Characteristics of Material Corrosion in Boiling Sulfuric Acid Environments

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1. Introduction

The fossil fuel depletion and the environmental pollution caused by use of fossil fuel. It can be solved by new energy source. Recently, hydrogen energy was highly regarded as alternative next generation energy source, because it is so clean that it does not emit carbon dioxide[1,2]. The sulfur-iodine (SI) process is one of the methods to produce the hydrogen. It is based on simple chemical reactions which are as follows;

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4 \quad (1)$$
$$2HI = H_2 + I_2 \quad (2)$$
$$H_2SO_4 = H_2O + SO_2 + 1/2O_2 \quad (3)$$

The reaction (1) has been known as the Bunsen reaction, where gaseous sulfur dioxide reacts with iodine and water producing an aqueous solution of iodic acid and sulfuric acid. Those reaction environments are very corrosive.

In the study, the corrosion tests of various materials were conducted in boiling sulfuric acid to select appropriate materials.

2. Experiment procedure

Reaction bonded SiC(RBS), sinterd SiC, Ni-Si-Ti-Nb and Ni-Si-Ti-Nb-B were tested in boiling 98wt% sulfuric acid. Dimension of the specimens and weight were measured. Ni-Si-Ti-Nb and Ni-Si-Ti-Nb-B were polished with #1500 abrasive paper, and then those were ultrasonically washed. Subsequently, specimens were heated by furnace in air condition and kept for 48hrs at 1000℃. The thermal treatment specimen is hereafter denoted as "Treated-Ni alloy", while the specimen without thermal treatment as "Non-thermal treated Ni alloy". Non- thermals treated Ni alloys were immersed in boiling 98wt% sulfuric acid for 3days, 7days and 14days. And Treated-Ni alloys were immersed for 7days, 30days, 60day and 120days, respectively. The sintered SiC, RBS were immersed in boiling 98wt% sulfuric acid for 1day, 7days, 15days, 30days, 60days, 120days and 300days, respectively

Corrosion rates were measured by means of the weight loss method after tests. The surface morphologies of tested materials were analyzed by using scanning electron microscope(SEM). The composition of tested specimens was examined by using energy dispersive x-ray spectroscopy(EDX).

3. Result

3-1. Corrosion rate

3-1-1. Non-thermal treated Ni alloy

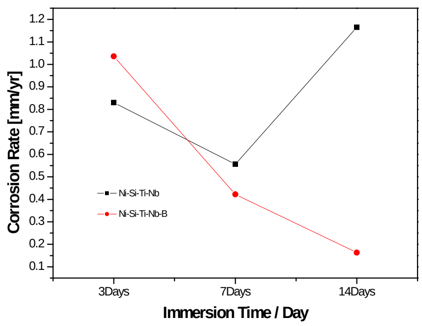

Fig.1 The corrosion rates in the boiling sulfuric acid

Corrosion rates of the Ni-Si-Ti-Nb-B were monotonously decreased during the immersion time. However, the corrosion rate of the Ni-Si-Ti-Nb was decreased by 7days, but it was increased after 7days. It was confirmed that the Ni-Si-Ti-Nb-B has corrosion resistance in boiling 98wt% sulfuric acid.

3-1-2. Ni-Si-Ti-Nb-B

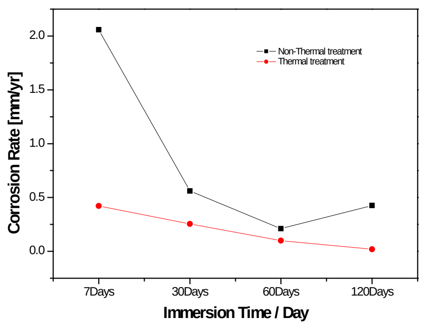

Fig.2 The corrosion rates in the boiling sulfuric acid

The corrosion rates of the thermal treated and non-thermal treated Ni-Si-Ti-Nb-B were decreased during the immersion time. However, corrosion rates of non-thermal treated specimens were to be nearly constant after 60days. On the other hand, it was confirmed that thermal treated specimens show excellent corrosion rate, because surfaces of specimens were formed with the oxide layer[3,4].

3-2. RBS and sintered SiC

3-2-1. Corrosion rates and bending strength

Table 1. Corrosion rates of RBS and sintered SiC as the immersion time.

Sample \ Day	1	7	15	30	60	120	300
Reaction Bonded SiC (RBS)	0.08 mm/yr	0.0002g WG 10Day	-	0.0016g WG	0.0258g WG	0.0595g WG	0.1625g WG
Sintered SiC	0.04 mm/yr	0.01 mm/yr	0.006 mm/yr	0.0047g WG	0.00535g WG	0.0115g WG	-

* *WG(weight gain) : The weight of specimens* were increased with the immersion time passed.

The RBS was immersed in boiling sulfuric acid for a long time. The weight of RBS was increased from 7days to 300days. The weight of sintered SiC was also increased from 30days to 120days. The weight of RBS and sintered SiC were increased with the immersion time in boiling 98wt% sulfuric acid.

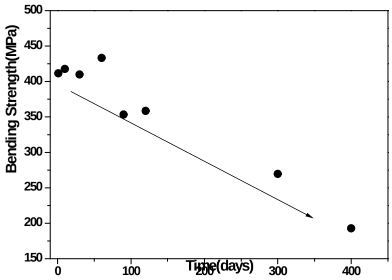

Fig 3. Bending strength of the RBS with the immersion time

It was found that bending strength of RBS was decreased with the immersion time.

3-2-2. Morphology of the RBS

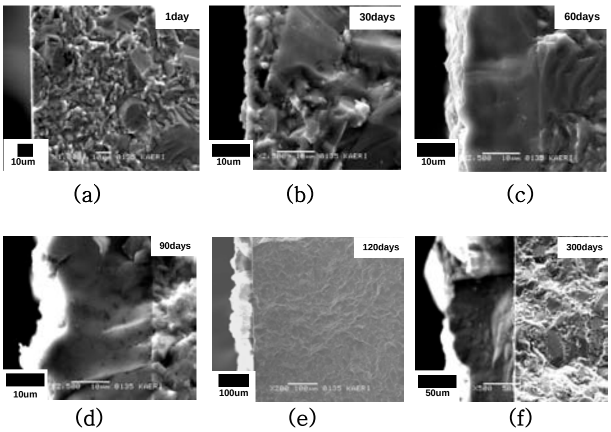

Fig. 4 The morphology of cross section of RBS in sulfuric acid (a) 1day (b)30days (c) 60days (d) 90days (e) 120days (f) 300days

SEM images of the RBS showed that thickness of oxide layer on surface was increased with immersion time.

4. Summary

This research was carried out to find materials tolerable in corrosion environments. The corrosion resistance of Ni-Si-Ti-Nb-B was better than Ni-Si-Ti-Nb in boiling 98wt% sulfuric acid. It was confirmed that thermal treated Ni-Si-Ti-Nb-B shows excellent corrosion rate, because surfaces of specimens were formed with the oxide layer. The weight of RBS and sintered SiC were increased with the immersion time in boiling sulfuric acid. It was found that bending strength of RBS was decreased with the immersion time. SEM images of the RBS showed that thickness of oxide layer on surface was increased with immersion time.

5. REFERENCES

[1] Hiroyuki Ota, et al., "Conceptual design study on sulfuric-acid decomposer for thermo-chemical iodine-sulfur process", 13th International Conference on Nuclear Engineering Beijing China, 2005, 1.

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[4] JAERI report, "IS Process for thermochemical hydrogen production", 94-006.