1. Introduction

Zirconium-based alloys have been used as nuclear fuel cladding in light water reactors for over 50 years, owing to their high neutron transparency, acceptable mechanical properties, and excellent corrosion resistance in regular operations of nuclear power plants. However, this cladding is susceptible to significant degradation under accident conditions, such as loss of coolant accident (LOCA). Temperatures beyond 700 °C and high-pressure steam cause rapid steam oxidation, hydrogen gas generation, and mechanical degradation of the cladding [1]. The ZrO2 formed has a phase transformation between 1100 °C and 1200 °C that leads to the spallation of the oxide film and further accelerates the oxidation [2,3]. Minor compositional changes in zirconium-based alloys yield satisfactory results in obtaining sufficient high-temperature oxidation resistance. Following the Fukushima accident in 2011, several concepts were proposed and developed to increase the high-temperature oxidation resistance of nuclear fuel cladding to develop accident-tolerant fuel. Coating with a material having high oxidation resistance on a zirconium-based cladding is receiving considerations as a method for obtaining both neutron transparency and accident resistance [4–13].

Transition metal silicides are suitable materials in the high-temperature industry owing to their high-temperature oxidation resistance and strength. For example, MoSi2 exhibits a protective and dense SiO2 film on the surface at temperatures of approximately 1400 °C and high-temperature oxidation resistance, although the SiO2 formed is unstable, causing pest oxidation and MoO3 formation in oxide films at low temperatures that are insufficient to form stable SiO2 layers on the MoSi2 surface [14,15]. In a high-temperature oxidation test of TiSi2, in contrast to the oxidation experiment conducted with MoSi2, both TiO2 and SiO2 were formed in the oxide layer, resulting in a higher oxidation rate of TiSi2 than that of MoSi2 [16,17]. ZrSi2 is a preferred coating material for the development of accident-tolerant fuel cladding, owing to its high-temperature strength and low neutron absorption compared to other silicides and iron-based oxidation-resistant alloys [18]. However, studies on the high-temperature oxidation of ZrSi2 are scarce. Geßwein et al. [19] reported that, through X-ray diffraction (XRD), the oxidation of ZrSi2 powder forms a tetragonal ZrO2 phase, monoclinic ZrO2 phase, and pure silicon phase. Yeom et al. conducted a ZrSi2 oxidation experiment for 5 h at temperatures of 700, 1000, and 1200 °C. At 700 °C, a Zr–Si–O amorphous phase was formed with silicon-rich oxide. A pure silicon phase and an isotropic layer-by-layer structure that are
estimated as ZrO$_2$ and SiO$_2$, were formed at 1000 °C and 1200 °C, respectively [20]. Studies on the high temperature corrosion resistance and heat transfer were conducted with ZrSi$_2$ coated on cladding [21]. Although ZrSi$_2$ exhibits superior oxidation resistance compared to zirconium-based alloys, an in-depth analysis of the oxide film formed on ZrSi$_2$ at high temperatures has not been actively pursued in the development of accident-tolerant fuel.

