Transactions of the Korean Nuclear Society Autumn Meeting
Busan, Korea, October 27-28, 2005

Corrosion Behavior of HANA alloy in SMART-Simulating Water Chemistry

Sang Yoon Park, Byoung Kown Choi, Byung Seon Choi, Ju Hyeon Yoon, Doo Jeong Lee, Young Hwan Jeong
Zirconium Fuel Cladding Team, Korea Atomic Research Institute, Daejeon, 305-353, Korea
nsypark@kaeri.re.kr

1. Introduction

HANA alloy, which were developed by Korea Atomic Energy Research Institute (KAERI) in collaboration with Korea Nuclear Fuel Company (KNFC) for high burn-up PWR nuclear fuel, showed an excellent out-pile corrosion resistance in PWR simulating loop conditions [1]. And in-pile corrosion resistance of the alloy, which was evaluated at the first interim inspection after ~185 FPD of irradiation in the Halden Reactor, was very excellent, too[2]. The objective of this study is to evaluate corrosion and hydrogen pick-up properties of the HANA alloy in ammonia water chemistry, which corresponds to the SMART (System-integrated Modular Advanced ReacTor) water chemistry. Long-term corrosion test in 360°C ammonia water chemistry was conducted and the corrosion rate constant and hydrogen pick-up rate were evaluated.

2. Experimental Procedure

Fuel cladding used in this study are HANA 3 (Zr-1.5Nb-0.4Sn-Fe-Cu), HANA 6 (Zr-1.1Nb-Cu) and reference alloy (Zircalloy(Zry-4) and A) claddings. Specimens which cut into 30 mm length, were surface treated by pickling in a solution of 10 vol.% HF, 30 vol.% HNO_3, 30 vol.% H_2SO_4 and 30 vol.% H_2O. Before corrosion test, some specimens were oxidized at 360°C pure water to develop 1 μm passivation layer on the cladding surface (SMART fuel process). Corrosion behavior was evaluated in ammoniated water adjusted to pH 10 at 360℃ under a pressure of 18.5 MPa using a circulating loop system. The water chemistries in the inlet of heating zone (autoclave) were maintained constant to be about 20 μg/ℓ of dissolved oxygen, 0.2 μg/ℓ of dissolved hydrogen, and 105 μS/cm of conductivity. The corrosion kinetics was determined by the gravimetric method. Hydrogen content of the specimen after corrosion test was analyzed with inert gas fusion thermal conductivity determination method using RH 404 hydrogen determinator (LECO Ltd.). Surface oxide layer and hydride morphology were examined by optical microscope (OM) and scanning electron microscope (SEM).

3. Results and discussion

3.1 Corrosion Behaviors

Figure 1 shows the long-term corrosion behavior of HANA alloys and Zry-4 at 360°C in a pH 9.98 ammonia aqueous solution. HANA alloys showed a better corrosion resistance than Zry-4 or A-alloy. Corrosion rates were changed periodically and accelerated at each transition time. Zry-4 showed 6 times of transition during 900 day corrosion and was accelerated its corrosion rate at each transition points. Table 1 shows the number of transition and transition periods. HANA 3 and HANA 6 alloy had 3 and 2 times of transition, respectively, and they showed an excellent corrosion resistance. It was also found that corrosion rate of HANA 6 is lower than that of HANA 3.

Figure 2 shows similar results for the pre-oxidized alloys corroded in a same corrosion environment. Although the first transition took place at same periods with the non-oxidized alloys, next transition periods were prolonged and their corrosion rates were reduced.

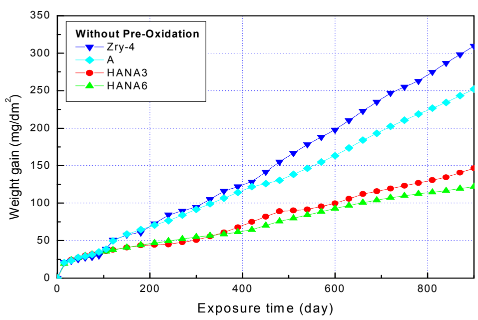

Figure1. Corrosion behavior of HANA alloy in pH 10 ammonia aqueous solution at 360°C

Table 1 The number of transition and transition periods

Alloys	Transition Time (day)					
	first	second	third	forth	fifth	sixth
Zry-4	90	180	240	420	600	780
A	90	260	480	630	840	
HANA3	330	560	840			
HANA6	390	630				

