Development of a Manufacturing Process for Nb containing Zr-based alloys

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1. Introduction

HANA(High performance Alloy for Nuclear Application) is a trademark of a developing zirconium-based alloy for a high burn-up fuel cladding material by the Korea Atomic Energy Research Institute. A series of out-of-pile and in-pile tests demonstrated that the HANA cladding tubes were superior to a commercial zirconium-base alloy in the mechanical properties as well as the corrosion properties [1,2]. Along with the research for a fuel cladding application using HANA alloys, their application to a spacer grid for a fuel assembly is also being investigated.

For robust mechanical properties of a spacer grid, an appropriate microstructure is needed. Especially, a recrystallized microstructure is desirable for proper mechanical properties, a corrosion resistance, a creep resistance, and a low irradiation growth [3]. In addition, an intermediate recrystallization is utilized to restore a ductility after a cold deformation process during a manufacturing. The recrystallization can be easily achieved when the alloy was heat-treated at high temperatures; however, an undesirable second phase particles such as β-Zr could be formed which deteriorate corrosion resistance of the alloy [4]. In that sense, the annealing temperatures should be controlled within proper ranges (practically below the monotectoid temperature of 600°C).

In this paper, the HANA-4 strip was manufactured at various annealing temperatures, and examined for the temperature which has not been considered to be desirable for its properties. It is suggested from this work that the higher temperature would also be applicable to the manufacturing. The effect of the annealing will be discussed in view of the proper mechanical and corrosion properties.

2. Methods and Results

The nominal chemical composition of the HANA-4 strip is Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr. The designated amounts of the solute atoms of Nb, Sn, Fe, Cr were added to a pure sponge zirconium. For homogenizing of the alloying elements, several meltings and betatizing at 1020°C for 15 min were introduced. To stabilize the b-Nb second phase particles, early annealing at 580°C for 10 h was done prior to deformation processes. Then the prepared ingots were hot-rolled and cold-rolled to have 0.66 mm thicknesses. The cold-rolling process consisted of three steps: 1st cold-roll of 35% reduction, 2nd cold-roll of 40% reduction, and final cold-roll with 65% reduction. The heat-treatments subsequent to every cold-rolling were conducted below and/or above a monotectoid temperature of about 600°C.

For the comparison, the early annealing was not carried out or an intermediate and a final annealing was done at 600°C or 620°C for 1 h. The cold-rolling and annealing conditions are presented in Table 1. For the heat-treatment, oxidation of the samples was prevented by using a quartz tubing with a vacuum. The heat-treated samples were tensile tested at room temperature in accordance with the ASTM B352 and E8. The strain rate was 0.0625 mm/mm/min through a 0.2% offset yield stress and 0.625 mm/mm/min after a yield stress. The corrosion behaviors of the samples were investigated in a 400°C steam environment in a manner consistent with the ASTM G2. For a reference, a commercial grade of the ZA outer strip was used.

Table I: Annealing conditions for the HANA-4 strip

Sample ID	Early annealing	Annealing after Cold-rolling		
		1st	2nd	3rd
H4A	O	570x3h	600x1h	600x1h
H4B	O		620x1h	580x1h
H4C	O			600x1h
H4D	O			620x1h
H4G	X	620x1h	620x1h	620x1h

2.1 Early Annealing

Annealing performed prior to the deformation process of a hot and cold rolling was termed as an early annealing. The early annealing was introduced to stabilize the β-Nb phase which is helpful for corrosion resistance, and to restrain the transformation of niobium-rich phase (β-Nb) into zirconium-rich phase (β-Zr) during heat-treatment at high temperature.

Figure 1 shows the transmission electron microscopy (TEM) image for the early annealed HANA-4 strip. After being beta-quenched from 1020°C, martensite structures were formed throughout the sample. The second phase particles were oversaturated into the zirconium matrix during the martensitic transformation. However, a heat-treatment at 580°C for 10 h induced a nucleation of the β-Nb second phase particles in the matrix as shown in Fig. 1. These results are consisten with our previous work for a Zr–*x*Nb binary alloy system [5].

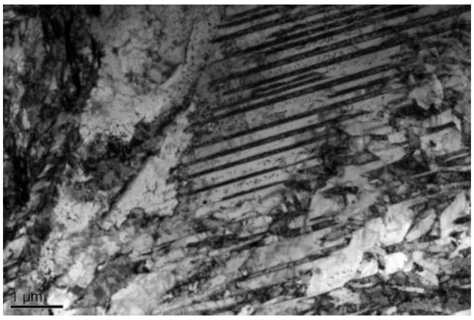

Fig. 1. TEM micrograph showing the precipitation of the second phase particles after the early annealing.

