Characterization of Corrosion Behaviors of Candidate Materials in Sulfuric Acid Environment

Injin Sah[*], Jae-Won Park, Eung-Seon Kim, Min-Hwan Kim
VHTR Technology Development Division, KAERI, Yuseong-gu, Daejeon 34057, Republic of Korea
[*]Corresponding author: injin@kaeri.re.kr

1. Introduction

A massive production of hydrogen along with electricity generation is expected through a heat transfer in a process heat exchanger (PHE) using a very high temperature gas-cooled reactor (VHTR) [1]. It is of interest to employ thermochemical water splitting by sulfur-iodine (S-I) cycle using the heat source from a VHTR system [2]. A small-scale gas loop for feasibility testing of a laboratory-scale has constructed and operated in KAERI as a precursor to an experimental- and a pilot-scale gas loop.

Following the S-I cycle proposed by GA, hydrogen and oxygen gas are products from the decomposition of reactants (hydrogen iodide and sulfuric acid) at about 450 and 850 ^{o}C, respectively. Due to the highly concentrated acid at elevated temperature of the S-I cycle, characterization of corrosion/oxidation behaviors of the candidate alloy/metal is of importance.

Corrosion testing for candidate alloy/metal has been carried out by many authors. Kim et al. performed the corrosion testing for commercial alloys (Fe-Cr, Ni-base, and stainless steel), model alloys (Fe-xSi, x=10, 13, 15, and 17 wt.%), reactive/refractory metals, and SiC; in 50 wt.% of H_2SO_4, they presented that Pt, Ta, Zr, SiC, Au and Fe-17Si have a good resistance without HI, but Au has a poor resistance with HI; Au, SiC and Fe-17Si alloy have a good corrosion resistance in 98 wt.% of H_2SO_4 with a poor resistance for Ta and Zr [3,4]. Similarly, Kubo et al. used SiC, silicon-impregnated SiC (Si-SiC), Si_3N_4, Fe-(15,20)Si, and silicon-enriched alloy SX (Fe-19Ni-17Cr-5Si-2Cu) for corrosion testing at temperatures of 320-452 ^{o}C under 2MPa; they addressed that SiC, Si-SiC, and Si_3N_4 have excellent corrosion resistance without any weight change [5]. Positive effect of SiC was also proposed by Park et al. by applying SiC coating on a Ni-base alloy [6]; however, quantitatively analysis of the corrosion behavior for SiC-coated alloy has not reported. Also, a refractory metal, Mo, is not paid much attention up to date.

Thus, a preliminary corrosion testing of the candidate materials in sulfuric acid environment is performed, and weight change and surface morphology are introduced in this study.

2. Methods and Results

2.1 Experimental procedure

Test materials for the corrosion testing are Ni-base alloy (Hastelloy X), SiC-coated Hastelloy X, and refractory metal (Mo). The chemical compositions of a commercial Hastelloy X are listed in Table I. Hastelloy X has high contents of Cr (~ 22 wt.%) for corrosion/oxidation resistance and has solid solution strengthening element (Mo and Co) in the matrix. As the extensive improvement of corrosion resistance of SiC is reported by many authors [3-6], SiC-coated Hastelloy X is also prepared. Details of the coating procedure are described elsewhere [6].

Immersing the specimens in highly concentrated sulfuric acid is carried out for corrosion testing. The aqueous solution is prepared by mixing 100 mL of H_2O and 150 mL of H_2SO_4 (98 vol.%). Corrosion cell is heated on a hot plate to maintain a boiling temperature; in this case, the boiling temperature of the aqueous solution is 150 ^{o}C and the immersion time is 5 h.

After the corrosion testing, the specimens are ultrasonically cleaned in ethanol for 10 minutes, and weight changes are measured. Scanning electron microscope (SEM) is applied to characterize the surface morphology of the test materials.