Coating technology is widely used in the materials industry to enhance the corrosion, oxidation, and wear resistance of materials notwithstanding maintaining the advantages of base materials. Currently, FeCrAl alloys are considered as undesirable coating materials owing to the formation of the eutectic phase caused by the interdiffusion of iron with Zr-based substrate. The interdiffusion can be prevented by coating molybdenum between a FeCrAl coating layer and Zircaloy-4 sheet by magnetron sputtering. The oxidation of the coated sheet is conducted at 1200 °C steam for 1 h, and the coated surface was covered by a 1.5-μm-thick Al$_2$O$_3$ layer after the oxidation [5]. Terrani et al. investigated the high-temperature oxidation resistance of zirconium slugs encapsulated in 310 stainless steel and FeCrAl alloy. Oxidation experiments were conducted at 1200 °C and 1300 °C. The change in the thickness of the oxide film of the encapsulated slugs formed under these temperatures was significantly less than that in the thickness of the bare slug. However, both samples experienced significant interdiffusion between the coating and zirconium substrate, causing failure of slugs encapsulated in 310 stainless steel [9]. For chromium, oxidation experiments were conducted on a Zircaloy-4 tube using the arc ion plate method and 3D laser coating, as analogous to the method used in this study. Oxidation experiments were carried out for 2000 s in 1200 °C steam/argon mixture. After oxidation, a ~1.5-μm-thick Cr$_2$O$_3$ layer was formed on the chromium layer coated by arc ion plating, and the tube coated with 3D laser had an oxide film of thickness less than 4 μm [6,8]. The oxidation experiment result of Zircaloy-4 sheet coated with silicon by laser beam scanning after plasma spraying is reported in literature. The experiment was conducted in 1200 °C steam/argon mixture for 2000 s. The silicon coating showed high oxidation resistance. Unlike other experiments, over 100-μm-thick ZrO$_2$ layers were formed between the coating and Zircaloy-4 substrate during oxidation because of the low adhesion [7]. The concept of coating a zirconium-based alloy on a molybdenum-based alloy tube that has a high melting point, high-temperature strength, and low oxidation resistance at temperatures below 600 °C is proposed for accident-tolerant fuel cladding [10]. Moreover, the high-temperature oxidation resistance of chromium-coated Zircaloy-4 tubes increased by the physical vapor deposition method [11]. Plasma spraying was used as a method for coating silicon on Zircaloy-4, and an unstable coating film was formed at temperatures up to 1200 °C, causing the formation of an interlayer ZrO$_2$ [7]. Cold spray coating techniques have been used to develop ATF cladding. Chromium, FeCrAl alloy, and Ti$_2$AlC MAX phases are deposited on Zircaloy-4 by the cold spray coating method. The coated Zircaloy-4 tube was oxidized at 1000–1300 °C for 20 min and showed good coating durability after oxidation [12]. In Ref. [13], Chromium was coated on a Zircaloy-4 tube using cold spray, followed by oxidation experiments and nanoindentation, demonstrating the superiority of cold spray. However, most of these methods are considered unfeasible in the industry because of their high cost or high-temperature and high-vacuum conditions requirements that are unsuitable for mass production. Particularly, if the coating is applied under high-temperature, the optimized microstructure of the zirconium-based alloy tube is destroyed. Cold spraying is relatively inexpensive and allows mass production compared to other methods, however, if using compounds such as FeCrAl, Ti$_2$AlC, ZrSi$_2$ as coating materials, the elemental powder cannot be used directly,
and powder of the compound is required with limited shape and size of powder for good quality of the coating.

In this study, we investigate the high-temperature oxidation behavior of bulk ZrSi2 as a candidate cladding coating material. An in situ XRD method, that can perform XRD analysis in real time under high-temperature oxidation condition is used to analyze the oxide film formed during the high-temperature oxidation process. A transmission electron microscope (TEM) analysis is performed to analyze the oxide film at high magnification and resolution.

Furthermore, coating is conducted on a Zircaloy-4 tube using a 3D laser coating. This study focuses on the microstructure characteristic of a ZrSi2-coated Zircaloy-4 tube and its oxidation behavior in a 1200 °C steam/argon mixture. The experimental results provide an assessment of whether ZrSi2 is suitable as an accident-tolerant fuel cladding coating.

2. Experimental procedure

2.1. High-temperature oxidation of bulk ZrSi2 in air

Bulk ZrSi2 samples were prepared using the powder metallurgy method. Zirconium powder (Sigma Aldrich, >99.99% with 3% Hf, 325 mesh pass) and silicon powder (Sigma Aldrich, >99.99%, 325 mesh pass), each with size less than 45 μm, were purchased and used for sample preparation. A mixture of the zirconium and silicon powders with a molar ratio of 1:2 was sintered by spark plasma sintering (SPS) (SPS-515, Fuji electronic industrial, Japan) without milling. The sintering was conducted at 1100 °C at a heating rate of 100 °C/min for 10 min, and an axial pressure of 50 MPa was applied under a high vacuum of less than 30 Pa. Sintered samples have a cylindrical dimension of 13 mm in diameter and 5 mm in height. The density of the sintered samples was measured using Archimedes’ method. The microstructure and crystal structure of the sintered samples were examined by SEM (Magellan 400, FEI) and XRD (D/MAX-2500, RIGAKU), respectively, to validate the formation of ZrSi2. The crystal structure of the samples during the oxidation was investigated by in situ XRD using Cu Kα1.2 ranges from 20° to 40°. The samples were oxidized at 900, 1000, and 1100 °C for 20 h each, and signals were collected hourly. SEM observation of the oxide film of the oxidized sample was conducted. TEM (Talos F200X, FEI) was utilized for an in-depth analysis of the oxide films. TEM samples were prepared using a focused ion beam (FIB) (Helios Nanolab 450 F1, FEI). In the TEM mode, the fast Fourier transform (FFT) was used to analyze the crystal structure of a specific phase in the oxide scale, and a compatible energy-dispersive spectroscopy (EDS) analysis was performed in the STEM mode.