2.2 Tensile Properties

Tensile properties of the manufactured HANA-4 strips, i.e. H4A, H4B, H4C, and H4D, were satisfied the required mechanical properties for a spacer grid; for a commercial application tensile strength of >379 MPa, yield strength of >296 MPa, and minimum elongation of 24% should be fulfilled. As compared to ZA strip, the manufactured HANA-4 strips were superior in tensile mechanical properties. The yield strength (YS) and ultimate tensile strength (UTS) of the manufactured strips were better than those of the ZA strip regardless of the annealing conditions. The elongations (EL) of the samples were increased as the annealing temperature was increased. Table II shows the obtained values of tensile strength.

Table II: Tensile mechanical strengths for the HANA-4 strips annealed at various temperatures.

Sample ID	Mechanical Properties [MPa]			Remarks
	YS	UTS	EL [%]	
H4A	412	535	32.8	
H4B	422	545	29.6	
H4C	417	544	30.5	
H4D	405	532	35.2	
ZA	365	485	31.3	

2.3 Corrosion Behaviors

Figure 2 shows the weight gains from the 150 days of corrosion test in the 400°C steam environment. The corrosion rate increased as the heat-treatment temperature increased. The hatched rectangle enclosed with dotted lines indicate the range of the oxide weight grains for the HANA-4 strips underwent a conventional manufacturing process and heat-treatment. All the strips except the H4G, which did not early annealed, revealed the lower oxide weight grain than the conventional strips of 155–187 mg/dm^2 in 150 days of the test.

In an equilibrium Zr–Nb alloy system, β-Zr phases precipitate at about 600°C. The more weight gain of the HANA-4 strip would result for the samples annealed at higher temperature over 600°C, because the β-Zr phase precipitates contribute to the acceleration of the corrosion [5]. In our case, the corrosion of the H4A–H4D specimens, which underwent a high temperature of the annealing, didn't accelerated nor surpass the oxide weight gains of the commercial strips because of the early annealing being enable to stabilize the β-Nb precipitates.

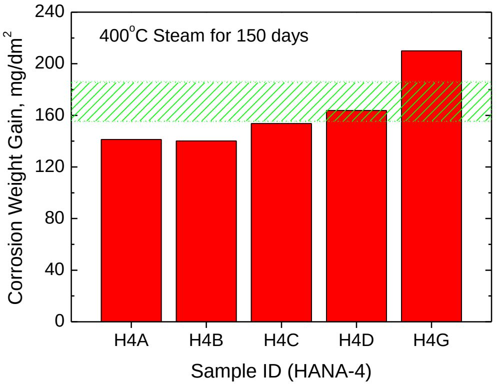

Fig. 2. Variations in weight gains of the HANA-4 strips for the corrosion test in a 400°C steam.

3. Conclusions

The effects of the early annealing and heat-treatment conditions for the HANA-4 strip were investigated. The tensile strength and corrosion properties were compatible to a commercial grade of a zirconium-based alloy. The developed process of an early annealing is applicable to a commercial manufacturing process for the HANA-4 strip as well as high strength alloys with high Nb contents.

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REFERENCES

[1] Y.H. Jeong, S.-Y. Park, M.-H. Lee, B.-K. Choi, J.-H. Baek, J.-Y. Park, J.-H. Kim, and H.-G. Kim, Out-of-pile and In-pile Performance of Advanced Zirconium Alloys (HANA) for High Burn-up Fuel, J. Nucl. Sci. Tech., 43[9], 977-983, (2006).
[2] K.W. Song, Y.H. Jeong, K.S. Kim, J.G. Bang, T.H. Chun, H.K. Kim, K.N. Song, High burnup fuel technology in Korea, Nucl. Eng. Tech., 40(1), 21-36, (2008).
[3] G.S. Lee, Nuclear Reactor Materials, Hyoilbooks, p.158 (2006). ISBN-89-8489-190-8
[4] Y.-I. Jung, M.-H. Lee, H.-G. Kim, J.-Y. Park, Y.-H. Jeong, J. Alloy. Compd., (2009) doi:10.1016/j.jallcom.2008.12.089.
[5] Y.H. Jeong, H.G. Kim and T.H. Kim, J. Nucl. Mater., 317, 1 (2003).