# High Temperature Oxidation Behavior of ZrSi$_2$ and Its Coating on the Surface of Zircaloy-4 Tube by 3D Laser Coating Method

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## 1. Introduction

A zirconium-based alloy has been used extensively for fuel cladding materials for more than five decades because of its excellent neutron transparency, mechanical properties, and corrosion resistance during normal operation of light water reactors (LWR). However, under an accident condition such as loss of coolant accident (LOCA), significant degradation of the zirconium-based alloy occurs. Above 700 °C, high pressure steam causes rapid oxidation leading to hydrogen emission [1]. In addition, zirconium oxide undergoes phase transformation upon temperature increase and it causes spallation of oxide scale and accelerates further oxidation [2][3]. Small compositional changes of a zirconium based alloy with other elements are not sufficient for satisfactory high temperature oxidation resistance. After the accident at Fukushima in 2011, many concepts for accident tolerance cladding have been proposed and developed to improve the high temperature oxidation resistance of cladding under LOCA conditions compared to the current zirconium base alloy cladding. Among the many concepts, coating of high temperature oxidation resistant materials on the cladding is getting attention which can obtain the accident tolerance at the same time as the high neutron economy.

Transition metal silicides have the potential to be applied in high temperature industry because of their outstanding oxidation resistance, strength at high temperature and relatively low density. The zirconium silicide has been proposed as one of the promising protective coating materials for accident tolerant fuel cladding due to its low thermal neutron absorption, high temperature strength. The oxidation of ZrSi$_2$ powder to 1550 ° C suggests the formation of ZrO$_2$, SiO$_2$ and ZrSiO$_4$ [4]. Oxidation experiments of ZrSi$_2$ for 5 hours at 700 °C, 1000 °C and 1200 °C were also carried out [5]. The amorphous Zr-Si-O layer was formed at 700 ° C, and the isotropic irregular layer by layer structure of ZrO$_2$ and SiO$_2$ was formed at 1000 ° C and 1200 ° C in the oxide layer. The thickness of the oxide scale in these experiments was even lower than that of the Zircaloy-4 tubes which were oxidized under the same conditions. However, the high temperature oxidation mechanism of ZrSi$_2$ is not well studied. The reason for the excellent oxidation behavior despite the existence of

ZrO$_2$, which is known to have a non-protective tendency in the oxide film, has not been explained yet.

In this study, the formation process of an oxide film of ZrSi$_2$ was investigated by means of in situ X-ray diffraction (XRD) over time during the oxidation at 900 °C, 1000 °C, and 1100 °C air for 20 hours each and microstructures of oxide scales were examined by scanning electron microscope (SEM). To identify the oxide scale of samples with high magnification and resolution, the oxide scale of each sample was imaged by a transmission electron microscope (TEM). Not only the ZrSi$_2$ oxidation but also a separate study was performed to coat ZrSi$_2$ on the surface of Zircaloy-4. As a coating method, a 3D laser coating was used which supplied zirconium / silicon powder mixture. The microstructure of oxidized ZrSi$_2$ coated Zircaloy-4 tube at 1200 °C steam was examined by SEM. The result of this study will provide the suitability of ZrSi$_2$ as an accident tolerance coating material on the Zircaloy-4 tube.