2.2. Three-dimensional laser coating of ZrSi2 on the Zircaloy-4 tube and steam oxidation test

A 3D laser coating was used for coating ZrSi2 on the Zircaloy-4 tube. The 3D laser-coating facility comprises a nozzle (NZ14Y01K, Yesystem), a powder supplier (Pwp14Y04K, Yesystem), and a laser source (PF–1500F, HBL). A continuous-wave diode laser, with a maximum output of 300 W was used. Fig. 1 describes a simple schematic of the 3D laser coating. The laser head that sprays the powder mixture and argon shielding gas for preventing oxidation, and the laser moves slowly in the direction of the tube where the cooling water flows, and the tube is rotated in the vertical direction.
of the head’s movement. The laser power was 120 W, hatching distance was 0.15 mm, and scan speed was 5 mm/s. Zirconium and silicon powders were used to form ZrSi2 coating. While the mixed powder was sprayed from the nozzle into the zircaloy-4 tube, some silicon powder was not coated but lost because the silicon powder had a lower density than the zirconium powder. To compensate for this loss, the silicon quantity added for the ZrSi2 coating was beyond twice the zirconium quantity. The zirconium-to-silicon molar ratio in the mixed powder were 1:5, 1:6, and 1:7. A Zircaloy-4 tube coated with ZrSi2 for high-temperature oxidation experiments was cut with a diamond wheel of length 1 cm. The cut tube was ultrasonically cleaned in ethanol for 5 min, and then dried. The high-temperature oxidation experiments were conducted using a thermogravimetric analyzer (TGA) (TGA-51H, Shimadzu) in a 1200 °C steam/argon mixture. The argon gas was used as a steam carrier and the flow rate of the mixed gas was 10 ml/min. The uncoated bare Zircaloy-4 tube was oxidized as a reference. The microstructures of the tubes before and after oxidation were examined by SEM.

3. Result and discussion

3.1. High-temperature oxidation of bulk ZrSi2 in air

The microstructure and crystal structure were investigated by SEM and XRD, respectively, confirming that the fabricated samples were well-sintered. Fig. 2 shows the microstructure of the sintered ZrSi2 sample. The EDS analysis result indicated that the matrix phase was ZrSi2, and a minimal volume fraction of pure silicon and mixed oxides were formed in the matrix. These oxide phases were estimated to be the oxides contained in the raw metal powder before sintering and those generated in the sintering process. The volume fraction of ZrSi2 calculated using image processing was 97.05%. The density of the fabricated sample measured using Archimedes’ method was 4.81 g/cm3 corresponding to 98.6% of the theoretical density of pure ZrSi2, and no porosity was observed. The actual measured density was slightly lower than the theoretical density because the sample contained pure silicon phases and oxides that had a lower density of 2.33 g/cm3 than that of ZrSi2. The XRD pattern of the fabricated sample is represented in Fig. 3. Because the volume fraction of pure silicon and oxide was small, diffraction peaks were hardly detected, and the ZrSi2 peak was only observed in the XRD pattern.

