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Surface Coating Technology on Zirconium-Based Alloy to Decrease High-Temperature Oxidation Rate

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1. Introduction

After the Fukushima accident, it has been recognized that hydrogen generation is one of the major concerns of reactor safety, as serious reactor damage can be caused by a hydrogen explosion. Hydrogen is generated by the corrosion reaction of zirconium alloys such as the fuel cladding, spacer grid, and channel box, and the corrosion reaction can be considerably increased with an increase in the environmental temperature [1, 2]. Thus, a decrease of the high-temperature oxidation rate of zirconium alloys was a key to decrease the hydrogen generation during the nuclear power plant accident.

The current method used to increase the corrosion resistance of zirconium alloy for a nuclear application basically adjusts the alloying elements such as Nb, Sn, Fe, or Cr, and their ratios. However, the oxidation rate of zirconium alloys at a high-temperature of 1200°C is not considerably changed with the alloy composition [3, 4]. Thus, it is a problem that the decrease in the oxidation rate of zirconium-based alloys at high-temperature is difficult to achieve using commercial materials. To overcome the acceleration of high-temperature oxidation of zirconium alloys, research the new material and concepts has been suggested [5, 6].

The coating technology is widely applied in other industrial materials to reduce the corrosion and wear damages, as the corrosion and wear resistances can be easily obtained by a coating technology without a change in the base material. Thus, surface coating technology on zirconium alloy was selected in this work after technical deliberation for a decrease in high-temperature oxidation rate, near term application, easy fabrication, economic benefit, and easy verification, although the high-temperature strength was reduced more than for other suggested technologies of hybrid and full ceramic materials. However, an optimized technology for the coating materials and coating methods must be developed for nuclear application, since the coating technologies for zirconium-based alloys to increase the high-temperature oxidation resistance have not been determined at the present time. Thus, this work studied the coating techniques for both coating methods and coating materials to reduce the oxidation rate of zirconium-based alloy in a high-temperature steam environment.

2. Methods and Results

A Zircaloy-4 (Zr-1.5Sn-0.2Fe-0.1Cr in wt.%) alloy sheet was used as a substrate with a dimension of 95 mm x 25 mm x 2.54 mm. The selection of the coated materials was based on the neutron cross-section, thermal conductivity, thermal expansion, melting point, phase transformation behavior, and high-temperature oxidation rate. After considering this point, the metal base materials of Si and Cr were selected as a coating layer for the surface coating on the zirconium-based alloy.

Two applied coating techniques are used this: for the first, pure Si powders are attached to the Zircaloy-4 sheet surface by a plasma spray (PS) coating method, and for the second, a Si-coated layer by a PS is treated by laser beam scanning (LBS) to increase the adhesion between the Zircaloy-4 matrix and Si-coated layer. Fig. 1 shows the schematic drawings of the plasma spray coating method and laser beam scanning method to make a Si-coated layer on the Zircaloy-4 sheet surface, and the appearance of the Si-coated layer using two methods.

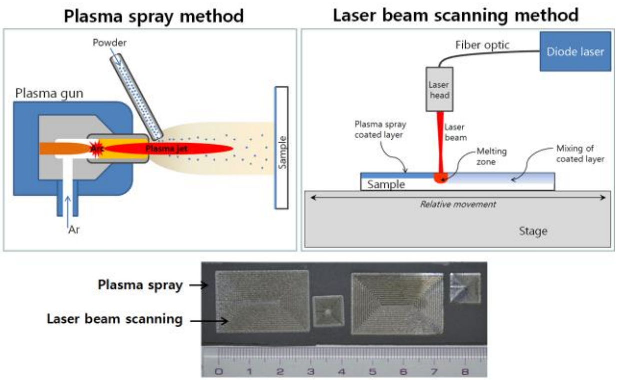

Fig. 1. Schematic drawing of plasma spray coating method and laser beam scanning method to make a Si coated layer on the zirconium metal surface.

After the coating treatments of the samples in both PS coating and LBS treatment after PS coating (PS + LBS), the microstructure and composition of a Si-coated layer for a cross-sectional direction has been determined using scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS), and a transmission electron microscopy (TEM) analysis. The samples for the TEM observation were prepared using focused ion beam (FIB) equipment.

To evaluate the oxidation behavior, the prepared samples were mounted in the test equipment for high-temperature oxidation, and a mixed gas of steam and Ar was then flowed at a 10 ml/min flow rate. The temperature of the samples rose 50°C/min, and the temperature was maintained at 1200°C for 2000 s.

