

# Materials Development for the Sulfuric Acid Decomposer in Iodine-Sulfur(IS)cycle for Nuclear Hydrogen Production System

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## 1. Introduction

The material used for the sulfuric acid gas channels for a mass production of hydrogen [1-2] is of importance because it is subjected to severe corrosion environment. Consideration is being given to surface modification of metallic materials. We selected Hastelloy X as the metallic substrate due to its good mechanical properties at a high temperature and SiC as a corrosion inhibiting coating material. In developing a surface coated metallic system, consideration needs to be given to how best to ensure the adhesion of the coating layer and how to reduce the defects in the coating. However we have solved this problem by employing an ion beam mixing (IBM) [3]. Other potential problems include the possible sublimation of the deposited film during a high temperature annealing in vacuum. This sublimation certainly gives rise to adverse effects such as loss of the film and/or its deterioration and non-stoichiometric structure formation [4]. In this paper, we show a result of in-depth sublimation suppression study of the SiC coated layer, and the corrosion study results of an immersion test in a 98 % sulfuric acid at 300.

## 2. Experiments and Results

In this section some of the experiments are described and the relevant results are presented..

### 2.1 Experiments

Prior to a SiC deposition, a sputter cleaning of the sample was carried with an N ion energy of ~10 keV and a current of 0.5 Ampere. Then, the deposition of the SiC was performed to 50 nm thickness, followed by a nitrogen ion beam mixing at 70keV with a dose of ~  $5 \times 10^{16}$  ions/cm<sup>2</sup>. A further SiC evaporative deposition up to a total of ~ 1  $\mu$ m was then conducted with a deposition rate of ~3 Å/s produced by an electron beam current of ~0.15 A. It is the outermost surface of the samples that was again N-irradiated (hammered) at 70 keV with a dose of ~  $1 \times 10^{17}$  ions /cm<sup>2</sup> to  $4 \times 10^{17}$  ions/cm<sup>2</sup> to increase their resistance to sublimation.

The samples were then placed in an alumina boat and annealed in a quartz tube vacuum furnace with a heating rate of ~7.5°C/min at temperature ranges of 550°C to 950°C for 2 hrs. The metallic substrate before the film

deposition and the coated samples were weighed before and after annealing with a micro balance to determine the sublimation rate.

Immersion corrosion test was performed in 98% H<sub>2</sub>SO<sub>4</sub> at 300°C during about 350hrs to see the difference between the bare and. the coated samples.

### 2.2 Results and Discussion

After heating at 950°C in both air and vacuum, SiC film was maintained as-coated on the Hastalloy-X surface in spite of a high difference in their CTEs. This is attributed to IBM to produce a highly adherent coated layer and an interfacial reaction during annealing [3]. As determined by the weight changes, the surface areas of the sample, and the SiC film thickness, the density of the SiC films is about 40% lower than that of the bulk SiC (3.217 g/cm<sup>3</sup>) [5].

As shown in Fig. 1, almost no sublimation occurs below 700°C, but the sublimation rate increases drastically as the temperature increases, that is, ~ 5% at 750°C, ~ 7% at 850°C, and ~ 30% at 950 (Fig 1a). The sublimation rate was determined by the weight decrease of the film with a careful exclusion of the substrate effects. However, when the N ions at 70 keV with a dose of  $5 \times 10^{17}$  ions/cm<sup>2</sup> were bombarded onto the film and then annealed in a vacuum of ~ $1.5 \times 10^{-5}$  torr, the sublimation was suppressed, but the sublimation rate is still measured by ~ 8% at 950°C [Fig.1b]. It is not decreased further as the ion dose increases up to  $4 \times 10^{17}$  ions /cm<sup>2</sup>. The reason why the ion beam irradiation does not eliminate the sublimation completely may be that the nuclear collisions between the impinging ions and the atoms in the nearer surface of the deposited SiC film are less probable.