In situ XRD was conducted to analyze the oxide layer formation on ZrSi2 under high-temperature oxidation. The samples were oxidized at 900, 1000, and 1100 °C in air for 20 h. XRD signals were collected for 20 min hourly, and measured again after cooling. Figs. 4 and 5 show the cross-sectional images of the oxidized ZrSi2 at each temperature for 20 h and weight gain per unit area of each sample after the 20 h oxidation. The oxide thickness of the oxidized sample at 900 °C ranged from 4.1 to 6.6 μm, that at 1000 °C ranged from 15.8 to 22.4 μm, and that at 1100 °C ranged from 62.5 to 74.1 μm. After the 20 h oxidation, the weight change was 3.2 mg/cm2 at 900 °C, 12.1 mg/cm2 at 1000 °C and 37.8 mg/cm2 at 1100 °C, consistent with the thickness of the oxide film. No spallation of oxide films was observed at any temperature. All oxides tested at three different temperatures contained pure silicon phases that appeared to be dark phases in the oxide film. The pure silicon phases were formed in the oxide base of a layer-by-layer matrix structure that is a relatively bright component in an oxide film described with a high-magnitude image in Fig. 4 (a). This result is consistent with that obtained by Yeom et al. in oxidizing ZrSi2 at 1000 °C and 1200 °C for 5 h [20]. Selective oxidation of zirconium resulted in the formation of an intermediate product of silicon phases. From Knittel et al., the thickness of the oxide film of MoSi2 oxidized at 1000 °C for 100 h was 430 nm and that of the film oxidized at 1100 °C was 470 nm [14]. Compared to these values, ZrSi2 formed a thicker oxide although it was oxidized for a shorter time of 20 h. A continuous pure SiO2 layer was formed in the MoSi2 oxide film. In Fig. 4, the oxide film of ZrSi2 comprise of pure silicon phases and a layer-by-layer structure of oxides. A continuous SiO2 layer was not formed, and thus, a higher oxidation rate was observed compared to that of MoSi2. Moreover, ZrSi2 did not form a continuous SiO2 oxide layer under high-temperature oxidation.
compared to silicides such as CoSi$_2$, CrSi$_2$, NiSi$_2$, and PtSi [22]. In the TiSi$_2$ oxide film formed in the high-temperature oxidation experiment, both SiO$_2$ and the metal oxide of TiO$_2$ were formed, causing a higher oxidation rate compared to that of MoSi$_2$ [17].

Fig. 6 shows the results of the in situ XRD conducted at each temperature. 0 h XRD pattern collected at room temperature before raising the temperature. The sample holder used was made of Al$_2$O$_3$, hence Al$_2$O$_3$ peaks were observed. As oxidation progressed at all temperatures, tetragonal ZrO$_2$ peaks and pure silicon peaks emerged and ZrSi$_2$ peaks remained unchanged, however its size decreased as the oxidation proceeded. Additionally, the size of the tetragonal ZrO$_2$ peak at 30° (101) gradually increased during the oxidation at each temperature, indicating the growth of the ZrO$_2$ phase in the oxide film. After completion of the oxidation, the samples were cooled to room temperature. The tetragonal ZrO$_2$ peaks disappeared and monoclinic ZrO$_2$ peaks at 28° (11-1) and 31° (111) were formed. This indicates a change in phase of the tetragonal ZrO$_2$ to a stable monoclinic ZrO$_2$ at relatively low temperatures. In the SEM backscattered electron image, the oxide layer had a pure silicon phase and two phases in the layer-by-layer structure; that is, oxidation products of three different phases were formed on the oxide film. However, the in situ XRD showed the oxidation products of only two different phase compositions, i.e., ZrO$_2$ and pure silicon, as the oxidation progressed. To examine the mismatch, a TEM analysis was performed to observe the oxide film at high magnification and resolution. The oxide film of the oxidized ZrSi$_2$ at 1000 °C was processed into a TEM specimen using FIB. The images in Fig. 7 are bright-field TEM images of an oxide film that includes a layer-by-layer structure and pure silicon, and a bright phase and dark phase FFT result constituting the layer-by-layer structure. Fig. 7 (b) and 7 (c) show the high magnification of each phase of the layer-by-layer structure observed in Fig. 7 (a). The FFT pattern of the bright part in Fig. 7 (d) shows no diffraction pattern implying that this part comprises of an amorphous structure. It is depicted in the bright-field image because the amorphous phase does not diffract the incident electrons. The diffraction pattern appears clearly in Fig. 7 (e), the FFT result of the image containing the dark image. This indicates that the dark phase has a crystalline structure, and the incident electrons are diffracted. The dark phases are darkly described in the bright-field image. This FFT pattern is the phase of monoclinic ZrO$_2$ detected in the in-situ XRD result after cooling and has a zone axis of [ T 2 3]. Indexing for each peak is shown in Fig. 7.