## 2. Experimental and Result

### 2.1 High Temperature Oxidation of Bulk ZrSi$_2$

Zirconium (Sigma Aldrich, > 99.99 % with 3% Hf) and silicon (Sigma Aldrich, > 99.99 %) powder were purchased for this study. For fabrication of bulk sample, powder metallurgy method was used. A mixture of zirconium and silicon powder with a molar ratio of 1: 2 was sintered without milling by spark plasma sintering (SPS). The sintering was carried out at 1100 °C with 100 °C / min heating rate for 10 minutes and 50 MPa of axial pressure was applied during the sintering. The density of the sintered sample was measured by Archimedes' method. For phase analysis during the oxidation, in-situ X-ray diffraction (XRD) (BRUKER, D8-Advanced) with Cu K$\alpha_1$ was used. Measurement range was $20^o \sim 80^o$ in two-theta. The samples were oxidized for 20 hours at 900 °C, 1000 °C, 1100 °C air, and signals were collected every hour for 20 minutes. For the microstructure analysis of the fabricated sample and oxide, a scanning electron microscope (SEM) (FEI, Magellan 400) and a transmission electron microscope (TEM) (FEI, Talos F200X) were used in conjunction with energy dispersive spectroscopy (EDS). The TEM sample was prepared by focused ion beam (FIB) (FEI, Helios Nanolab 450 F1).
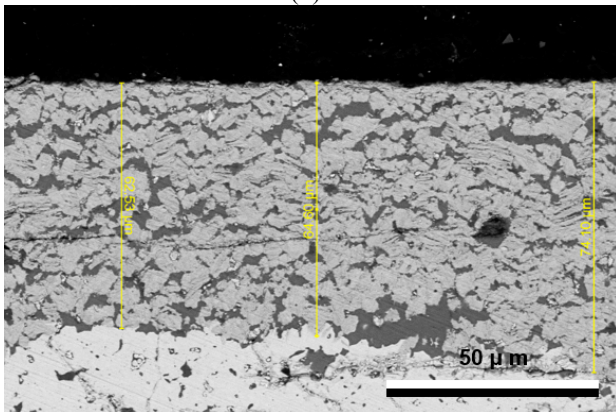
SEM-BSE images of oxide scales of oxidized $ZrSi_2$ for 20 hours at each temperature air are shown in Fig. 1. Oxide scale thickness at 900 °C is in the range of 4.1 ~ 6.6 $\mu$m, at 1000 °C is 15.8 ~ 22.4 $\mu$m, and at 1100 °C is 62.5 ~ 74.1 $\mu$m. All of the oxides tested at three temperatures contained a pure silicon phase that appeared dark in the oxide film. The relatively bright part was composed of oxide of layer-by-layer structure. Fig. 2 shows the in-situ XRD pattern results before oxidation, after 5 hours of oxidation, after 20 hours of oxidation, and after cooling at different temperatures. Unmarked peaks are alumina peaks used as sample holders. As oxidation progresses, tetragonal $ZrO_2$ peaks and pure silicon peaks were grown and the $ZrSi_2$ peak tends to decrease as the oxide film grows.
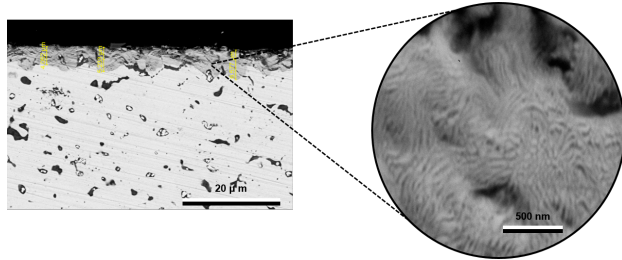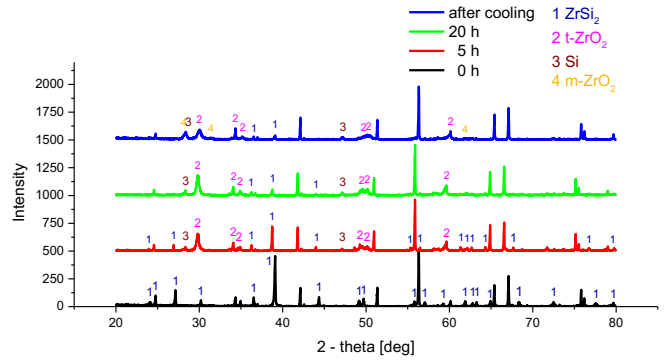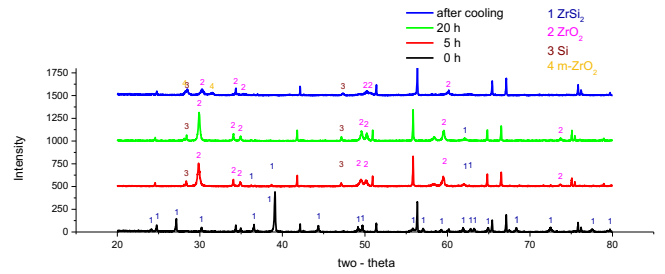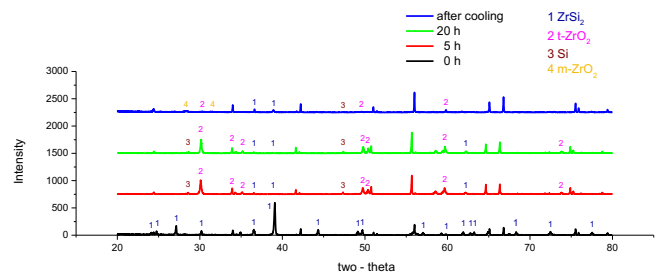