Fig. 2 shows a cross-sectional SEM observation together with an EDS analysis of the Si-coated layer by a PS on the Zircaloy-4 sheet. Thickness of Si-coated layer was determined from SEM image and EDS profile. In this figure, the thickness of the Si-coated layer was increased with repeated spraying numbers of one to six passes. In the first pass, the mean thickness of the Si-coated layer was 15 μm, and the variation of the thickness was ± 3 μm. Thus, a uniform layer thickness cannot be obtained by a one pass PS treatment of Si powder. The mean thickness of the Si-coated layer after three and six passes reached 70 and 130 μm, respectively. Pores of irregular shape were observed in the Si-coated layer, and density of pores was increased with an increase of the repeated straying numbers.

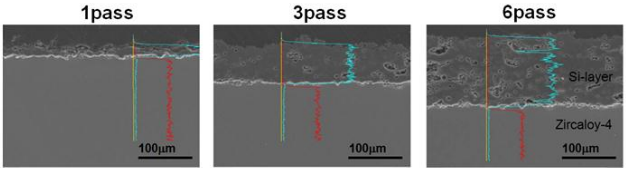

Fig. 2. Cross-sectional SEM observation of the Si-coated layer on the Zircaloy-4 sheet by PS with spraying times from one to six passes.

The Si-coated layer was not fully melted in the case of the low laser power condition; therefore, the diffusion zone between the Si and Zr was not formed, and the pores observed in the Si-coated layer by a PS were not completely removed. In the case of the high laser power condition, the Si-coated layer by a PS was broken down by the excessive mixing between Si and Zr elements. The LBS treatment after PS coating (PS + LBS) was performed on the samples of a three pass Si-coated layer to remove pores and to improve the adhesion to Zircaloy-4 substrate. Fig. 3 shows the SEM observation and EDS analysis images for the boundary between the PS and PS + LBS treatments to compare the microstructure characteristics with the coating methods of the Si-coated layer. When compared to the Si-coated layer by a PS shown in the left part of the SEM image, the pores fully removed, and a diffusion zone between Si and Zircaloy-4 was formed by the LBS treatment.

After the coating of the Si using the PS as well as PS+LBS methods, the oxidation behaviors were evaluated by the cross-sectional microstructure observations for the Si-coated layer. The oxidation resistance of the Si-coated layer is superior to that of the Zircaloy-4 sheet, because the severe oxidation reaction is suppressed in the Si-coated layer by a PS. However, the adhesion property of the Si-coated layer by a PS was considerably decreased during the high-temperature oxidation test at 1200^{o}C, as the severe oxidation was progressed at the interface region between the Si-coated layer and Zircaloy-4 substrate at the side of the tested samples. From the cross-sectional observation of Si coating by the PS + LBS treatment after the oxidation test, the oxidation resistance of the Si-Zr mixed layer is superior to that of Zircaloy-4, and a good adhesion property can be obtained.

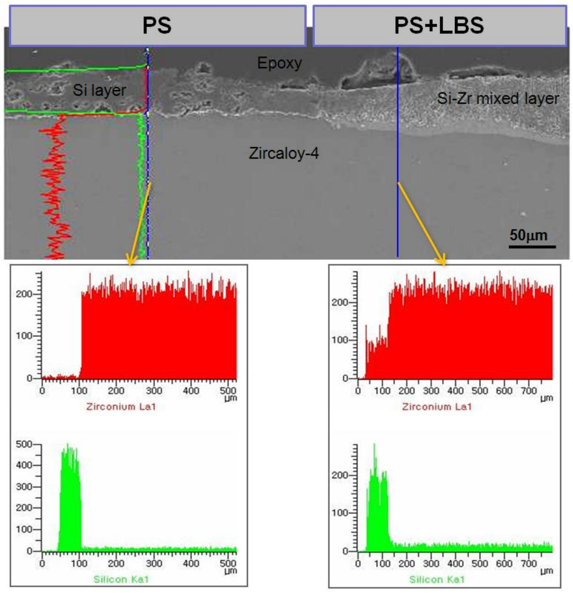

Fig. 3. Cross-sectional SEM observation in the upper part and EDS profile analysis for the Zr and Si element profiles in the lower part to compare the microstructure characteristics.

3. Conclusions

The coating techniques for both the coating methods and coating materials to reduce the oxidation rate of zirconium-based alloy in a high-temperature steam environment were studied. Two technologies, plasma spray (PS) and laser beam scanning (LBS) after a PS, were selected as the coating method, and the Si was selected as a coating layer for the surface coating material on zirconium-based alloy.

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