Fig. 7. Bright-field TEM image of oxide scale with low magnification (a), high magnification of bright part in layer-by-layer structure (b), high magnification of dark part in layer-by-layer structure (c), FFT pattern of the bright part (d), and FFT pattern of the dark part (e).
In summary, the crystalline dark phases in the layer-by-layer structure are monoclinic ZrO$_2$ transformed from tetragonal ZrO$_2$ after cooling. Moreover, the bright phases in the layer-by-layer structure were amorphous, thus, not identified in the in situ XRD. A STEM-EDS analysis was performed to examine the atomic composition of these phases. The high-angle annular dark field-STEM and EDS mapping images of the oxide scale of ZrSi$_2$ are shown in Fig. 8. The atomic composition at each point in the image is shown in Table 1. The point EDS result showed that phase (a) was pure silicon; (b) was ZrO$_2$, observed in the in situ XRD result and described as a dark layer phase in the bright-field TEM image; and (c) was SiO$_2$, that was not observed in the in situ XRD and defined as an unknown amorphous phase.

Normally, ZrO$_2$ exists above 1100 °C in the tetragonal phase. All temperatures in this experiment were lower than the phase transformation temperature, however, during oxidation, a tetragonal phase was formed at all temperatures analogous to the report by Geßwein et al. [19]. Gravie et al. discussed the formation of tetragonal ZrO$_2$ under 1145 °C [23]. From Ref. [23], the surface energy of tetragonal ZrO$_2$ is lower than that of monoclinic ZrO$_2$. Therefore, if a grain size of less than 30 nm is formed, the tetragonal ZrO$_2$ with relatively low surface energy becomes more stable, whereas monoclinic ZrO$_2$ becomes unstable, owing to the large surface area. Therefore, tetragonal ZrO$_2$ may be formed, although it has higher Gibbs free energy than monoclinic ZrO$_2$ at temperatures below the phase transformation temperature. The ZrO$_2$ in the layer-by-layer structure in Figs. 4 and 8 exhibited a thin thickness of several tens of nanometers and a large surface area by forming a long layer. Therefore, in the in situ XRD analysis, tetragonal ZrO$_2$ peaks were observed during oxidation and the tetragonal phase transformed to a monoclinic phase that was stable at low temperatures.

<table>
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<tr>
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<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<tbody>
<tr>
<td>Zr [at%]</td>
<td>0.1</td>
<td>33.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Si [at%]</td>
<td>99.6</td>
<td>4.3</td>
<td>35.7</td>
</tr>
<tr>
<td>O [at%]</td>
<td>0.3</td>
<td>62.4</td>
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Fig. 9. Classification of oxide formation of disilicides [25].
temperatures and at room temperature after oxidation. The pure silicon phase was observed in in-situ XRD and electron microscopy images at all three temperatures. From the thermogravimetric/differential thermal analyzer (TG-DTA) experiment of ZrSi$_2$, the oxidation of ZrSi$_2$ proceeds by the following equation:

$$\text{ZrSi}_2 + 2\text{O}_2 \rightarrow \text{ZrO}_2 + \text{SiO}_2 + \text{Si} \quad (1)$$

Above 1000 °C, the second oxidation step commences, and the remaining silicon begins to oxidize. Beyond 1400 °C, oxidation of the silicon phase continues and the weight change continues to increase [19]. This is consistent with the result of the existence of pure silicon phase in this study. This phenomenon indicates that the zirconium in ZrSi$_2$ has a higher oxygen affinity than silicon and is preferentially oxidized to form pure silicon phase that is not oxidized and remains in the oxide film. If the oxidation time is prolonged and the complete oxidation of the specimen occurs, the remaining silicon phase changes to SiO$_2$ and disappears.

In this study, ZrSiO$_4$ was not observed at any temperature at which the oxidation experiments proceeded. Curtis et al. determined the temperature range where ZrSiO$_4$ was formed, through the heat treatment of a mixture of ZrO$_2$ powder with various crystal structures of SiO$_2$ powder [24]. The lowest temperature for ZrSiO$_4$ formation was 1315 °C. It was formed at a rapid rate from ~1420 °C to ~1540 °C. Considering the temperature at which ZrSi$_2$ oxidation proceeded in this study, no ZrSiO$_4$ was formed in the oxide film.