(a)
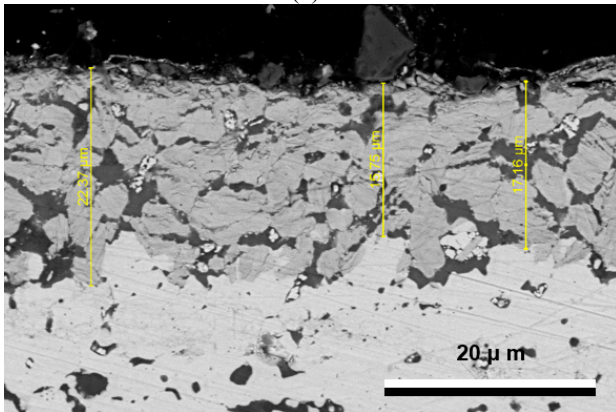


(b)



(c)

**Fig. 1 Cross-sectional SEM BSE images of oxide scale oxidized at (a) 900 °C, (b) 1000 °C, (c) and 1100 °C.**



(a)



(b)



(c)

**Fig. 2 In-situ XRD pattern at (a) 900 °C, (b) 1000 °C, and (c) 1100 °C air for 20 h.**

Fig. 3 is TEM image of layer by layer structure in oxide scale of $ZrSi_2$ oxidized at 1100 °C. As noticed in the SEM-BSE image, there are two phases in the TEM image, which appear as bright and dark areas. The results of FFT analysis of the bright and dark areas, respectively, are shown in Fig. 4. There is no diffraction

pattern in the bright phase FFT results. That is, the bright phase is judged to be an amorphous phase. It is therefore brightly depicted in the TEM image because it does not diffract the electrons. On the other hand, FFT analysis of the dark part reveals that the diffraction pattern appears. This dark phase is crystalline phase and is therefore appeared dark in the TEM image. Matching the XRD results, it can be concluded that the dark phase of the TEM image in the layer by layer is $ZrO_2$ and the bright unknown phase is not in the XRD pattern because it is an amorphous phase. In order to interpret the composition of these phase, STEM-EDS analysis were carried out. The high angle annular dark field (HAADF) STEM image and EDS mapping images of the oxide scale of $ZrSi_2$ are shown in Fig. 5. The chemical compositions of the points indicated in the image analyzed with EDS are in Table. 1. According to EDS analysis, it is found that (a) is pure silicon, (b) is pure $ZrO_2$ which was confirmed in the XRD result and the dark phase in TEM image, (c) is pure $SiO_2$ which was unknown amorphous phase in TEM image. HAADF has Z contrast, the brightness of each phase is proportional to the atomic number. Therefore, unlike the TEM image, crystalline $ZrO_2$ appears bright and amorphous $SiO_2$ appears relatively dark.
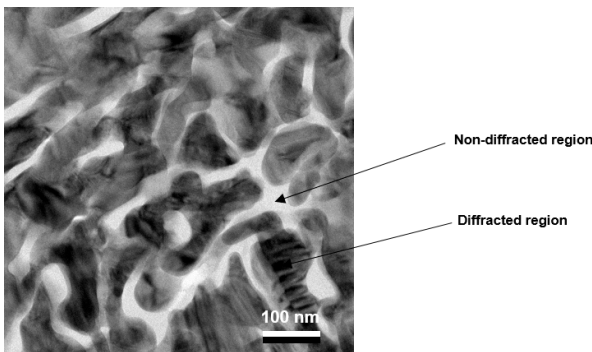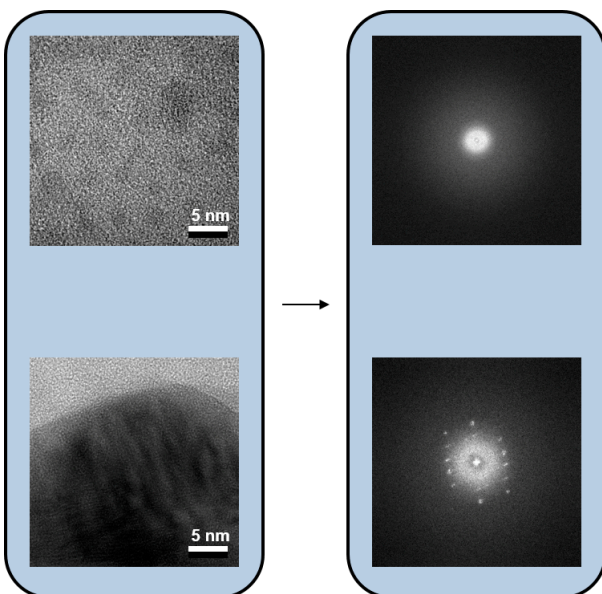


