

## Surface Modification Technology on Zirconium Alloy for High-Temperature Application

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### 1. Introduction

After the Fukushima accident, it was recognized that a hydrogen-related explosion is one of the major concerns of reactor safety during high-temperature corrosion of zirconium alloys. It was reported that hydrogen is generated by a corrosion reaction of zirconium alloys, such as the fuel cladding, spacer grid, and channel box at a high-temperature steam environment. Thus, the decrease of the high-temperature corrosion rate of zirconium alloys is an attractive solution to a nuclear power plant accident. Recently, the development concept of zirconium alloys has focused on a decrease of the corrosion rate under normal operation conditions to increase the operation economy and safety margin [1-3]. However, it is unclear whether the corrosion resistance of zirconium alloys at normal operation in a 300°C-water environment can be maintained at up to a high-temperature steam condition of a 1200°C-steam environment. In general, the corrosion rate of zirconium alloys is considerably increased with an increase in the environment temperature regardless of the alloy compositions [4]. Thus, the improvement of the corrosion rate of zirconium based alloys at high-temperature is a difficult problem using the commercial materials. To solve this problem, it is necessary to develop an advanced technology such as the coating of incorrodible materials on a zirconium surface. The coating technology is widely applied at the other industrial materials to reduce the corrosion damage, as the corrosion resistance can be easily obtained by a coating technology without a base material change. However, the optimized coating technology containing the materials and methods must be developed, since the chemical and mechanical failures of the coating layer are a serious concern in coating technology. Thus, this work studied the coating techniques to reduce the corrosion rate of a zirconium based alloy in a high-temperature steam environment.

### 2. Methods and Results

Decreasing the corrosion rate of zirconium based alloy at a very high-temperature of up to 1200°C is limited by the compositional design of the alloying element of zirconium, as it was reported that the corrosion rate is not decreased with the alloy composition in commercial cladding materials [4]. The corrosion barrier property of the ZrO<sub>2</sub> phase, which is spontaneously formed on zirconium alloys by a

corrosion reaction, is maintained for a long time at a reactor operation temperature of about 300°C, whereas the corrosion barrier property of that phase is sharply degraded with an increase in temperature at a high-temperature of more than 500°C. Thus, we considered the coating (surface modification) methods as a corrosion barrier layer on zirconium based alloys.

#### 2.1 Consideration of corrosion barrier materials

To apply the nuclear material, it is necessary to check the neutron cross section and other physical properties (phase transformation temperature, melting point, thermal expansion coefficient, and thermal conductivity). Thus, we checked the coating material properties, as shown in Table 1. Among them, ceramics (Y<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>), carbides (Cr<sub>3</sub>C<sub>2</sub>, SiC, ZrC), and nitrides (ZrN, TiN) were generally used as coating materials for high-temperature application components as they have a high melting point, and corrosion and wear resistance. However, ceramics, carbides, and nitrides have a problem controlling the stoichiometry during the general coating process, and another problem is a weak adhesion to zirconium based metal and a higher neutron cross-section. Thus, a pure metal such as Cr and Si was selected as a coating material as the first work. Regarding the Si, it can be anticipated that Si was changed into a SiO<sub>2</sub> phase (quartz) during the oxidation; therefore, a SiO<sub>2</sub> layer can be made by pure Si coating on the zirconium matrix. Also, Cr<sub>2</sub>O<sub>3</sub> layer can be achieved by pure Cr coating on the zirconium matrix.

Table I: Summary of the basic properties of coating materials

Materials	Phase Transform. Temp. (°C)	Melting Point (°C)	Thermal Expansion Coeff. (x 10 <sup>-6</sup> /K)	Thermal Conductivity (W/mK)	Neutron Cross Section (barn)
Y <sub>2</sub> O <sub>3</sub>	none	2690	8.1	1.0	1.28(Y) 0.0002(O)
SiO <sub>2</sub>	Depend on pressure	1600	12.3	1.3	0.177(Si) 0.0002(O)
ZrO <sub>2</sub>	M(970)/ T(1205)/ Cubic	2130	10.1	1.8-3.0	0.182(Zr) 0.0002(O)
Cr <sub>2</sub> O <sub>3</sub>	none	2400	90.	-	3.05(Cr) 0.0002(O)
Cr <sub>3</sub> C <sub>2</sub>	none	1895	10.3	13	3.05(Cr) 0.0035(C)