The oxidation of transition metal silicide is governed by an affinity for oxygen, diffusivities of silicon and oxygen, and vapor pressure of metal oxides. To understand the oxidation mechanism, the factors illustrated in Fig. 9 require consideration [25]. The first classification relies on the oxygen affinity of the metal and silicon. Molybdenum in MoSi$_2$ has a lower oxygen affinity compared to silicon. However, zirconium in ZrSi$_2$ and titanium in TiSi$_2$ have higher oxygen affinity than silicon, as illustrated in Fig. 10, showing the Gibbs free energy of formation of the oxide if the metal elements were oxidized by 1 mol of oxygen molecule [26,27]. Between 800 °C and 1200 °C, the Gibbs free energy of ZrO$_2$ and TiO$_2$ was lower than that of SiO$_2$, whereas the Gibbs free energy of MoO$_3$ was higher than that of SiO$_2$. The second classification involved a comparison of diffusivity of silicon in silicide and oxygen in silicon oxide. Because the formation reaction of SiO$_2$ oxide layer occurred at the interface between the oxide film and substrate, sufficient silicon supply from the substrate silicide is required to the interface to form a continuous SiO$_2$ layer. If the supply of oxygen to the interface was faster than that of silicon from the substrate, the remaining oxygen starts to react with the metal atom in silicide. From the in situ XRD and TEM analyses above, for comparison, the diffusivity of oxygen in amorphous SiO$_2$ and diffusivity of silicon in ZrSi$_2$ can be compared in ZrSi$_2$ oxidation. The diffusivity of oxygen in amorphous SiO$_2$ was measured using a secondary ion-mass spectrometer that is greater than that of silicon in ZrSi$_2$ at high temperatures [28,29]. The final criterion is the vapor pressure of metal oxide formed. In MoSi$_2$ oxidation, MoO$_3$ was well-volatilized at a temperature beyond 1000 °C that enabled the formation of a pure protective SiO$_2$ layer. However, at a relatively low temperature, the volatility was low and MoO$_3$ was formed with SiO$_2$ in the oxide scale; thus, the oxidation rate was higher than that at a high temperature. In ZrSi$_2$, the metal oxide ZrO$_2$ was not volatile at high temperature, and in contrast to MoSi$_2$, both pure SiO$_2$ and ZrO$_2$ in the oxide film were formed, as shown in this study.

![Gibbs free energy of formation of oxides with temperature](image1)

Fig. 10. Gibbs free energy of formation of oxides with temperature [26,27].

![Laser coating equipment and coated tube](image2)

Fig. 11. Laser coating equipment (left) and a photo of coated and bare tubes (right).
ZrSi₂ showed a lower oxidation rate compared to that of Zircaloy-4 investigated previously. The oxidation of zirconium and silicon proceeded with the oxygen anion passed through the already formed oxide, reacted with the metal substrate, and the oxide film grew. The diffusion of oxygen ions in ZrO₂ occurred along the grain boundaries and through the grains. However, in ZrSi₂ oxidation, a dense amorphous SiO₂ layer was formed in the oxide layer that provided a lower oxidation rate to ZrSi₂ than the oxidation rate of Zircaloy-4, because the diffusivity of oxygen was a few orders greater in tetragonal ZrO₂ compared to amorphous SiO₂ in the temperature ranges of the oxidation experiments in this study [28–30]. This inhibited the diffusion of the oxygen anion to the substrate. Furthermore, alternate to the Zircaloy-4 oxide film, the oxide film of ZrSi₂ observed a stable oxide film with no cracks and spallation contributing to a reduction in the oxidation rate.

3.2. Three-dimensional laser coating of ZrSi₂ on the Zircaloy-4 tube and steam oxidation test

The laser power used in coating was 120 W. The hatching distance was 0.15 mm, that is the interval between the laser sweeps on the cladding surface and the coating speed was 5 mm/s. Fig. 11 shows a macroscopic image of the coated tube and zirconium and silicon powders sprayed on a Zircaloy-4 tube using laser 3D printing. By establishing optimal coating conditions, a uniform...
ZrS\textsubscript{2} coating layer of ~100 \textmu m thickness was obtained without oxidation and cracks. Fig. 12 shows the SEM-BSE cross-sectional microstructure of tubes coated with a zirconium-silicon mixture with molar ratios 1:5, 1:6, and 1:7. During the coating process, deformation of the tube by thermal stress did not occur, because of the cooling water flowing inside the tube. A thin ZrSi layer was formed owing to the high zirconium concentration on the substrate site at the interface between the ZrS\textsubscript{2} coating. The Zircaloy-4 substrate is expected to make the adhesion of this coating stronger. This interdiffusion layer had a thickness of 1.1–1.5 \textmu m, regardless of the zirconium to silicon ratio of coating. The silicon phase fraction on the surface of the coating layer increased with increasing silicon fraction in the powder mixture. Thus, the oxidation experiment was performed with a tube coated at a ratio of 1:5 where the ZrS\textsubscript{2} fraction in the coating layer was the highest.

