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Development of High Temperature Oxidation Resistant High Entropy Alloys for Coating Materials of Accident Tolerance Fuel Cladding

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1. Introduction

After Fukushima accident in 2011, the development of new cladding materials for light water reactors has been intensively investigated to prevent steam oxidation that causes the production of hydrogen and heat during Loss of Coolant Accident (LOCA). Various concepts have been proposed and several designs have been investigated. One of these ideas is the coating of the zirconium alloy cladding with a protective layer of oxidation-resistant materials, such as silicon carbide (SiC) [1], iron-chromium-aluminum (FeCrAl) alloy [2], and MAX phase materials [3]. A promising coating material for accident tolerant fuel cladding must have not only high temperature oxidation resistance, but also low neutron absorption, high adherence to the substrate, and thermal expansion similar to Zircaloy to prevent the interfacial stress caused by the thermal expansion difference between the coating and the substrate. Although existing attempts have an excellent performance in terms of high temperature oxidation resistance, several drawbacks have also been raised, such that SiC coating showed a yield strength limit at higher temperatures above 650 ℃, FeCrAl alloy coating has high thermal expansion coefficient than Zircaloy and showed unsatisfactory irradiation embrittlement, and MAX phase coating suffered difficulties in coating on the metal substrate.

The concepts of high entropy alloy were defined for the first time by Yeh et al. [4] as alloys which contain more than five elements with equal or near equimolar atomic percent. Although HEA has compositional complexity, the preference of formation of solid solution phase have been observed and that preference is caused by high configurational entropy of mixing between constituent elements. Usually, BCC structure high entropy alloy has much higher hardness than that of stainless steel and FeCrAl alloy and coatings of high entropy alloys on the surface of stainless steel were successful using laser surface alloying. [5][6]

In this study, the fabrication process and property evaluation of high entropy alloys that have high temperature oxidation resistance were investigated to develop protective coating materials for accident tolerant fuel cladding. New high entropy alloys containing Al, Cr, Fe, Mo and Ni were fabricated with various compositions. Those elements were selected by considering thermal neutron cross-section, high temperature oxidation resistance, and high temperature mechanical behavior. Several thermodynamic constants such as the average enthalpy of mixing between elements (ΔH_{mix}), the average entropy of mixing between elements (ΔS_{mix}), the unitless factor indicating the atomic radius differences between elements (δ), and Valance Electron Concentration (VEC), which determine phase and crystal structure, were calculated for each composition of the alloys. After fabrication, microstructures, crystal structures, oxidation behaviors of alloys were measured. The results of these experiments evaluate suitability of various compositions of AlCrFeMoNi high entropy alloys as coating materials on the Zircaloy for accident tolerance fuel cladding.

2. Experimental Plan

The effect of the concentration of molybdenum on the mechanical behavior of $AlCrFeMo_xNi$ alloys has been investigated [7]. An increase in the molybdenum concentration in alloys results in a hardness enhancement and a severe brittleness by forming a sigma phase in the alloy. The irradiation embrittlement was observed with increasing Cr concentration in the Fe-Cr system and the FeCrAl alloy [8,9]. The experimental strategy, based on the Taguchi method, was used to investigate the effect of the concentration of aluminum, chromium and molybdenum on the oxidation behavior of alloys. The purity of the raw materials in this study is shown in Table 1. Alloys were made by vacuum arc melting. Based on the previous investigations and orthogonality between the individual experiments, compositions of alloys were designed as Table 2. The concentration of iron and nickel has the same value which is 100 minus the sum of the concentration of aluminum, chromium and molybdenum divided by 2.