SiC(CVD)	none	2545	<5	330	0.177(Si) 0.0035(C)
ZrN	none	1960	7.24	10	0.185(Zr) 1.9(N)
ZrC	none	3540	7.01	12	0.185(Zr) 0.0035(Cr)
Cr	none	1907	4.9	93.9	3.05(Cr)
Si	none	1414	2.6	149	0.177(Si)
Zr	HCP(863)/ BCC	1850	7.2	10	0.185(Zr)

## 2.2 Developing the coating method

Many coating methods such as a plasma spray, chemical/physical vapor deposition, and laser beam scanning have been developed and applied in the commercial industry field. Among them, we considered the direct application method on fuel assembly components having a complex shape (cladding tube, guide tube, and spacer grid). Since the length of the cladding and guide tube is 4 m, the coating method having a high vacuum control is not acceptable from an economical point of view. Also the coating can be applied to an irregular surface, as the coated area is not flat (tube and irregularly formed grid). For these reasons, the laser beam scanning method was selected in this study.

## 2.3 Coating and high-temperature oxidation test

Melted pure Si particles and a zirconium surface were well mixed by a laser beam heating and fast cool down during the coating, as shown in Fig. 1. Thus, a Si layer was uniformly formed on one side of the zirconium alloy sheet (Zircaloy-4). The coated layer thickness can be controlled by the laser power and Si feeding. After the coating, the sample was tested in a high-temperature steam environment. The test temperature and time were 1000°C and 1000 s, respectively.

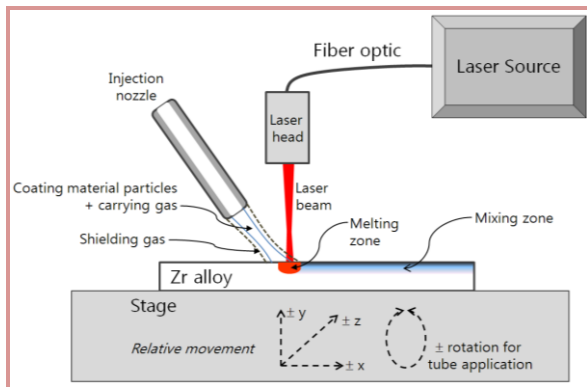


Fig. 1. Schematic drawing of laser beam scanning methods for the formation of Si coated layer on the zirconium metal surface.

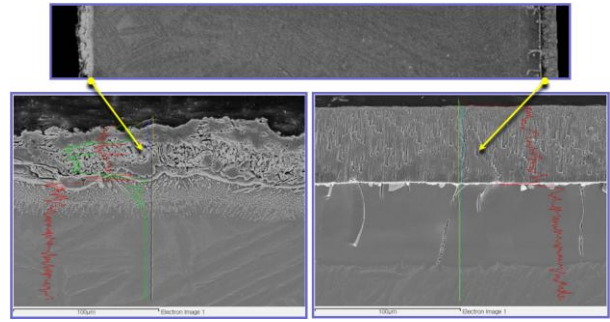


Fig. 2. Cross-sectional SEM observation of Si coated zirconium surface (left side) and not coated zirconium surface (right side) after the high-temperature oxidation test at 1000°C for 1000 s.

Fig. 2 shows the cross-sectional observation results after the oxidation test to evaluate the Si coating effect on zirconium alloy. The Si coating layer was maintained without peeling off after the high-temperature oxidation test. This means that the coated pure Si layer by laser beam scanning is not separated by the thermal expansion of zirconium alloy at up to 1000°C. On the Si-coated surface, a very thin oxide layer, which was lower than a few microns, was formed on the Si layer. In addition a reaction layer between the Zr and Si was shown at the coated interface. However, the  $ZrO_2$ , which was formed by the oxidation of zirconium, was observed on the zirconium alloy surface. The thickness of  $ZrO_2$  was about 75 microns. From this result, it is known that the Si coated layer acted successfully as a corrosion barrier layer to resist the high-temperature corrosion of zirconium alloy.

## 3. Conclusions

A pure Si layer was successfully coated on a zirconium alloy surface by laser beam scanning. The pure Si layer showed a better oxidation resistance than zirconium alloy at a high-temperature of 1000°C for 1000 s in a steam environment, and the layer was not separated by the thermal expansion of zirconium alloy at up to 1000°C.

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