2.2. Weight loss

Fig. 1 shows the weight loss of the test materials after the corrosion testing. All specimens lose their weight during 5 h of corrosion testing. While the as-received Hastelloy X changes about 1 mg/mm^2, weight change of SiC-coated Hastelloy X is far less (~ 0.1 mg/mm^2) than

Table I: Chemical compositions of the materials used in this study (wt.%).

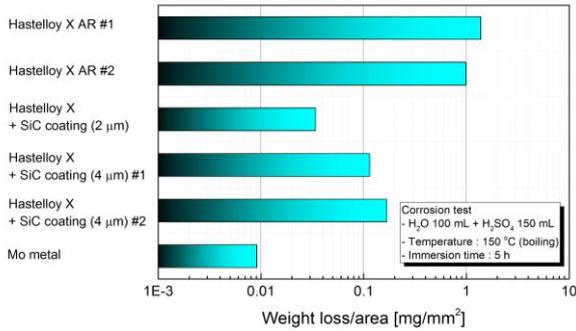| Materials	Ni	Cr	Fe	Mo	Co	W	Remark
Hastelloy X	Bal.	21.46	18.96	8.66	1.11	0.45	0.42Si, 0.30Mn, 0.21Al, 0.01Ti, 0.09Cu, 0.014P, 0.003B, 0.0001S, 0.06C
SiC-coated Hastelloy X	-	-	-	-	-	-	Coating: SiC (4 μm) through EB-PVD + IB mixing Substrate: Hastelloy X
Refractory metal	-	-	-	99.99	-	-	-

Fig. 1. Weight loss of test materials after corrosion testing. All specimens are immersed in aqueous sulfuric acid environment for 5 h.

that of the as-received. It would be attributed to the presence of the SiC at the outermost layer, implying that substrate is prevented from the direct contact with the aqueous sulfuric acid. It is not surprising that good/excellent corrosion resistance of Si-containing materials in sulfuric acid environment has been already reported [3-5].

It is of worth to note that the weight loss of Mo is even lower (~ 0.01 mg/mm^2) than the SiC-coated Hastelloy X. Conventionally, Ni-base alloys have Cu, Cr, Mo, and/or W to improve the surface stability; however, much attention was not paid to evaluate the effect of Mo in sulfuric acid environment. Of course, the effect of Si is well documented by Kim et al., but there is also an interesting result for the tested Ni-base; that is, Mo contents in the matrix of Alloy 690, Haynes 556, Hastelloy X, and Hastelloy C-276 are 0, 3, 9, and 15 in wt.%, respective; the corrosion resistance is increased in a sequence of Alloy 690 (194 mpy), Haynes 556 (9 mpy), Hastelloy X (8 mpy), and Hastelloy C-276 (1.3 mpy) in 50 wt.% of H_2SO_4, and Haynes 556 (7 mpy), Alloy 690 (4 mpy), Hastelloy C-276 (1 mpy), Hastelloy X (0.4 mpy) in 98 wt.% of H_2SO_4 [4], indicating that high Mo-containing alloys have better corrosion resistance.

2.3. Surface morphology

Fig. 2 shows the surface morphology before and after the corrosion testing. Before the corrosion testing, Hastelloy X has clean surface with some holes developed during the specimen preparation (Fig. 2(a)). SiC-coated Hastelloy X has SiC film islands formed during the heat treatment (Fig. 2(b)). Note that several heat treatments are applied at 950 $^{\circ}$C to remove the residual stress evolved during the deposition of SiC on the substrate [6], and coefficient of thermal expansion (CTE) of two neighboring materials are quite different (SiC: 5.0×10^{-6} at 1000 $^{\circ}$C and Hastelloy X: 16.6×10^{-6} at 980 $^{\circ}$C). However, any detachment of the SiC-coated layer is not observed, which might be resulted from the ion-beam mixing during the coating process. Lastly, scratches are found in Mo metal like as-received Hastelloy X (Fig. 2(c)).

