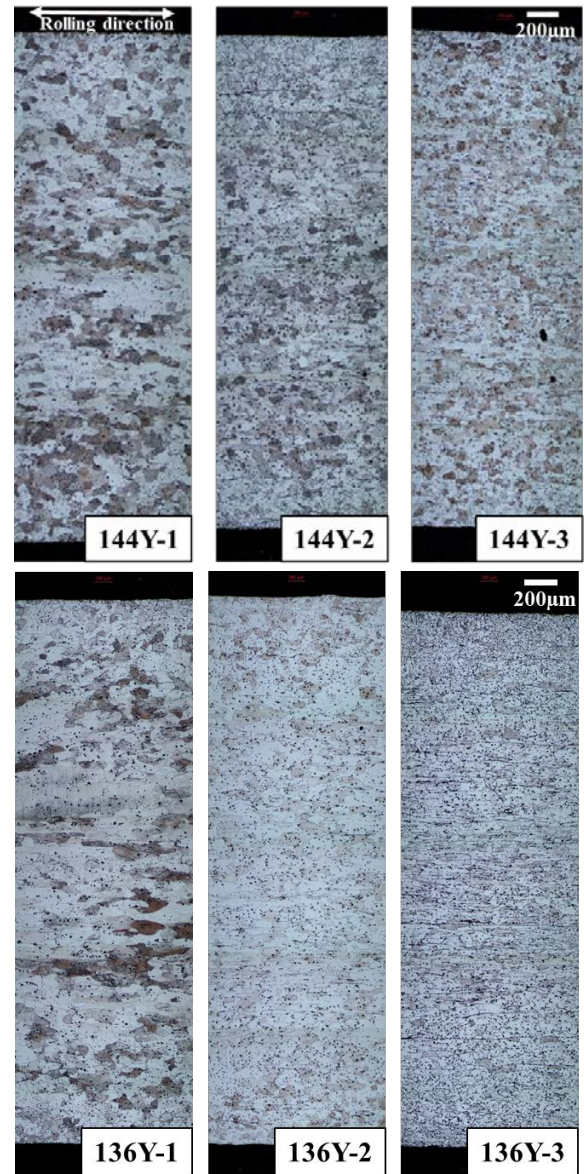


Fig. 2. Optical microscope image (x50 magnification) of the longitudinal plane (cross-section) of each as-received samples.

3.2. High temperature steam oxidized samples

Table 2 shows the weight gain results of the corroded samples. Although there is little variation in the values and repeatability should be confirmed, the kinetic behaviors of the initial oxidation (10 min) and the long-term oxidation (1 hour or more) are estimated to be different depending on the Y content. In the case of 136Y-2 (Fe13Cr6Al + 0.143Y), the oxidation resistance was the worst among Fe13Cr6AlY samples at the initial oxidation kinetics, but it became the best at the long-term oxidation kinetics.

As a result, the sample with the lowest weight gain in the 3-hour corrosion test was 136Y-2 alloy, and thickness of the uniform Al oxide of 136Y-2 was the thinnest (see Fig. 3).

Table 2. Weight gain results of corroded samples

(WG: Weight gain, mg/cm²)

Y wt.% Time	Fe14Cr4Al + Y			Fe13Cr6Al + Y		
	0.03 Y	0.149 Y	0.254 Y	0.032 Y	0.143 Y	0.268 Y
10m WG	0.22	0.57	0.14	0.17	0.48	0.19
1h WG	0.87	0.35	0.37	0.34	0.31	0.36
3h WG	spalled	spalled	9.71	9.93	4.61	5.39

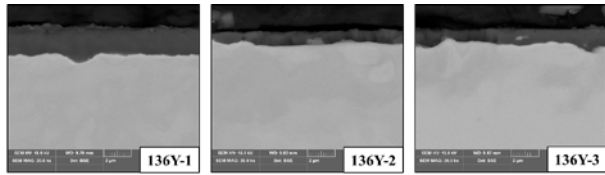


Fig. 3. SEM cross-sectional image of 136Y-1, 136Y-2 and 136Y-3 after 3 hour oxidation tests under 1200 °C steam/Ar

The surfaces of the all corroded samples have a reticular structure as shown in Fig 4. Al oxide is formed in most of the surface and Fe-Cr oxide is formed at the grain boundary.

As shown in Fig. 5, as the corrosion time increased, cavities and cracks were formed in the Fe-Cr oxide at the grain boundary. 136Y-2 sample shows the least cavities and cracks at grain boundaries.

