Development of Fuel Cladding for Further High Fuel Burnup
− Suppression of Corrosion and Hydrogen Pickup by Surface Modification Technology, Fresh Green −

Background

In light water reactors, fuel burnup is gradually being increased in order to enhance plant availability and reduce fuel and fuel cycle costs by suppressing amount of spent fuels. In order to increase the fuel burnup further, the amount of hydrogen pickup into fuel cladding must be reduced because the dwell time of fuel cladding subjected to the reactor coolant becomes longer. There are countermeasures to cope with the hydrogen pickup by modifying material compositions and by controlling crystal structures.

We have been proposing surface modification methods to mitigate hydrogen pickup. We invented the surface modification technology of titanium, Fresh Green (FG), by oxidizing and carburizing titanium on its surface. The formed carbon-doped titanium oxide layer is closely packed, intimately adheres to a base matrix and exhibits the superior corrosion resistance. This infers that the same FG surface modification of the zirconium alloy (Zircaloy) fuel cladding can suppress corrosion and hydrogen pickup, since zirconium is classified in the same 4A group of elements as titanium.

Objectives

The purpose of this study is to investigate corrosion and hydrogen pickup behavior of a BWR Zircaloy-2 fuel cladding with the FG surface modification in an accelerated autoclave experiment, and to explore the applicability of FG surface modification to the conventional fuel cladding manufacturing process.

Principal Results

1. Crystal Structure of FG Layer

XRD and XPS analyses indicated that a modified layer on zirconium surface is carbon-doped zirconium dioxide, in which some oxygen atoms in monoclinic zirconium dioxide are replaced by carbon (Fig. 1). The FG surface modification of titanium is, therefore, applicable to zirconium as well.

2. Optimized FG Conditions to Suppress Corrosion and Hydrogen Pickup

The FG surface modification is applied to commercial Zircaloy-2 fuel cladding tubes at three temperature levels (500℃, 580 oC and 660℃) and for two dwell times (1 h and 4 h). The finish annealing has already been applied to all the specimens in vacuum at 580℃ for 2 h before the FG treatment. Experiments are conducted for three representative conditions [*1] using an autoclave. The Fresh Green surface modification at 500℃ for 1 h and 580℃ for 1 h reduces both the corrosion and hydrogen-pickup amounts to a half of them without FG treated base material (Fig. 2). Hydrides were found in the base material without treatment, though they were scarcely observed in the FG treated specimen at 500℃ and 580℃ (Fig.3). This is because the FG layer is closely packed and adhered intimately to the base material. The FG surface modification at 660℃, accelerates, in turn, corrosion and hydro-gen-pickup. FE-TEM micrographs show enlarged inter-metallic compounds in the base material for such high-temperature surface modification, resulting in susceptible to corrosion.

3. Applicability of FG Surface Modification to Cladding Manufacturing Process

Since the optimized operating temperature (500℃, 1 h) of the FG process is lower than the final annealing temperature of BWR cladding material Zircaloy-2 in a manufacturing process, the process does not affect the material property and crystal structure. The FG process, which is operated at slightly higher pressure than ambient, can be introduced in the conventional manufacturing process without much complicity.

Future Developments

We will carry out autoclave experiments for a long period close to the reactor condition (360℃) to investigate corrosion and hydrogen pickup performances, and in-pile experiments to examine irradiation performance.

Main Researchers:
Masahiro Furuya, Ph. D., Senior Research Scientist, Sector Nuclear Reactor System Safety, Nuclear Technology Research Laboratory
Moriyasu Tokiwai, Dr. Eng., Research Advisor;
Nobuyuki Tanaka, Technology Transfer Group, Center for Intellectual Property and Technology Licensing, Senior Research Scientist

Reference

M. Furuya, M. Tokiwai, N. Tanaka, M. Horie, 2009, 2006, “Corrosion Control and Anti-Hydrogen-Pickup of Fuel Cladding by Surface Modification Technology, Fresh Green”, CRIEPI Report L08014 (in Japanese).
M. Furuya, M. Tokiwai, N. Tanaka, M. Horie, 2007, “Surface Modification Technology of Titanium, ‘Fresh Green’ - Durability and Photocatalytic Activity of Carbon-Doped Titanium Dioxide Surface,” Ti-2007 Science and Technology, JIMIC 5, Japan Institute of Metals, Vol.II, pp.1727-1730, 2007.

＊1：The autoclave experiments were conducted under the three representative conditions: uniform corrosion (400℃, 336 h), nodular corrosion (500℃, 24h), and super-critical water corrosion (500℃, 24h).