Corrosion products are dominantly observed for Hastelloy X (Fig. 2(d)), while Kim et al. reported the preferentially attacked grain boundary, some precipitation of carbides, and dissolution or detachment of carbides [3,4]. The substrate is not revealed because the the surface is fully covered with corrosion products. Further analysis is in progress to identify the corrosion products.

In case of SiC-coated Hastelloy X, it is obvious that SiC-coated region is unchanged after the corrosion testing (Fig. 2(e)). However, corrosion products, which might be same as those formed for Hastelloy X, are extensively developed in some regions. It seems that when SiC-coated film islands are detached from the substrate for some reasons, corrosion products are formed on the surface of Hastelloy X, leading to the further detachment of the SiC-coated layer from the substrate. In short, while SiC material has good corrosion resistance, the adherence of the SiC-coated layer to the substrate is of concern.

The surface morphology of the corroded Mo is easily distinguishable from the above (Fig. 2(f)). Within the scope of the test condition, any corrosion products are not occurred on the surface, which is consistent with the weight loss shown in Fig. 1. Further corrosion testing is necessary to figure out the reaction of Mo metal in aqueous sulfuric acid environment.

2.4. Strategy for material selection

Through the preliminary corrosion testing performed in this study, it seems that Si, SiC, and/or Mo play an essential role to improve the corrosion resistance. As there is no commercial alloys containing high Si (> 15 wt.%) in the matrix, SiC and Mo would be of interest. Si and/or SiC coating on an alloy is an alternative, but the adherence between the coated layer and the matrix would be a problem as shown in Fig. 2(e). In case of refractory Mo metal, poor oxidation behavior in ambient environment in high temperature ranges is of concern, so high Mo-containing Hastelloy family (B, C, N, S, W, and/or X) could be the candidate materials.

Manufacturing process for a micro-channel type PHE should be considered as well. In other words, even though the selected material has a good/excellent corrosion resistance, the diffusion bonding technique, which is one of solid-state welding methods to join similar/dissimilar alloy/metal, is required to maintain the integrity of a PHE.

