

Corrosion of materials in sulfuric acid for hydrogen production by using VHTR

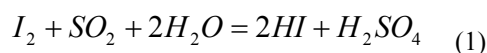
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1. Introduction

Hydrogen which can be stored and transported for a long distance with a lower loss when compared to electricity is one of the promising major energy sources in the future. Moreover a necessity for hydrogen as a clean energy source is increasing more due to significant climate changes [1,2].

Iodine sulfur process (IS process) which splits water thermochemically can produce a large amount of hydrogen without an emission of greenhouse gases by using a high temperature nuclear energy with a thermal efficiency above 40% [3].

IS process which was first proposed by General Atomics [4] and demonstrated as a closed cycle at JAEA [5] is composed of the following three chemical reactions.



Here, reaction (1) is known as the Bunsen reaction, where gaseous sulfur dioxide reacts with iodine and water producing an aqueous solution of iodic acid and sulfuric acid. Thermal decomposition of hydrogen iodide (2) and that of sulfuric acid (3) produces hydrogen and oxygen, respectively. By carrying out these three reactions sequentially, as a net material balance of the process, water can be decomposed into hydrogen and oxygen [6].

Sulfuric acid from a Bunsen reactor is purified and concentrated and then is decomposed into SO_3 and SO_2 thus producing oxygen again. Therefore materials composing an IS process should withstand high temperature and highly concentrated sulfuric acid environments. Moreover, high pressure differences during a normal operation and transient conditions elevate the boiling temperature and sulfuric acid decomposition temperature, which accelerates the corrosion of materials.

Therefore considering that the IS process is operated under very severe environments of iodic and sulfuric acids at a wide temperature range from room temperature to 900°C, material corrosion must be an important issue for an accomplishment of a successful IS process. Especially, a corrosion resistant material applicable to highly concentrated sulfuric acid of a high temperature should be found.

In the present work, corrosion behaviors of some commercial materials and fabricated materials were investigated in boiling sulfuric acid.

2. Experimental

Corrosion tests of various materials were performed in a 50wt% boiling sulfuric acid condition at 125°C and a 98wt% sulfuric acid condition at 320°C. Moreover, a corrosion test for materials showing a good corrosion resistance in a 50wt% boiling sulfuric acid condition was conducted in 50wt% boiling sulfuric acid including HI of 0.5mol, when considering HI as an impurity

Materials such as Alloy 690, Hastelloy C276, Hastelloy X, Haynes 556, Ta, Zr, Au, Fe-xSi alloys(x=6, 10, 13%) and SiC were tested. Dimensions of the specimens were 20mm x 20mm x 1mm with a 5mm diameter circular hole to be held over the specimen holder.

Corrosion cell made of a pyrex glass flask with a capacity of 1L was used. The corrosion cell was heated on a hot plate to maintain a stable boiling condition. Evaporated sulfuric acid was liquidified in a reflux condenser to minimize the evaporation loss. The immersion period was defined as the time between the moment when a boiling begins and the moment when the heater is shut off.

The weight before and after the immersion test was measured by using an electronic balance of the Mettler model AT261. Specimens were washed ultrasonically in acetone for 5 minutes before weighing them and then dried. Corrosion rate was calculated by dividing the weight loss by both the specimen surface area and the immersion period. The surface morphologies of the corroded materials were examined by using SEM equipped with EDS(JSM6360).

3. Results and discussion

Fig. 1 presents the potentiodynamic curves for Fe-6Si, Fe-10Si and Fe-13Si in 50wt% sulfuric acid at room temperature with a scan rate of 5mV/s. At -0.4V(SCE), a corrosion potential was observed, irrespective of the Si amount, which was consistent with the equilibrium potential of an Fe dissolution [7]. At this corrosion potential, passive SiO_2 was thermodynamically stable according to the E-pH diagram. In the active-passive transition region and the passive region, the measured current was decreased with an increase of the Si amount. Additionally, a passive current was measured above about 0.4V(SCE) where Fe_2O_3 is formed [7].

At the corrosion potential, Fe dissolves and exposes a Si enriched surface. Exposed Si is oxidized to a passive

SiO₂ which is thermodynamically stable at this potential. As an applied potential increases, it is expected that the surface coverage of passive SiO₂ is increased with an increase of the Si amount leading to a decrease of the measured current in the active-passive transition region and the passive region. For the Fe-13Si specimen, an active-passive transition caused by an Fe₂O₃ formation was less obvious, which could be due to the large coverage of SiO₂ already formed on the surface during an anodic sweep of the applied potential.