**Fig. 3 TEM image of oxide scale.**



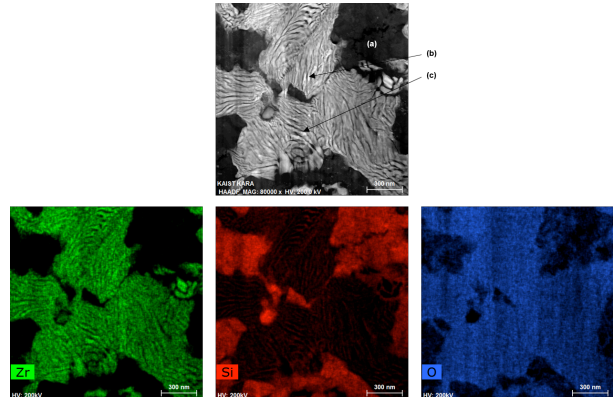**Fig. 4 FFT of bright and dark region in TEM image.**



**Fig. 5 STEM image and EDS mapping analysis of oxide scale.**

|            | (c)  | (a)  | (b)  |
|------------|------|------|------|
| **Zr [at%]** | 2.9  | 0.1  | 33.3 |
| **Si [at%]** | 35.7 | 99.6 | 4.3  |
| **O [at%]**  | 61.4 | 0.3  | 62.4 |

**Table. 1 Chemical composition of the points indicated in Fig. 10**

*2.2 3D Laser Coating on the Zircaloy-4 Tube and Steam Oxidation Test*

For coating on the Zircaloy-4 tube, 3D laser coating method was used. A photo of the constructed 3D laser coating facility is shown in Fig. 1 which consists of a nozzle (Yesystem, Nz14Y01K), powder supplier (Yesystem, Pwp14YO4K), and laser source (HBL, PF-1500F). The laser head, spraying mixed powder, argon gas, and laser, moves slowly in the direction of the tube in which the cooling water flows is rotated in the vertical direction. During the powder injection process, the loss of silicon powder was caused by the difference in size and density of zirconium, silicon powder. Therefore, silicon powder was mixed more than twice as much as the zirconium powder in order to compensate for powder loss. After coating, the cross section of the coated zircaloy-4 tube was observed by scanning electron microscope. High temperature steam oxidation was conducted with thermo gravimetric anlayzer (TGA) (Shimadzu, TGA-51H) in 1200 °C steam and argon mixture with a flow rate of 10 ml/min. The heating rate was 50 °C /min and only argon gas was supplied during the heating. After oxidation, the cross-section of the oxidized tube was observed also.