In the steam oxidation of cladding, zirconium reacts with oxygen released from the steam, causing hydrogen generation, as shown in the following equation:

\[ \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \]  

(2)

If the cladding surface temperature increases owing to accidents such as LOCA, the cladding reacts more actively with the steam. This reaction is an exothermic, and during oxidation, the temperature of the cladding surface rises. The amount of hydrogen gas generated is directly proportional to the degree of cladding oxidation. The quantity of hydrogen generated reduces with the decreasing oxidation rate under accident conditions, hence increasing accident tolerance.

The oxidation experiments were conducted in a 1200 °C steam/argon mixture for 2000 s. A cross-sectional image of the oxidized coated tube and high-magnification image of the coated part after oxidation are shown in Fig. 13. It is observed that the thickness change of the outer side of the coating is small compared to that of the inside of the tube, where ZrS\textsubscript{2} coating is not performed. On the inner side of the uncoated part, a thick \text{ZrO}_2 layer of ~300 \textmu m was formed, whereas the thickness of the oxide scale on the coating was ~10–30 \textmu m, as illustrated in Fig. 13 (b). In the thin film of the coating, a pure silicon phase and a layer-by-layer structure of the oxide were observed as analogous to that of the oxide film of the bulk ZrS\textsubscript{2} oxidized in the atmosphere as shown above. The results of the line EDS analysis of the coating side are shown in Fig. 14. Zirconium, silicon, and oxygen were detected at a thickness of 30 \textmu m outside the coated part. Inside the oxide layer, ZrS\textsubscript{2} coating that was not oxidized; unreacted zirconium during the coating process; and a thin ZrSi layer were found between the oxide and the tube.

Compared to other materials coated on the Zircaloy-4 tube introduced above, ZrS\textsubscript{2} coating has an oxide thickness of 10–30 \textmu m that is thicker than the values shown for FeCrAl and Cr coating cases. However, because the oxidized bare Zircaloy-4 has an oxide thickness of more than 300 \textmu m under the same conditions, ZrS\textsubscript{2} coating plays a significant role in increasing the high-temperature oxidation resistance of Zircaloy-4. Additionally, because of the high adhesion caused by the formation of a thin ZrSi phase between the coating and substrate, there is no spallation of coating after high temperature oxidation.

4. Conclusion

The high-temperature oxidation behavior of ZrS\textsubscript{2} that is used as a coating material for nuclear fuel cladding, was investigated for the development of accident-tolerant fuel cladding. The bulk ZrS\textsubscript{2} samples used in the oxidation experiments were prepared by powder metallurgy. The zirconium and silicon powder mixture was sintered at 1100 °C for 10 min by SPS. The oxidation was analyzed by in situ XRD; the samples were oxidized at 900, 1000, and 1100 °C for 20 h; and XRD signals were collected hourly. From the SEM analysis, cracks and spallation were not observed in the oxide films at the temperatures of the oxidation experiments conducted. The results of the in situ XRD and TEM analysis revealed that the oxide layer comprises pure silicon phases and a layered structure of crystalline \text{ZrO}_2 and amorphous SiO\textsubscript{2}. The amorphous SiO\textsubscript{2} layer formed in the oxide film significantly contributed to the high-temperature oxidation resistance of ZrS\textsubscript{2}. A ZrS\textsubscript{2} coating was applied to the Zircaloy-4 tube using laser 3D printing. The coating formed uniformly without any crack. The coated Zircaloy-4 tubes were oxidized for 2000 s at a 1200 °C steam/argon mixture. It was observed that the inner surface of the tube was seriously oxidized, forming a thick oxide film, whereas the outer surface of the coated surface had insignificant thickness change. The result indicated that the generation of hydrogen by high-temperature steam oxidation under the accident condition can be reduced through ZrS\textsubscript{2} coating using laser 3D printing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.net.2020.02.018.

References