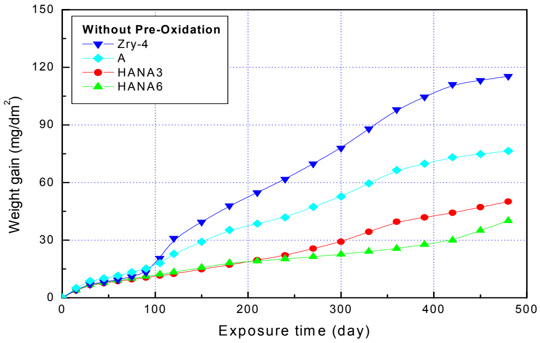

Figure2. Corrosion behavior of pre-oxidized HANA alloy in pH 10 ammonia aqueous solution at 360°C

HANA 3 and 6 alloys had an excellent corrosion resistance rather than Zry-4 and A-alloy in SMART water chemistry.

3.2 Hydrogen Pick-up

During the corrosion, Zr-alloys have a reaction with water as follows:

$$2H_2O + Zr \rightarrow ZrO_2 + 2H_2 \qquad (1)$$

Some of the hydrogen resulting from the reaction of the alloy with water to form ZrO_2 is absorbed into metal, and the rest is dissolved into water. Hydrogen pick-up fraction is the ratio of absorbed hydrogen content into the metal to the total generated one. Figure 3 shows the linear increase of hydrogen contents in the alloys with exposure time.

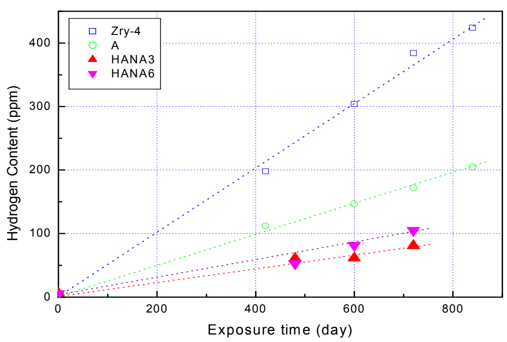

Figure 3 Hydrogen content of HANA and reference alloys with the corrosion time

And this hydrogen pick-up fraction could be calculated by equation (2)[3]:

$$HPUF(\%) = \frac{\left(\frac{m_O}{M_{Ti}} - \frac{\Delta m}{2M_O}\right)M_{Ti}\frac{(C_H - C_{Hini})}{10^6}}{2M_H\left[\Delta m - \left(\frac{m_O}{M_{Ti}} - \frac{\Delta m}{2M_O}\right)M_{Ti}\frac{(C_H - C_{Hini})}{10^6}\right]/M_O} \times 100 \qquad (2)$$

where m_o, C_{Hini}, C_H, Δm, M_O, M_H and M_{Zr} are sample mass(g), initial and final hydrogen content(ppm), weight gain(g), molecular mass of oxygen, hydrogen and Zr. Table 2 shows the hydrogen pick-up rate (HPUR) and pick-up fraction (HPUF) during the corrosion in simulated SMART condition calculated by eq.(2). HPUR and HPUF of the HANA alloys were lower than that of reference alloys.

Table 2 Hydrogen pick-up rate and pick-up fraction of the test alloys during the corrosion in 360°C ammonia water chemistry

Alloys	HPUR		HPUF
	ppm/d	ppm/y	%
Zry-4	0.517	189	22.9
A	0.234	85	13.1
HANA3	0.102	37	8.5
HANA6	0.133	49	10.3

3. Conclusion

In this study, the corrosion behavior of the HANA alloy at 360°C in a pH 10 aqueous ammonia solution was evaluated. The corrosion resistance of HANA alloys was superior to the reference alloys and hydrogen pick-up fraction was lower than that of reference alloys. The corrosion resistance of HANA6 alloy was slightly higher than that of HANA3, but hydrogen pick-up properties of HANA3 was slightly superior to that of HANA 6.

ACKNOWLEDGMENTS

This work has been carried out under the Nuclear R&D Program by MOST.

REFERENCES

[1] Y.J. Park et.al. Proceedings. Of the Korean Nuclear Society Autumn Meeting, Yongpyong, Kores, Oct. 2004, p905
[2] Y.H.Jeong et.al., 2005 Water Reactor Fuel performance Meeting, Oct 3-7, Kyoto, Japan(2005)
[3] M.Tupin, M.Pijolat, F.Valdivieso, M. Soustelle, A. Frichet, P. Barberis, J. Nucl. Mater. 317, pp 130-144, 2003.