Fig. 6 is cross-sectional images of $ZrSi_2$ coated Zircaloy-4 tube with different zirconium to silicon ratio for mixed powder. Fig. 7 is the cross section of oxidized coated Zircaloy-4 tube. The inner surface of the uncoated tube formed a thick $ZrO_2$ oxide film of about 400 micrometers, but the outer surface of the $ZrSi_2$ coated film shows little change in thickness considering the basic coating thickness. As a result, the $ZrSi_2$ coating shows a significant improvement in the high-temperature oxidation resistance of the Zircaloy-4 tube.
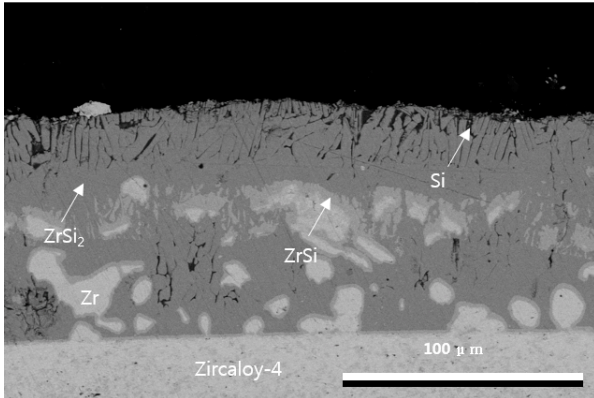


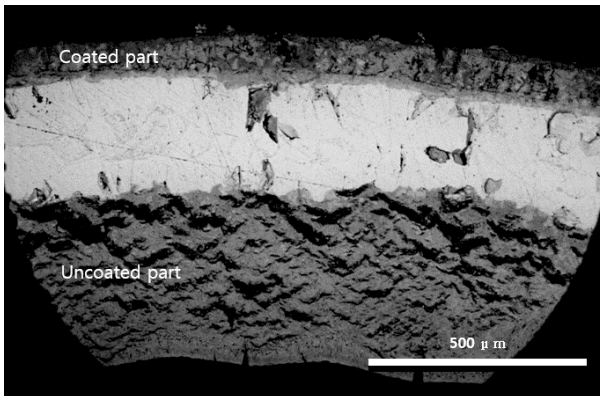**Fig. 6 Cross-sectional SEM-BSE image of coated Zircaloy-4.**



**Fig. 7 Cross-sectional SEM-BSE image of oxidized coated Zircaloy-4**

### 3. Conclusions

For the development of accident tolerance fuel cladding, high temperature oxidation of zirconium silicide, which is used as a coating material for nuclear fuel cladding, was conducted at 900 °C, 1000 °C, and 1100 °C. Powder metallurgy method was used for bulk sample fabrication, and zirconium and silicon powder mixture was sintered at 1100 °C using SPS. The density measurement using the Archimedes' method yielded a sample with a relative density of 98.6% of the theoretical density. In-situ XRD, SEM, and TEM analyzes were used for the oxidation mechanism analysis. As a result of SEM analysis, it was determined that the oxide film was formed continuously at all the temperatures and spallation did not occur. Therefore,

the oxide film had high oxidation resistance which is much better than that of Zircaloy. In situ XRD results show that tetragonal $ZrO_2$ and pure silicon are formed during oxidation. TEM analysis revealed that pure silicon, crystalline $ZrO_2$ and amorphous $SiO_2$ were formed in the oxide film. It has been determined that the glassy $SiO_2$ layer formed here plays a significant role in the high temperature oxidation resistance of $ZrSi_2$. A $ZrSi_2$ coating with 3D-laser was applied to the Zircaloy-4 tube. Because of the difference of powder size, density, silicon powder was needed more than twice of zirconium powder to make uniform $ZrSi_2$ coating. The coating was formed with a uniform thickness and the zirconium hardly melted from the tube side to coating due to the cooling water flowing through the tube. Therefore, it is expected that using $ZrSi_2$ powder can provide a better quality coating instead of the mixture of zirconium and silicon powders. Coated Zircaloy-4 tubes were oxidized for 2000 seconds at 1200 °C steam / argon mixture. As a result, it was confirmed that the outer surface of the coating was hardly changed in thickness, but the uncoated inner surface was seriously oxidized. This study has confirmed that the $ZrSi_2$ coating significantly increases the high-temperature oxidation resistance of Zircaloy-4 cladding.

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