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Microstructure and Corrosion Characteristics of HANA-alloy with Manufacturing Process

H.G. Kim[a,*], B.K. Choi[a], Y.H. Jeong[a], K.T. Kim[b], C.H. Park[b], S.D. Kim[b]
[a] *Zirconium Fuel Cladding Team, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea*
[b] *Korea Nuclear Fuel Co., Ltd. Daejeon 305-353, Korea*
[*] *hgkim@kaeri.re.kr*

1. Introduction

The corrosion resistance of fuel claddings has been considered to be one of the key properties to control the performance and the safety of nuclear reactor. Zr-based alloy such as Zircaloy-4 has been used as fuel cladding materials for the last few decades. Since, the corrosion of fuel claddings is the most critical issues in high burn-up operating condition in PWRs, the development of the advanced Zr-based fuel cladding with an improved corrosion resistance was demanded.

The HANA-alloy designed in KAERI was one of the newly developed materials having an improved corrosion resistance. It was reported that the corrosion properties of Zr-based alloys were very sensitive to their microstructural properties such as texture, dislocations and precipitate characteristics [1-3]. The microstructural characteristics of Zr-based alloy were determined by the performed manufacturing process conditions. Therefore, to obtain the good corrosion resistance, the Zr-based alloy as fuel cladding was applied to the optimized manufacturing process which was found by different parameter studies. The purpose of this investigation is to get the optimized manufacturing process of HANA-alloy.

2. Experimental procedure

The HANA-alloy was manufactured by the sequence of the vacuum arc re-melting of 4 times to promote the homogeneity of the alloying element, β-quenching at 1050℃, and hot and cold rolling. To study the manufacturing parameter such as annealing temperature and hot and cold rolling effect, the β-quenched HANA-alloy was hot-rolled after pre-heating at 580 or 610℃ for 30 min and than applied the cold rolling steps of different times. The cold-rolled samples were intermediate-annealed at 580 or 610℃ for 3 hours and than some samples were final-annealed at 580 or 650℃ for 3 hours. Therefore, the sheet type HANA-alloy having different 8 conditions was manufactured shown as table 1.

The microstructure with annealing temperature and rolling sequence was observed using optical microscope with polarized light. The precipitate characteristics were analyzed using transmission electron microscope equipped with energy dispersive spectra. Specimens for TEM observation were prepared by twin-jet polishing with a solution of C_2H_5OH (90 vol.%) and $HClO_3$ (10 vol. %) after mechanical thinning to about 70μm.

Table 1 Manufacturing process of HANA-alloy

[X: not performed]

Process	1	2	3	4	5	6	7	8
Ingot melting	VAR							
Beta annealing	1050℃x30min							
Cooling rare from beta region	Water quenching at 1050℃							
Hot rolling	610℃ x20min	580℃ x20min	610℃ x20min	610℃ x20min	610℃ x20min	610℃ x20min	610℃ x20min	610℃ x20min
Vacuum annealing	X	X	580℃ x3hr	X	580℃ x3hr	X	580℃ x3hr	580℃ x3hr
Cold rolling	X	X	X	50%	50%	50%	50%	50%
Vacuum annealing	X	X	X	X	X	580℃ x3hr	580℃ x3hr	650℃ x3hr

The corrosion test was performed in a static autoclave of 400℃ steam under saturated pressure of 10.3 MPa. Corrosion testing specimens of 15mm x 25mm x 1mm in size were cut from the prepared sheets and mechanically ground up to 1200 grit SiC paper. Also, the ground specimens for the corrosion test were pickled in a solution of H_2O (40 vol.%), HNO_3 (30 vol.%), HCl (25 vol.%) and HF (5 vol.%). The corrosion resistance was evaluated by measuring the weight of the corroded samples after suspending the corrosion test at a periodic term.

3. Results and discussion

The microstructure observation was performed to evaluate the grain shape and precipitate characteristics with the manufacturing process, since it is well known that corrosion properties of Zr alloys is highly depended on the microstructural characteristics [3].