3. Conclusions

Characteristics of corrosion behaviors of Hastelloy X, SiC-coated Hastelloy X, and Mo metal are presented for the application of a PHE in the S-I cycle. Through the preliminary corrosion testing, the weight changes are significant in a sequence of Mo metal, SiC-coated Hastelloy X, and Hastelloy X. Even though SiC material has good corrosion resistance in aqueous sulfuric acid,
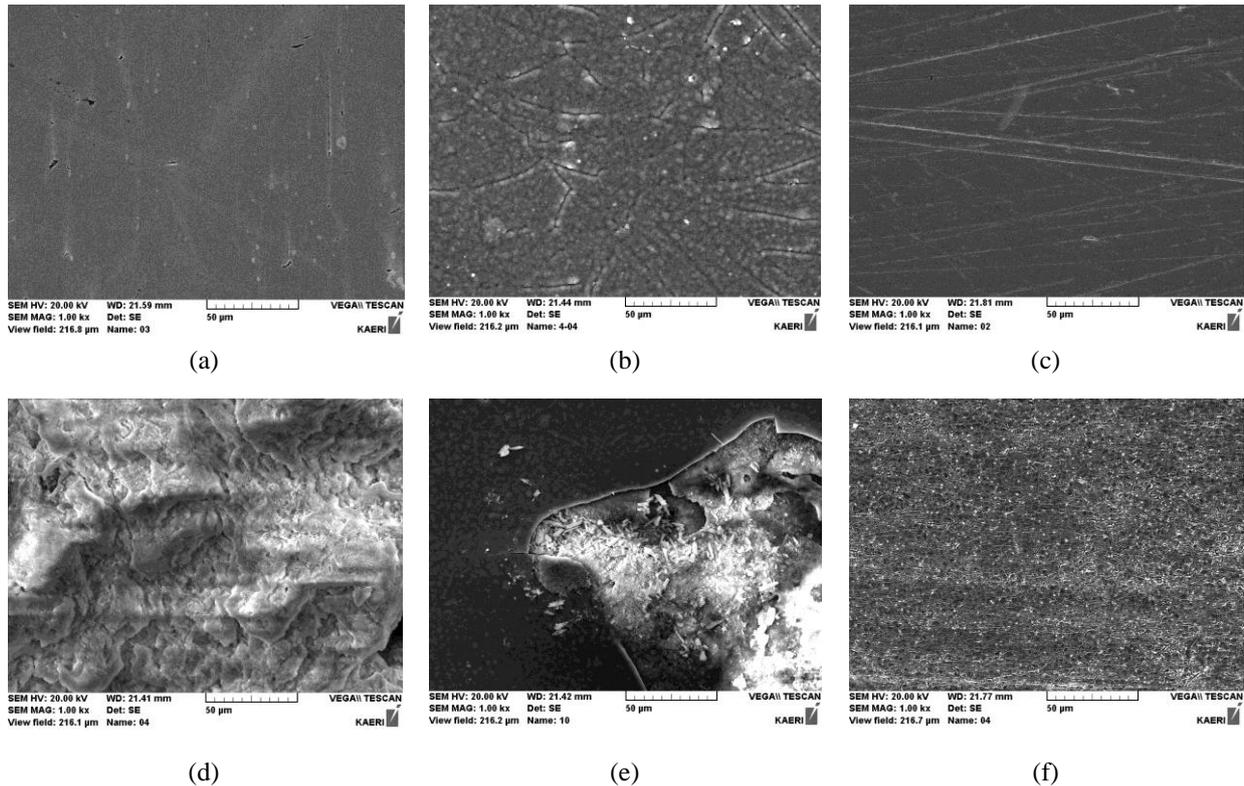
Fig. 2. SEM micrographs for the surface of: (a) as-received Hastelloy X, (b) as-coated Hastelloy X (thickness of 4 μm SiC), (c) refractory Mo metal, (d) corroded as-received Hastelloy X, (e) corroded as-coated Hastelloy X, and (f) corroded refractory Mo metal. Corrosion test is carried out in boiling condition (150 $^{\circ}$C) of aqueous sulfuric acid ($H_2O:H_2SO_4 = 100:150$).

the adherence of the SiC coating layer from the substrate leads to weight loss to some extent.

REFERENCES

[1] J. Chang, Y.-W. Kim, K.-Y. Lee, Y.-W. Lee, W.J. Lee, J.-M. Noh, M.-H. Kim, H.-S. Lim, Y.-J. Shin, K.-K. Bae, and K.-D. Jung, A Study of a Nuclear Hydrogen Production Demonstration Plant, Nuclear Engineering and Technology, Vol.39, No.2, p.111, 2007.

[2] X. Vitart, A.L. Duigou, and P. Carles, Hydrogen Production Using the Sulfur-Iodine Cycle Coupled to a VHTR: An Overview, Energy Conversion & Management, Vol.47, p.2740, 2006.

[3] D.-J. Kim, H.H. Lee, H.C. Kwon, H.P. Kim, and S.S. Hwang, Corrosion of Selected Materials in Boiling Sulfuric Acid for the Nuclear Power Industries, Corrosion Science and Technology, Vol.6, No.2, p.37, 2007.

[4] H.P. Kim, D.-J. Kim, H.C. Kwon, J.Y. Park, and Y.W. Kim, Corrosion of the Materials in Sulfuric Acid, Journal of Engineering for Gas Turbines and Power, Vol.131, 2009.

[5] S. Kubo, M. Futakawa, I. Ioka, K. Onuki, and A. Yamaguchi, Corrosion Resistance of Structural Materials in High-Temperature Aqueous Sulfuric Acids in Thermochemical Water-Splitting Iodine-Sulfur Process, International Journal of Hydrogen Energy, Vol.38, p.6577, 2013.

[6] J.-W. Park, H. Kim, S.-D. Hong, and Y. Kim, Materials Development for Process Heat Exchanger (PHE) in Nuclear Hydrogen Production System, Nuclear Engineering and Design, Vol.271, p.318, 2014.