Table 1. Purity of law materials

Component	Al	Cr	Fe	Mo	Ni

Purity [%]	99.95	99.95	99.99	99.95	99.99

Table 2. Compositions of alloys using Taguchi's orthogonal array

Concentration	Al [at%]	Cr [at%]	Fe [at%]	Mo [at%]	Ni [at%]
Alloy-1	15	10	Rest	10	Rest
Alloy-2	15	12.5	Rest	12.5	Rest
Alloy-3	15	15	Rest	15	Rest
Alloy-4	20	10	Rest	15	Rest
Alloy-5	20	12.5	Rest	10	Rest
Alloy-6	20	15	Rest	12.5	Rest
Alloy-7	25	10	Rest	12.5	Rest
Alloy-8	25	12.5	Rest	15	Rest
Alloy-9	25	15	Rest	10	Rest

After the fabrication of alloys, the exact composition and microstructure of the alloys were examined using a combination of scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) was used to study the crystal structure of alloys. Prior to oxidation experiments, the samples were polished with 1200 grit SiC papers to remove native oxide film on the surface of alloys. Oxidation tests of each alloy were performed at 1200 -^{o}C in air using a box furnace. The tests were performed for 50 hours. The mass of the samples was measured every 5 hours. In order to ensure reproducibility of the experiments, each specimens were tested more than two times. After oxidation tests, the crystal structure and the chemical composition of the oxide layers of each sample were examined with XRD and SEM-EDS.

3. Result and future plan

Figure 1. shows the SEM-BSE image of alloy-9. There are 3 phases. The black phase is almost pure aluminum, which was not completely distributed during the arc melting. Blight gray phase is aluminum and nickel rich phase and dark gray is chromium, iron and molybdenum rich phase. Table 3. shows the composition of each phase. The XRD patterns of alloy-9 are shown in Figure 2. There are three phases that are an aluminum-rich chromium phase and the others are BCC structural phases. This XRD result is well correlated with the number of phases in the SEM image. To overcome the heterogeneity of the alloy, a heat treatment has to be carried out. After the heat treatment, the crystal structure and the microstructure of the alloy are re-examined, and the oxidation behavior of each alloy is examined as discussed above.

Table 3. Chemical composition of three different phases

Component	Al [at%]	Cr [at%]	Fe [at%]	Mo [at%]	Ni [at%]
Black	99.1	0.9	0.0	0.0	0.0
Dark gray	12.4	20.7	36.4	15.2	15.3
Blight Gray	32.0	8.3	15.7	7.4	36.6

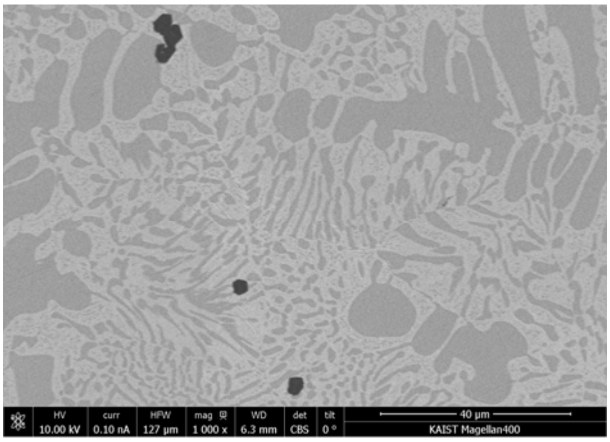

Figure 1. 1000x SEM-BSE image of alloy-9

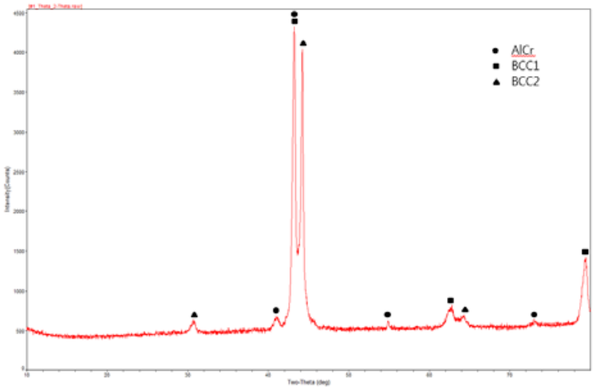

Figure 2. XRD pattern of the alloy-9

4. Conclusions

In this study, microstructure and oxidation behavior of 9 different compositions of AlCrFeMoNi high entropy alloys were investigated. The effects of aluminum, chromium and molybdenum on the oxidation behavior of alloys were investigated with a minimal number of experiments using the Taguchi's method. The results of these experiments evaluate the suitability of various compositions of AlCrFeMoNi high entropy alloys as coating materials on the Zircaloy for accident tolerance fuel cladding.

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