

Surface Coating Technology on the Zirconium Base Alloy for High Temperature Application

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1. Introduction

The Fukushima Nuclear Power Plants were struck by the Pacific Ocean Earthquake and the ensuing tsunami on March 11, 2011. It was a very serious nuclear accident in the most recent. In this accident, the hydrogen related explosion was one of the major concerns of the reactor safety after the Earthquake attack. It was known that the hydrogen was generated by the corrosion reaction of the zirconium base alloys such as fuel cladding, spacer grid, and channel box at a high temperature steam environment. Thus, the high temperature corrosion of zirconium base alloy was attracted to the NPPs accident. Recently, the concept of zirconium alloy development was focused on the decrease of corrosion rate at a normal operation condition of NPPs to increase the operation economy [1-3]. However, it is unclear that the normal operation corrosion resistance of zirconium alloy can be maintained up to high temperature steam condition. Since it was known that the decrease of high temperature corrosion rate of zirconium base alloy was caused for a lot of hydrogen generation, it is necessary to reduce the hydrogen generation up to high temperature steam condition. So, this work is studied on the coating techniques to reduce the corrosion rate of zirconium base alloy at a high temperature steam environment.

2. Methods and Results

To improve the corrosion resistance of zirconium base alloy at very high temperature up to 1200°C, it is difficult by the compositional design of alloying element because the zirconium matrix and ZrO₂ have a phase transformation during the increase of the environment temperature [4]. By the phase change, the corrosion rate of zirconium base alloy was considerably increased with increasing the temperature. So, we considered the coating methods on the zirconium base alloys.

2.1 Coating material

To apply the nuclear field of the material, it is need to check the neutron cross section and other physical properties (phase transformation temperature, melting point, thermal expansion coefficient, and thermal conductivity). So we checked the coating material properties as shown in table 1. Among them, the

ceramics (Y₂O₃, SiO₂, ZrO₂, Cr₂O₃) and the inter-metallic compounds (Cr₃C₂, SiC, ZrN, ZrC) were generally used in coating materials in the field of high temperature application because they had a higher melting point as well as were resistance than metal base materials. However, the ceramics and inter-metallic compounds had a problem to control the stoichiometry during the coating process, and the other problem was the adhesion to the zirconium base metal. So, the pure metal such as Cr and Si was selected as a coating material in this work. Regarding the Si, it can be anticipated that Si was changed to the SiO₂ phase (quartz) during the oxidation; therefore, SiO₂ layer can be made by pure Si coating on the zirconium matrix. Also, Cr₂O₃ 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 ⁻⁶ /K)	Thermal Conductivity (W/mK)	Neutron Cross Section (barn)
Y ₂ O ₃	none	2690	8.1	1.0	1.28(Y) 0.0002(O)
SiO ₂	Depend on pressure	1600	12.3	1.3	0.177(Si) 0.0002(O)
ZrO ₂	M(970)/ T(1205)/ Cubic	2130	10.1	1.8-3.0	0.182(Zr) 0.0002(O)
Cr ₂ O ₃	none	2400	90.	-	3.05(Cr) 0.0002(O)
Cr ₃ C ₂	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 Coating method

Many coating methods were known in material research field. Among them, we considered the direct

application on fuel assembly components (cladding tube, guide tube, and spacer grid). Since the length of cladding and guide tube is 4 m, the coating method having high vacuum control is not acceptable in an economical point of view. Also the coating is possible to apply to the irregular surface, because the coated area is not flat (tube and irregularly formed grid). From these reasons, the plasma spray method was selected in this study.

2.3 Coating and Oxidation Test

The melted pure Si particles were attached on the zirconium surface and then fast cool down by plasma spray coating method. Thus, the Si layer was uniformly formed on the one side of zirconium alloy sheet (Zircaloy-4). The coated layer thickness was controlled by spraying time. After the coating, the sample was tested at a high temperature steam environment. The test temperature and time was 1000°C and 1000 s, respectively.

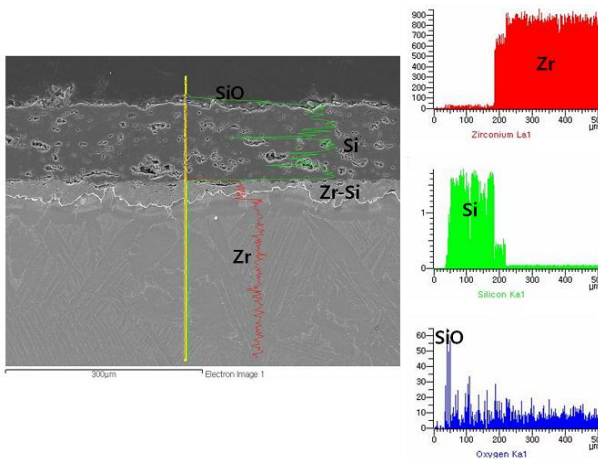
test. It means that the plasma coated pure Si layer is not separated by thermal expansion of zirconium alloy up to 1000°C. On the Si coated surface, a very thin oxide layer, which was lower than 3 micron, was formed on the Si layer. And the reaction layer between Zr and Si was shown at the coated interface. However, the ZrO₂, which was formed by oxidation of zirconium, was observed on the zirconium alloy surface. The thickness of ZrO₂ was 35 micron. From this result, it was known that the Si coated layer was successfully acted as the corrosion barrier layer to resist the high temperature corrosion of zirconium alloy.

3. Conclusions

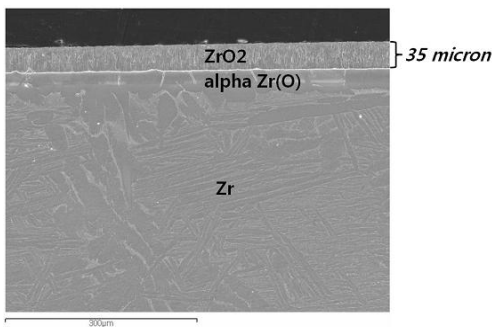
The pure Si layer was successfully coated on the zirconium alloy surface by the plasma spray coating. The pure Si layer showed better oxidation resistance than zirconium alloy at the high temperature of 1000°C for 1000 s in a steam environment, and that layer was not separated by thermal expansion of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

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(a) Si coated surface



(b) Zirconium surface

Fig. 1. Cross-sectional SEM observation of Si coated zirconium surface (a) and not coated zirconium surface after the high temperature oxidation test at 1000°C for 1000 s.

Fig. 1 shows the cross-sectional observation results after oxidation test to evaluate the Si coating effect on zirconium alloy. The Si coating layer was maintained without peeling off after high temperature oxidation