Fig. 1 shows the optical microstructures of HANA-alloy with different manufacturing process. Their microstructural characteristics were largely changed by manufacturing process shown as table 1. The martensite structure (prior β phase) was formed at water quenched samples from β region of 1050℃. The massive large grains were observed in the case of process (1), (2) and (3), and the elongated grains were observed in the case of process (4) and (5). The small recrystallized grains were observed in case of process (6), (7) and (8). From the results of microstructural observation, homogenous microstructure such as small recrystallized grains was formed by the process of annealing after cold rolling.

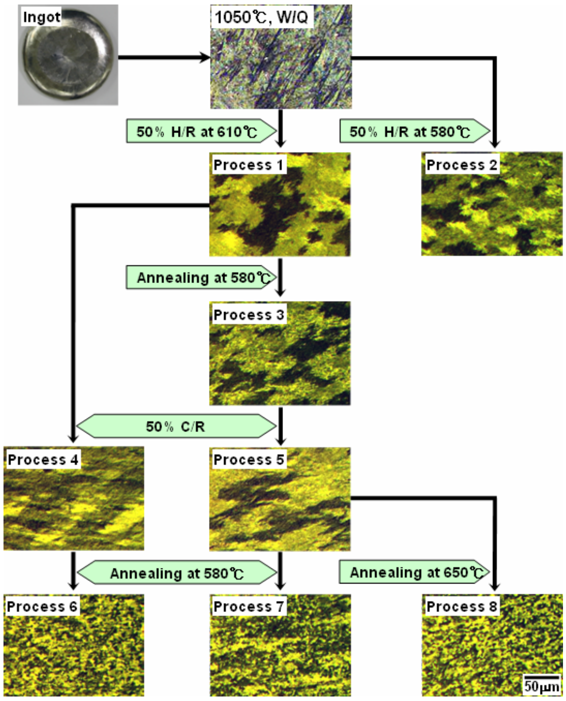

Fig. 1 Optical microstructures of HANA-alloy with different manufacturing process

From the result of precipitate analysis using TEM, the alloying elements of HANA alloy were homogeneously supersaturated in the martensitic matrix, because the precipitates were not observed in the martensite structure formed by water quenching. The precipitate in the matrix was observed after hot rolling process of 590 or 610℃. It was observed that the precipitate type such as β-Zr and ZrNbFe phase was determined by different manufacturing process.

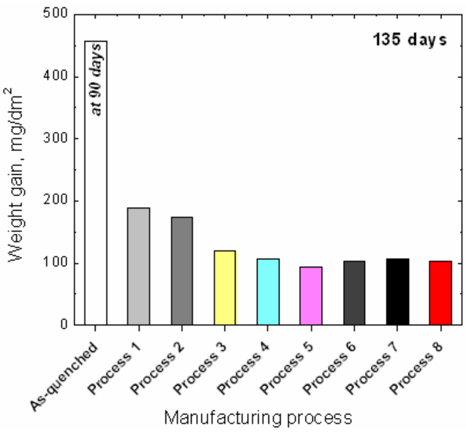

Fig. 2 Corrosion behaviors of HANA-alloy with the different manufacturing process

Fig. 2 shows the corrosion behavior of HANA-alloy manufactured by different process in an autoclave of 400℃ steam condition up to 135 days. The corrosion resistance of HANA-alloy was largely affected by the manufacturing process conditions. The corrosion resistance of that alloy was highly increased by the process of hot-rolling steps and it was somewhat increased by the next process of annealing and cold rolling steps.

From the results of microstructure and corrosion studies, it was assumed that the corrosion rate was correlated with the precipitate characteristics since the correlation between optical microstructure results and corrosion behavior was not observed. The lower corrosion rate of HANA-alloy was showed when the precipitates were homogenously distributed in the matrix. Also it was revealed that the Nb-concentration of β-Zr phase was affected by the corrosion resistance because the corrosion resistance was increased with increasing Nb-concentration in β-Zr.

4. Conclusion

The newly developed HANA-alloy that was made by various manufacturing process were investigated in order to get the optimized manufacturing process. The microstructural characteristics of HANA-alloy were largely changed by the manufacturing process conditions. The corrosion resistance of HANA-alloy was mainly affected by the formation of precipitates in the matrix. From the analysis of precipitate characteristics, it was assumed that the good corrosion resistance of HANA-alloy was obtained by decreasing the Nb-concentration in the matrix.

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