From these results, it is plausible that the coverage of the passive SiO₂ is increased with an increase of the Si amount in the Fe-xSi during an immersion in 98wt% boiling sulfuric acid. Corrosion resistance of Fe-Si with the Si amount is caused by a coverage and thickness increase of the passive SiO₂ as a function of the Si amount.

Fig. 2 shows the potentiodynamic curves for Fe-6Si in 50wt% sulfuric acid at room temperature and 60°C with a scan rate of 5mV/s. As the solution temperature increased, the corrosion rate at the corrosion potential increased and the measured current in the active-passive transition region and the passive region increased. Moreover the potential where a passive current was measured increased slightly. As an applied potential increases anodically, Fe dissolves vigorously with a temperature increase leaving a Si enriched surface and hence, forming a passive SiO₂. The measured current decreases abruptly at a potential where a passive film of Fe₂O₃ is formed. It seems that the passivities of Fe₂O₃ and SiO₂ decrease with a temperature increase from the fact that the measured current increases with a temperature increase. And a region where Fe₂O₃ is stable is narrower as the temperature increases according to the E-pH diagram [7] leading to a shift of the active-passive transition potential.

4. Conclusion

1. Ta, Zr, Au and SiC showed an excellent corrosion resistance in 50wt% boiling sulfuric acid. However corrosion resistance of Au was degraded by adding 0.5mol HI.
2. Au and SiC showed an excellent corrosion resistance in 98wt% sulfuric acid while Ta showed a poor corrosion resistance. Oxides were observed on the surfaces of Au and SiC, which could lead to an excellent corrosion resistance in the 50 and 98wt% sulfuric acids.
3. With regards to Fe-xSi(x=6, 10, 13%), corrosion rates for Fe-6Si, Fe-10Si and Fe-13Si in 98wt% boiling sulfuric acid were decreased with an increase of the Si amount. It is expected that the corrosion resistance of Fe-Si is attributed to a passive SiO₂ formation on the surface, which was explained reasonably by analyzing the results of the potentiodynamic curves and E-pH diagram.
4. After an appropriate annealing, corrosion rate for Fe-6Si was greatly decreased and its corrosion rate was

decreased with the immersion time. It seems that a surface modification during an annealing provides a passivity against a corrosion.

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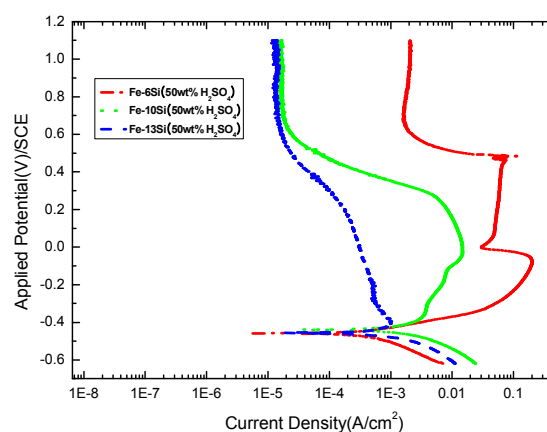


Fig. 1. Potentiodynamic curves for Fe-6Si, Fe-10Si and Fe-13Si in 50wt% sulfuric acid at room temperature with a scan rate of 5mV/s.

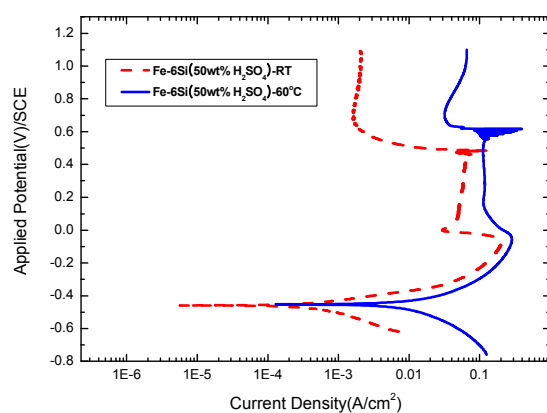


Fig. 2. Potentiodynamic curves for Fe-6Si in 50wt% sulfuric acid at room temperature and 60°C with a scan rate of 5mV/s.