The characters of materials in sulfuric acid environments

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1. Introduction

The studies on next generation energy sources have been conducted due to the finite resources and environmental pollution. Recently, hydrogen energy is the most actively research part, cause of many merits such as simplicity of the storage and transportation [1][2]. Hydrogen energy does not emit carbon dioxide also. Iodine sulfur (IS) process is one of the methods to product hydrogen energy. IS Process was proposed by GA(General atomic company).

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

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

In these studies, it is found that the material has a suitability to apply to IS process environments. Therefore corrosion tests of various materials were performed in sulfuric acid to select appropriate materials compatible with the IS Process.

2. Methods and Results

The kinds of specimens were Fe-6Si, Fe-4.5Si, Ni-4.5Si, Ni-Si-Ti-Nb and Ni-Si-Ti-Nb-B which were tested in boiling sulfuric acid. Sizes of those specimens were length 10, width 10 and thickness 1.Those were ground with #1500 abrasive paper. And to remove the extra impurities, those specimens were handled by an ultra sonic treatment, and the surfaces of those were oxidized at 1100℃. The time of oxidation was 48hrs. The terms of experiment were 3days, 7days and 14days. For the decomposed sulfuric acid, experimented specimens were Hastelloy-X, Alloy 617, Alloy 800H and Haynes 230. and Sizes of those specimens were length 15, width 15 and thickness 2. Testing time was 1day. Corrosion rates were measured by using the weight change after an immersion. The surface morphologies of the experimented materials were analyzed by using SEM. The composition of the tested specimens was examined by using EDX and XRD.

2.1 The liquid phase of sulfuric acid

2.1.1 Corrosion rates in boiling 98wt% sulfuric acid

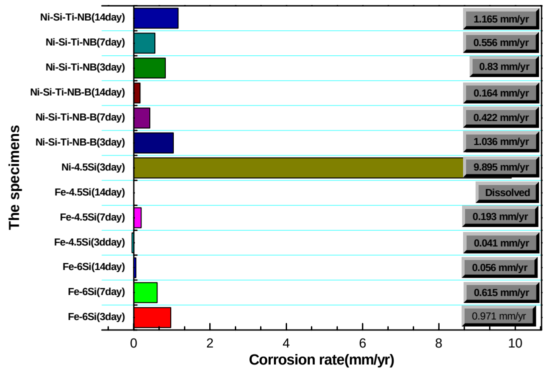
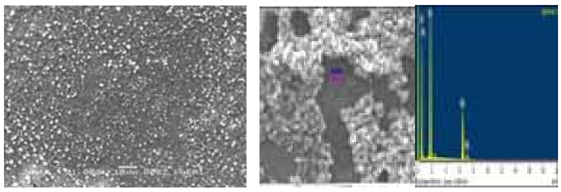


Fig.1 The corrosion rates in the boiling sulfuric acid

The corrosion rates of the Fe-6Si and Ni-Si-Ti-Nb-B were decreased as the time passed. Ni-4.5Si was dissolved during the testing time. And the corrosion rates of the others were increased according to the flowing at that time. These difference of the corrosion rate depended on the density which was created on the surface.

2.1.2 The surface morphology of specimens in liquid phase sulfuric acid

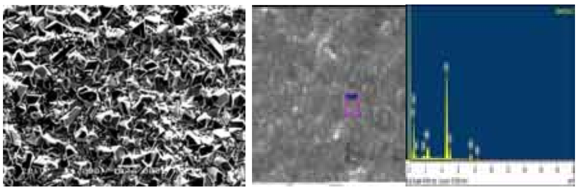
Due to the thermal treatment, the oxidation layer forming the surface of Fe-6Si was very dense. According to the flowing at that time, the particle increased in the size. The oxidation layer was composed of a duplex film structure after immersion test. The inner layer of the oxide is dense and less porous but the outer layer had big particles and more porous.



(a) (b)

Fig. 2 The morphology of the specimens was obtained from the SEM and the compositions were acquired from the EDX
(a) The surface of the Fe-6Si was oxidized in the furnace and a period of time was 48hrs. (b) The compositions of the Fe-6Si after experimenting in the sulfuric acid for 14days

The compositions of the surface were silicon oxide. The silicon oxide compound was the most resistance character in the sulfuric acid [3],[4].



(a) (b)

Fig. 3 The morphology of the specimens was obtained from the SEM and the compositions were acquired from the EDX
(a) The surface of the Ni-Si-Ti-Nb-B was oxidized in the furnace and a period of time was 48hrs. (b) The compositions of the Ni-Si-Ti-Nb-B after experimenting in the sulfuric acid for 14days

The Ni-Si-Ti-Nb-B formed dense oxide particles. The composition of an oxide particle mainly consisted of nickel oxide (not shown, here). After the Ni-Si-Ti-Nb-B was tested in sulfuric acid for the 14days, the oxide compositions of the Ni-Si-Ti-Nb-B changed to the titanium oxide and silicon oxide. Those oxide particles function as a passive film which resists the corrosive environments.

2.2 The gas phase of sulfuric acid

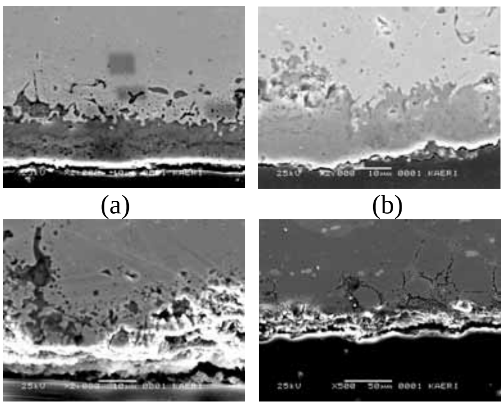
2.2.1 Corrosion rates in the gas phase of sulfuric acid

Table I: The corrosion rate of high temperature material in gas phase sulfuric acid

	Hastelloy-X	**Alloy 800H**	**Haynes230**	**Alloy617**
Corr.rate (mm/yr)	**0.31**	**-0.35**	**0.36**	**0.47**

The Alloy 800H specimen among the experimented materials was the most resistance to corrosion in the gas phases of sulfuric acid. The other specimens showed a similar corrosion rate.

2.2.2 The morphology of the specimens in the gas phase of sulfuric acid



(a) (b) (c) (d)

Fig. 4 The morphology of cross section in the gas phase of sulfuric acid for 30days

(a) Alloy 800H (b) Hastelloy-X (c) Alloy 617 (d) Haynes 230

The tested specimens had the ability of a resistance to corrosion environments. But the Alloy and Haynes 230 were corroded at the grain boundary.

3. Conclusions

This research was carried out to find materials which have a the ability of a resistance to corrosion environments. The Fe-6Si and Ni-Si-Ti-Nb-B among the selected specimens were shown to have the most stability in the liquid phase sulfuric acid. Those specimens stability in the corrosive condition was caused by dense passive film which protected the metal ions from the bare metal. In the gas phase sulfuric acid, the Alloy 800H among the tested materials was the most stably resistance ability.

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