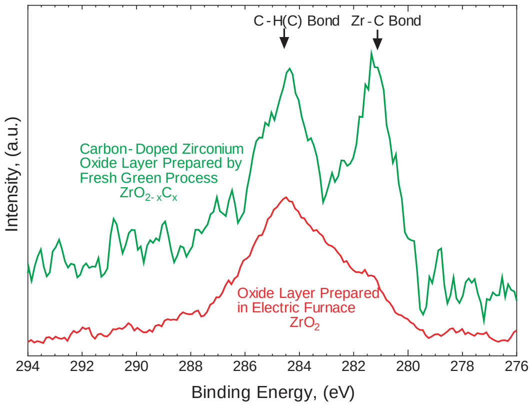

Fig.1 X-Ray Photoelectron Spectroscopy of C 1s Test

The FG layer is carbon-doped zirconium dioxide, in which some of oxygen atoms in monoclinic zirconium dioxide are replaced by (not isolated) carbon with Zr-C bonding.

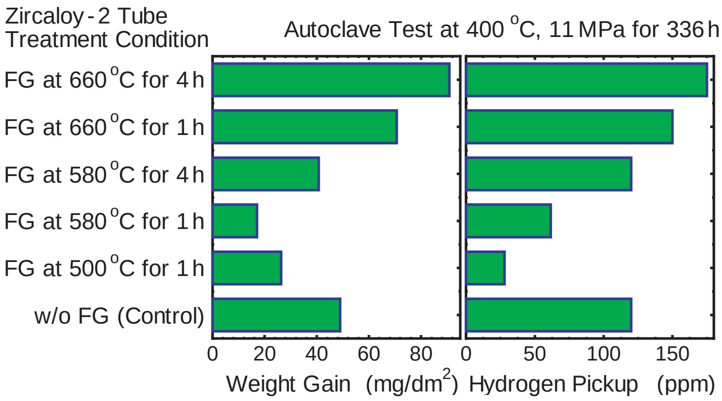

Fig.2 Weight Gain and Hydrogen Pickup after General Corrosion

FG treatment at 500 ℃ for 1 h suppressed corrosion to a half and and hydrogen pickup to one-fifth of those of untreated specimen. Similar results were acquired in other autoclave conditions[*1].

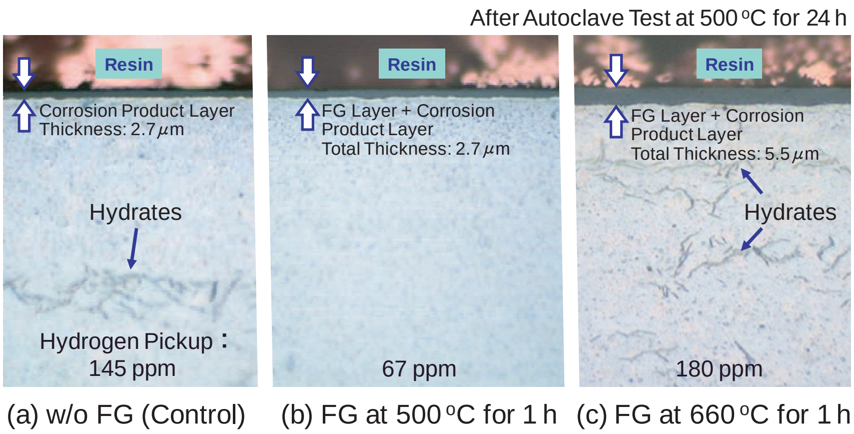

Fig.3 Optical Micrographs of Hydrate Alloy

Hydrides were found in the base material without treatment and with high temperature (660 ℃) FG treatment, though they were scarcely observed in the Fresh Green treated specimen at 500 ℃ for 1 h, since hydrogen pickup is less than solid solubility limit.

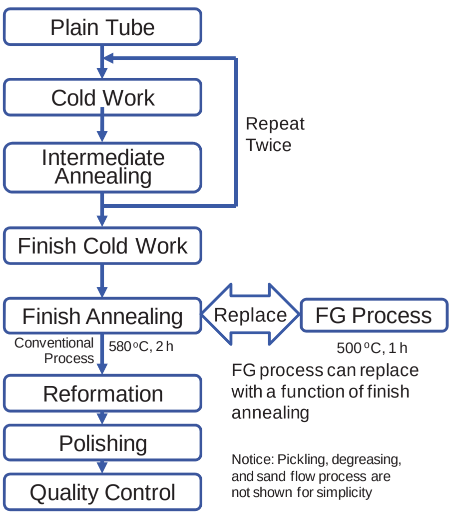

Fig.4 Manufacturing Process of BWR Fuel Cladding

FG process can replace the finish annealing process for both annealing and surface modification of the alloy.

5