Figure 2 shows weight retain rates of the as-received Hastelloy X and the both side coated Hastelloy X samples as a function of the immersion time (hours) in 98% sulfuric acid at 300°C. The coated sample with IBM retains the weight almost unchanged, but the weight of the uncoated reduces rapidly. The process heat exchanger is supposed to be used in the environment of the decomposed sulfuric acid gas above 900°C, but this test is performed in a 98% sulfuric acid at 300°C which is a very severe corrosion

environment and exhibits the difference in a shorter period.

Figure 3. is a cross sectional observation of as-received and SiC coated Hastelloy X sheets bending-machined as a real shape for the decomposed sulfuric acid channel before and after immersing in 98% H<sub>2</sub>SO<sub>4</sub> for 80 hrs and 348hrs at 300 °C. The upper two sheet samples are SiC coated samples annealed in vacuum and air at 950 °C. The lowest is the as-received sample. The annealing atmosphere does not affect the corrosion behavior. Even after 80hrs immersion we can see a considerable difference in the thickness of the samples and, after 348 hrs, the as-received sample is corroded out from the edge. Although the corrosion rate is quite different, the thickness of the coated sample is also reduced. This may be attributed to the progress of the corrosion through the coalescent pores formed during the crystallization of the amorphous SiC film. The corrosion through the coalescent pores may have resulted in the film peeling-off.



Figure 3. A cross sectional observation of as-received and the SiC coated Hastelloy X sheets shaped for the decomposed sulfuric acid channel before and after immersing in 98% H<sub>2</sub>SO<sub>4</sub> for 80 hrs (a) and 348hrs (b) at 300 °C.

### 3. Conclusions

We report the SiC coating on Hastelloy X can be sustained at a high temperature in spite of the high difference in CTE, when IBM is applied. The mechanism may be that the ion beam mixing fastens the SiC coated layer with the Hastelloy X substrate until the interfacial reaction occurs. Then, the new phase is formed at the film/substrate interface, which acts as a functionally degraded layer. The final ion irradiation on the deposited film produces a sublimation barrier. The corrosion tests of the resultant samples suggest that the SiC coated Hastelloy X should improve the lifetime of the process heat exchanger. The PHE system manufactured in this way certainly has a merit that it does not hamper the manufacturability of process heat exchanger of I-S cycle as compared to the whole ceramic system.

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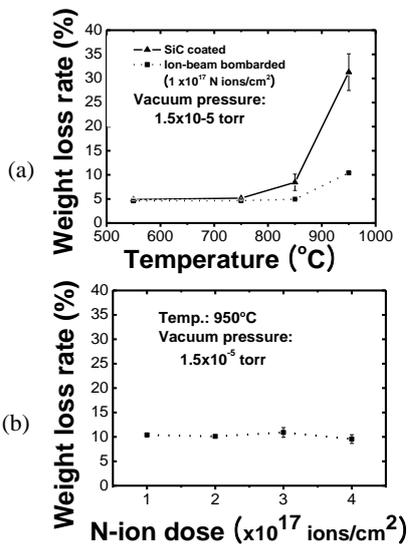


Fig. 1. The sublimation occurs vigorously at 950 °C, but it is greatly suppressed upon the N ion beam bombardment onto the film (a). At 70 keV, ion doses more than 1x10<sup>17</sup>/cm<sup>2</sup> do not affect the sublimation rate that much (b).

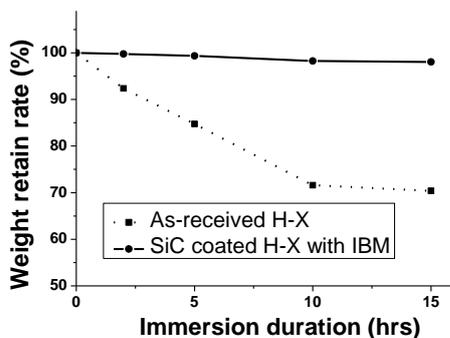


Figure 2. Corrosion rates of the as-received and SiC coated Hastelloy X samples in 98% sulfuric acid at 300 °C