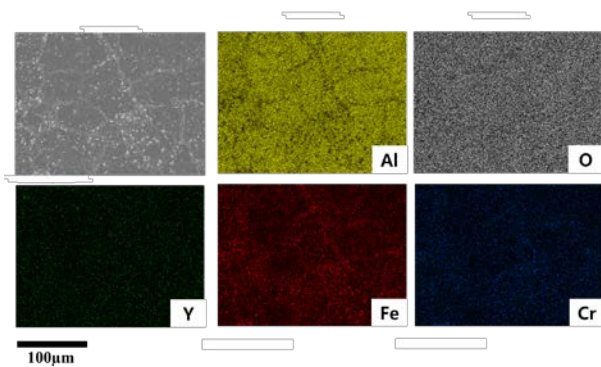
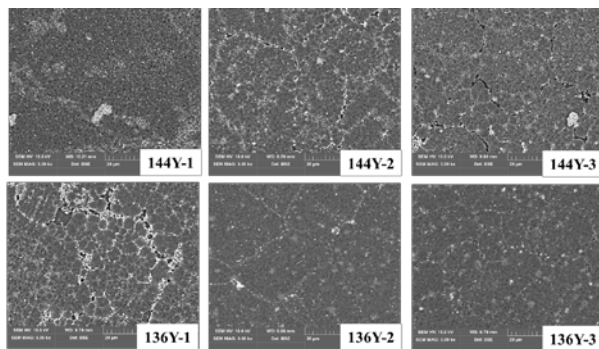


Fig. 4. Surface SEM image of 144Y-3 (x1,000 magnification) corroded for 10 minutes under 1200 °C steam/Ar



20µm

Fig. 5. Surface SEM image of FeCrAlY model alloy corroded for 3 hours under 1200 °C steam/Ar (x3,000 magnification).

3.3 Yttrium effect

In all of the specimens of this study, yttrium is segregated at the grain boundary and Al ion and oxygen penetrate along the yttrium from the surface to form an oxide as shown in Fig. 6.

Yttrium is initially present as a Y-Fe intermetallic compound, but Y₂O₃ particles are selectively formed in grain boundaries as oxidation progresses, thus acting as a nuclei for Al₂O₃ formation and a short circuit path to oxygen diffusion. As a result, Al₂O₃ grows around Y₂O₃, and eventually Y₃Al₅O₁₂ particles are formed by the reaction of these two compounds.

The addition of small amount of yttrium causes dense Al₂O₃ formation, which reduces the diffusion of oxygen and Al ion, but if the yttrium content exceeds a certain level, the mass gain increases due to the rapid diffusion rate of oxygen through Y₃Al₅O₁₂ particles. Therefore, proper yttrium content addition is very important for high temperature oxidation resistance.

In this study, the corrosion resistance was superior at the 0.143 wt. % yttrium among the three Fe13Cr6AlY alloys corroded for 3 hours.

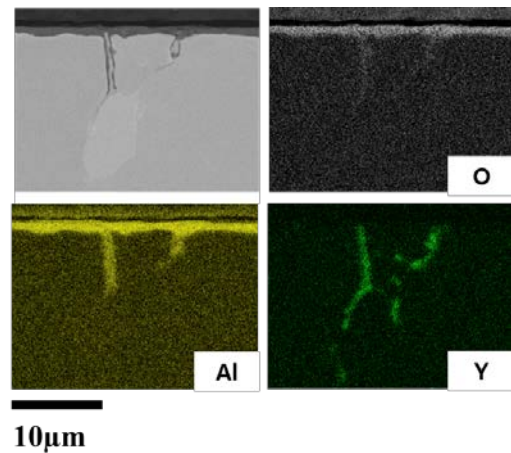


Fig. 6. The Y rich oxide and the surrounding Al oxide observed at the cross section of 136Y-3 alloy corroded for 1 hour under 1200 °C steam/Ar.

Future work

The microstructure analysis will be conducted after exposing 136Y-2, which has the highest oxidation resistance, for 8 hours and 24 hours at 1200°C under steam/Ar environment. The commercial FeCrAl alloy, Kanthal APMT is also planned to be compared the high temperature oxidation resistance with 136Y-2 at the same exposure time.

In this study, the 136Y-2 alloy was considered to have the highest oxidation resistance, but the fabricability is expected to poor because of the high Al

content. The analyzed Al chemical composition of 136Y-2 was 5.5 wt. %. However, when the Fe13Cr6Al0.15Y of 38kg size ingot was rolled under the same manufacturing process, the whole specimen was cracked despite of 10% thickness reduction. The analyzed Al content was 6.1 wt. %.

And it is necessary to improve the tensile properties as well as the fabricability. Tensile tests were carried out at the room temperature and 360°C for Fe14Cr4Al alloys, which is non-yttrium containing alloy, ultimate tensile stress (UTS) was 519 and 395 N/mm², respectively. The UTS of zirconium alloy (Zr-Nb-Sn alloy) is 768 N/mm² at room temperature and 551 N/mm² at 365 °C, which is significantly higher than that of Fe14Cr4Al alloy.

The average size of yttrium particle was 2 to 10 μm, which is large to have solid solution strengthening. Therefore, it is necessary to add minor elements such as Mo, Ti, C or Nb and C in order to improve fabricability and mechanical properties. Long-term corrosion tests are also required under the operating conditions of the nuclear power plant, Fe14Cr4Al, Fe13Cr6Al and Fe13Cr6Al0.15Y are currently being tested. He ion irradiation experiments are carried out to evaluate neutron irradiation characteristics.

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